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D.O.E./D.S.T.
Thermal Power Systems Workshop
on
Selective Absorber Coatings

6-8 December 1977

Solar Energy Research Institute
Golden, Colorado

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PROCEEDINGS: D.O.E./D.S.T. THERMAL POWER SYSTEMS WORKSHOP ON SELECTIVE ABSORBER COATINGS

DECEMBER 6-8, 1977

PATRICK CALL
MATERIALS BRANCH

AUGUST 1978

Solar Energy Research Institute
1536 Cole Boulevard
Golden, Colorado 80401

A Division of Midwest Research Institute

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Session 4: Advanced/High Temperature Coatings (M. Adams, Chairman)

Moderating Panel

P. Call	SERI
D. Elliott	DOE/SAN
J. Vossen	RCA
W. Carroll	JPL
G. McDonald	NASA
L. Melamed	DOE
J. Richmond	NBS
D. Pettit	Sandia
B. Butler	SERI

WORKSHOP SUMMARY

The DOE Absorber Coatings Workshop, hosted by SERI on December 6-8, 1977, was organized to address four topics:

1) What goals should exist for a selective surface coatings program; explicitly addressing the three temperature regimes: <350°, 350-500°C and >500°C? What are the elements of a complete program to meet these goals?

2) Considering economic constraints, thermal and environmental stability and ease of fabrication, are there techniques and/or materials that should be added (deleted) to(from) current research efforts?

3) What refinements of the current Coatings Program within the Thermal Power Systems R&D Branch can be made to better address the needs of the Central and Distributed Receiver Program?

4) Is there a need for a dedicated facility to provide controlled thermal testing and optical characterization of selective coatings at working temperatures?

The workshop produced specific discussions of improved measurement capabilities and potential environmental stressing concerns. It was concluded that problems of nomenclature and techniques for optical measurement have previously been resolved and that new and old members of the solar optical coatings program must make an effort to educate themselves with reference to a recognized bibliography[1-4].

A need for absorptance and emittance measurements at operating temperatures was established; in addition, the complete understanding of coating behavior will require that these measurements be made as a function of wavelength and angle of incidence. A preliminary inventory of available facilities appears in the proceedings as Appendix I.

Although it was not possible to make a comprehensive list of critical issues for absorber coatings, Table I summarizes the parameters that concern coatings development and for which standardization of testing procedures may

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[1] NBS Technical notes 910 series (1 & 3 currently available).

[2] NBS Monograph 160.

[3] International Lighting Vocabulary, 3rd Ed. CIE pub. 17, 1970 (available through Jack Teck at NBS).

[4] Wright Air Development Center, WADC-TR-59-510 Standardization of Thermal Emittance Measurements, Part IV. Normal spectral emittance 800-1400°K.

need to evolve. Table II represents a checklist that the program might compile on the status of each coating under development.

The issue of coating repairability was discussed. Repairability and durability are related issues; however, loss of coolant accidents or mechanical damage to the receiver may exceed reasonable coating design criteria and recoating using vacuum or CVD techniques will almost certainly be limited to those receiver designs where the coated component can be easily removed.

The importance of solar spectrum photons at high irradiance with regard to the stability of absorber coating optical properties was emphasized. Test facilities to explore this effect at operating temperatures are coordinated by the Solar Thermal Test Facility (STTF) Users Association (contact C. Bishop, SERI and see Appendix I).

Considerable confusion results from the admixture of British and SI units. In keeping with international trends future workshop and program communications should be expressed in metric units with British units in parentheses where appropriate.

Workshop discussion, when not specifically occupied with technical issues, tended to drift to the topic of general philosophy of an Absorber Coatings Program. Opinions were generally found between two extreme positions: 1) absorber costings development should be reactive, i.e., coatings should be developed for specific receiver designs where appropriate; 2) coatings development should provide a variety of coatings characteristics from which systems designers may choose, i.e., systems designs should not be limited by the lack of appropriate coatings. The appropriate balance between philosophies 1 and 2 will be make on the basis of the importance of coatings to the generic systems in terms of net annual energy output.

Addressing the four topics which appeared at the beginning of the summary, the workshop concluded:

1) The goals for selective absorber coatings R&D are to provide thermal systems designers with cost-effective, reliable and well-characterized coatings. The cost of maximizing substrate adhesion and solar absorptance and minimizing the degradation rate and the thermal emittance should be balanced with the value of the coating to the thermal systems. Specific program elements

to achieve these goals include: systems analysis to assess cost/benefit, development of specific coatings as needs are determined by systems analysis, vigorous test and characterization programs and basic research leading to understanding of optical processes and degradation mechanisms in selective absorber coatings. Specific program elements by temperature include:

<350°C: Investigation of operating conditions for black chrome and identification of alternatives.

350-500°C: Identification and development of current projects to meet this temperature regime. Identification of optical characterization capability at operating temperature.

>500°C: Extension of JPL-type systems analysis to specify high temperature designs and to assess potential benefit of selective coatings (e.g., optimized $10MW_e$ central receiver [open] and parabolic dish with open receiver).

2) Critical areas of concern were identified for a number of projects within the program; recommendations for deletion or addition of new development projects were not expressed. Refinements of existing projects were suggested.

3) Refinements to the current program should include improved and more specific systems analysis, improved testing and characterization including the development of durability standards and a data base of the optical properties of materials of construction as well as specialized coatings. The optimum optical properties of surfaces for cavity applications needs to be determined.

4) The issue of a dedicated facility proved controversial. The resolution of the discussion appears to be that a primary responsibility of the program management will be to identify proper test facilities and coordinate sample testing. In the early stages of coating development individual contractors could rely on standards to maintain the comparability of diverse measurements.

The recommendations for program direction compiled by the review panel and individual summaries of the workshop sessions are included.

Table I

Maximum sustained operating temperature.

Maximum sustainable thermal transients, gradients and duration (cloud passage, LOC accident).

Optical properties as a function of temperature, wavelength and incident angle $[\alpha, \varepsilon (T, \lambda, \theta)]$.

Geometric Concentration Factor and the effect of photochemistry at high temperatures on optical properties.

Rate of change of α_s and ε_t as a function of temperature and irradiance above operating temperature.

Repairability of absorber coating.

Optical properties as function of incident solar spectrum (effect of pollution, high n for AMn spectra from far field mirrors).

Effect of dust, rain, humidity, contamination of working fluid, atmospheric contamination from pollution.

Effect of contamination from coating to transparent envelope (e.g., outgassing from paint).

Cost per unit area.

Materials resource limitation or vulnerability.

Geometrical constraints in application.

Effect of shaping or forming after coating.

Substrate candidates.

Table II

Coating	Example
	Black Chrome
Environment	Air (30%,RH)
Temperature of optical measurement (^{o}C)	25
Optical Properties (as produced)	
α_s	0.95
ϵ_t	0.08
Operation	
Temperature (^{o}C)	250
Duration (hrs)	1000
$\Delta\alpha_s$	
$\Delta\epsilon_t$	
Cycle temperature (ΔT)	230
Number of cycles	10,000
Duration of cycle (hrs)	.1
$\Delta\alpha_s$	
$\Delta\epsilon_t$	
Maximum temperature - 24 hours (^{o}C)	500
$\Delta\alpha_s$	
$\Delta\epsilon_t$	
Maximum temperature - 1 hour (^{o}C)	700
$\Delta\alpha_s$	
$\Delta\epsilon_t$	
Peak Irradiance (W/m^2)	5×10^4
Temperature (^{o}C)	250
duration (hrs)	100
$\Delta\alpha_s$	
$\Delta\epsilon_t$	
Substrate	Copper
Morphology	
TEM	x
SEM	x
Compositional Profile	
AES	
SIMS	x
ESCA	
Changes in composition or morphology as function of test conditions (note)	
Confidence in evaluation	B*

A - proven commercial (>100 analyses and field evaluations)
B - laboratory demonstration/early commercialization (>10 analyses)
C - laboratory development (1 - 10 analyses/no field experience)
D - laboratory prototype (∿1 analysis)

Recommendations on Programmatic Directions

- Program funding level is appropriate and should not be reduced.
- Selectivity/Benefit analysis should be improved, refined and incorporated into the program structure as an interim buffer to facilitate communication between systems designers and coatings developers.
- System operating parameters should be defined and incorporated into previous item.
- Redirection of coatings development will require identification of systems parameters.
- Coatings developers should move to standardize optical measurement techniques. α and ε should be measured as a function of temperature incident angle and wave length as appropriate to the application.
- Centers of optical expertise should be identified or developed where necessary to maintain the needed measurement facilities. DOE and SERI may have to coordinate general use testing as part of the coatings program.
- Communication between users, developers and the DOE community should be improved. The formation of a standard distribution for coatings reports generated by this group is suggested. The initial list would be the attendees.
- As the program develops a need for simulation of high energy photon fluxes, utilization of the 5MW solar thermal test facility should be explored.
- The need for consistent environmental testing was stressed. Environments such as "vacuum" and air should interact with samples heated close to their operating limit to determine changes in α and ε at the usual operating temperatures.

Session 1: Users Forum (D. Elliott)

- Choice of cavity vs. external receiver for future central receiver applications will be made on an individual system basis. Selection of external receiver for Barstow does not preclude the choice of a cavity design for the next demonstration.
- Loss of Coolant (LOC). Thermal inertia in the MDAC external receiver is worth 10-15 seconds in a LOC accident (time to defocus heliostats). Martin Marietta indicated that two minutes of inertia is available with the water in drum boiler. Rocketdyne indicated that tests of the external receiver for 1 minute without coolant have been performed.
- Constraints on external receiver coatings: ease of refurbishment, no down time, 10,000 thermal cycles (30 year life), survival of rain and dust environment.
- One percent increase in α_s is equivalent to increasing the α_s/ε ratio from 1 to 2 at $\alpha_s = .95$ and corresponds to ∿$7/KW cost reduction for the McDonnell Douglas 10 MW design.
- α_s on a plane surface may be saturated at a value of .98. As the coating designer approaches this value further coating improvements will require reduction in ε.
- Distributed Energy System temperature requirements range from 200°C for process heat to 800°C for high performance electrical generation systems.
- For concentration ratios >100 coatings research should emphasize increasing α.
- An inventory of facilities for optical measurements and in particular measurements at operating temperatures was solicited.

Central Receivers (A. C. Skinrood)

- Selective coatings are not used in present designs.
- High absorptivity is essential.
- A document will be written by Sandia which better defines desired coatings properties.
- If these properties are met, selective coatings may be able to make a small but significant improvement in performance. Specific responses should be solicted as to how (or whether) these requirements can be met.
- The central receivers program should <u>not</u> be used as justification for a major selective coatings research program.

- It is not correct to assume that all receivers operating above 500°C. will be cavities.

- Measurement of absorptivity at temperature as a function of angle for the Barstow plant will be done. The only questions are where, by whom, and with what. It is possible that more than one coating will be used if more than one coating is qualified. I would like to receive the list of potential measurement sources.

Dispersed Power Systems (J.A. Leonard)

- Temperature: >Ambient (40°C) for process heat concentrators

  >200°C for irrigation and solar total energy applications

  >300°C for electric power only applications

  Presently line focusing systems are tending to be limited to ∿300°C by temperature limitations of absorptive coatings and heat transfer fluids.

- Diurnal and thermal shock: Ambient to operating temperature or reverse in about 1/2 hour.

- Temperature excursions with coolant loss: 200°C over operating temperature in 15 minutes has been experienced.

- Thermal expansion: Longitudinal expansion plus bending and flexing must be considered-- tube bundles and expansion joints especially.

- Incident angles: For line focus concentrators normal incidence is rare. For point focus receivers most absorbing surfaces will also be non-normal but incidence angles tend to be constant throughout the day. Line focus systems will try to get operation started within an hour after sunrise (15° above horizon--75° from normal at the receiver for equinox on E-W horizontal collector).

- Substrate materials: Carbon steel, stainless steel, copper tubing, zirconium copper, aluminum, incoloy 800 (Central Rec).

- Atmospheres: 10^{-3} torr or softer. Roughing pump vacuum is probably all that can be maintained for long times in most designs although some glass/glass seals are being investigated. Glass envelopes with air or air cavities are frequently seen in designs. Some consideration being given to low conductivity gases in mechanically sealed tubes.

- Handling and Assembly: Tubes are frequently welded to flanges or to adjacent tubes. Compressive fittings sometimes used. Heat sinks can be used to minimize heat affected zone. Consideration must be given to handling needs for packaging, shipping, and assembly operations.

- Performance effect: Selective coating has 20% effect on efficiency for 50x or less concentrators (compared to non-selective).

Session 2: Optical Properties Measurements (K. Masterson)

- A need to establish a single solar spectrum for weighing spectral absorptance measurements exists.

The techniques and nomenclature for appropriate optical characterization are in hand.

Although much of the instrumentation and expertise to make the measurements was developed in the '60s, a lot has been mothballed and staffs dispersed. Only a few, probably one or two, good facilities are intact.

New developments make many old instruments obsolete.

- Auger, SEM, etc., analyses are indeed important support facilities and should be utilized. DOE should either continue to support the dedicated facility or encourage inclusion of funds for subcontracting analysis in contracts.

- Pyromark paint held up well in White Sands tests. Measurements of oxides of high temperature alloys should be extended into IR.

- Basic research on black chrome is still not adequately funded in light of the emphasis on it in distributed systems presently installed or being installed.

- The selective/non-selective and central-distributed measurements facilities controversy masked the real purpose of discussing measurements. It was, however, fairly clear that a very important quantity to measure is $\alpha(\theta,\lambda,\tau)$ over the solar spectrum. The angular dependence is the directional-hemispherical measurement. This can be adequately done in an integrating sphere reflectometer of the Edwards type. It can be made to operate at elevated temperatures also.

The engineer designing systems needs $\alpha(\theta,\lambda,\tau)$. The researcher developing coatings may need bi-directional reflectance measurements also. The different requirements in optical characterization between engineers and coatings researchers surfaced several times.

Emittance measurements can be made calorimetrically or optically. Both are needed in order to cross-check results. Optically, one needs specular optical systems of the Coblentz sphere type or similar.

Round-robin tests of a few selected samples and the availability of NBS standard test specimens is a satisfactory means of assuming measurement consistency.

Session 3: Semiconductor/Metal Systems (B.O. Seraphin)

- The session included reports on four advanced coating designs: the first two based on the principle of the absorber reflector tandem, and the last two on the spectral selectivity of composite systems.

- Seraphin of the University of Arizona reported on a multi-layer stack deposited by CVD. This approach expanded conventional thin film technology to first, high temperature applications and, secondly, to economic large area fabrication. Recent developments replace the absorber by a CVD layer of amorphous silicon, and the present silver reflector by a molybdenum film deposited by CVD. The discussion centered on the protection of molybdenum films over extended periods of time, on the better match of molybdenum to the silicon absorber and on the cost of the process, judged to be only a fraction of the price of the substrate.

- Griffith of Brookhaven elaborated on the benefits of an amorphous silicon absorber. He judges--from his theoretical considerations--the absorptance to increase to 91% at $400^{o}C$. The discussions suggested to actually verify this estimate on experimental stacks including amorphous silicon.

- Gittleman of RCA reported on Composite Dielectric Films that consist of suspensions of gold particles in Al_2O_3 hosts, and show promising spectral selectivity. The discussion asked why the supression of the front surface reflection possible by a gradation of the particle density was not emphasized more. Gittleman acknowledged this possiblity and discussed also the temperature performance of these composites, which will be measured in the future.

- Sievers of Cornell University included the inhomogeneous profile of the optical density of the composites and, therefore, considers the attractive possibility of reducing the front surface reflection. Solar Absorptance of 0.94 and emittance of 0.1 had been obtained in the experimental verification of this approach.

- The general discussion at the end of the session centered on the benefit of coatings in view of the insensitivity of the cavity receiver concept to the character of the intercepting surface. Melamed emphasized the value of keeping the designer's options open by asking researchers to provide alternatives for existing but in-process designs. It is not to be desired to freeze the program into the direction of the cavity receiver, for instance, simply because the neglect of the coatings program does not leave any alternatives.

- JPL intercepted the discussion at this point and promised to give an evaluation of the benefits of coating work in the afternoon session that would make this type of discussion more fruitful.

Session 4: Advanced High Temperature Coatings (P. Call)

- A. Muenker reported Exxon research on seven high temperature paints with solar absorptance between 0.95 and 0.98 which have withstood a prescreening test of 24 hours at 500°C in air.

- J. Dickson indicated that Engelhard Industries has developed a silver matrix copper oxide film on stainless steel with an α_S of 0.9 and ε of 0.1-0.2 at 500°C. Discussion addressed the costs of metal matrix films.

- R. Blickensderfer reported on oxynitride carbides of group IV metals. α/ε values as high as 40 have been observed with α up to 0.9. Potential flat plate applications were discussed with the caveat that the stability of these coatings in air is poor.

- L. Wen and R. Caputo have performed a systems analysis of a point focus distributed solar power conversion system. The effect of a absorber coating on the receiver was analyzed in addition to other parameters. Although limited benefit is expected under design conditions, coatings may improve systems performance during off-design insolation and load situations. A selective coating will tend to moderate the operating temperature sensitivity of system performance.

- M. Adams presented a methodology developed at JPL for assessing the benefits of absorber coatings over a wide range of possible system configurations. The true benefit to an operating system is site and system specific: even though the benefit at a given operating point can be calculated the range of operating conditions must be used to "weight" the benefits obtained.

- A suggestion was made in discussion that a sacrifice in high α to achieve low ε may be an appropriate pursuit for the development of a cavity coating. It was further suggested that a "white" coating for cavity applications may be desirable to obtain a uniform flux distribution and reduce risk of boiler burnout.

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Development of Selective Absorber Coatings for Solar Thermal Power Systems

Louis Melamed
DOE/HQ

1.0 Introduction

The Solar Thermal Power Systems group (STPS) within the Division of Solar Technology has the responsibility of developing and demonstrating the technology of generating electricity, generally by the use of turbines powered by high temperature working fluids. This requirement has resulted in the support of a wide spectrum of system concepts including central receiver, dispersed power, total energy, and irrigation. These systems have different design philosophical end goals, solar energy collection techniques, and user requirements. Despite the wide diversity of collector sophistication, tracking requirements, and energy transport unique to each system, a common goal is the efficient thermal conversion and transfer of the collected solar energy to useful working fluid.

To perform efficient conversion, the receiver placed at the focus of the collector generally requires a surface with engineered optical properties. These properties may be summarized as consisting of a very high absorptivity for the solar spectrum out to ca. 2 μm, followed by a sharp change to high reflectivity beyond 2 μm. The advantages of a high solar absorptance are obvious; the requirements of a high I.R. reflectance provides a low surface emittance at operational temperatures thereby inhibiting black body reradiation losses. There are no known materials which simultaneously possess these two spectrally selective properties, and the present DOE coatings program is an attempt to develop artificial materials, composites, etc., which will be superior in performance to the (naturally) oxidized steel surfaces of typical receiver designs.

1.1 Central Receiver

A solar energy receiver located on a tower several hundred meters high is at the focal point of an artifact "paraboloid of revolution" consisting of several thousand individual two-axis tracking heliostats (Fig. 1, 2). Typical heliostats are nearly plane and may measure 6 meters in diameter.

The tower may be located either at the center of the heliostat field or at the north extremity of the field; in the latter case the heliostat array comprises an off-axis paraboloid. Typical solar concentration at the receiver ranges from about 200 : 1 to about 2000 : 1. Typical operating temperatures are ∿500°C.

1.2 Distributed Collector

The distinguishing feature of this approach is that unlike the "point" focus Central Receiver, the thermal energy collected from individual modules is manifolded and transported to a removed site for electricity generation and distribution. A typical collector frequently specified is the parabolic trough array usually oriented E-W.

Solar concentration is approximately 40 : 1; operating temperature is about 300°C. The array is built up from individual modules assembled in either series or parallel fashion. Typical basic module dimensions are approximately 2 meters wide and 5 meters long (Fig. 3).

Unlike the Central Receiver which has a maximum practical size, the Distributed Collector is basically a modular system which can be increased or decreased in capacity over a wide range without a significant sacrifice in performance efficiency. The efficient operation of either system concept will be sensitive to how much of the incident solar energy is transferred as heat to the circulating working fluid. The receiving surface at the collector focus should therefore have as high a solar absorptance as possible while minimizing thermal losses. Of the three loss mechanisms, conduction, convection, and radiation, only the last will be considered in this paper. The selective coating problem may then be stated as follows: how may a surface be designed to have very high absorptance, α , in the solar spectrum and a low emissivity, ε , in the black body emission spectrum.

2.0 Characterization; Theory of Coatings

2.1 Background

Spectrally selective surfaces were first proposed by Tabor in 1955.(1) Shaffer's (2) calculations showed that selective thermal devices are capable of very high overall efficiencies. The advantages of spectrally selective surfaces also were shown by theoretical considerations of Tabor,(3) Hibbard,(4) Liebert and Hibbard,(5) and Edwards.(6) Tabor conceived of a selective surface consisting of two layers. The outer layer has high solar absorptance but is transparent to long wavelengths. The underlying layer is highly reflective. The combination provides good solar absorptance while being a poor emitter of longwave thermal radiation. Layered composites of this type are known as absorber stacks, and their performance depends upon the properties of each layer. Semi-conductors have the general characteristics of shortwave absorptance and longwave transparency while metals such as silver, copper, aluminum, and gold have excellent longwave reflectance.

2.2 Elementary Theory

The need for a selective surface is illustrated in Fig. (4) which gives the spectral profiles of the solar flux incident at the earth's surface and the black body re-emission for bodies at temperatures of 300°K, 550°K, and 1000°K.

The blackbody radiation occurs predominantly at wavelengths longer than 2 μm, while the solar flux is almost entirely below this wavelength. A surface with the optical characteristics of an ideal absorber, Fig. (5), will absorb the solar flux efficiently and simultaneously suppress reradiation losses because of its low emittance in the infrared. This spectrally selective surface would be an efficient solar-thermal converter.

An ultimate limitation on any selective absorber is the energy overlap region between the incident solar spectrum and the re-emission spectrum. With increasing temperatures, the overlap region grows. At temperatures up to $\sim$ 400°C (773°K) the overlap is ignorable as may be seen from Fig. (4). At temperatures higher than the ca. 500°C contemplated for the Central Receiver power plant, this restriction grows stronger. Thus, selective coatings will be useful primarily in the low to moderate temperature regimes (up to $\approx$ 400°C). An analysis has been performed by Gurev et al.(7) and is presented in Fig. (6) which shows the effect on the maximum attainable fluid temperature achievable by reducing the emittance from 1.0 (solid lines) to 0.05 (dashed line).

The "absorption of merit, is defined as,

$$\alpha_m = \frac{Q}{X\tau\phi} = \frac{\text{Heat flux rate into working fluid}}{\text{Solar flux incident on absorber}}$$

$$\text{or } \alpha_m = \alpha - \frac{\varepsilon\sigma T^4}{X\tau\phi} \qquad (1)$$

= solar absorptance less the fraction reradiated when conduction and convection losses are ignored where,

α = solar absorptance
ε = total hemispherical emittance
σ = Boltzmann constant
T = absorber temperature (°K)
X = collector concentration ratio
τ = fraction of intercepted energy transferred through optical system to absorber surface
ϕ = incident solar flux

To prepare Fig. (6), it was assumed that

$\alpha \cong 1$
$\tau \cong 1$
$\phi = 10^3$ W/M^2

From Fig. (6) it may be seen that for $\alpha_m = 0.7$ (70 percent energy extraction), a black body receiver with $\varepsilon = 1$ and operating in a 10x concentration ratio collector, the maximum temperature of the working fluid $\cong$ 225°C. Upon reducing ε to 0.05 (dashed line) the achievable operating temperature $\cong$ 725°C. From Fig. (6) it may also be seen that a receiver with an $\varepsilon = 0.05$ and a 10x concentration ratio will achieve the same operating temperature of 725°C (at $\alpha_m = 0.7$) as will a receiver with $\varepsilon = 1.0$ operating in a 200x concentration ratio collector. There are many ways in which the dependence of α_m on the parameters in equation (1) may be depicted. Thus, Fig. 6a shows perhaps more clearly the sensitivity of α_m to ε for a more realistic $\alpha = 0.95$, at a fixed temperature of 873°K (500°C) and where the system concentration ratio is varied from 60 ($\approx$ upper limit for a parabolic trough) to 2000 ($\approx$ upper limit for a central receiver). The $X = 250$ line is approximately representative of the parameters for the 10 MW$_e$ pilot plant to be constructed at Barstow, California, using the MDAC 17 meter high external receiver. However, the reader is cautioned that conductive-convective losses have not been displayed. Hence, the actual α_m anticipated for the pilot plant will be substantially lower than indicated in Fig. 6A.

Considerable attention has been given in the literature to maximizing the ratio of α/ε as a measure of receiver performance. If performance is judged by this ratio, lowering ε becomes increasingly important as $\varepsilon \to 0$. However, studies by McCulloch(8) and others show that in a practical system design, a high α has a greater impact on collector efficiency than the α/ε ratio considered alone. The results of McCulloch's study are presented in Fig. (7) and reveal that the improvement in performance per unit decrease in ε is not a strong function of ε; i.e., changing ε from 0.6 to 0.5 is approximately equal in effect to changing it from 0.2 to 0.1. Furthermore, collector improvements by incrementally increasing absorptivity are more effective and probably much less difficult than corresponding decreases in emissivity, e.g., a 0.05 increase in absorptivity achieves the same result as decreasing the emissivity by 0.02. These facts may be obscured by considering the data of Fig. (7) in terms of the ratio of absorptivity to emissivity only.

2.3 Desirable Properties of Candidate Coatings

The effective collection and utilization of the incident solar flux requires collector surfaces with the following optical and physical properties:

1. The absorbing surface must have maximum absorption over the solar spectrum of approximately 0.35-2.2 μm.

2. The collector surfaces must afford maximum suppression of blackbody thermal reradiation. (low emissivity)

3. The spectral transition between the regions of high absorption and low thermal emittance should be as sharp as possible.

4. Finally, both optical and physical properties of the absorber surface must remain stable under long-term operation at elevated temperature and under repeated thermal cycling. Material diffusion, solid phase reactions, chemical reactions, oxidation, mechanical stresses, weathering, and the temperature dependence of the optical properties of the constituent materials must all be carefully considered.

From a practical point of view, these spectrally selective surfaces should be easily manufactured. In addition, the completed absorber must be economical in terms of production costs and in terms of the total energy used during manufacture. Several methods can be utilized to obtain the required spectral selectivity of the absorber surface. Each method exploits a different physical principle or a combination of principles. The first, and ideal solution, is to find or create a single material whose intrinsic properties yield the desired spectral characteristics. At present, no such material is known although some materials such as HfC, LaB_6 and SiP_2 possess spectral properties that are a first approximation to those desired.(9) More recently, partially oxidized Mo films have been shown to exhibit some spectral selectivity. Thus, a Mo-MoO_3 thin film deposited on a SiO_2 substrate and protected from oxidation by an SiO_2 thin overlayer has demonstrated an α = 0.75 at air mass 2 and an ε = 0.06 at 500°C. (Private communication from University of Arizona)

3.0 State-of-the Art Coatings

Several coatings have been developed in recent years to achieve selective absorption. These materials are characterized by having a fairly high solar absorptance and a moderate to low emittance and include black chromium, black nickel, "AMA" and semi-conductor paints. These will be described briefly and characterized.

3.1 Black Chromium

Probably the most successful coating is "black chromium." This is a variable composition Cr-Cr_2O_3 electrolytically deposited coating about 1800 Å thick (10, 11, 12) and is generally deposited on a sulfamate nickel film (to provide high near IR reflectance) which is in turn deposited on the steel collector substrate. Typical values are α = 0.96, ε = 0.06 with useful operating temperatures up to about 350°C. Limited life-time high-temperature studies by Masterson et al.(49) at the University of Arizona on black chromium films supplied from two independent sources show, however, that these values may deteriorate with increasing temperature. For one supplier, after 15 hours of on-off cycling at 550°C α dropped to 0.88 and ε rose to 0.36. The other coating sample revealed a drop of α to 0.84 and a rise in ε to 0.34 under the same conditions. On the other hand, when the maximum temperature was 350°C, there was little or no degradation of performance for either sample. To achieve a high solar absorptance and a low thermal emittance, the thickness must be carefully controlled. This is accomplished by careful monitoring of plating time and current density.(13) Mattox claims that a black chrome coating 1500 - 1800 Å thick is optimum for high α with a low ε. This thickness is obtained with a current density of 0.19-0.22 amp/cm^2 for 2-4 minutes in a fresh black chrome bath at 24°C prepared and used according to manufacturers specifications. Film properties will change with bath "break-in-time," bath use, and with the addition of replenishers. Exact plating conditions must be determined for each plating geometry. Unfortunately, ε is more sensitive to plating conditions than is α. This means that plating conditions must be established using ε measurements which are more difficult to make than are α measurements. Considerable difficulty has been encountered in the past in obtaining high α low ε black chrome coatings from commercial suppliers because of lack of good process specifications and/or process controls. These problems are exacerbated by the need to perform in situ measurements on the α, ε performance as the plating progresses. This will result in the need to train the electroplating industry in the use of scientific apparatus in their plants or perhaps to turn the "art" of producing optimum coatings into a "science." One advantage of black chromium is that the high solar absorptance of 0.96 is maintained up to angles of 50° off normal incidence. Fig. (8) (48) compares the absorptive properties of electrolytically deposited black nickel and black chrome with an idealized solar absorber.

3.2 Black Nickel

Electroplated black nickel coatings have been extensively reported and have been shown to have good solar selective properties.(14-18) Pettit and Sowell (11) have studied the properties of this material as deposited on bright nickel electroplated in turn on a steel substrate. α in the range of 0.8 to 0.96 and ε (100°C) of about 0.07 were reported. Unfortunately, black nickel has only fair environmental resistance. It is not useful above about 250°C and does not resist humidity well.(20) Black nickel deteriorates even more rapidly at high temperature life-time cycling than does black chromium.(13)

3.3 AMA Coatings

"AMA" selective absorbers (20, 21) are multi-layer vacuum deposited coatings consisting typically of $\sim$ 600Å Al_2O_3 on $\sim$ 300Å MoO_x on $\sim$ 600Å Al_2O_3 on $\sim$ 6000Å Mo onto the stainless steel substrate. The thick Mo layer acts as the high IR reflector with the other three layers acting as an interference filter to provide high visible light absorptance. An α of about 0.85 and an ε of about 0.1 have been reported.(22) Although this four-layer stack has performed well, the performance may degrade depending on the particular stainless steel used as the substrate. Degradation results from diffusion of oxygen and carbon from the stainless into the stack. Type 321 and 347 S.S. have proven superior in this regard to type 304. A nickel intermediate layer between the Mo and S.S. has been used with varying success to limit the diffusion. A promising and simple technique is to pretreat the substrate at $\sim$700°C. This produces an anti-diffusion Cr_2O_3 layer. Operation up to $\sim$600°C is possible if the substrate is carefully chosen. However, two hours at 850°C will completely destroy the coating. The AMA coating has the disadvantage characteristic of interference films of requiring precise control of film thickness for satisfactory performance. In addition, the vacuum deposition requirement adds to the cost and complexity. The rather substantial molybdenum requirement could pose a materials problems for large scale applications. It does not seem that AMA would be suited to large volume production requirements. Finally, an inherent disadvantage of an interference-film device, be it absorber, anti-reflection coating, etc., is the wavelength shift (to shorter λ) that results for non-normal angles of incidence. This is a very general conclusion and does not depend on the particular film employed.

3.4 Selective Paints

Semi-conductor paints consisting of a high temperature silicone binder mixed with very small particles of PbS, Ge, or Si have been described in the literature.(11,16,23,24) H. Mar(44) has compiled data on the performance of a candidate list of pigments and binders for selective black paints. A paint has the intrinsic advantage of being easily applied in the field either for repair or initial installation. The solar selective properties rely on the intrinsic energy band gap structure of the pigment. Thus, for PbS, Ge, and Si, the corresponding transition wavelengths between high solar absorptance and transparency occur at about 3 μm, 1.8 μm and 1.1 μm, respectively. Although the solar absorptance at normal incidence of all paints was high (PbS = 0.96, Ge = 0.91, Si = 0.83), the emittance at 300°C varied from 0.7 to 0.9. Mar(24) has reported on a very thin (1.3 μm) paint film which had an $\alpha = 0.92$ and an $\varepsilon = 0.36$. Normal paint film thicknesses are about 40 μm. Of the three pigments, PbS has received the most study although Ge which becomes transparent at 1.8 μm would seem to provide the best a priori performance. The high emittances of these paints are due to the thicknesses of the binders used. Thus, in one instance, increasing the paint thickness from 7 μm to

50 μm increased the emittance from 0.2 to 0.7 at 300°C for PbS paint. Such paints are useful up to about 300°C in air. Higher temperature operation should be possible for typical distributed collector applications where the coated collector is located inside of evacuated concentric U.V.-opaque glass tubes. However, these paints are not suitable as solar selective coatings unless the amount of silicone binder can be reduced or a low emittance binder can be found.

3.5 Other Coatings; Materials; Techniques

In addition to the coatings described, many other materials have been suggested in the literature.

These have included(23) chemically blackened metals such as Ebanol-C treated copper (forms a CuO-Cu_2O layer), Ebanol-S treated steel, Ebanol-SS treated stainless steels, and NH_4S treated copper (forms a Cu_2S layer).

Techniques employing textural effects and/or multiple scattering have been suggested to achieve spectral selectivity. Materials that can be deposited as a dense matte of whiskers and rods often have high absorption in the solar spectrum due to multiple reflections and light trapping effects. In the infrared where the wavelength of light is longer than the size of the surface features, the surfaces appear quite smooth and highly reflecting with a consequent reduction of the infrared emittance. This effect has been used with rhenium oxide(25), dendritic tungsten,(26,41) and lead sulphide on aluminum.(27) Other examples of reflective-absorbing surfaces are wire mesh surfaces,(28,42,43) V-grooved surfaces,(29) and the rough surfaces formed by various deposition, chemical conversion, and chemical etching techniques.(45) A weakness of such surface morphology absorbers is the strong dependence of absorptivity on the angle-of-incidence of the incident radiation. In a somewhat analogous manner, dispersions of metallic or absorbing particles in a dielectric medium can provide absorption at shorter wavelengths by multiple scattering among particles, while retaining higher reflectance at longer wavelengths.(30) (See Section 4.4.) Mie scattering films have been suggested as selective absorbers. Such films use finely divided particles to give forward scattering and multiple internal reflections to absorb radiation. The gold smokes are good examples of this effect. A problem with the smokes is their poor thermal transport properties. If the particles are in a matrix, the thermal transport properties are improved. Example of this system are tin particles in a MgF_2 matrix,(32,33) the semi-conductor paints previously discussed, and some of the electrodeposited systems where metal particles are codeposited with an oxide matrix.(34) Generally, it is found that the coating system with the best solar absorbing properties utilizes several of these effects. Examples of this are the control of the coating thickness to minimize volume emittance and to obtain destructive interference of radiation reflected at the interface, control of the surface morphology to increase light trapping, and the inclusion of fine particles in the absorbing matrix to take advantage of the Mie effect. A desirable property of absorbing surfaces is that the absorptivity should be independent of the angle of incidence up to about 60°. Other important aspects of the coatings are their stability under service conditions which may include: elevated temperature, temperature cycling, thermal shock, air exposure, ultraviolet radiation, handling, and moisture. Several coatings systems, e.g., PbS paints, have been found to be unstable in the presence of ultraviolet radiation and oxygen. Failure may occur from loss of adhesion, changes in composition, diffusion between layers, and changes in optical properties. Table I prepared from references (48) and (12) list the properties of some of the coatings discussed above.

4.0 Overview of Current Coatings Research

This section is not intended to be an exhaustive review of current coatings research but merely to highlight some more promising areas. A common feature is the use of semi-conductors for the absorbing medium. The basic optical properties that make such materials promising, high solar absorptance followed by a rather sharp transition to transparency in the near IR, were discussed briefly in Section 3.4.

4.1 Bulk Semi-Conductor/Metal Stack

A silicon-silver selective absorber "stack" has been under continuous development by Seraphin et al.(19,35,7,25) at the University of Arizona for the past three years and will be described in some detail. Unlike the coatings described in the previous section, the U. of A. composite is capable of operation at temperatures up to about 800°C. A silicon thin film absorber is deposited by chemical vapor deposition (CVD) on a thin film silver reflector. This optical stack is fabricated at temperatures in excess of 800°C, and the CVD technology is amenable to large scale production in a flow-through system. At 500°C the Si-Ag system has typical absorptance and normal emittance values of 0.75 and 0.06, respectively. This absorptance is far too low to be acceptable to system designers. Samples have been fabricated which maintained their high spectral selectivity after 2000 thermal cycles between 150°C and 450°C, and after 100 hours at 600°C. Further studies underway indicate that the solar absorptance can be improved to better than 0.85 by employing a Si-Ge multilayer absorber and that the operating range of the stacks can potentially be raised to the 800-900°C range by employing a refractory metal thin film reflector such as tungsten or molybdenum in place of silver. A cross-section view of the stack is presented in Fig. (9).

Layer 1: The silicon absorber is deposited to a thickness of 1.5 to 1.7 μm by CVD. The silicon layer thus formed absorbs strongly at wavelengths below 0.75 μm, and is sufficiently low in free carriers to be transparent in the near infrared when measured at 500°C. Because of silicon's inherently high index of refraction, its reflectivity in the visible range is quite high (about 35 percent).

Layer 2: To obviate this reflection problem SiO_2 and Si_3N_4 are deposited by CVD (at 800°C) over the Si as a quarter wave antireflecting (AR) coating. The thickness is selected to minimize the reflected light at wavelengths near the peak of the solar spectrum (about 0.6 μm).

Layer 3: In the IR range, the silver reflector presents a low emittance surface and suppresses reradiation losses. Evaporated Ag has the highest known IR reflectance of any metal, but it has the bothersome tendency to agglomerate rapidly at temperatures above 200-300°C.

Layer 4: To prevent this agglomeration during the high temperature fabrication processes, or during service life, the Ag film is overcoated with a thin (100-200Å) chromium oxide stabilizer film. The chromium oxide stabilizes the silver film against agglomeration and does not contribute noticeably to the IR emissivity of the stack.

Layer 5: A chromium oxide barrier layer is formed on the surface of the substrate either by thermally growing a native-oxide or by reactive deposition of a chromium oxide layer. This layer both improves the adhesion of the Ag and impedes any metallurgical action between the Ag and the ferrous substrate.

Current research is underway to simplify the stack by replacing the silver and its anti-agglomeration layers of chromium oxide with the refractory metals, tungsten and molybdenum. However, this variation will succeed only if a deposition technique is developed which can provide a high IR reflectance for the refractories. One outstanding advantage of the U. of A. approach is the amenability of the CVD process to successive and continuous deposition of the several stack elements at room temperature and pressure. Thus, long tubing may be readily coated without the need for retaining vacuum chambers. An inherent problem in the use of a semi-conductor absorber is the high refractive index for visible light resulting in high Fresnel reflection losses. These losses are given by the familiar expression

$$\%R = \frac{(n-1)^2}{(n+1)^2}$$

for radiation at normal incidence to a surface having a relative index n. Thus, for Si, PbS, and Ge, the indices for visible light are in the range of about 3.6 to 4.1 with corresponding reflection losses of about 32 percent to 37 percent. It is evident that a high intrinsic absorptivity is of little value unless means are devised to reduce reflection losses. One elaborate and usually expensive technique was mentioned in the previous section--an anti-reflection quarter-wave interference coating. Numerous other techniques have been discussed in the literature to circumvent the high reflection losses of Si or Ge. These include amorphous semi-conductors, graded index semi-conductors, and granulated semi-conductors.

4.2 Amorphous Semi-Conductors

Attempts are underway to improve the net absorptance of crystalline silicon films by developing the technique of depositing textured amorphous silicon onto suitable metal substrates. There is evidence(36) that amorphous silicon deposited with "micro-voids" in a film $\sim$ 1 μm thick can be prepared with a room temperature absorption coefficient much larger than is the case for crystalline silicon (Fig. 10). In addition, it may be possible to shift the normal absorption edge (1.1 ev energy band gap) to longer wavelengths.

Mattox and Kominiak(47) observe that the absorptivity of germanium films can be increased greatly by gas evaporation in a 20 mTorr Argon atmosphere due, apparently, to changes in film surface morphology. The feasibility of extending such desirable behavior to realistic operating temperatures for a selective coating ($\sim$ 400°C) is under study. It is hoped to reduce the high visible light reflection losses by depositing the silicon with suitably sized micro-pores or nodules that will trap the visible wavelengths thus reducing the Fresnel losses, while remaining transparent for the longer IR wavelengths. One possibility is the direct deposition of the amorphous material onto a micro-roughened metal substrate. If the twin advantages of a higher visible light absorption constant and the band gap shift can be economically achieved, very low cost selective absorbers should be possible. This is especially true if cheap metallurgical grade silicon were used costing about $1 per kilogram. In this case the material cost for a 1 μm coating thickness would be approximately 0.24 cents per square meter of absorber.

4.3 Graded Index Semi-Conductors

A well known technique for optical "impedance-matching" useful in minimizing losses in transmitting light from a low index medium (air, $n_1 \cong 1$) to a high index medium such as silicon, where $n_2 \cong 4$, is to provide an intermediate surface with an index n' where ideally n' is the geometric mean between n_1 and n_2. Thus $(n')^2 = n_1 n_2$ or $n'=2$. Still better would be to provide two surfaces of different n, each providing a geometric mean between its neighboring layers. In the limit one may conceive of an infinite number of layers providing a smooth transition from n=1 to n=4. A simple way of achieving this condition is to deposit a material with the property that n varies uniformly from about 1.5 to 4 from the outer to the inner surface. One way of achieving this goal is to apply the Maxwell-Garnet theory of particulate mixtures. The theory predicts that a mixture of small particles (e.g., a semi-conductor dispersed in a dielectric) will have optical properties intermediate between those of the bulk semi-conductor and bulk dielectric depending on particle size and relative concentration. Programmed co-deposition of the two materials could, in principle, achieve a single film graded in composition from 100% dielectric at the outer surface to 100% semi-conductor in the interior.

4.3 Particulate Metal-Dielectric Composites

Composite materials consisting of small metal particles suspended in a dielectric medium have been proposed as selective absorbers by Sievers(37) and Austin.(38) Such artificial dielectrics are known by many names including colloids, (e.g., gold particles in a glass matrix to form ruby glass) cermets, aggregated films and granular films. Baumeister(39) has published a brief review of the history of artificial dielectrics. Such materials have optical properties very different from the bulk metal. Sievers has predicted the optical properties of such materials based on a modification of Maxwell-Garnet(40) theory. Appropriate composites may be designed to have strong absorption in the visible spectrum (resulting from the submicroscopic texture) and high reflectance in the near infrared due to the metal-like conductivity at the longer wavelengths. Suggested preparation techniques include plasma spraying and vacuum evaporation. In the latter case, simultaneous evaporation of the metal and dielectric occur onto a single substrate. Typical material combinations are chromium and SiO_2, chromium and magnesium oxide, titanium and aluminum oxide, and titanium and magnesium oxide. Among the advantages of a particulate composite selective coating are:

a) a high angle of incidence possible,

b) precise tailoring of optical properties are theoretically possible,

c) high temperature capability.

The anticipated disadvantages include:

a) the necessity for vacuum deposition,

b) lack of compatibility with mass production techniques,

c) high cost.

5.0 Conclusions

It is convenient to summarize the status and goals of selective absorber technology in terms of three temperature regimes. These are ∿ 300°C (Distributed Collector) ∿ 500°C (Central Receiver) and 700 → 1000°C. The latter has not been discussed in this paper and is a future area of interest for advanced concepts such as Brayton cycles employing helium or air. Its priority is low at present.

For all temperature regimes and all possible system configurations, a high absorptance remains the primary goal of any candidate absorber. The importance of this goal can not be overstated since system studies consistently demonstrate that the heliostat field represents about one-half of typical solar power plant costs, and system performance directly relates to receiver absorptivity. A secondary goal is a low emittance; however, the significance of a "low" emittance will vary with the particular system. In general as the concentration ratio increases, system efficiency becomes less dependent on the emissivity. Thus, although Central Receivers (CR) usually operate at a higher temperature than do Distributed Collectors (DC), their concentration ratio is also 10 to 50 times higher. Thus, despite the higher T^4-dependent radiation losses, the overall sensitivity to a low emissivity is about 3 to 15 times greater for the DC regime than for the CR regime.

$$\left(\frac{773°K^4}{5/3°K}\right) \div 30 \simeq 0.11$$

Conceptually this is equivalent to saying that the higher concentration ratios imply smaller receiver areas; even at unit emissivity, a small radiating area reradiates a small net quantity of energy. The needs of the DC regime are, at present, adequately met by the use of black chrome which performs well to ∿350°C although surrogate materials will be developed. The principal draw back of black chrome is the lack of understanding of how to consistently and reliably produce optimum coatings; i.e., to minimize ε without degrading α. The deposition parameters of black chrome will require further study before its use can be made low-cost. If successful, the "art" of producing optimum black chrome coatings would become a science, and consistent coatings could be easily reproduced by industrial personnel. Additional selective absorber candidates that need investigation for the DC regime would include paints with low-emissivity binders and a better tailoring of the semi-conductor pigments to match the solar spectrum. The requirements of the CR regime are somewhat variable due to the large variation in receiver geometry employed. These vary from external cylinders, exposed to air, to quasi-black body configurations consisting of a box-like receiver with a relatively small entrance aperture. In the former case black body radiation is uninhibited; in the latter, losses are effectively controlled by utilizing a small entrance aperture. In the limiting case, no selective coating is needed since the resultant geometry approaches a classical radiator no matter what the inner absorbing walls are. Practical receivers, present and future, will lie between these two extremes and justify continuing research in this temperature regime. The semi-conductor-metal sandwich absorbers such as Si-Ag are still in an early stage of development, and many problems remain. The most significant of these is achieving a higher net absorptance. Among the approaches suggested have been substituting germanium or other semi-conductors for the silicon resulting in an extension of the solar absorptance from 1.1 μm (Si) to 1.8 μm (Ge) or beyond but not too far beyond in order not to compromise control of the IR emissivity. Another obstacle to high absorptance is in the high, visible light Fresnel losses associated with high index materials. The use of antireflection coatings is costly and requires vacuum apparatus. Cheaper alternatives will be investigated to achieve a low surface reflectance. These will include investigations of the effects of surface morphology, substitution of amorphous silicon for crystal silicon, and graded index metal-dielectric deposits. One troublesome problem with amorphous silicon is in its tendency to re-crystallize at elevated temperatures.

Little work is proceeding in developing absorbers, selective or not, for the 700°C → 1000°C regime. Clearly, material survivability becomes crucial at these temperatures. On the reasonable assumption that a high operating temperature will require a high concentration ratio, perhaps in excess of 1500, initial needs will be to develop high absorptance materials without special regard to their emittance properties. Refractory oxides and nitrides have been suggested, as well as ceramic paints and ceramic enamels. Absorber selectivity will become less meaningful at elevated temperature for the further reason that the black body emission overlaps more of the visible spectrum. Initially high temperature absorbers will be developed for the 500°C to 800°C region with extension ultimately to $\sim$ 1000°C. Finally, a need exists to document the high temperature optical properties of candidate materials. Published figures on absorptance, reflectance, index of refraction, emittance, etc. are generally measured at room temperature and may be inaccurate at operating temperatures leading to false estimates of selective coatings performance.

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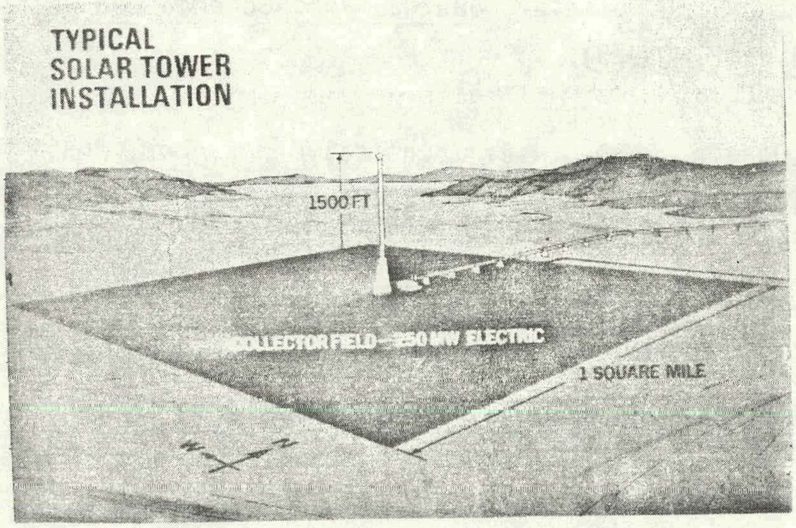

TYPICAL
SOLAR TOWER
INSTALLATION
1500 FT
COLLECTOR FIELD—250 MW ELECTRIC
1 SQUARE MILE
W
N

FIG. 2

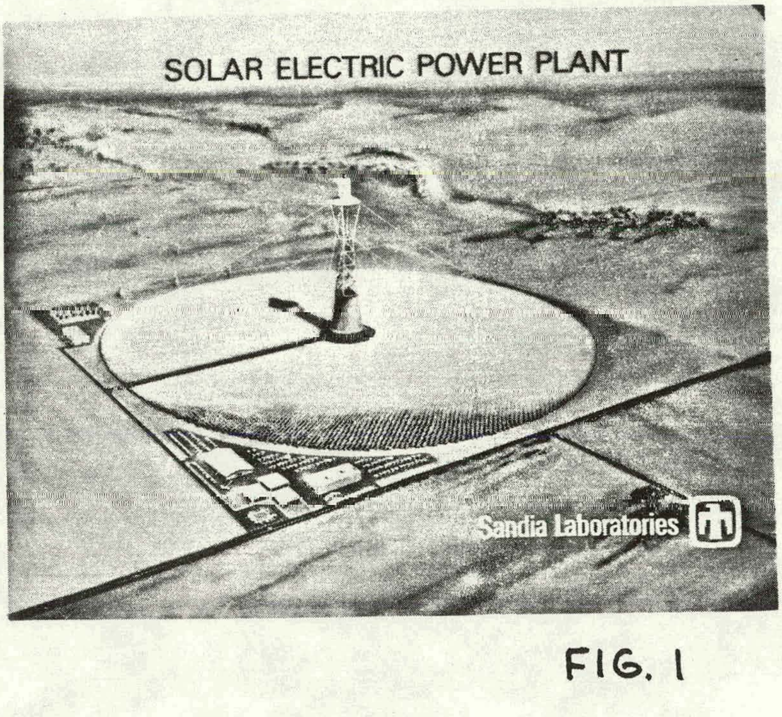
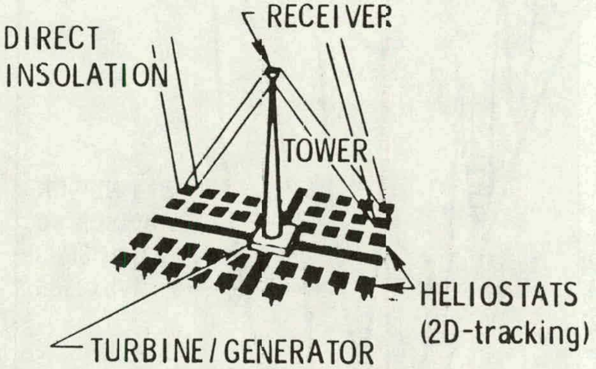
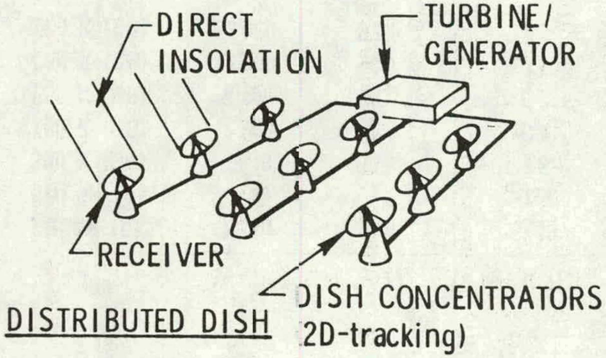

SOLAR ELECTRIC POWER PLANT
Sandia Laboratories

FIG. 1

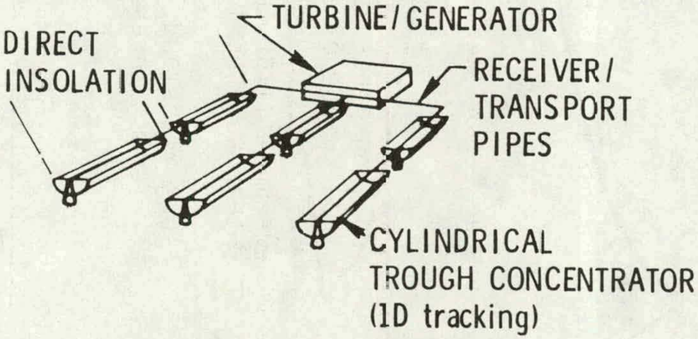
Typical Solar Thermal System Concepts



CENTRAL RECEIVER



DISTRIBUTED DISH



DISTRIBUTED TROUGH

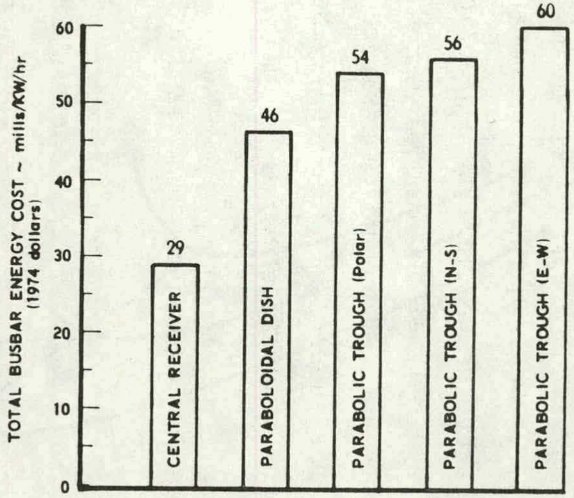
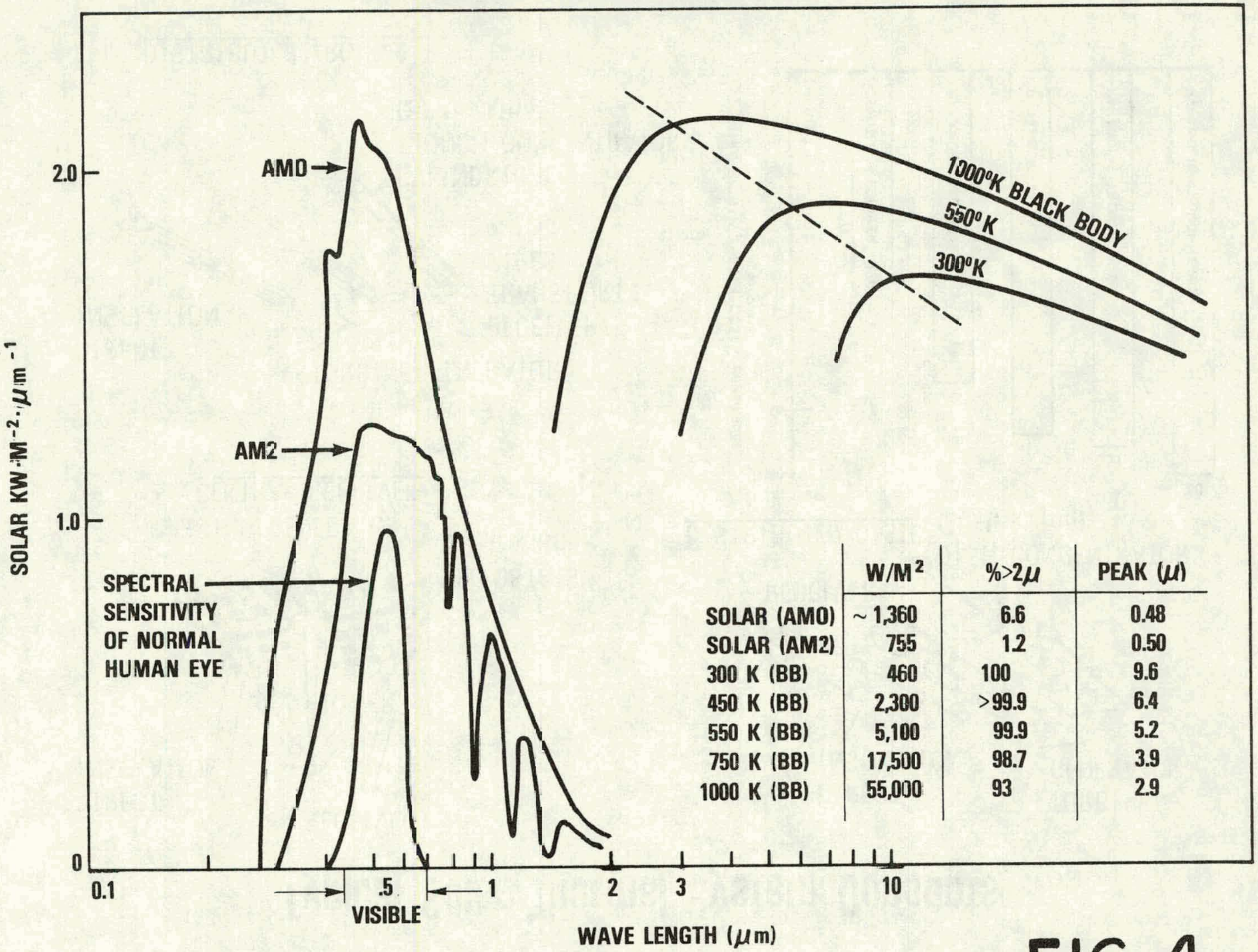


FIG. 3

COMPARISON OF SOLAR SPECTRUM AND BLACK BODY EMISSION ($\epsilon = 1$)



	W/M²	%>2μ	PEAK (μ)
SOLAR (AM0)	~ 1,360	6.6	0.48
SOLAR (AM2)	755	1.2	0.50
300 K (BB)	460	100	9.6
450 K (BB)	2,300	>99.9	6.4
550 K (BB)	5,100	99.9	5.2
750 K (BB)	17,500	98.7	3.9
1000 K (BB)	55,000	93	2.9

FIG. 4

OPTICAL PROPERTIES OF AN IDEAL SELECTIVE ABSORBER

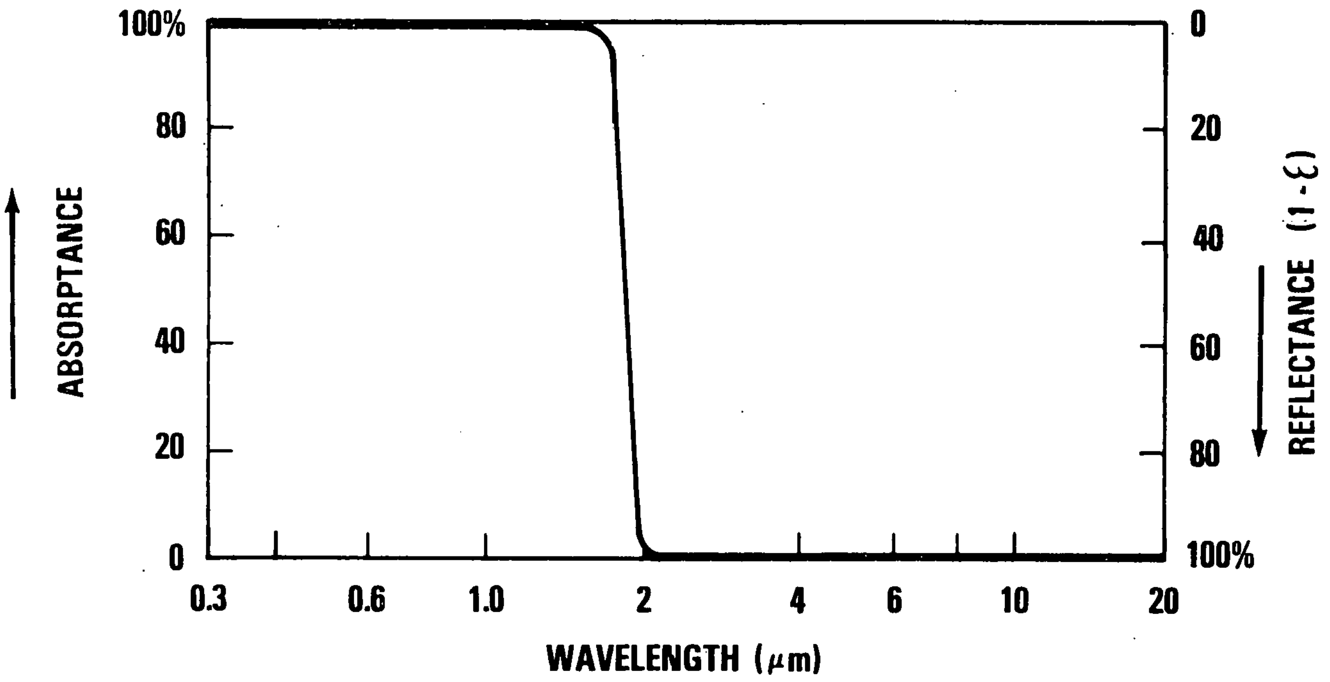
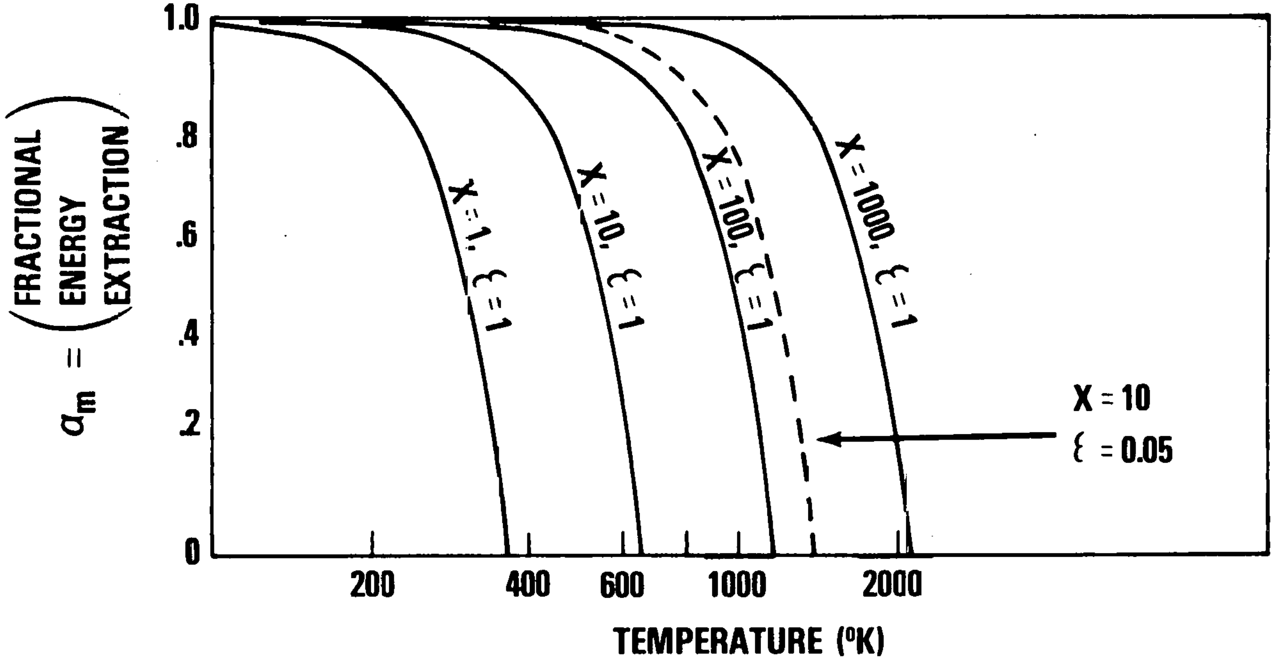


FIG. 5



MAXIMUM THEORETICAL ENERGY EXTRACTION VS. OPERATING TEMPERATURE FOR BLACK BODY ABSORPTION ($\alpha=1$ $\varepsilon=1$)

FIG. 6

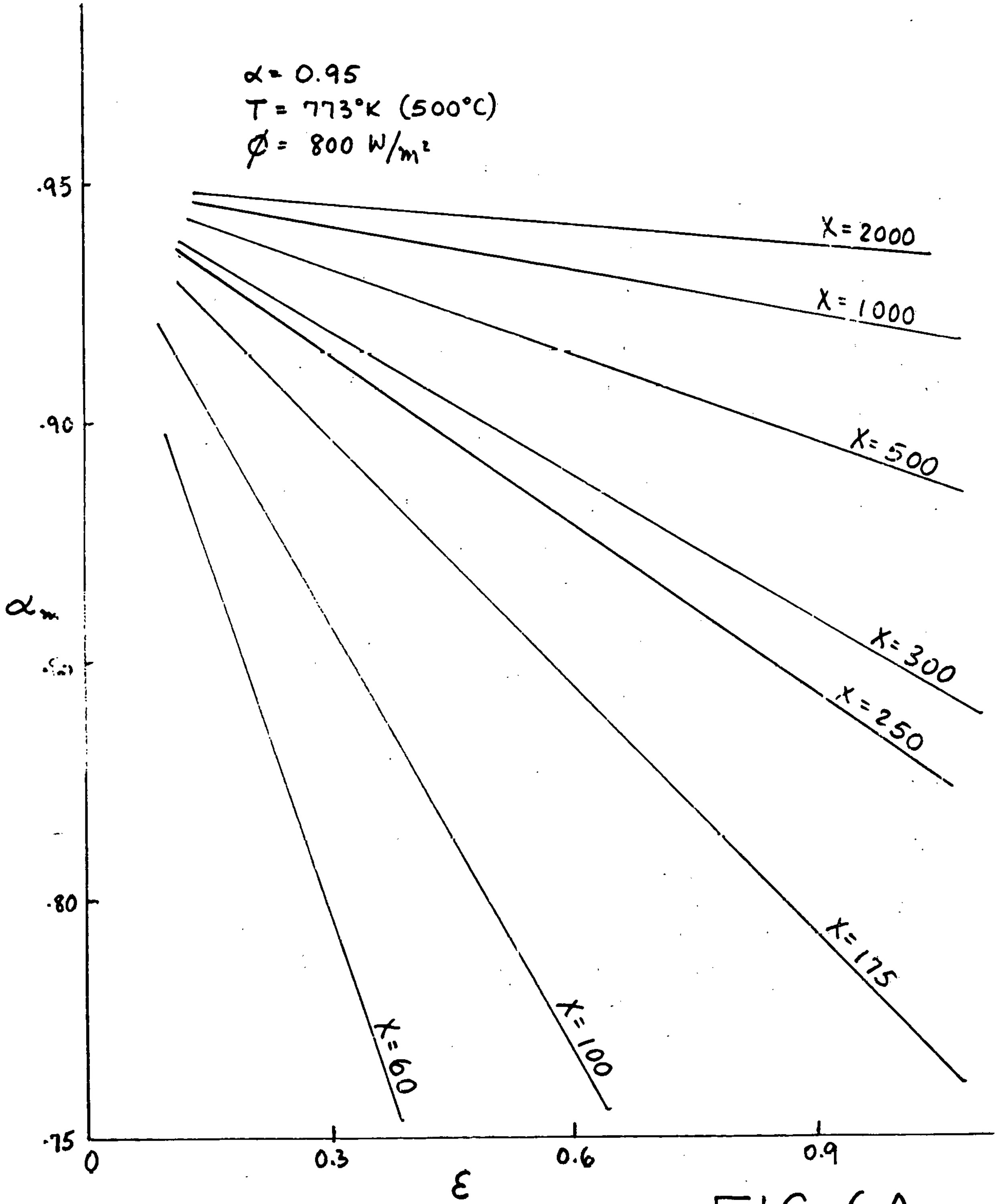

α = 0.95
T = 773°K (500°C)
Ø = 800 W/m²
.95
.90
α_m
.85
.80
.75
0
0.3
0.6
0.9
ε
X = 2000
X = 1000
X = 500
X = 300
X = 250
X = 175
X = 100
X = 60

FIG. 6A

SENSITIVITY OF COLLECTOR EFFICIENCY TO α, ε

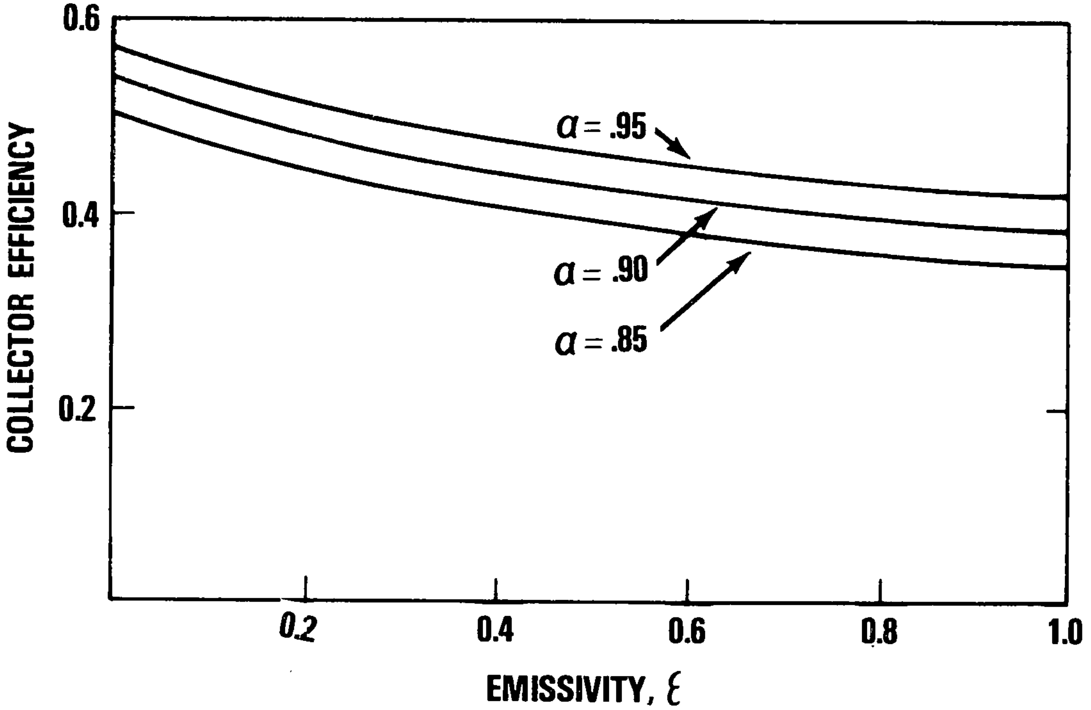


FIG. 7

RELATIVE COATINGS PERFORMANCE

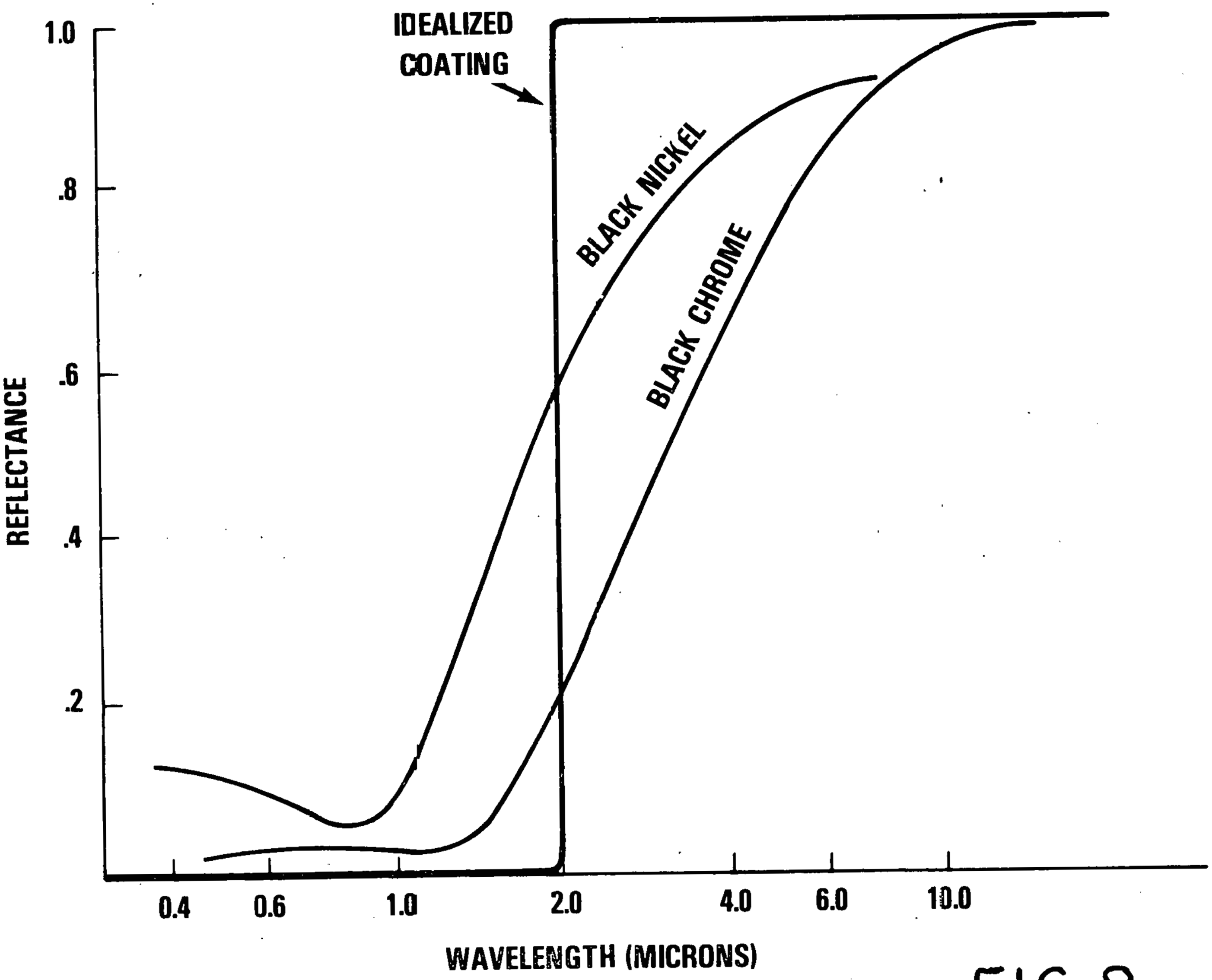


FIG. 8

Si-Ag SELECTIVE ABSORBER CROSS-SECTION

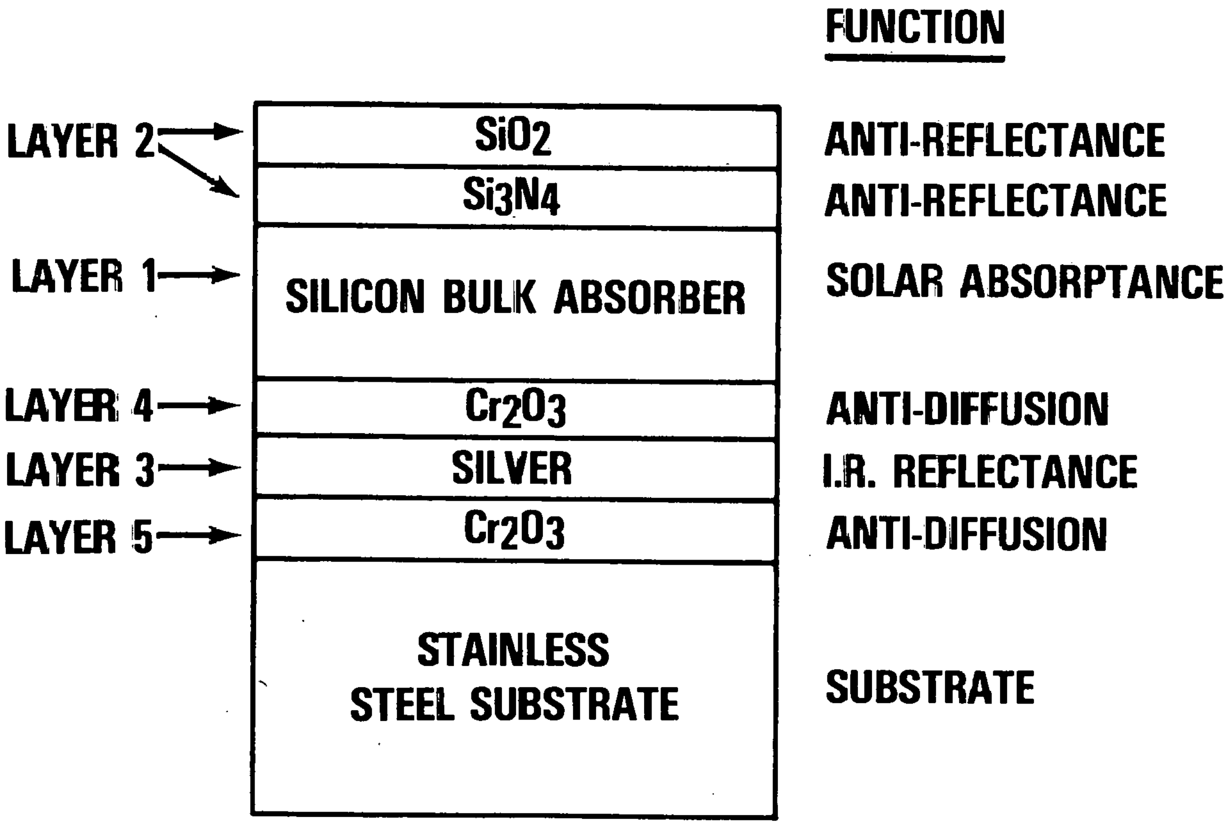


FIG. 9

SPECTRAL DEPENDENCE OF OPTICAL ABSORPTION CONSTANT FOR AMORPHOUS AND CRYSTALLINE SILICON FILMS ~ 1µ THICK

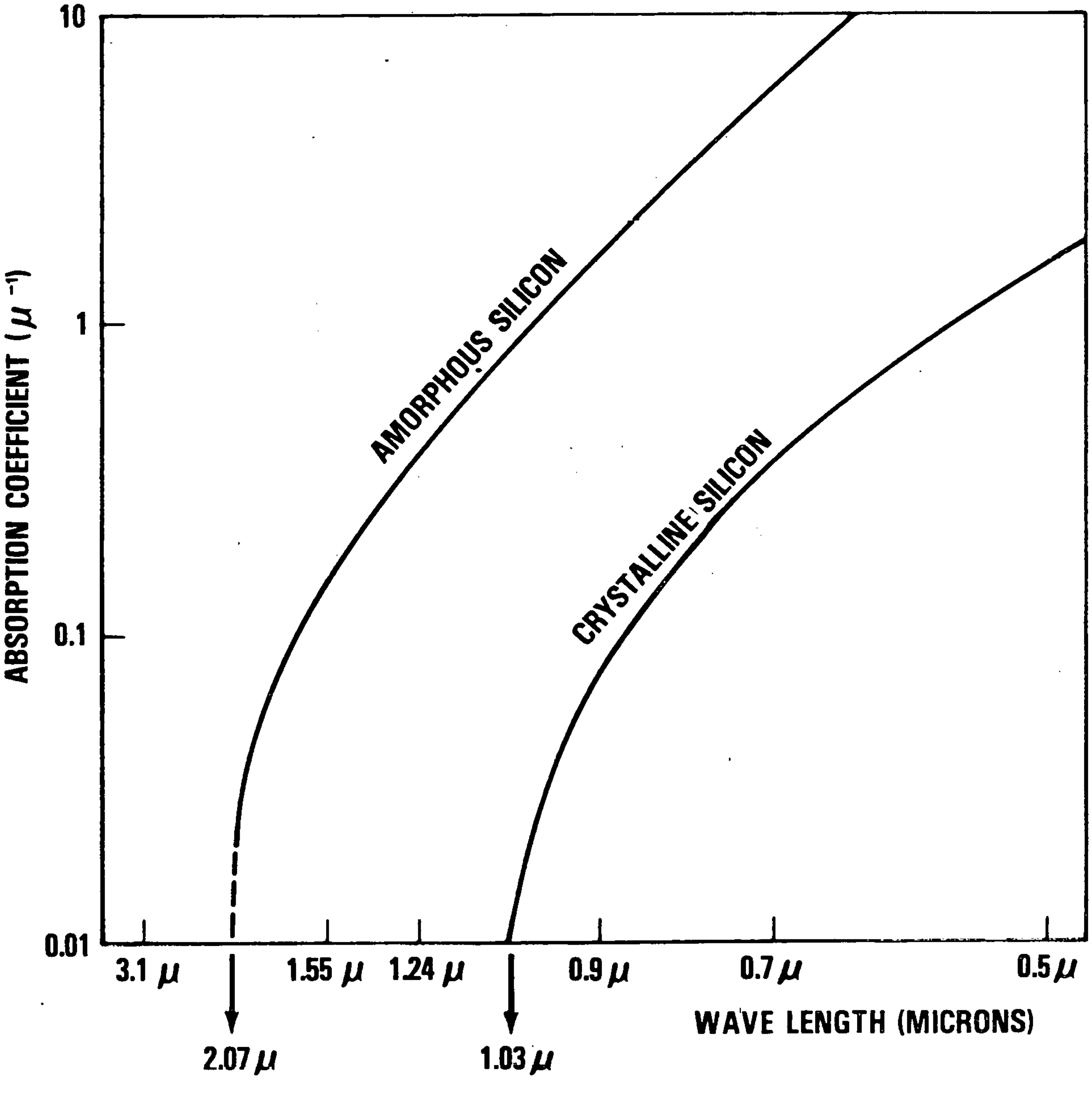


FIG. 10

TABLE I PROPERTIES OF SOME SELECTIVE COATINGS

MATERIAL	PREPARATION	α	ε (LOW T)	ε (HIGH T)	STABILITY
GOLD SMOKE	EVAPORATION	> .99	< 0.1		< 100°C
GERMANIUM	PAINT (SILICONE BINDER)	0.9	0.8 (200°)		
SILICON	PAINT	0.8	0.7 (200°)		
LEAD SULPHIDE	PAINT (SILICONE BINDER)	0.94	0.8 (200°)		
BLACK COPPER	CHEMICAL	0.91	0.16 (100°)	0.4 (200°)	
BLACK NICKEL	ELECTROLYSIS	0.9	0.1		< 250
BLACK CHROME	ELECTROLYSIS	0.9	0.1		< 350
AMA	VACUUM EVAPORATION	0.9	0.34 (100°)	0.4 (350°)	< 900

Solar Central Receiver Program

Alan C. Skinrood

Sandia Laboratories, Livermore, California

Summary of Presentation

A two year research and development program to develop technology for a 10 MWe solar central receiver pilot plant has been completed. This represents a major milestone in the Department of Energy Program to collect and utilize solar energy on a commercial scale. The plant, the first of its kind, will be built in Barstow, California, starting in 1978, and will be operational in 1980. It will provide economic and operating data so that the commercial potential of solar central receiver power plants can be evaluated.

The central receiver concept consists of a field of individually controlled mirrors, or heliostats, that redirect the sun's energy to a receiver mounted on top of a tower. In the receiver, highly concentrated solar flux heats a circulating fluid; the thermal energy is then used to drive a turbine or is stored for later use.

Three contractor teams - consisting of groups headed by Honeywell, Martin Marietta, and McDonnell Douglas, carried out parallel competing conceptual designs for a pilot plant and for a commercial plant. Concurrent to these efforts, a fourth contractor, Boeing Engineering and Construction designed a heliostat that could be incorporated into the other plant designs. During this period, the contractors built and tested experimental collectors, receivers, and energy storage subsystems to assess the technical feasibility of several designs. Sandia Laboratories evaluated the technology and recommended a conceptual design for the pilot plant to the Department of Energy. The concept selected for the pilot plant utilizes glass collector mirrors, an external boiler as the receiver, and an oil/rock thermal storage subsystem. Much of this technology was developed by the McDonnell Douglas team although certain features developed by other contractors will be incorporated. A team of utility companies headed by Southern California Edison is providing the site, the turbine generation subsystem, and will operate the facility.

The development of second generation technology has begun. Contracts have been awarded to Boeing and McDonnell Douglas for improvements on their heliostat designs. New heliostat designs are being developed by the General Electric Company and Solaramics, Inc. These studies are of nine months duration and one or more of these contractors will be extended to do a one year experimental program. Advanced system development has begun at Atomics International and General Electric on sodium receiver designs, at Boeing on a closed cycle air receiver, and at Martin Marietta on a molten salt receiver. The technology developed from these one year studies will be evaluated and one or more will be extended into the experimental phase. Other Department of Energy advanced studies are being done at Sanders (open Brayton cycle) and at Sandia Laboratories (direct energy absorption in a molten salt). The possibility of adding solar energy system to existing fossil fuel power plants is being studied at the Public Service Company of New Mexico.

Many of the central receiver designs utilize absorptive coatings and there are several factors which determine the requirements for these coatings. Two types of receivers are being developed: the external design where energy is absorbed on the outer surface of a structure composed of tubes carrying a coolant, and the cavity design where energy is absorbed on the inner walls of a cavity. Necessary coating characteristics are high absorptivity and long life at temperatures in the 300°C to 1100°C range, while being exposed to incident solar fluxes at up to 2 MW/m^2. For external receivers, selective coatings could potentially improve receiver efficiency as much as 5 percent depending on the size, incident flux, and operating temperature of the receiver design. For cavity receivers, selectivity is relatively unimportant since re-radiation losses are already minimized by receiver geometry. At the higher temperatures, the potential gains are of course limited by the greater overlap between the solar and radiative spectra.

In summary, high absorptivity coatings are important to the central receiver program and selective coatings can be useful in plant designs using external receivers.

SOLAR CENTRAL RECEIVER PROGRAM

FIRST GENERATION

- R & D PROGRAM COMPLETED
- CONCEPT SELECTED FOR PILOT PLANT

ADVANCED DEVELOPMENT

- ADVANCED SYSTEMS STUDIES
- PROTOTYPE HELIOSTAT PROGRAM
- REPOWERING
- HYBRID STUDY
- NEW CONCEPTS

USE OF COATINGS WITHIN THE PROGRAM

PURPOSE OF THE PILOT PLANT

PRINCIPAL

TO ESTABLISH THE TECHNICAL FEASIBILITY OF A SOLAR THERMAL POWER PLANT OF THE CENTRAL RECEIVER TYPE.

TO OBTAIN SUFFICIENT DEVELOPMENT, PRODUCTION AND OPERATING DATA TO INDICATE THE POTENTIAL ECONOMIC OPERATION OF COMMERCIAL POWER PLANTS OF SIMILAR DESIGNS.

TO DETERMINE THE ENVIRONMENTAL IMPACT OF SOLAR THERMAL CENTRAL RECEIVER PLANTS.

ADDITIONAL

TO GATHER OPERATIONAL DATA THAT CAN BE ANALYZED TO DETERMINE SYSTEM STABILITY AND SAFETY CHARACTERISTICS.

TO DEVELOP BOTH UTILITY AND COMMERCIAL ACCEPTANCE OF SOLAR THERMAL THERMAL CENTRAL RECEIVER SYSTEMS.

TO STIMULATE INDUSTRY TO DEVELOP AND MANUFACTURE SOLAR ENERGY SYSTEMS.

TO ENHANCE PUBLIC ACCEPTANCE AND FAMILIARITY WITH SOLAR THERMAL CENTRAL RECEIVER TYPES OF SYSTEMS.

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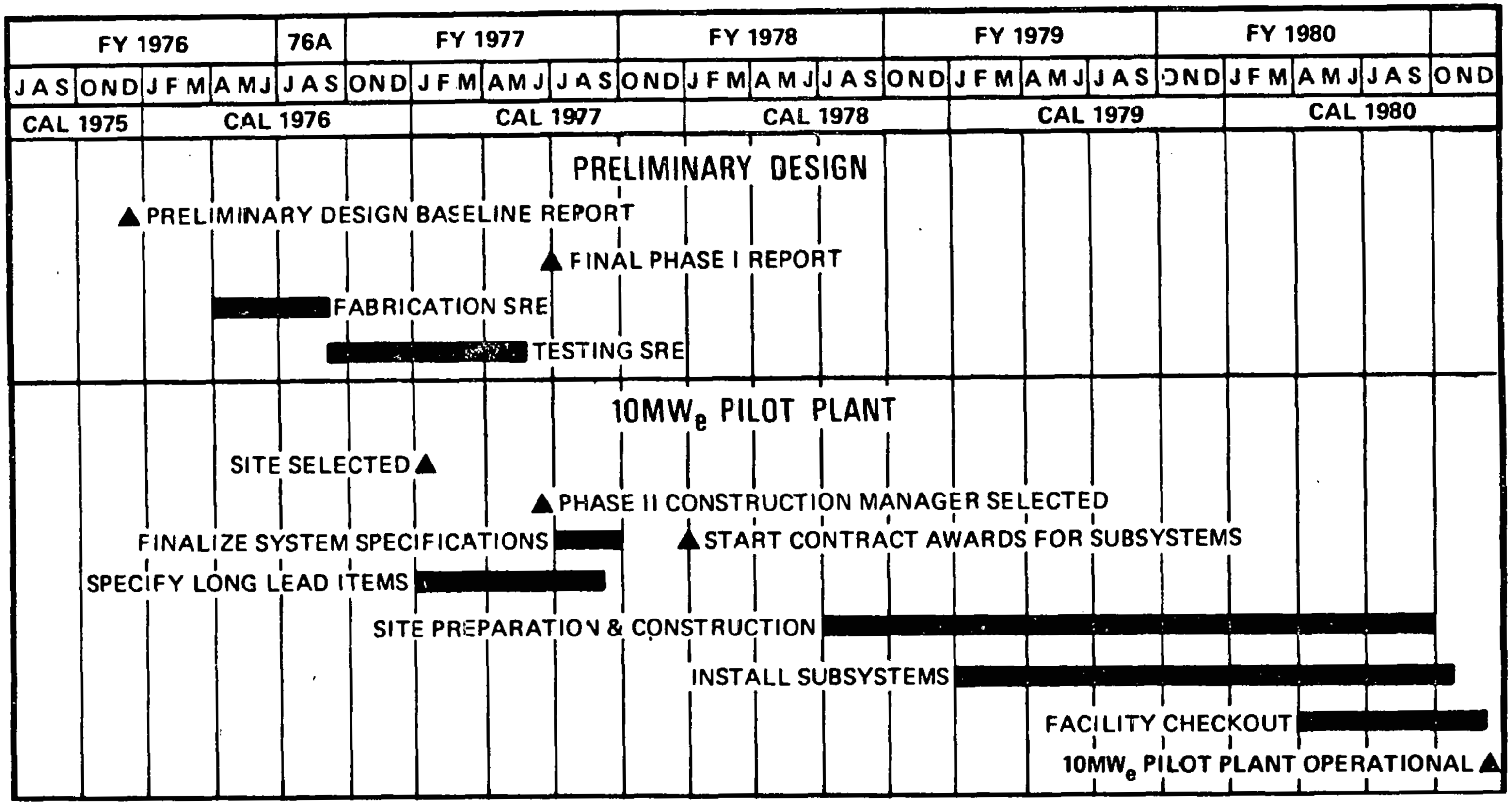
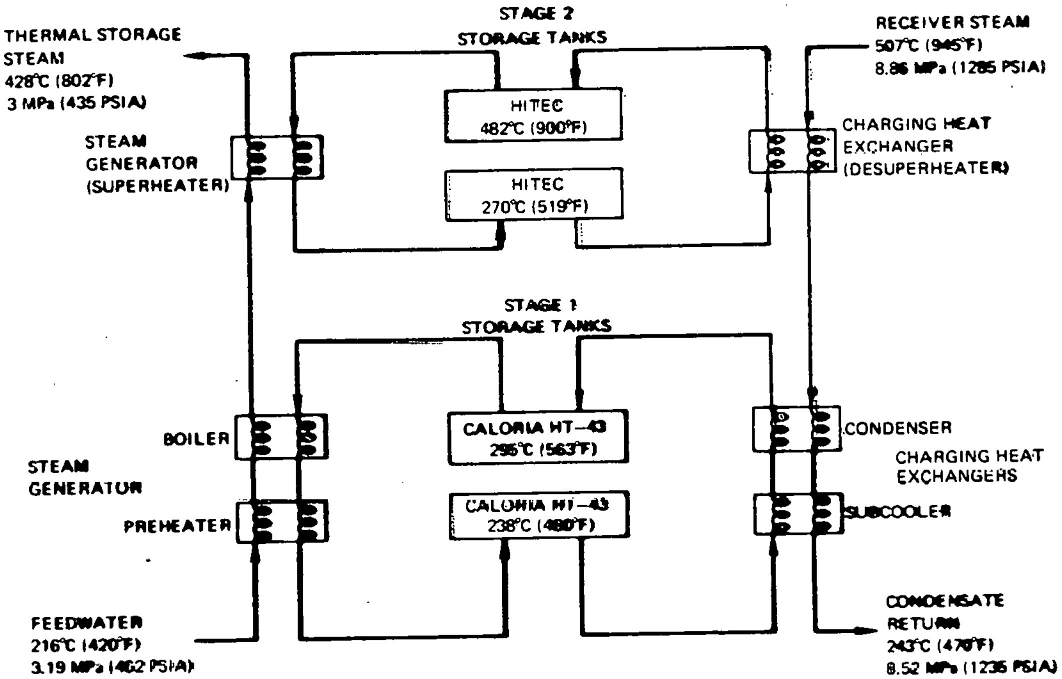
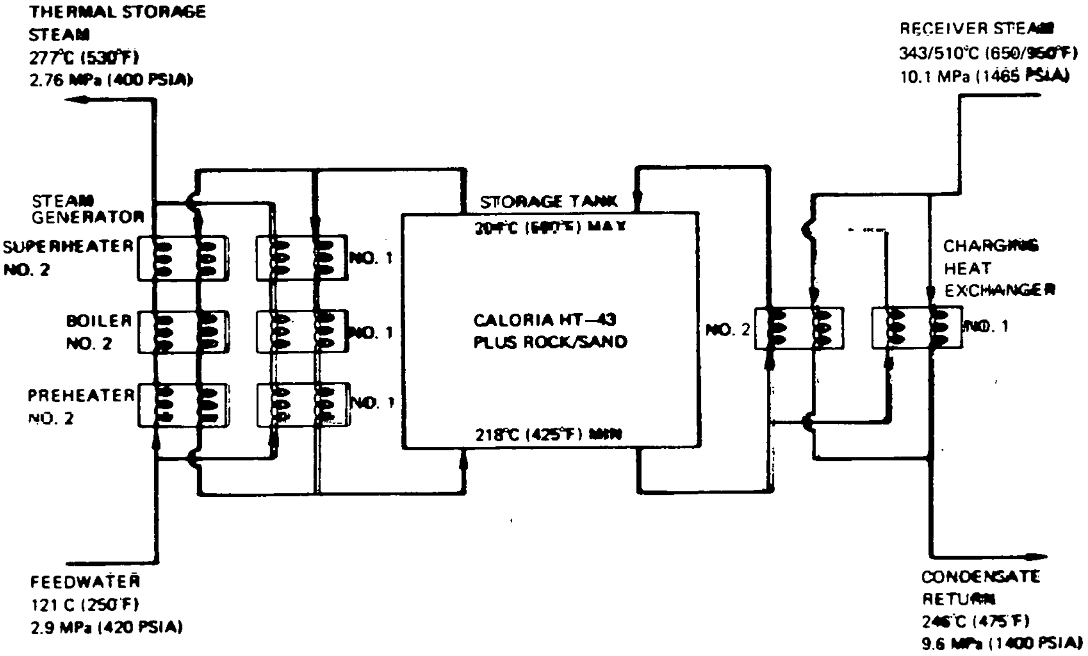


10 MW_e Pilot Plant Project 5 Year Milestone Schedule

Martin Marietta Pilot Plant Thermal Storage



McDonnell Douglas Pilot Plant Thermal Storage



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RECOMMENDED PILOT PLANT CHARACTERISTICS

RECEIVER SUBSYSTEM

TYPE	EXTERNAL RECEIVER
TOWER HEIGHT	100 METERS

COLLECTOR SUBSYSTEM

HELIOSTAT	McDONNELL DOUGLAS TYPE
NUMBER OF HELIOSTATS	2,300
REFLECTIVE AREA PER HELIOSTAT	38 M^2
TOTAL REFLECTIVE AREA	87,400
LAND AREA	40 X 10^4 M^2 (22% COVERAGE)

STORAGE SUBSYSTEM

TYPE	SENSIBLE HEAT - THERMOCLINE
STORAGE MATERIAL	OIL/ROCKS
CAPACITY	36 NW_E

MASTER CONTROL

AS DEFINED BY THE MASTER CONTROL SUBSYSTEM EVALUATION TEAM

ELECTRICAL POWER GENERATION SUBSYSTEM

SOUTHERN CALIFORNIA EDISON RESPONSIBLE

BALANCE OF PLANT

DEFINED DURING DETAILED DESIGN

ADVANCED SYSTEM DEVELOPMENT

SCOPE: COMMERCIAL PLANT CONCEPTUAL DESIGN

ESTIMATE COSTS

DEFINE DEVELOPMENT PROGRAM, INCLUDING EXPERIMENTS, PILOT PLANT, MATERIALS

DURATION: 1 YEAR

TOTAL COST: $2.6 M, PHASE I

CONTRACTORS: BOEING--CLOSED BRAYTON, AIR, CAVITY RECEIVER

GENERAL ELECTRIC--SODIUM, EXTERNAL RECEIVER

MARTIN MARIETTA--MOLTEN SALT, CAVITY RECEIVER

ROCKWELL--SODIUM, EXTERNAL RECEIVER

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ADVANCED HELIOSTAT DEVELOPMENT

SCOPE: CONCEPTUAL DESIGN OF HELIOSTAT, FOUNDATION, LOCAL CONTROL SYSTEM, AND PRODUCTION TOOLING

MATERIALS DEVELOPMENT AS NEEDED

COST ESTIMATION

TEST PLAN FOR PHASE II

DURATION: 9 MONTHS

TOTAL COST: $2.45 M, PHASE I

CONTRACTORS: BOEING

GENERAL ELECTRIC

McDONNELL DOUGLAS

SOLARAMICS

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HYBRID CONCEPT

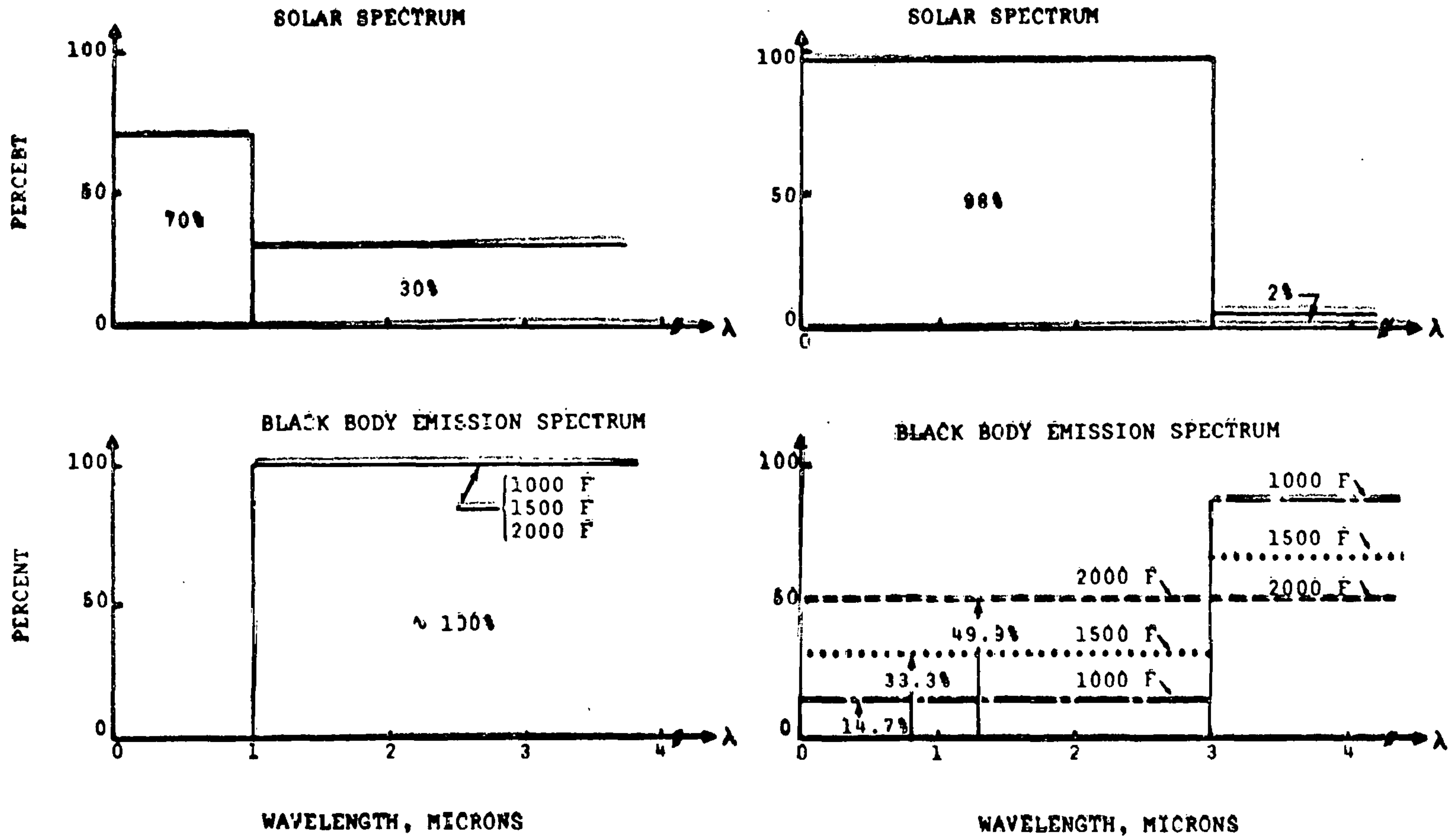
- SOLAR CENTRAL RECEIVER COMBINED WITH NON-SOLAR SOURCE
- RFP TO BE RELEASED IN JUNE 1978
- REPOWERING STUDY AT PUBLIC SERVICE OF NEW MEXICO

FACTORS INFLUENCING USEFULNESS OF COATINGS TO CENTRAL RECEIVER PROGRAM

- RECEIVER GROMETRY
- OPERATING TEMPERATURE

COATING REQUIREMENTS

- STABILITY AT HIGH TEMPERATURES
- RESISTANCE TO SEVERE THERMAL TRANSIENTS
- HIGH CYCLE LIFE
- HIGH ABSORPTANCE TO SOLAR SPECTRUM


SOLAR SPECTRUM
PERCENT
100
50
0
70%
30%
λ
SOLAR SPECTRUM
100
50
0
98%
2%
λ
BLACK BODY EMISSION SPECTRUM
PERCENT
100
50
0
1000 F
1500 F
2000 F
∿ 100%
0
1
2
3
4
λ
WAVELENGTH, MICRONS
BLACK BODY EMISSION SPECTRUM
100
50
0
1000 F
1500 F
2000 F
2000 F
49.9%
1500 F
33.3%
1000 F
14.7%
0
1
2
3
4
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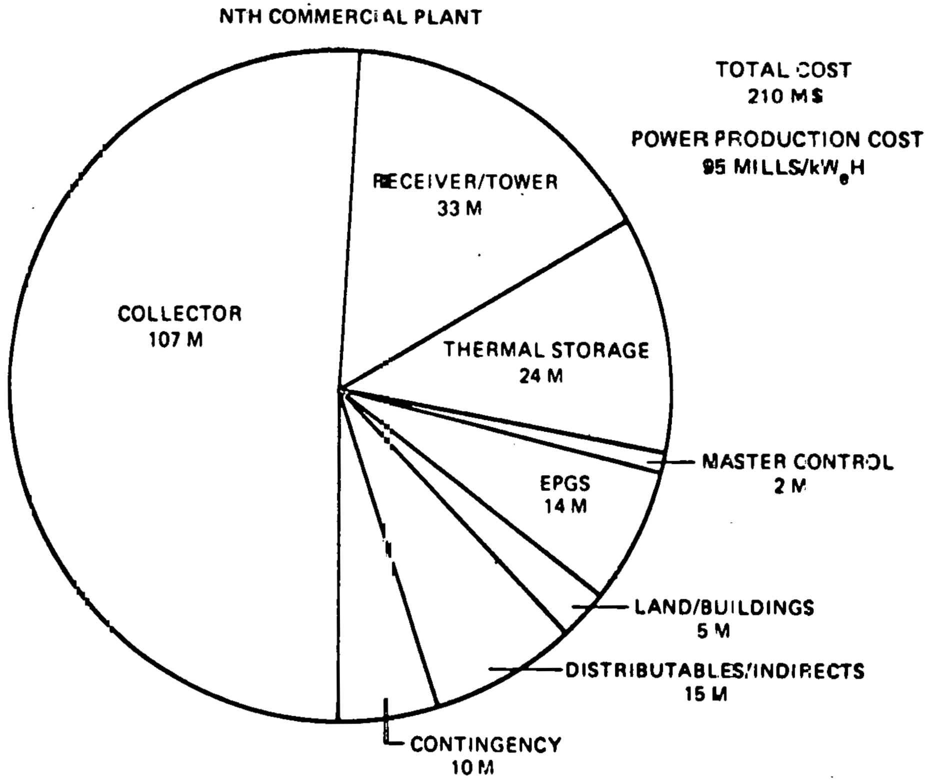
WAVELENGTH, MICRONS

SUMMARY

SELECTIVE COATINGS MAY BE USEFUL TO CENTRAL RECEIVER PROGRAM

CURRENT DESIGNS DO NOT USE SELECTIVE COATINGS



COMMERCIAL PLANT COST ESTIMATES. SANDIA REVISED COST ESTIMATES FOR RECOMMENDED SUBSYSTEM DESIGNS; SOLAR MULTIPLE OF 2; STORAGE CAPACITY OF 7 HOURS AT 70 MW$_e$.

MR. RICHMOND: I didn't quite understand on those advance concepts where they were using in one case the air Brayton cycle and in other cases they were using either a salt or sodium as a heat transfer fluid. They can't use that directly, they have some sort of a heat exchanger to a working fluid for the heat engine, don't they have?

MR. SKINROOD: Yes, and I didn't mention that, perhaps I should have.

Sodium cycles use water steam prime movers, and there is a heat exchanger where you make super heated steam. It is intended that the operating temperature of the sodium be somewhere in the 1100 to 1300° F range and that you operate with steam at about 1050° F or so.

The Brayton cycle, of course, can operate directly. The salts are the same, except the operating temperatures in the salts, I think, may be in the 1050 to 1100 range, possibly a little bit low, almost certainly less than the sodium.

MR. CAU: Can you quantify the severe thermal transients which you have listed as one of the design criteria?

MR. SKINROOD: Well, in what way? We can produce analytical solutions for temperature transients that are made. There is a fair temperature transient within the thickness of the front surface of a tube. The front to back present design of the front surface of the tube, the gradient, I think, is like 100 degrees, possibly 150 in certain zones, in the super heater zones.

There is also, of course, a gradient as you go around the thickness or go around the circumference of the tube.

MEMBER OF THE AUDIENCE: Is that F or C?

MR. SKINROOD: That is F. I mix units. Some I can remember, some I can't.

MR. RICHMOND: Those are gradients, not transients?

MR. SKINROOD: Yes, I am sorry. I answered the wrong question, didn't I?

Those are gradients. The transients also can be calculated, I don't really remember what they are. But, they are fairly easy to calculate.

MR. RICHMOND: That's essentially when a cloud goes over?

MR. SKINROOD: Right, that's your most severe condition. You do have a fair amount of thermal inertia in the tubing, so it is not instantaneous while you lose your flux, and I didn't mention it, but some of the fluxes are up in the 2 MW/M^2 range for the advanced designs. When you lose your flux, you still have a fair heat sink behind you.

So, it may not be quite as bad as it seems.

MR. SCHWARTZ: The Boeing Brayton--is the top temperature of that 1600 F?

MR. SKINROOD: Yes, 1550, 1600.

MR. SCHWARTZ: Well, really in the advanced systems, you are really not looking beyond 1600 F or 800 degrees C?

MR. SKINROOD: Well, I didn't cover it, but Black and Veatch is being funded by EPRI, and their system operates at 2200 F, the last I heard.

Let me add one more comment on it, and that is that there is development being done at Sanders Associates, which is --

CHAIRMAN ELLIOTT: A semi-open cycle.

MR. SCHWARTZ: It is about 1900, 2000 F.

MR. SKINROOD: Right.

MR. SCHWARTZ: I have a follow-up question, since you brought up the Black and Veatch systems, not that I haven't looked at all the systems, the thing that is peculiar, there is a conflict in a sense between Boeing which shows efficiencies of 44 percent with a top temperature of 1600 F, and Black and Veatch at a top temperature nominally of 1900 to 2000 F with something like efficiencies of 37, 38 percent.

MR. SKINROOD: One thing you have to be careful about when you read efficiencies is be careful that the denominator is defined the same way. You can define efficiencies all kinds of ways for solar systems anywhere from total energy incident on the ground for the heliostat field to going all the way back through the system and defining it only for the turbine, only for the receive, and --

MR. SCHWARTZ: The best I can determine in reading both reports, the numbers I have given you are on the same basis.

MR. SKINROOD: Nobody is violating any laws of thermodynamics, and I think if you will go back, I know it is hard to define or find it out sometimes, you have to be very careful and look at those definitions. I would not propose though to define those numbers.

MR. SERAPHIN: Coming back to Pat Call's thermal transients, do you consider the loss of coolant situation, and if so, what's your temperature margin?

MR. SKINROOD: Well, we consider the loss of coolant situation. This is still being analyzed, and there is a fair amount of work being done to look at loss of coolant.

We do feel that there is 10 to 15 seconds worth of thermal inertia in some of the receiver designs so that you can stand loss of coolant.

But, you have got to get those heliostats off in less than a minute, or you are very soon going to melt things. But, those calculations are not all completed.

MR. SERAPHIN: What's the particular temperature margin that you consider safe that you have to assume in design of the intercepting surface? How high can they run in case of an accident like that? Let's say the operating temperature is 550 C, for instance, how would you lay out the coating in order to be safe for these 10, 15 seconds that it takes to turn the --

MR. SKINROOD: I think it would depend on the particular design. The thermal inertia behind you is considerably different for each design. I really don't know what the answer to that is. Charlie Bolton from Martin Marietta may have done some calculations. You probably haven't looked at coatings very much?

MR. BOLTON: I don't know. Our cavity design with a drum would last about two minutes. So, we weren't that sensitive to the immediate transient loss of coolant. We utilize the water that is in the drum to generate the steam to keep it cool. So, I don't have an answer to that.

MR. SKINROOD: The once-through design of McDonnell-Douglas is more sensitive to the loss of coolant.

MR. TOBIN: We essentially build, design, and test it. We did demonstrate at least a minute in operation without coolant in the radiant heating facility.

In terms of an operating temperature, the material itself, it is not a "braced" structure, it is a welded structure, so it is whatever you are willing to take on the material, and of course, its melting point is around 24, 2500 F.

Of course, you may lose the paint and have to repaint it. I don't know what coat is on it, maybe you won't be able to reuse it again if you exceeded some temperature.

But, I don't know of any limits yet on that.

MR. SKINROOD: I should point out too that there are several different flux levels for the McDonnell-Douglas design. The pilot plant is designed for .3 MW/M^3, commercially proposed design is .85. I am not sure, Ron, whether you still have that time at .85?

MR. TOBIN: You have a little less at .85.

MR. SERAPHIN: As far as alpha goes, we may be close to saturation in the sense that probably from a material science point of view, we can't go much higher.

MR. TOBIN: Right.

MR. SERAPHIN: Whether or not we want to suppress the emissivity is a decision that we can make. So here are these $7.00 per kilowatt savings that we can get by going towards selectivity?

MR. TOBIN: Right.

MR. SERAPHIN: I was very glad about the last conclusion. We probably can't do anything about raising alpha much above 98 percent.

MR. SERAPHIN: But, about the emissivity, we can do something and can get that savings.

The other question was the degradation of alpha, to what extent has the optical performance of a coating been evaluated at the operating temperature? By degradation, you just mean heating the surface, cooling it down and then measuring it?

MR. TOBIN: Right. No, it has not been evaluated at temperature--it is difficult.

MR. SERAPHIN: It is difficult to do it, but it must be done.

MR. TOBIN: That would be a good area to look at.

MR. SERAPHIN: Because many of these refractory materials that can stand high temperature are either insulators or semi-conductors, and it is a fundamental property of these materials that their reflectivities go up considerably at these operating temperatures.

So, you may design a plant for an alpha of 98 percent, and find yourself sitting there with something that has 65% absorptance.

MR. TOBIN: That's a good point.

MR. SERAPHIN: But, we must measure these things at the temperature at which the plant is supposed to run.

MR. TOBIN: As I say, all we have measured is the total emittance of the material at elevated temperature, but not at solar wavelengths.

MR. RICHMOND: Joe Richmond, Bureau of Standards. I just wanted to comment that you made a very common error in your terminology when you talked about integrating the spectural reflectance, actually what you are doing is taking the weighted average. Using the solar central distribution or the "Planck"distribution as the weighting factor.

MR. TOBIN: Yes, that's what I meant to say. That is the way it was done.

MR. SKINROOD: My question is not directed at Ron, but at the audience. What facility exists for determining the absorptivity at temperature?

MR. SERAPHIN: There are about three or four high temperature reflectometers in this country.

MR. SKINROOD: We have looked around, and I would be very dismayed if we had a pilot plant built at an incorrect site because of this.

MR. SERAPHIN: It is a very crucial point that optics by and large has been a room temperature application. What solar energy conversion is going to teach us, and we have to learn this, is that we are doing optics. Solar energy conversion is interaction of radiation with matter, and it has been done at room temperatures or below so far.

Now, we have to look at 500 C and above. We know very little, it is a back border area of physics really.

MR. GROSSKREUTZ: TRW measured the absorptance for Black and Veatch of silicon carbide at room temperature and at 1800° F, and it was .85 within ± .01, there was no degradation of the absorptance of silicon carbide.

MR. SCHWARTZ: You give the values of α for pyromark as .95? Have you included the geometry effect between the adjoining tubes? Because you get a black body effect there, increasing α, have you looked at that?

MR. TOBIN: No, we haven't. It would tend to help us, but no we haven't.

That is just a direct measurement really.

MR. SCHWARTZ: You may find that you have $700-thousand sitting there waiting to be tapped.

To follow on that again from a geometry standpoint, have you looked at vanes instead of coatings? So that basically, the thing that you are building into your tubes is a black body cavity or approaching a cavity?

MR. TOBIN: The problem here is partly the tremendous heat flux that we are putting in, making sure that the vanes are at an acceptable temperature, and exactly how do you design to a boiler code with that type of a configuration? The cavity effect is nice, but we are talking about basically low conductivity materials.

So, unless we had a way of putting a high conductivity vane on there, we would be in trouble.

MR. SCHWARTZ: Finally, a follow-up to a comment by Dr. Seraphin from Arizona, the impression I had from his final comment to you was that there was an advantage in moving to lower epsilon, from a practical standpoint, we can't do that. It would be nice if you could go .95 at an epsilon of 0.1, usually in order to get that selectivity--

MR. TOBIN: That's right, alpha drops.

MR. SCHWARTZ: So, as far as I can see, with a central tower concept I don't see selectivity unless the concentration factors are low.

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Absorptive Coatings Evaluation for Solar Tower Receiver Application

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Rocketdyne Division, Rockwell International
Canoga Park, California 91304

Summary of Presentation

Efforts to select and evaluate a suitable high solar absorptance coating for solar tower receiver application were initiated in 1974 in a company funded project. The evaluation was continued in varying degrees in two separate ERDA contracts relating to the solar tower receiver concept. Emphasis in the latter efforts was directed toward evaluation of the prime candidate coatings under simulated solar tower operating conditions utilizing electrical, solar furnace and radiant heating test facilities.

In the initial screening process prime consideration was given to the basic system requirements relating to coating durability and/or easy on-site refurbishment. A review of the thermal efficiency relations associated with highly concentrated solar energy indicated that high solar absorptance was more important than selectivity; with a 3 percent gain in α_S about equivalent to a 10:1 gain in selectivity (α_S/ε) ratio. Based on the foregoing, in conjunction with the large surface areas involved in the receiver concept, the more complex chemical surface treatments were not considered.

Two groups of nine different candidate surface treated (Incoloy 800 substrate) specimens were evaluated. One group in the as-received condition and the other after 90 hours in an ASTM weatherometer. These surface treatments included: 1) as machined (for reference purposes), 2) mechanical (grit blasted), 3) chemical (oxidized), 4) plasma spray, and 5) high temperature paints. Spectral reflectance (0.23 to 24 microns) and total emittance (at 1200°F) measurements were made of all specimens.

The results of this screening evaluation indicated the superiority of two high temperature black paints (on a grit blasted surface) with solar absorptance values ranging from 0.95 (unweathered) to 0.93 (weathered). The most promising of the paints (denoted S-31) in terms of durability (based on use history) was selected for use in a test program involving the feasibility demonstration of the once-through boiler concept.

Difficulties with the initial curing and resultant durability of the S-31 paint led to consideration of a commercially available (Pyromark) paint as a back-up. Both paints were evaluated in an electrically heated test section using different cure techniques to determine their surface adherence characteristics.

In addition, both the S-31 and Pyromark paints were evaluated in the White Sands Solar furnace. As of 28 July 1977, the paint samples have been cycled 144 times for an accumulated time of 256 hours at an average heat flux level of 0.3 MW/m^2 and a peak of 0.6 MW/m^2. Average surface temperature was 600°F with peak values of 1375°F. Periodic measurements have indicated no degradation in solar absorptance. Adherence of the paint to the Incoloy substrate has been satisfactory.

The paints were also evaluated under typical solar tower operating conditions using a radiant heating facility in conjunction with a full size once-through boiler panel. In excess of forty hours were successfully accumulated on the paints at peak heat flux levels of 0.3 MW/m^2 at maximum temperatures of greater than 1200°F.

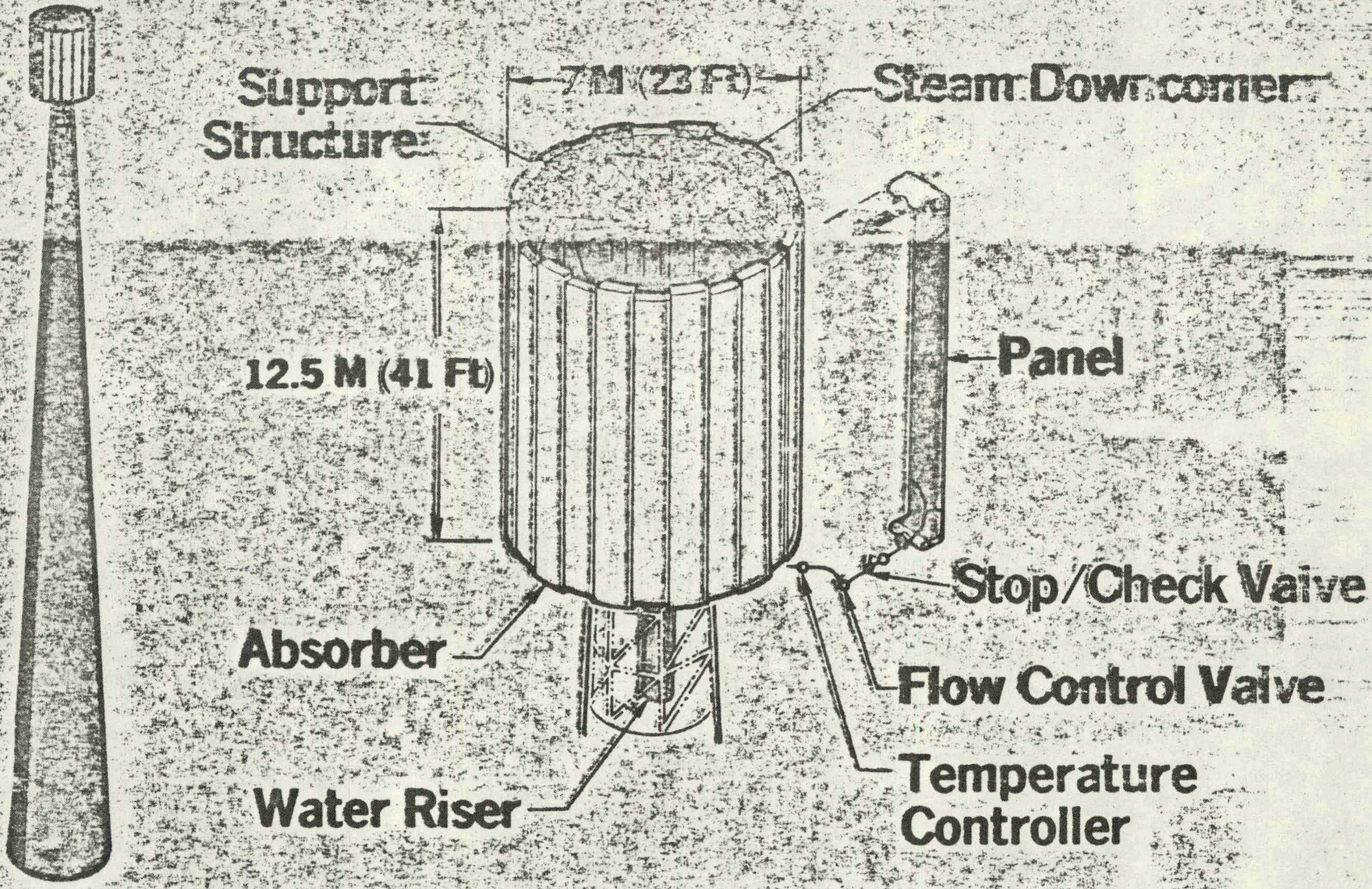
The results of these various tests have indicated the feasibility of high temperature, high absorptance paints for solar tower application. Future efforts should be directed toward increase in absorptance levels above the currently demonstrated value of 0.95 or increase in selectivity without significant solar absorptance degradation.

SUMMARY OF EFFORT

- COMPANY SPONSORED - NOVEMBER '74 TO APRIL '75
    - SCREENED CANDIDATE COATINGS FOR APPLICABILITY
    - MEASURED SOLAR ABSORPTANCE OF SELECTED CANDIDATE COATINGS
    - SELECTED COATING FOR USE ON SOLAR TOWER PANEL TEST SECTIONS
- ERDA CONTRACT E(04-3)-1103, "SOLAR RECEIVER HEAT FLUX CAPABILITY AND STRUCTURAL INTEGRITY," JUNE 1975 TO MAY 1976
    - EVALUATED COATING DURABILITY UNDER HIGH RADIANT HEAT FLUX OPERATION AND LIMITED DURATION
- DOE CONTRACT EY-76-C-03-1108, "CENTRAL RECEIVER SOLAR THERMAL POWER SYSTEM," JUNE 1975 - PRESENT
    - COATING THERMAL CYCLING USING ELECTRICALLY HEATED TUBES
    - COATING THERMAL CYCLING IN WHITE SANDS SOLAR FURNACE
    - EVALUATED COATING DURABILITY ON FULL-SIZE STEAM GENERATOR PANEL OPERATING FOR EXTENDED DURATIONS AT PILOT PLANT RADIANT HEAT FLUX LEVELS

PILOT PLANT RECEIVER

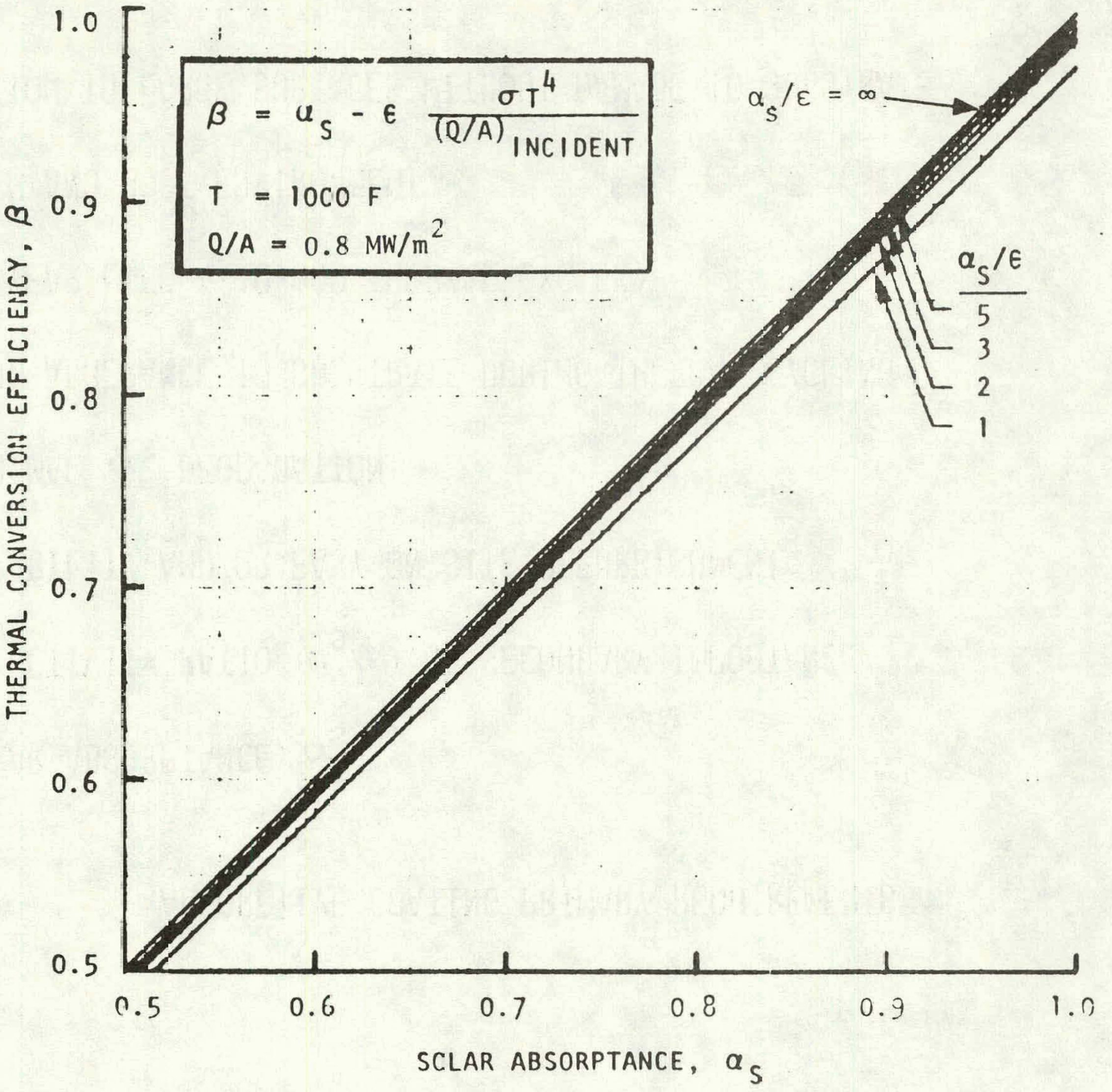
3AK-89137



ABSORPTIVE COATING PRIMARY REQUIREMENTS

- HIGH SOLAR ABSORPTANCE, α_s
  - SELECTIVITY RATIO (α_s/ϵ) OF SECONDARY IMPORTANCE
- GOOD DURABILITY AND/OR EASY ON-SITE REFURBISHMENT
  - MINIMAL α_s DEGRADATION
  - GOOD ADHERANCE TO SUBSTRATE DURING THERMAL CYCLING
  - 30 YEAR LIFE (~10,000 THERMAL CYCLES)
  - RAIN AND DUST ENVIRONMENT
- APPLICATION TO LARGE SURFACES WITHOUT DAMAGE TO SUBSTRATE

EFFECT OF SOLAR ABSORPTANCE ON THERMAL CONVERSION EFFICIENCY



ABSORPTIVE COATINGS FOR SOLAR TOWER RECEIVER

NO. OF SAMPLES	SAMPLE DESIGNATION	DESCRIPTION OF SAMPLE SURFACE PREPARATION
2	1A AND 1B	AS MACHINED - SURFACE FINISH $\overset{32}{\surd}$
2	2A AND 2B	OXIDIZE AT 1000-1200 F FOR 2 HOURS
2	3A AND 3B	GRIT BLAST (SIZE 20 GRIT)
2	4A AND 4B	GRIT BLAST AND THEN OXIDIZE AS ABOVE
2	5A AND 5B	GRIT BLAST AND PLASMA SPRAY - TUNGSTEN CARBIDE AND COBALT (12 PERCENT)
2	6A AND 6B	GRIT BLAST AND PLASMA SPRAY - CHROMIUM CARBIDE AND COBALT (12 PERCENT)
2	7A AND 7B	GRIT BLAST AND PLASMA SPRAY - FERRITE COATING
2	8A AND 8B	GRIT BLAST AND SHERWIN-WILLIAMS HIGH TEMPERATURE PAINT (BLACK)
2	9A AND 9B	GRIT BLAST AND B-1 DIVISION HIGH TEMPERATURE PAINT
18	TOTAL	

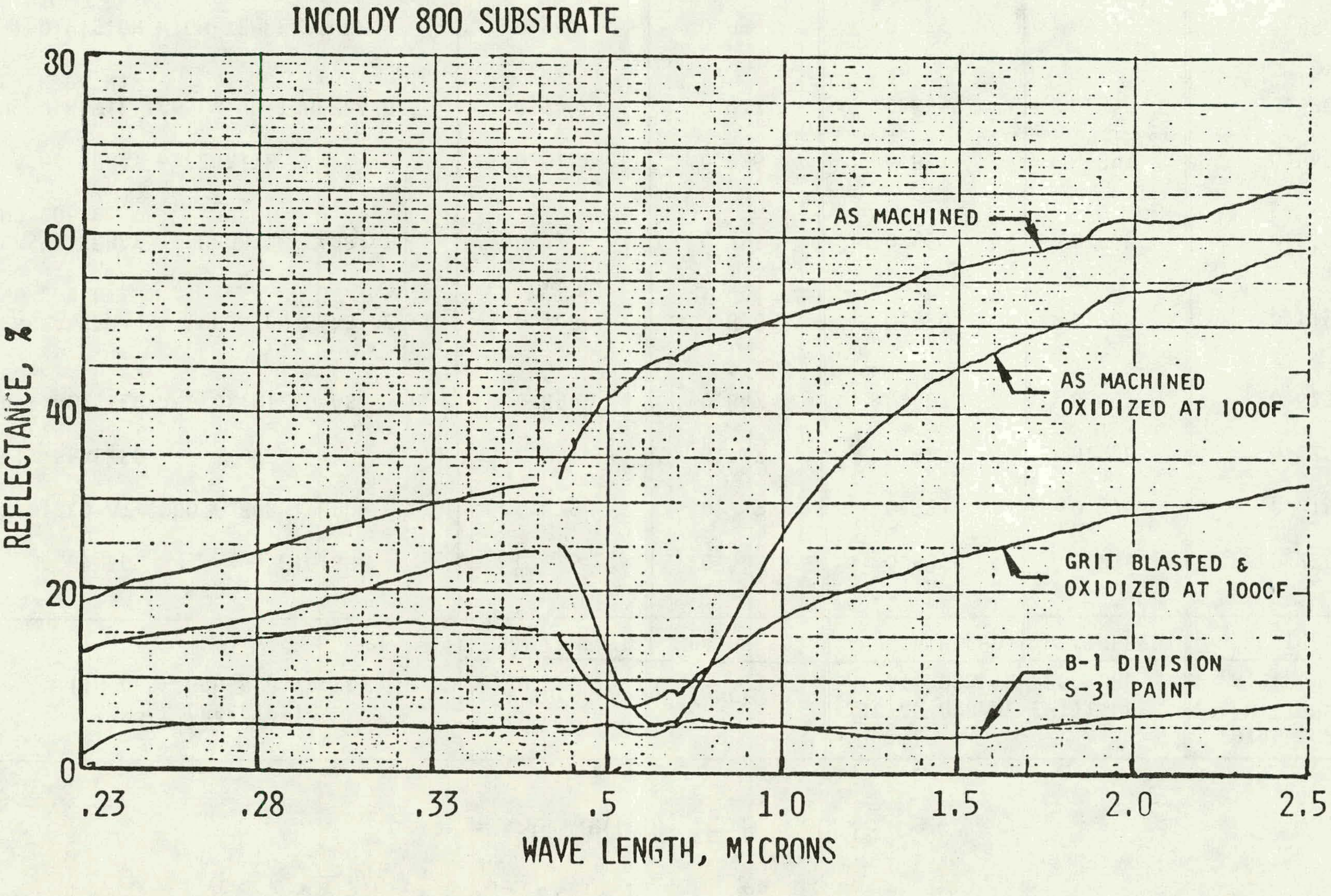
SAMPLES ARE INCOLOY 800 CIRCULAR DISKS 31/32 IN. DIAMETER X 0.090 IN. THICK

ABSORPTIVE COATINGS FOR SOLAR TOWER RECEIVER

TEST PROCEDURE AT B-1 DIVISION

- TWO IDENTICAL GROUPS OF 9 TEST SPECIMENS
  - FIRST GROUP - REFLECTANCE AND EMITTANCE MEASURED AS RECEIVED
  - SECOND GROUP - ASTM WEATHEROMETER FOR 90 HOURS AND THEN REFLECTANCE AND EMITTANCE MEASURED
- SOLAR ABSORPTANCE DETERMINATION TECHNIQUE
  1) MEASURE REFLECTANCE VERSUS WAVELENGTH (0. 23-25 MICRONS) AT ROOM TEMPERATURE
  2) INTEGRATE UNDER EXPERIMENTAL REFLECTANCE CURVE TO DETERMINE SOLAR AND TOTAL NORMAL EMITTANCE AT ROOM TEMPERATURE
  3) MEASURE TOTAL NORMAL EMITTANCE AT $T \approx 1000$ F
  4) COMPARE TOTAL NORMAL EMITTANCE AT ROOM TEMPERATURE AND 1000 F TO DETERMINE IF THERMODYNAMIC CHANGE IN SURFACE
     A. IF NO CHANGE THEN ROOM TEMPERATURE SOLAR α VALUE VALID
     B. IF SIGNIFICANT CHANGE THEN ROOM TEMPERATURE SOLAR QUESTIONABLE
- ASTM WEATHEROMETER TESTS
  - SUBJECTS SAMPLES TO ACCELERATED WET AND DRY LOW TEMPERATURE CYCLES WITH SOLAR SIMULATED RADIATION

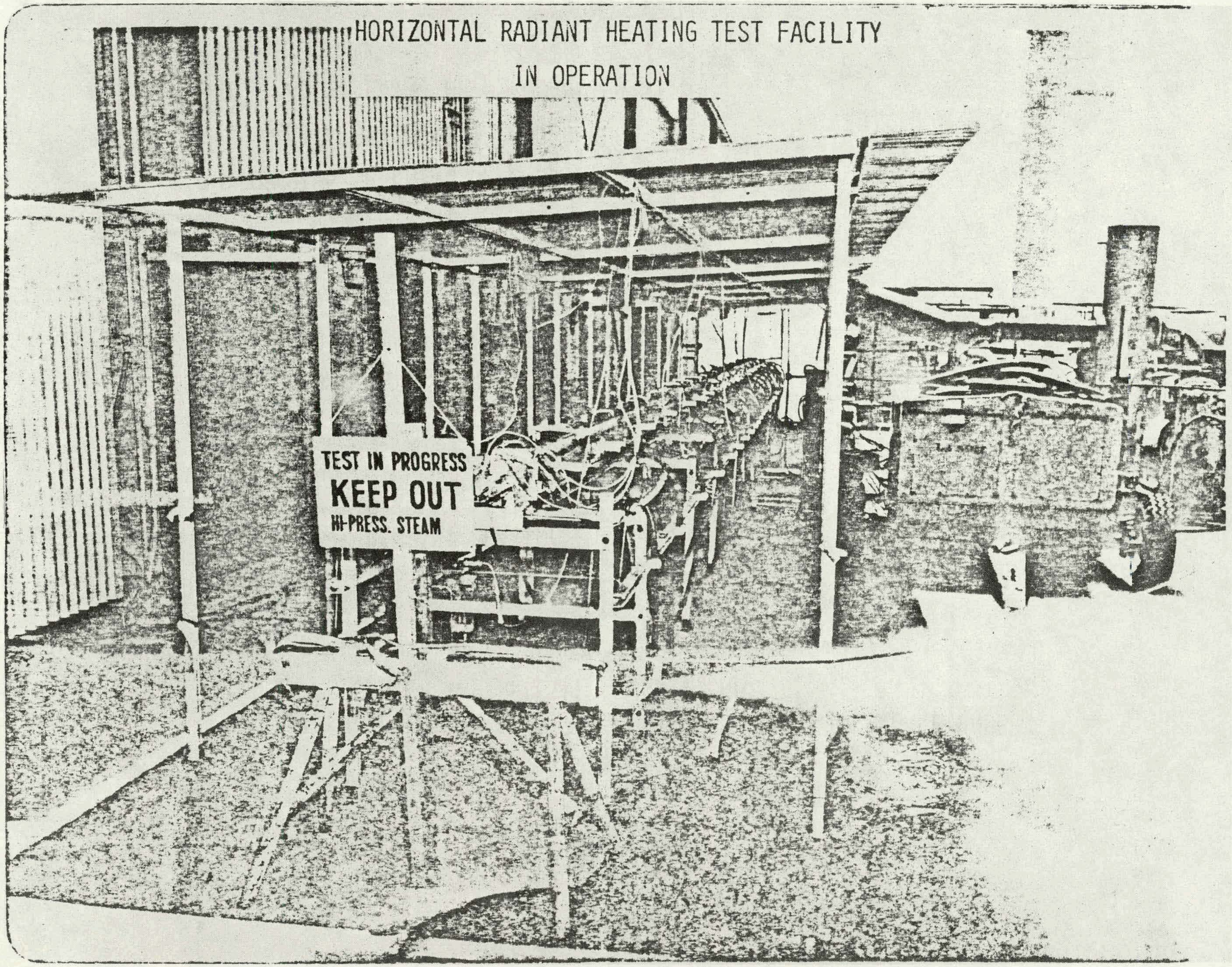
SURFACE REFLECTANCE IN SOLAR WAVE LENGTH BAND



SUMMARY OF TEST RESULTS

SAMPLE DESCRIPTION (INCOLOY 800 SUBSTRATE)	SOLAR ABSORPTANCE		TOTAL NORMAL EMITTANCE AT ROOM TEMPERATURE		TOTAL NORMAL EMITTANCE AT 1200 F
	UNWEATHERED	WEATHERED	UNWEATHERED	WEATHERED	UNWEATHERED
AS MACHINED $\overset{32}{\surd}$ FINISH	0.526	0.449	0.587	0.222	0.220
OXIDIZED AT 1000 F FOR 1 HOUR	0.779	0.759	0.223	0.370	0.215
GRIT BLASTED	0.731	0.727	0.529	0.578	0.620
GRIT BLASTED AND OXIDIZED AS ABOVE	0.854	0.847	0.607	0.607	0.625
*PLASMA SPRAY - TUNGSTEN CARBIDE AND COBALT	0.708	0.878	0.520	0.768	0.515
*PLASMA SPRAY - CHROMIUM CARBIDE AND COBALT	0.771	0.751	0.566	0.568	0.610
*PLASMA SPRAY - FERRITE	0.912	0.926	0.883	0.899	0.855
*SHERWIN WILLIAMS HIGH-TEMPERATURE BLACK PAINT	0.944	0.927	0.855	0.849	0.820
*B-1 DIVISION HIGH-TEMPERATURE PAINT	0.950	0.934	0.875	0.870	0.880

*SAMPLES GRIT-BLASTED PRIOR TO APPLYING SURFACE COATING



HORIZONTAL RADIANT HEATING TEST FACILITY

IN OPERATION

HIGH HEAT FLUX RADIANT HEATING TESTS

- OBJECTIVE
  - EVALUATE FULL-LENGTH ONCE-THROUGH STEAM GENERATOR PANEL UNDER SIMULATED COMMERCIAL RECEIVER CONDITIONS
    - ASCERTAIN S-31 AND PYROMARK PAINTS DURABILITY
- APPROACH
  - HORIZONTAL RADIANT HEATING FACILITY - GRAPHITE HEATERS
  - SINGLE TUBE AND 5-TUBE PANEL TEST SECTIONS - 65 FT LONG
- TEST SUMMARY
  - NUMBER OF TESTS - 34
  - HEAT FLUX - 0.25 TO 1.16 MW/m^2
  - MAXIMUM TEMPERATURE > 1500°F
- RESULTS
  - EXTENSIVE SPALLING OF S-31 PAINT
    - ATTRIBUTED TO IMPROPER CURE
  - MINIMAL SPALLING OF PYROMARK PAINT

COATING THERMAL CYCLING - ELECTRICAL HEATING

- OBJECTIVE
  - EVALUATE PYROMARK AND S-31 PAINTS ADHERENCE CHARACTERISTICS UNDER THERMAL CYCLING CONDITIONS
- APPROACH
  - ELECTRICAL RESISTANCE HEATED TUBES COATED WITH PAINTS
  - NATURAL CONVECTION AIR COOLED
- TEST SUMMARY
  - RATE = 3 CYCLES/HR
  - TEMPERATURE RANGE = AMBIENT TO 1200°F
  - TOTAL NUMBER OF CYCLES > 300
- RESULTS
  - NO SPALLING OF PROPERLY CURED PAINTS

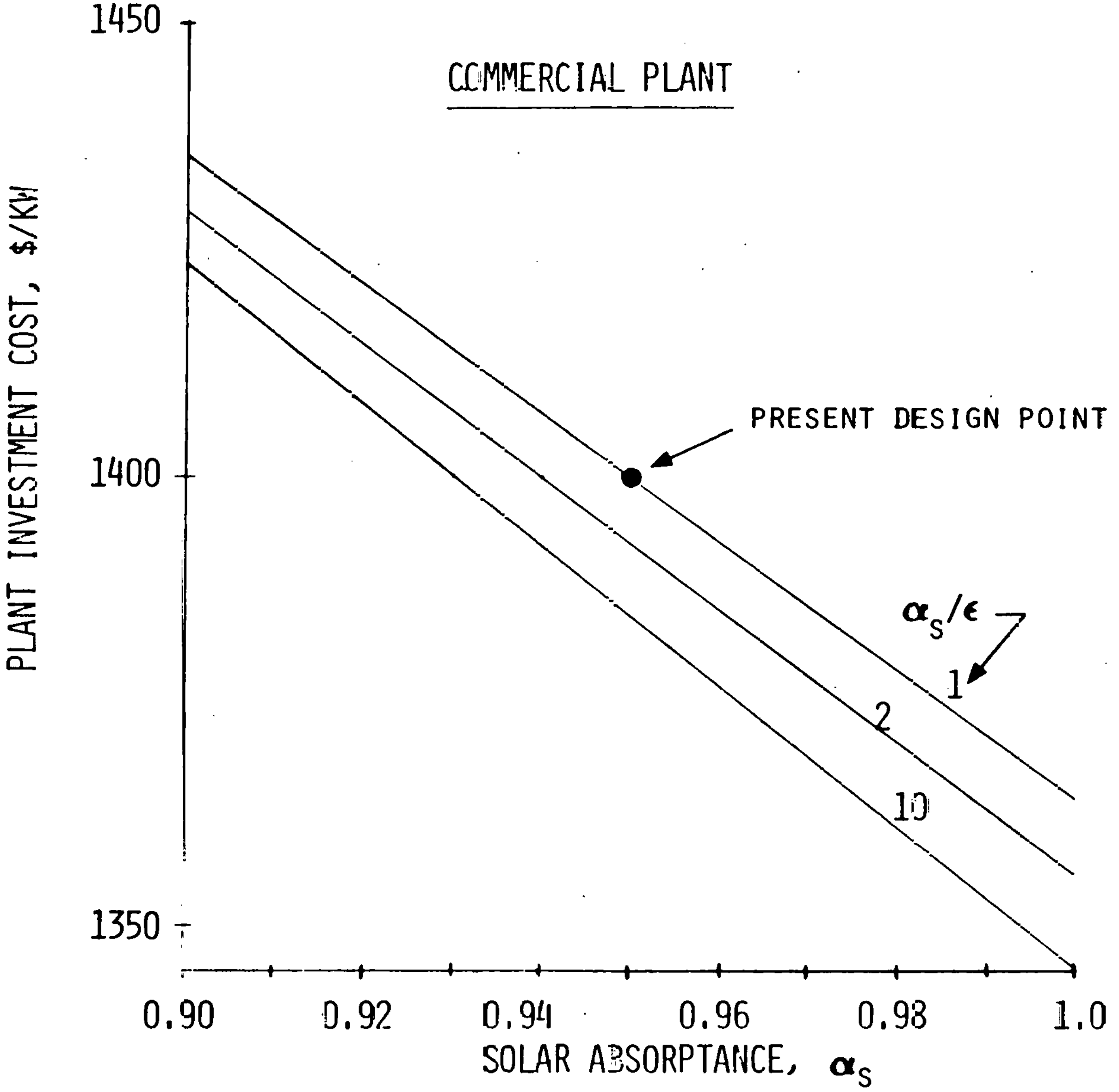
COATINGS THERMAL CYCLING - SOLAR FURNACE

- OBJECTIVES
  - EVALUATE PYROMARK AND S-31 PAINTS IN SOLAR ENVIRONMENT
  - EVALUATE VARIOUS PAINT CURING TECHNIQUES
    - THERMAL CYCLING SIMULATION
    - THERMAL GRADIENT SIMULATION
  - EVALUATE DEGRADATION OF SOLAR ABSORPTANCE
- APPROACH
  - WHITE SANDS TEST FACILITY - SOLAR FURNACE
  - WATER COOLED COPPER TEST SECTION
    - ALTERNATING PAINTED STRIPS
  - SURFACE TEMPERAURE CONTROLLED BY HEAT FLUX LEVEL
  - PERIODICALLY MEASURE SOLAR ABSORPTANCE
- TEST SUMMARY
  - NUMBER OF CYCLES = 144 } AS OF 28 JULY 1977
  - TOTAL DURATION = 256 HRS }
  - HEAT FLUX LEVEL = 0.3 - 0.6 MW/M^2
  - SURFACE TEMPERATURE, PEAK/AVERAGE = 1375/600°F
- RESULTS
  - NO SPALLING OF PAINTS
  - NO DEGRADATION OF SOLAR ABSORPTANCE ($\alpha_s \approx 0.95$)

RADIANT HEATING TESTS

- OBJECTIVE
  - EVALUATE FULL SIZE ONCE-THROUGH STEAM GENERATOR PANEL UNDER SIMULATED PILOT PLANT CONDITIONS
    - ASCERTAIN PYROMARK PAINT DURABILITY AND α_S DEGRADATION
- APPROACH
  - RADIANT HEATING FACILITY - INCONEL AND GRAPHITE HEATERS
- TEST SUMMARY
  - ACCUMULATED TEST DURATION IN EXCESS OF 40 HRS
  - NUMBER OF CYCLES ~ 50
  - PEAK HEAT FLUX LEVEL = 0.3 MW/M^2
  - MAXIMUM TEMPERATURE > 1200°F
- RESULTS
  - NO SPALLING OF PAINT
  - NO DEGRADATION OF SOLAR ABSORPTANCE

SOLAR TOWER COST BENEFITS - IMPROVED ABSORPTIVE COATINGS



CONCLUSIONS

- DEMONSTRATED FEASIBILITY OF HIGH TEMPERATURE, HIGH ABSORPTANCE PAINTS FOR SOLAR TOWER APPLICATION
    - MINIMAL α_s DEGRADATION
    - GOOD ADHERENCE TO SUBSTRATE UNDER THERMAL CYCLING
    - CAPABLE OF SUSTAINED OPERATION AT TEMPERATURES IN EXCESS OF 1200°F
    - READILY REFURBISHED ON-SITE
        - NO DOWN TIME REQUIRED
- SIGNIFICANT PLANT INVESTMENT COST SAVINGS POSSIBLE WITH INCREASED SOLAR ABSORPTANCE AND/OR SELECTIVITY
    - 1 PERCENT GAIN IN $\alpha_s \sim$ \$7/KW COST REDUCTION
    - SELECTIVITY RATIO INCREASE ($\alpha_s = .95$) OF 2:1 $\sim$ \$7/KW COST REDUCTION

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Dispersed Power Systems - Projects and Requirements

James A. Leonard

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Albuquerque, NM 87115

Summary of Presentation

The national Dispersed Power Systems program within the Department of Energy's Division of Solar Energy consists of three subprograms: Solar Total Energy, Irrigation Systems, and Small Power Systems. Sandia Laboratories has been assigned the responsibility of providing program management support for Solar Total Energy and Irrigation, while the Jet Propulsion Laboratory of Pasadena, California, manages the Small Power Systems Applications.

Two Solar Total Energy Large Scale Experiments are in the preliminary design phase. The first LSE is to provide electrical power and thermal energy to a troop housing complex at Ft. Hood, Texas. Westinghouse Electric Corporation has selected a field of line focusing parabolic trough collectors which will operate at an outlet temperature of 260°C to drive a steam turbine. The second LSE is for a knitwear factory in Shenandoah, Georgia. General Electric has selected a distributed field of two axis tracking, point focusing parabolic dish collectors which will elevate the temperature of a heat transfer fluid to 300°C or 400°C to drive a steam turbine. Strong consideration is being given to the possibility of constructing in the near future an LSE which features a small central receiver.

DOE's first irrigation project near Willard, New Mexico, has been in operation since the spring of 1977. A field of parabolic trough collectors by Acurex-Aerotherm are used to produce 215°C of fluid to drive an organic Rankine cycle turbine. The second irrigation project in Coolidge, Arizona, has also been awarded to Acurex-Aerotherm, which will install an advanced version of their parabolic trough.

The first Small Power System Experiment is just getting underway. Proposals for the conceptual design contract have been solicitied by JPL and are now being evaluated. This project will be for electric power only and will produce about 1 MW peak. The plant will have a field of either line focusing, or point focusing distributed collectors, or central receivers. This collector field will be designed to operate at temperatures of at least 550°C. The possibility of operating plants at 800°C or higher in the near future is being investigated.

It is evident from this brief overview that the Dispersed Power Systems Program includes a very heterogeneous mixture of highly application sensitive systems which involve a great variety of solar collector concepts operating over a wide range of temperatures and other conditions.

The balance of this summary will consist of a requirements oriented discussion describing what the Dispersed Power Systems designers need and expect of absorptive coatings and some of the conditions and environments such coatings must survive.

Temperature

For line focusing collectors, most applications will be below 330°C with significant applications below 250°C in the irrigation and process heat areas. Point focusing collectors will tend to be operated at around 550°C but with some applications down to 300°C and strong future interest in much higher temperatures.

Thermal Shock

Because solar energy is an intermittent source, all collectors are subject to at least diurnal thermal cycles. Some cycling throughout the day due to cloudiness will also be encountered.

Temperature Excursions

Any concentrating collector is subject to loss of coolant flow while in focus. Most systems have an emergency defocus mechanism, but should this protection fail, temperature excursions of several hundred degrees above the operating temperature within a few minutes are possible. Designers would, of course, prefer coatings which can survive such incidents. If serious degradation is inevitable, then knowledge of the time/temperature degradation relationship is needed to help set requirements on emergency defocus systems.

Energy Density

Concentration ratios for focusing collectors vary from about ten for low temperature concentrators to several thousand for central receivers. Line focusing collectors typically operate at 25-40x and point focusing dish collectors at 100-1000x.

Geometry

Receivers of line focusing collectors are usually designed with round pipe, flattened tubing or extruded rectangular stock. The receivers of point focusing systems can vary greatly in design, but a tube bundle welded to a plate or cavity wall is common.

Atmosphere

In the vicinity of the receiver, ambient air, soft vacuums down to one micron, or low conductivity inert gases such as argon may be encountered. In many receiver designs, little or no protection from the ambient is provided. In these cases the absorber coatings may be subjected to dust, smog, salt fog, industrial pollutants, or fumes from leaking heat transfer fluid.

Incident Angle Effects

Due to the geometry of receivers and the non-normal incidence of the incoming solar energy for many collector designs, normal energy incidence on the absorbing surface is the exception rather than the rule. An effective coating must be able to accept a wide range of incident angles without serious loss of performance.

Materials

Line focusing collectors commonly employ receiver tubes of low carbon steel pipe, stainless steel or copper tubing. Receivers in point focusing systems may use a variety of steel alloys or more exotic materials such as zirconium copper. As collector operating temperatures get higher in the future, super alloys, refractory metals, and even ceramics will be specified by receiver designers.

Absorptance/Emittance Tradeoff

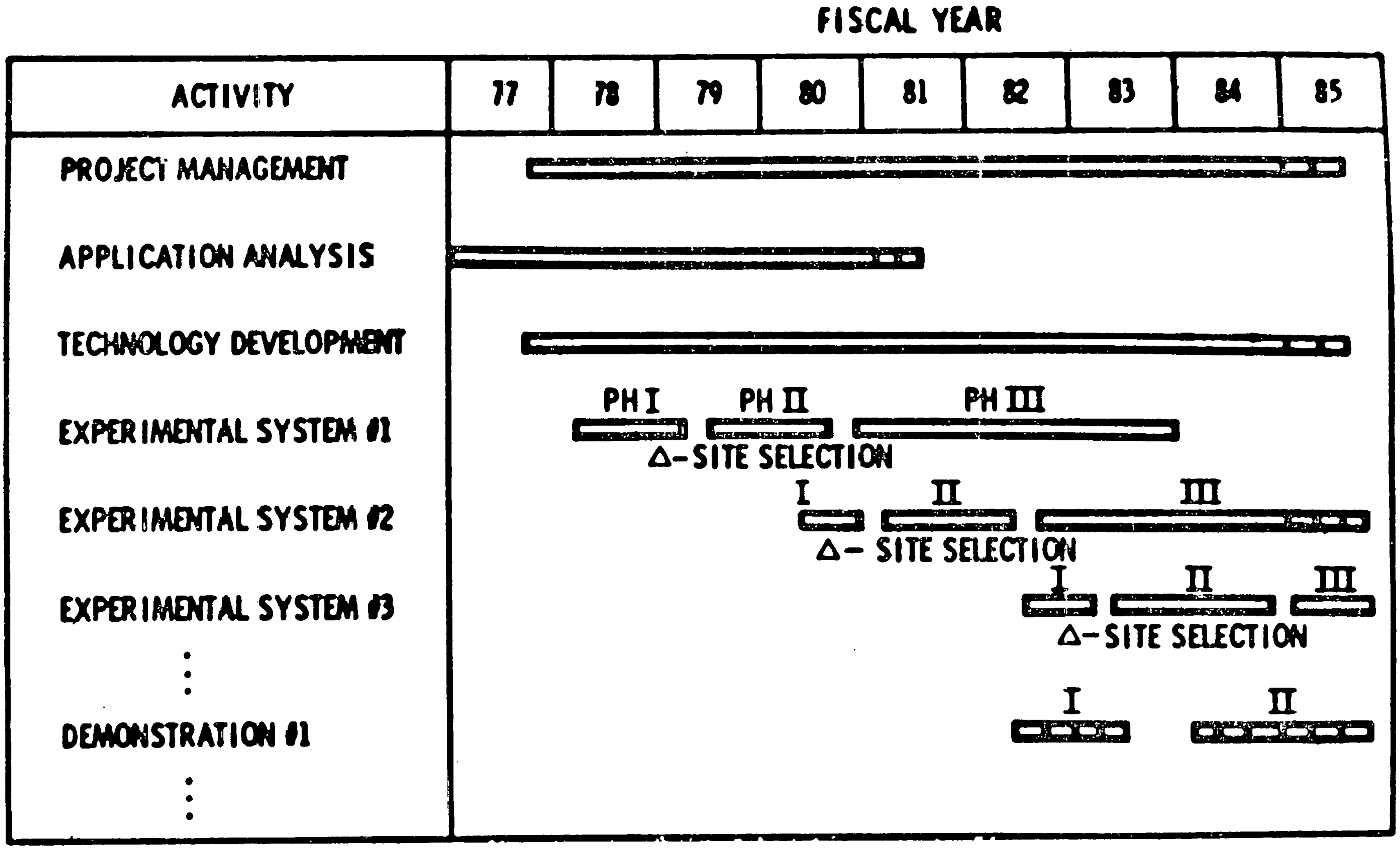
Because absorption by the receiver is a first order effect and radiation losses are second order, high absorptance is generally more important to the designer than low emittance. The tradeoff ratio varies for different designs.

Cost Leverage

Because the absorbing surface of a concentrating collector is small compared to the collector aperture, the designer can afford to pay a relatively high price for a small performance increase in a selective absorber coating. First order performance increases translate to a proportional reduction in collector field size for a given power plant rating.

It should be noted that the relative performance of a selective vs. non-selective coating in any solar collector is dependent on operating temperature, receiver geometry, and concentration ratio (relative radiating area), and that these performance ratios must be traded off against system costs before one can determine the worth of a selective coating. Analysts at various agencies are studying these questions, and this workshop will no doubt produce spirited discussion in this area.

SMALL POWER SYSTEMS PLAN

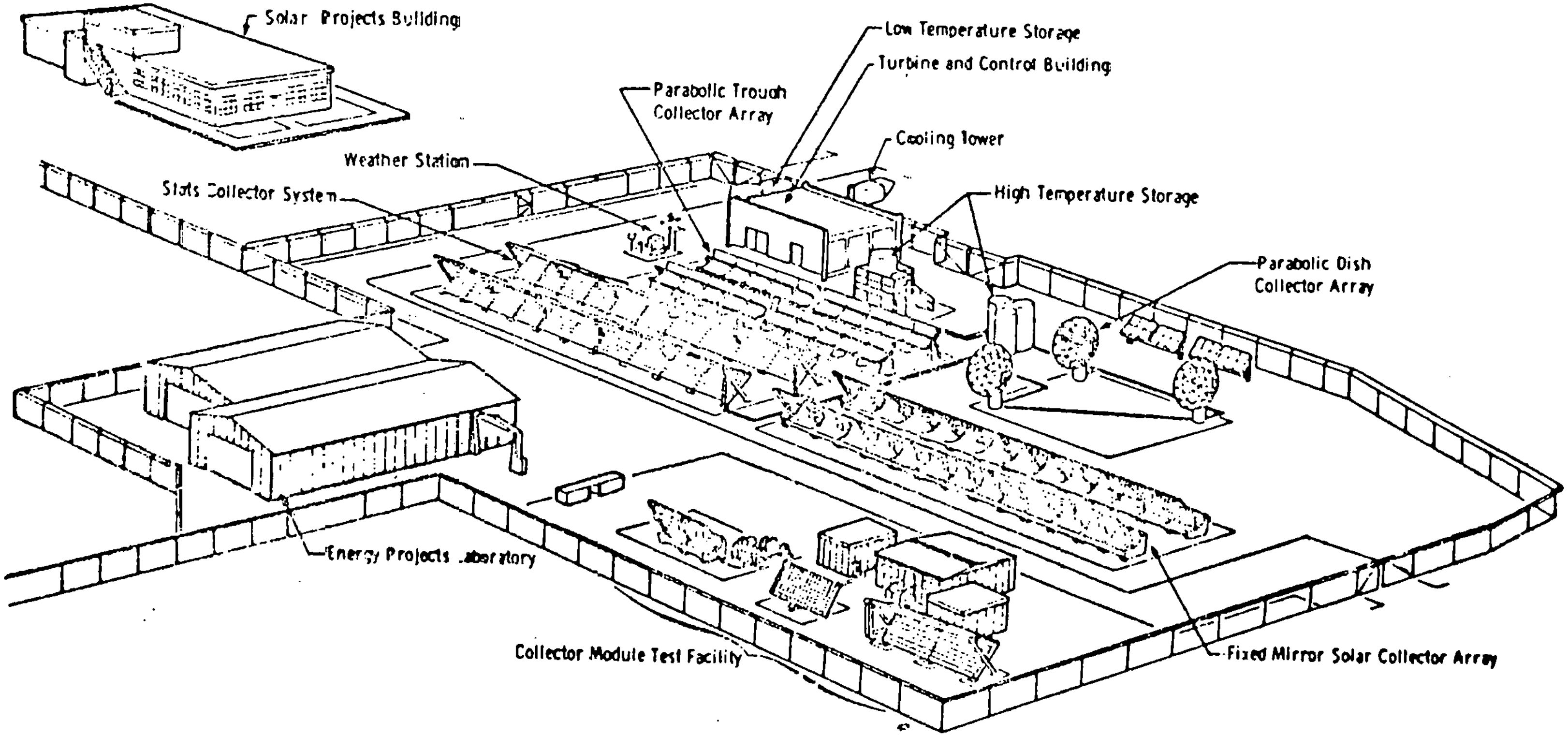


COURTESY OF JPL

SMALL POWER SYSTEMS DEFINITION

- 1 to 50 MWe SIZE RANGE
- TECHNOLOGY OPTIONS INCLUDE
  - POINT-FOCUSING DISTRIBUTED COLLECTOR SYSTEMS
  - LINE-FOCUSING DISTRIBUTED COLLECTOR SYSTEMS
  - SMALL CENTRAL RECEIVER SYSTEMS
  - RANKINE, BRAYTON, STIRLING CONVERSION
- POTENTIAL USERS INCLUDE
  - SMALL COMMUNITIES
  - ISOLATED LOADS
  - RURAL ELECTRIC APPLICATIONS
  - INDUSTRIAL APPLICATIONS

COURTESY OF JPL


Solar Projects Building
Low Temperature Storage
Turbine and Control Building
Parabolic Trough Collector Array
Cooling Tower
Weather Station
Stats Collector System
High Temperature Storage
Parabolic Dish Collector Array
Energy Projects Laboratory
Collector Module Test Facility
Fixed Mirror Solar Collector Array

SOLAR TOTAL ENERGY TEST FACILITY PROJECT

OBJECTIVES

TO SUPPORT APPLICATION PROJECTS OF THE NATIONAL SOLAR TOTAL ENERGY AND OTHER DISPERSED POWER PROGRAMS BY:

- PROVIDE A VERSATILE FACILITY WHICH CAN BE USED AS A NATIONAL COMPONENT EVALUATION CENTER
- ESTABLISH A FACILITY OF SUFFICIENT SIZE TO PROVIDE REALISTIC SYSTEM DESIGN AND INTEGRATION EXPERIENCE
- GENERATE PERFORMANCE AND COST DATA ON SUBSYTEMS
- ACCUMULATE OPERATING AND MAINTENANCE EXPERIENCE
- DEVELOP PRIVATE SECTOR EXPERTISE
- DISSEMINATE RESULTS WIDELY

OCTOBER 1977

STE-LSE #1
FT. HOOD, TEXAS
SUMMARY PARAMETERS

COLLECTOR FIELD APERTURE AREA (N-S HORIZONTAL PARABOLAS)	13,950 M^2	(150,000 FT^2)	
COLLECTOR FIELD EXIT TEMPERATURE	288°C	(550°F)	
COLLECTOR FIELD INLET TEMPERATURE	193°C	(380°F)	
TURBINE THROTTLE TEMPERATURE (DERATED STEAM TURBINE)	260°C	(500°F)	
THROTTLE PRESSURE	2520 KPA	(365 PSI)	
GENERATOR RATING	250 KWE		
AIR CONDITIONER RATING	200 TONS		
HIGH TEMPERATURE STORAGE CAPACITY (SENSIBLE HEAT OIL)	265 M^3	(70,000 GAL)	HOT
LOW TEMPERATURE STORAGE CAPACITY	136 M^3	(36,000 GAL)	HOT/CHILLED

11/77

STE-LSE #2

SHENANDOAH, GEORGIA

SUMMARY PARAMETERS

Collector Field Aperture Area (7M Parabolic Dish)	10,400 M^2	(110,000 FT^2)
Collector Field Exit Temperature	315°C	(600°F)
Collector Field Inlet Temperature	245°C	(475°F)
Turbine Throttle Temperature (Derated Steam Turbine)	300°C	(570°F)
Throttle Pressure	3400 kPa	(500 psi)
Process Steam Conditions	170°C, 1070 kPa	(337°F, 157 psi)
Generator Rating	450 kWe	
High Temperature Storage (Trickle Oil/Rock)	76 x 10^6 kJ	(72 x 10^6 BTU)

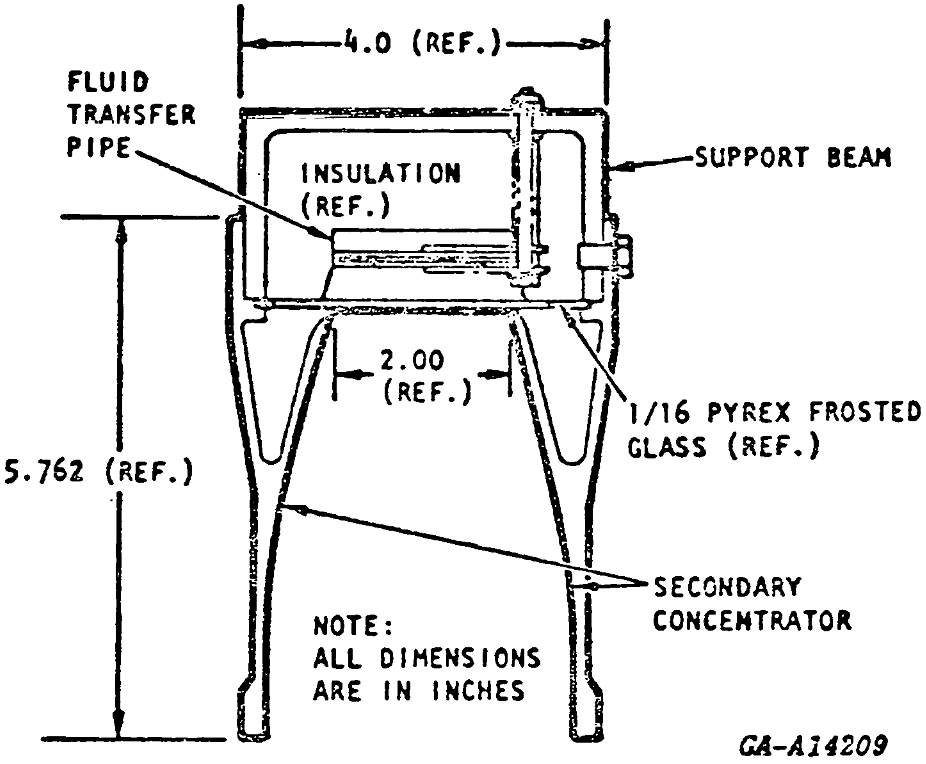
11/77

DISPERSED POWER SYSTEM COLLECTORS

ABSORPTIVE COATINGS APPLICATIONS, ENVIRONMENTS, REQUIREMENTS

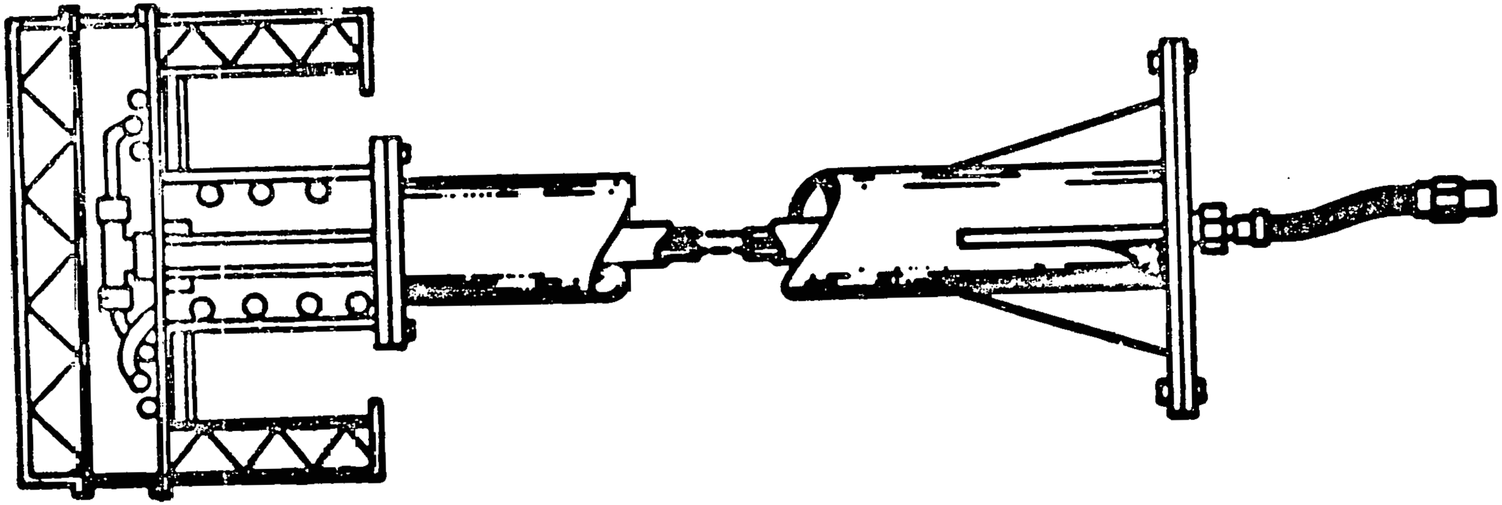
TEMPERATURE	OPERATING TEMPERATURES THERMAL SHOCK TEMPERATURE EXCURSIONS THERMAL EXPANSION
ENERGY DENSITY	CONCENTRATION RATIO INCIDENT ANGLES COST LEVERAGE
MATERIALS & GEOMETRY	RECEIVER TUBES CAVITIES
ATMOSPHERE	VACUUM GASES
ABSORPTANCE/EMITTANCE TRADEOFF	

11/77



Heat receiver assembly cross section

RAYTHEON PARABOLIC DISH COLLECTOR RECEIVER--CROSS SECTION



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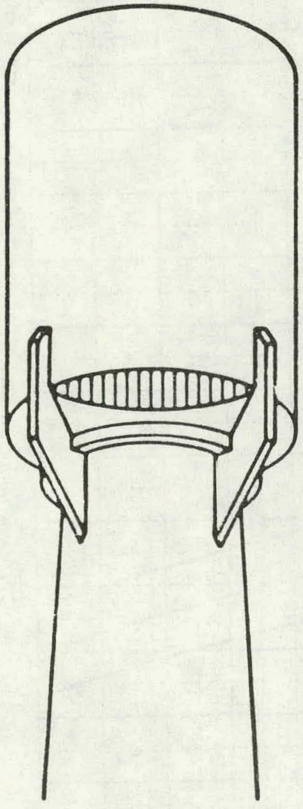
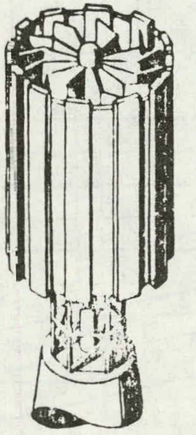
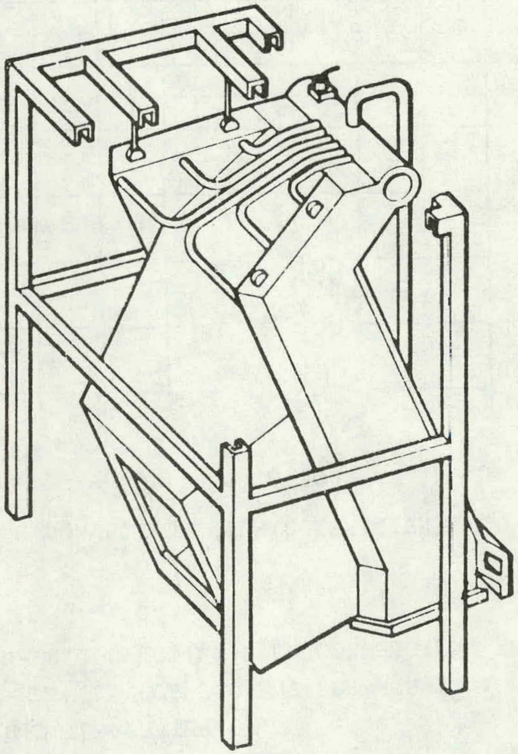


HONEYWELL

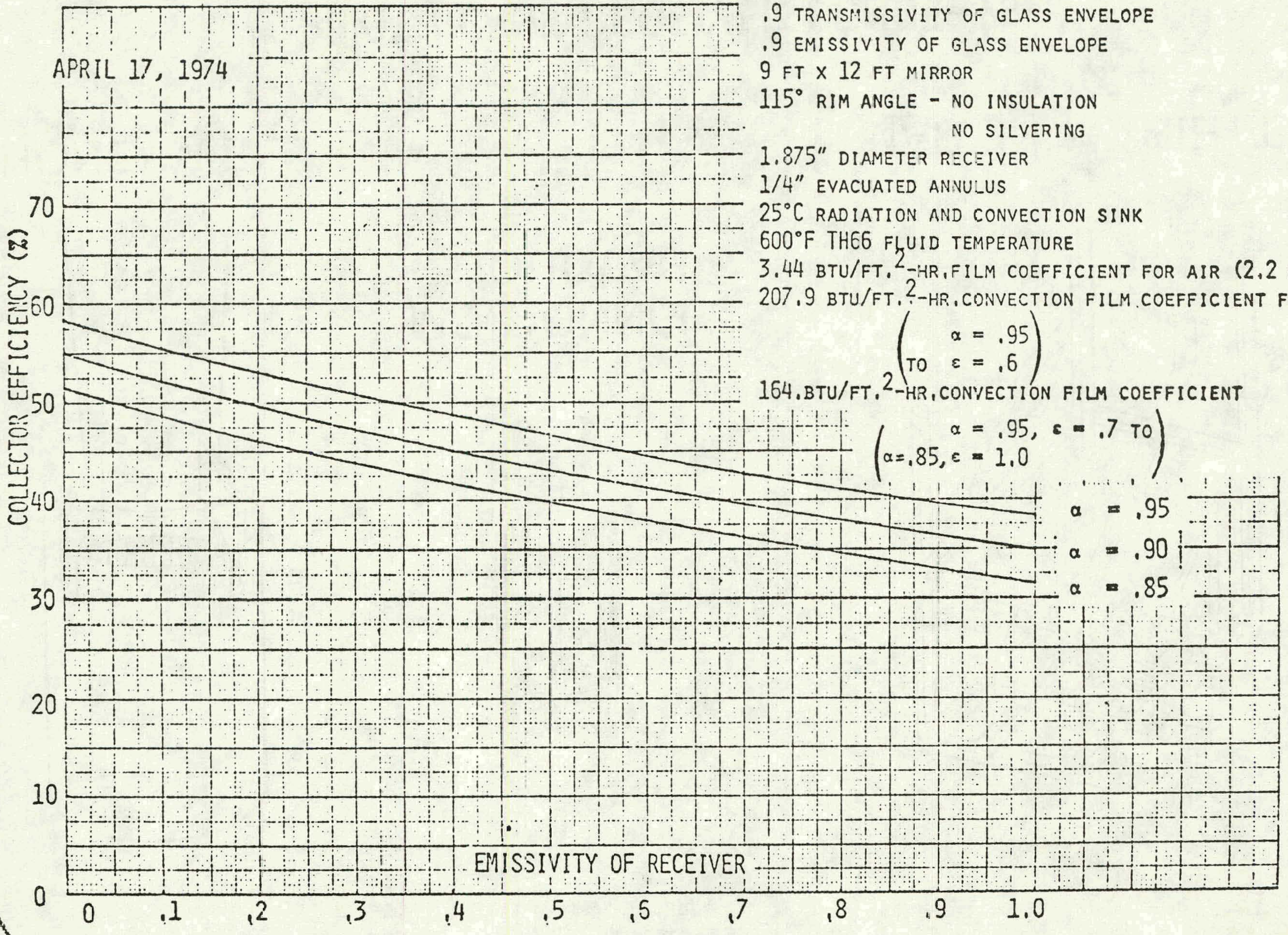


MC DONNELL
DOUGLAS



MARTIN MARIETTA

PILOT PLANT RECEIVER CONCEPTS



GIVEN: 318 BTU/FT.^{2}-HR. - NORMAL SOLAR INPUT
.9 ABSORPTIVITY OF RECEIVER
.78 REFLECTIVITY OF MIRROR
.9 TRANSMISSIVITY OF GLASS ENVELOPE
.9 EMISSIVITY OF GLASS ENVELOPE
9 FT X 12 FT MIRROR
115° RIM ANGLE - NO INSULATION
NO SILVERING
1.875" DIAMETER RECEIVER
1/4" EVACUATED ANNULUS
25°C RADIATION AND CONVECTION SINK
600°F TH66 FLUID TEMPERATURE
3.44 BTU/FT.^{2}-HR. FILM COEFFICIENT FOR AIR (2.2 M/SEC.)
207.9 BTU/FT.^{2}-HR. CONVECTION FILM COEFFICIENT FOR TH66
$\left(\begin{matrix} \alpha = .95 \\ \text{TO } \varepsilon = .6 \end{matrix} \right)$
164. BTU/FT.^{2}-HR. CONVECTION FILM COEFFICIENT
$\left(\begin{matrix} \alpha = .95, \ \varepsilon = .7 \text{ TO} \\ \alpha = .85, \ \varepsilon = 1.0 \end{matrix} \right)$

MR. SERAPHIN: I was disappointed that your talk did not address the importance of angle of incidence.

MR. LEONARD: I forgot to mention that. That is an extremely important --

MR. SERAPHIN: It's an interesting point because all of the systems that you have shown are what the optical designer calls fast optics and flux amplification ultimately implies large angles of incidence.

MR. LEONARD: Especially important for line focusing systems which have very shallow angles of incidence in early light.

MR. SERAPHIN: In defining a system like this, we should speak of the speed of the optics or at least the angle of acceptance for the absorptance. I wonder if there are any numbers available for the acceptance angle that the coating has to provide. I think the fact that your experimental studies exceeded the calculations may simply be that the coating has a particular directional characteristic that we have to know in order to model the system properly.

MR. LEONARD: There has been experimental work done on angles of incidence at our lab on black chrome, I am certain, and perhaps Bob Sowell will show some of those results.

The cosine effect is not the only important one--

cylindrical reservoirs with round cross sections are important, too. The energy that impinges away from the center line is finally reflected away and lost.

The entire diameter of the cylindrical reservoir is not usable and system designers need to be extremely careful either with specifying how good the coating must be or being aware of the limitation in designing the all-day performance.

You typically see efficiencies presented as peak noontime efficiencies, but the all-day capability is extremely important, and in fact, it is the important thing for an actual load.

MR. GROSSKREUTZ: If I heard you correctly, you said that the temperature regime for the small power systems would be generally above 1000 F?

MR. LEONARD: Yes.

MR. GROSSKREUTZ: Can you elaborate on why that requirement has been made?

MR. LEONARD: Well, basically, I assume because one is interested in electric power production only, and the cycle efficiency is simply better.

In the case of solar total energy, where one has a market for the waste heat, the cycle efficiency of the power production process is not quite as important. But, for electrical only, one wants to go for high efficiency, and that implies high temperature. Here again, it would be a cost tradeoff if you could do it more cheaply at a lower temperature and lower efficiency, then you win.

MR. GROSSKREUTZ: Doesn't that eliminate line focusing collectors?

MR. LEONARD: The approaches limit line focusing collectors, although I guess they have not been thrown out yet. A good line focusing collector is capable of those temperatures at reduced efficiency, and would have to therefore compete very favorably with a point focusing system on cost in order to be successful.

MR. GILLIGAN: I want to follow up a little on Bernie's comments.

A number of the slides showed transparent plastic covers over some of these devices. If you are going to be looking at the acceptance angle of the system, then you have to look at all of the components, not just the surface coating.

MR. LEONARD: That's right. Most of them were glass envelopes, although General Atomic does employ a tedlar film window, I believe. The transmittance of glass becomes lower and lower at shallow angles as well.

MR. GILLIGAN: The other point I was going to make in that regard is that it isn't just the transmittance, I think you have to do directional transmittance. The standard way of measuring transmittance is not adequate or appropriate. So you have to make a biangular directional measurement. It is very important because diffuse transmittance is not what you want, you are after the normal transmittance.

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DOE Solar Heating & Cooling and Agricultural/Industrial Process Heat Programs

S. Sargent

DOE Solar Heating & Cooling R & D Branch

S. Moore

Los Alamos Scientific Laboratory, Solar Energy Group

Summary of Presentation

Cost-effective collectors are essential for widespread use of solar energy to meet the thermal energy needs of building as well as agricultural and industrial process heating applications. Various coatings have been developed to improve the performance of solar collectors, e.g., anti-reflection coatings, infrared reflecting coatings, high absorptivity coatings and selective surfaces. A major DOE, Heating and Cooling Branch program is research and development of selective surface coatings. A need for this type of research was recognized early in the solar program and funded by the NSF. Some of these programs were later transferred to ERDA for management. This presentation will outline the present and future selective surface programs and describe some of their accomplishments.

In addition to funding and managing research programs, the DOE has sponsored special workshops and conferences on coatings for the presentation of important selective coatings contributions. These conferences/workshops have helped formulate the heating and cooling selective surface state-of-the-art and research objectives.

Presently active programs and some of their accomplishments are as follows:

Honeywell, Inc. - "Optimization of Coatings for Flat Plate Collectors." This program has involved investigations of selective paints, plated coatings and vapor deposited coatings. Past programs have investigated coatings preparation, optical performance, durability and weatherability, and economics.

ITT Research Institute - "Exposure Testing and Evaluation of Solar Collector Materials." Many selective surfaces are undergoing accelerated and normal exposure testing. One full year of exposure has now been imposed on many specimens. Review and publication of results is expected in the near future.

Los Alamos Scientific Laboratory - "Collector Research and Development." Collector development studies included interaction with industry in producing 8000 ft^2 of mild steel collectors with Nickel/Black-chrome electroplated coatings having average properties of $\alpha=.94$ and $\varepsilon=.08$.

Included in the National Program Plan for Research and Development in Solar Heating and Cooling, ERDA 76-144, are various selective surface tasks. Initiation of these tasks has been implemented through the issuance of PRDA EG-77-D-29-0002 and 0003 and RFP EG-77-R-04-0022 solicitations. The basic categories of absorber operating criteria are based on the following:

1. Non-concentrating collectors operating at low temperature (70-120°F), medium temperature (120-170°F) and high temperature (170-230°F).

2. Concentrating collectors of 3X or of 10X.

As a result of these solicitations the following selective surface contracts have been announced and when combined with present on-going programs represent the majority of the FY 78 coatings effort:

Berry Solar Products - "Commercial Selective Surfaces Applicable to Copper, Aluminum, and Stainless Steel, Their Cost Effective Improvement and Evaluation of Potential Durability in Solar Absorbers."

De Soto, Inc. - "Solar Selective Absorber Coatings by Electrodeposition of Paint."

Honeywell, Inc. - "Selective Paint and Black Chrome Coatings Development."

Owens-Illinois, Inc. - "Improvement of Solar Selective Coating Stability."

Penn-State University - "Black Germanium Selective Absorber Surfaces."

Telic Corporation - "Development of Selective Surfaces."

Additional unsolicited proposals are continually being evaluated for funding.

SELECTIVE ABSORBER COATINGS PROGRAM OBJECTIVES

SPONSOR RESEARCH AND DEVELOPMENT ON SELECTIVE ABSORBER COATINGS FOR SOLAR HEATING/COOLING AND AGRICULTURAL/INDUSTRIAL PROCESS HEAT APPLICATIONS WHICH HAVE:

- IMPROVED ABSORBTIVITY AND EMISSIVITY
- REDUCED INITIAL AND LIFE CYCLE COST
- ENHANCED DURABILITY
- APPLICATIONS TO PASSIVE, FLAT PLATE OR CONCENTRATING COLLECTORS

HEATING AND COOLING

- PASSIVE SYSTEMS (70-160°F)
- NON-CONCENTRATING COLLECTORS
  - LOW TEMPERATURE (70-120°F)
  - MEDIUM TEMPERATURE (120-170°F)
  - HIGH TEMPERATURE (170-230°F)
- CONCENTRATING COLLECTORS (200-350°F)
  - ABSORPTION CHILLERS
  - RANKINE ENGINE/VAPOR COMPRESSION CHILLERS
- AIR HEATING (200-500°F)
  - DESICCANT CHILLERS

AGRICULTURAL AND INDUSTRIAL

- HOT WATER: 150-250°F
  - FOOD PROCESSING
  - FOOD CONTAINER WASHING
  - LAUNDRY APPLICATIONS
  - TEXTILE: PROCESSING AND DRYING
- STEAM: 212-400°F
  - INDUSTRIAL PROCESSES
  - STERILIZATION
  - CHEMICAL PROCESSING
- AIR: 200-350°F
  - GRAIN DRYING
  - FOOD DEHYDRATION
  - PULP AND PAPER DRYING

SELECTIVE ABSORBER COATING PROGRAM EVOLUTION

- NATIONAL SCIENCE FOUNDATION PROGRAMS
- TRANSFER TO DoE
- UNSOLICITED PROPOSALS
- TECHNICAL ASSESSMENT
- DIRECTED R&D PROGRAM PLAN
- PROGRAM IMPLEMENTATION: PRDA'S AND RFP'S

TECHNICAL ASSESSMENT

STATE OF THE ART

- CATEGORY OF COATING
  - ELECTROPLATED SURFACES
  - VAPOR DEPOSITED COATINGS
  - PAINTED SURFACES
  - COATINGS ON GLASS
- TYPES OF STUDIES
  - DURABILITY
    - VARIATIONS IN PARENT MATERIALS
    - SUBSTRATE TYPE & THICKNESS
    - OXIDE, INTERFERENCE OR PAINTED SURFACE
    - PROTECTIVE OVERCOATS
    - VACUUM EFFECTS
  - OPTICAL PROPERTIES
  - TEMPERATURE LIMITATIONS
  - ECONOMIC

R&D PLAN EMPHASIS

- BLACK CHROME
  - STUDY COMMERCIALIZATION OF Bl Cr ON Cu, Al, S.S.
  - DEVELOP Bl Cr ON FOILS
  - INCREASE DURABILITY
  - DECREASE Ni THICKNESS
  - DEVELOP OVERCOATS
  - DECREASE Bl Cr COST
- PAINT COATINGS
  - INVESTIGATE NEW FORMULATIONS
  - IMPROVE MECHANICAL DURABILITY
  - IMPROVE THICKNESS CONTROL
  - INVESTIGATE APPLICATION TECHNIQUES
- BLACK GERMANIUM
  - STUDY SPUTTERED COATINGS
- COATINGS ON GLASS EVACUATED COLLECTORS
  - IMPROVE PROPERTIES
  - IMPROVE DURABILITY
- RESEARCH IN NEW COATINGS AND APPLICATION TECHNIQUES

CURRENT PROJECTS

- HONEYWELL, INC.-"OPTIMIZATION OF COATINGS FOR FLAT-PLATE COLLECTORS."
- IIT RESEARCH INSTITUTE-"EXPOSURE TESTING AND EVALUATION OF SOLAR COLLECTOR MATERIALS."
- LOS ALAMOS SCIENTIFIC LABORATORY-"COLLECTOR RESEARCH AND DEVELOPMENT."

PRDA AWARDS

- BERRY SOLAR PRODUCTS-"COMMERCIAL SELECTIVE SURFACES APPLICABLE TO COPPER, ALUMINUM AND STAINLESS STEEL."
- DE SOTO, INC.-"SOLAR SELECTIVE ABSORBER COATINGS BY ELECTRODEPOSITION OF PAINT."
- HONEYWELL, INC.-"SELECTIVE PAINT AND BLACK CHROME COATINGS DEVELOPMENT."
- OWENS-ILLINOIS, INC.-"IMPROVEMENT OF SOLAR SELECTIVE COATING STABILITY."
- PENN-STATE UNIVERSITY-"BLACK GERMANIUM SELECTIVE ABSORBER SURFACES."
- TELIC CORPORATION-"DEVELOPMENT OF SELECTIVE SURFACES."

SELECTIVE SURFACE COATINGS

SOLICITATION	CATEGORY	PROPOSALS RECEIVED	AWARDEES	PROJECT
PRDA-3	SAS-I	25	HONEYWELL, INC.	SELECTIVE PAINT & BLACK CHROME DEVELOPMENT
			DE SOTO, INC.	ELECTRODEPOSITION OF PAINT
			PENN. STATE UNIVERSITY	BLACK GERMANIUM SELECTIVE SURFACES
			TELIC CORP.	DEVELOPMENT OF SELECTIVE SURFACES BY SPUTTERING
			BERRY SOLAR PRODUCTS	COMMERCIAL SELECTIVE SURFACES ON CU, AL AND S.S.
PRDA-2	AER-I	10	OWENS - ILLINOIS	IMPROVEMENT OF COATING STABILITY ON GLASS
RFP-22	SEL-I	13	NO AWARDS TO DATE	STUDY TECHNIQUES OF PRODUCING SELECTIVE SURFACES EVALUATE PROPERTIES AND STABILITY STUDY ECONOMICS

MR. NELSON: Who is developing the black chrome on foils?

MR. SARGENT: This is Barry Solar Products in New Jersey. There may be other companies, in fact, doing that, but this is the only one that we are sponsoring.

MR. NELSON: Also, you said 76-144 is being revised, when will that be out?

MR. SARGENT: We are hoping by about February. If not better, at least thicker than the previous version.

The R&D program plan was reviewed by the Solar Energy Industry Association, plus numerous individuals, and all their comments have been taken into account. I am not saying that we necessarily incorporated them, but they certainly have been considered.

MR. BLICKENSDERFER: Did you state the temperature at which you measured emissivity?

MR. SARGENT: For which particular application? Are you speaking of Los Alamos?

MR. NELSON: Your results on the panel that you measured?

MR. SARGENT: I believe it is room temperature, is it not?

MR. MOORE: We used a number of different instruments. We used Dick Pettit's information, and at that time, with the removable filter, you were capable of 100 C in room temperature; is that correct?

MR. PETTIT: Yes, we are also capable of 300 C. I would guess that the data presented there is probably near ambient.

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Summary of Discussion

CHAIRMAN ELLIOTT: I will summarize what I think I heard as the key points to provide some sort of basic structure, and I would like to call for elaboration or discussion of these points or any others that I seem to have missed.

The first thing I think we heard is that absorptivity dominates over emissivity. Absorptivity is more important than selectivity at the high concentration ratios, particularly the high concentration ratios that we see in the central receiver program.

In the realm covered in Jim Leonard's topic, Jim felt that about a 100X concentration was the basic point at which you begin to want to really think about selectivity.

And certainly we heard from Steve that selectivity is going to be extremely important if we get to the lower levels, and yet Ron told us that there is a point up there when you start pushing the absorptivity much above .95, .96, that you may begin to want to think about the trade-offs for the kind of selectivities that we saw in the last few slides, if these live at the high temperatures. They may begin to be worth considering on an economic basis when we start trying to make even central receiver plants pay off.

So, I think the question is not closed, in fact, it is very much open, and allied to it are the questions whether use of integrated solar spectra, or a properly weighted solar spectrum? We tend to have been rather careless about the angles at which the tests are made. We are pretty good at distinguishing between normal and global optical tests, but some of the effects of angle are rather interesting.

There are some factors both plus and minus that we have to address and keyed to this is the very vital question of what temperature do we make our optical measurements at, and are those measurements that we make at ambient temperature indeed credible when we are talking about extrapolating to temperatures like 500 C?

MR. RICHMOND: There were several statements made in the discussion this morning about the need for measurement at temperature. I just wanted to point out that there was a system developed at the National Bureau of Standards back in the mid '60-s for measuring directional hemispherical reflectance at temperatures up to 2500 K. Unfortunately, that equipment has been largely cannibalized. A few of the parts are still left. It could be put back in operation.

I do have a number of copies of the NBS tech note describing that work, and if any of you want to write to me asking for it, I will be glad to send you a copy. That's Joe Richmond, National Bureau of Standards, Washington, DC 20234.

MR. SCHWARTZ: I have a question as a follow-up to what Joe stated. Does anyone here know whether any at-temperature alpha measurement is available in the country?

CHAIRMAN ELLIOTT: I would like to bounce that question off Bernie Seraphin, if I may.

MR. SERAPHIN: Assuming that we are dealing with opaque materials, of course, a high temperature reflectometer should do the job, and as I mentioned before, there are about three or four in this country.

MR. SCHWARTZ: Where are they? Who has them?

MR. SERAPHIN: Well, we have one at the Optical Sciences Center.

MR. SCHWARTZ: Yes, but that is for specular, as I understand?

MR. SERAPHIN: That is for specular, and is being expanded into a hemispherical operation.

There is the equipment at China Lake under the direction of Hal Bennett.

MR. SCHWARTZ: Isn't that specular again?

MR. SERAPHIN: That's also specular.

MR. SCHWARTZ: Is there anything at high temperature, not only for specular, but for diffuse, both?

MR. SIEVERS: The Cornell group has a diffuse reflectometer for measuring up to 300 C.

MR. GILLIGAN: We have one under design right now that will go up to 1200 F.

MR. RICHMOND: I might mention that there was some work done at the Bureau of Standards some years ago on the use of the Carey White 90 reflectometer which is a modified hemispherical reflectometer making measurements at temperatures up to something on the order of 400 C. Now, this was a directional hemispherical reflectance measurement.

MR. JURISSON: We have a hemispherical reflectance measurement up to 500 degrees C, but unfortunately, some of the equipment has been cannibalized.

MR. SCHWARTZ: Now, those are emittance measurements?

MR. SERAPHIN: Spectral equipment?

MR. JURISSON: Yes, spectral emittance, you do get the same absorptance.

MR. SCHWARTZ: I really want spectral at the short wavelengths, in other words, at the solar spectrum.

MR. JURISSON: Right.

MR. SCHWARTZ: What kind of instrument is it?

MR. JURISSON: It is a Beckman.

MR. SERAPHIN: I think it is very important, like Herman did, to distinguish between instruments that give you the calorimetric information. There are dozens available.

MR. SCHWARTZ: Hundreds.

MR. SERAPHIN: These are helpful if you want to evaluate a finished coating or compare different coatings. If you want to improve things, you need the spectral information, and this is much harder to do at the elevated temperature, and even harder to do in the directional mode.

MR. RICHMOND: It is also very hard to do at short wavelengths because you don't have much energy to work with.

MR. SCHWARTZ: Apparently, am I right, the consequence is that we do have some instruments? The instrument, particularly the one at Cornell, that goes up to 300C?

MR. SIEVERS: Right.

MR. SCHWARTZ: 300 C is reasonable, but it is nowhere near what is needed obviously for something like the Barstow plant. The Barstow plant is nominally 500 C degrees, so we are short 200 degrees. Is there any other one but that one?

MR. GILLIGAN: We have two or three different pieces of equipment. We measure the emittance out to 25 microns, hemispherically or directionally. We have directional gear capable of temperatures right now that are about 1000 degrees and 1200, or something like that, and that can go higher. There is no reason why they can't go much higher than that.

MR. SCHWARTZ: But again, it is the short wavelengths that we want.

MR. GILLIGAN: We can go to any wavelengths you want. We are not limited to wavelength at all.

CHAIRMAN ELLIOTT: You do have the sensitivity to work very short wavelengths?

MR. RICHMOND: What kind of detectors are you using now?

MR. GILLIGAN: You name the wavelengths, we have got the detector for it.

MR. RICHMOND: We are talking now about the wavelength range from about 0.25 μm to 2.5 μm

MR. GILLIGAN: For very short wavelengths. The shortest we go down to is about .325 μm

MR. RICHMOND: That's short enough. At what temperatures?

MR. GILLIGAN: About 1000 F.

CHAIRMAN ELLIOTT: What detector would you use at the short wavelengths?

MR. GILLIGAN: PM-2.

MR. RICHMOND: Your energy is down by about a factor of 10 over what it would be up at the peak?

MR. GILLIGAN: We developed this equipment on an Air Force contract, and the sensitivities are something like .01. That's pretty low. That's all wavelengths between .325 μm and 10.6 μm

CHAIRMAN ELLIOTT: It might be useful if this meeting could lead to a tabulation of these resources. Since you seem to be most interested, could I ask you to haul out a piece of paper and get the people to list briefly their resources, and if any publication comes out of this, that could be incorporated in it also?

MR. SCHWARTZ: Yes.

MR. CARROLL: I would like that to include enough description of the equipment so that we could understand what the designs are what they are measuring. It should indicate detectors and the basic instrument used.

MR. RICHMOND: There are publications describing it.

MR. CARROLL: That's fine as long as there are publications.

CHAIRMAN ELLIOTT: Enough to make it possible to chase down the resource and make some assessment on how useful it will be.

MR. CARROLL: I have a statement and a question. Joe, how far down in wavelength can TRW go with that parabaloid reflectometer?

MR. RICHMOND: I don't know for certain, but I think they can go right down through the entire solar range.

MR. CARROLL: There is a system that as far as I know they can go to about 800 C.

MR. McDONALD: I talked to them a few days ago, and they said that they couldn't make those kinds of measurements now, but they expected with slight modification they could make them.

MR. CARROLL: With the parabaloid system?

MR. McDONALD: Yes.

MR. CARROLL: In addition, they have built an intermediate or low temperature reflectometer in the solar spectrum that operates on a relative mode that will go up to 250 or 275 C. I don't know what the status is. It was a jury rig that they built for a program at JPL last spring.

MR. SKINROOD: I want to make two comments. Currently as part of my specification, there is a specification on absorptivity at temperature, and it does include an angular specification. We haven't figured out how to measure things like that, but that didn't stop us from putting it in the specification.

It is still of major interest because of the way the pilot plant is being procured. The heliostats are procured in one batch, and all of the rest of the plant is another procurement.

Secondly, I am not sure I understood the summary of the use of selective coatings and concentrations. I think Jim mentioned 100X as a threshold, I don't think you mean that to be a general rule of thumb to say that above 100X selectivity is not of interest because I think it may be.

MR. LEONARD: On the contrary, what I said was that a theoretical black body absorber with unit emittance compared to black chrome at .95 absorptivity, has a cross over at about 100X. But qive me a nonselective surface like pyromark where the absorptance is equal and the selectivity beats it everytime. You have to improve absorptance if you are nonselective.

CHAIRMAN ELLIOTT: I apologize for misquoting Jim for the sake of getting a discussion going, but I think we saw in the last curve that Ron showed that we are definitely not disinterested in emissivity now that we have good absorptivity.

MR. SERAPHIN: You may include in your summary, Doug, the point that Ron Tobin made, namely, the determination of the time, temperature, degradation characteristics of the coatings which is particularly important, I feel, in the case of black chrome simply because it is so close to the operating temperature. If you want to use black chrome in a design that is supposed to run anywhere between 250 or 300 C, we are very close to where things happen to black chrome.

CHAIRMAN ELLIOTT: From what you have said, am I correct in saying that the central receiver operating temperatures may take you completely out of the realm of black chrome?

MR. SERAPHIN: That is my personal opinion, I don't know how many share this. But black chrome degrades permanently at about 300 C. About 1000 hours at 350 C or something like this. At 400 C black chrome is gone definitely.

MR. LIN: I would like to ask Jim, do you have any idea what temperature is at the glass jacket that you get in the trough design?

MR. LEONARD: From memory, I think the answer is in the low 200 F.

MR. LIN: The reason I am asking this question is that we developed an inverse selective coating for glass, maybe that would be applicable to concentrated collectors.

MR. LEONARD: But, is it temperature sensitive?

MR. LIN: Not at 200 degrees F.

MR. LEONARD: Pettit says that he is recollecting more like 150 F.

MR. LIN: This particular coating is stable at 350 C.

MR. PETTIT: One quick question, could you repeat the temperature that the AMA coating is stable to --

MR. JURISSON: We have appraised it up to 1050 degrees F for 500 hours.

MR. PETTIT: What about in air?

MR. JURISSON: I would guess it is roughly 3 to 400 degrees C, atmospheric.

CHAIRMAN MASTERSON: What about the measurement of absorptance or reflectance in the infrared in terms of inferring emittance from those measurements?

MR. RICHMOND: Well, first of all, you can't use a normal integrating sphere in the infrared because the reflectance of the normal sphere coatings becomes very low at wavelengths longer than about 2.5 μm , and you really need to measure out to at least 20 μm and preferably out to about 30 μm

There are several methods by which this can be done. The most common if you want to measure reflectance is to use some sort of an integrating mirror to collect the reflected flux. Those mirrors are usually either an ellipisoidal mirror, a paraboloidal mirror, or a hemispherical mirror.

Another method that is used is the Hohlraum reflectometer where the sample that is being measured is inserted into a heated cavity. The specimen is water cooled during the measurement. You view it through a very small hole in the cavity, and you view the specimen and the wall of the cavity alternately, and you put the radiant energy that is coming out through a monochromator, and you compare that reflected by the sample to that coming from the wall and the ratio of the two gives you the reflectance at that wavelength.

This is a function of wavelength, and taking one minus that to get your spectral absorptance, and an average in which you weight it by the spectral distribution of black body radiation at the temperature of interest.

MR. PETTIT: Could you briefly describe some of the results that you obtained from the integrating sphere reflectometer that was able to measure reflectance properties of samples heated from room temperature up to 2000 F?

MR. RICHMOND: I didn't bring any of that with me. I can tell you that the reflectance of graphite is almost independent of temperature over that range. Very, very slight effect at several wavelengths.

In most of the other materials that we measured, the reflectance decreased with an increase in temperature. But the amount was quite small. The type of materials that we were measuring were generally refractory materials.

With tungsten, the reflectance increased with temperature. I think we observed the same effect in rhodium. Those were the only two metals that we measured. All the others were high temperature oxides, primarily, and most of those reflectances went down slightly with temperature. A very rough order of magnitude was about one percent of the measured value per hundred degrees K. It could vary from that by at least a factor of two for different materials.

MR. SCHWARTZ: Let's take a look at this epsilon term in the equation. It is another term that would be nice to get, but in the infrared, very seldom do we ever see it measured, and usually the thing that is measured is the $\varepsilon(\lambda)$ normal, or the $\varepsilon(\lambda)$, basically the total hemispherical.

By virtue of the fact that you can't get this, I wonder if it isn't just as good to forget the lambdas, if you will, and just go directly to the epsilon total hemispherical? So again, in this equation here, we concentrate on the total hemispherical since you can't get the ultimate which is the $\varepsilon(\lambda,\Theta)$, and over here, since you can get the details quite readily for the angular reflectance in the solar spectrum, is that generally true? Because I have never seen the measurement of $\varepsilon(\lambda,\Theta)$ in the infrared.

MR. RICHMOND: It has been done by different people. Most of it was done way back in the early 1900s, maybe that's why you didn't find it.

But the relationship between the normal emittance and the hemispherical emittance is quite well known as a function of the emittance so that you can make a conversion emperically and probably not have an error of more than one percent at the most, probably more on the order of a half a percent.

MR. SERAPHIN: The suggesion that Herman made is more important in that $\varepsilon(\lambda)$ is really a very interesting quantity because in the infrared, it is supposed to go up with temperature, but for those materials in the near infrared and in the visible, it goes down with the temperature. That means most materials lose less energy at high temperatures than they do at low temperatures, and a systematic study of this sign inversion shows the temperature coefficient to be very important because it opens a possibility to synthesize materials that have this sign inversion way out into the infrared, and therefore, help us in suppressing the emittance as the temperature goes up. I think you made a very important, potentially very influential, suggestion.

MR. RICHMOND: I might say something about these reprints; this is something that I prepared that we are going to pass around and let people look at the hopefully we will discuss this at the review session.

The whole thing is involved with the question of trying to get everybody to make the conversion from the spectral reflectance data to solar absorptance the same way, use the same solar absorptance curve and the same method of making the computation. Apparently now, there are about five different solar energy distributions being used, and four different methods of making the computation, and I think a lot of the discrepancies in the value between different laboratories are due to the method of making the computation.

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Historical Perspective --

Coatings for Solar Collectors

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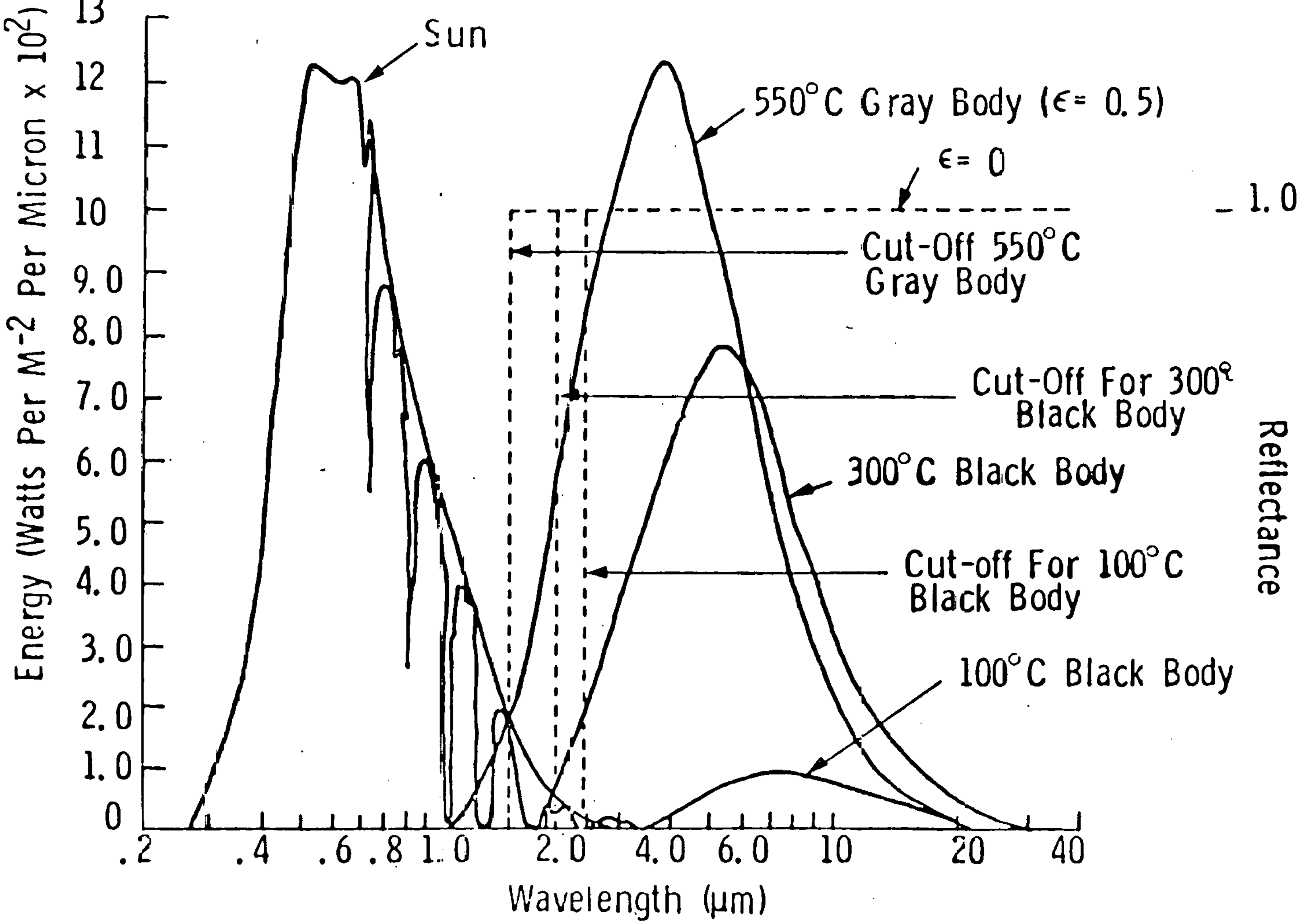
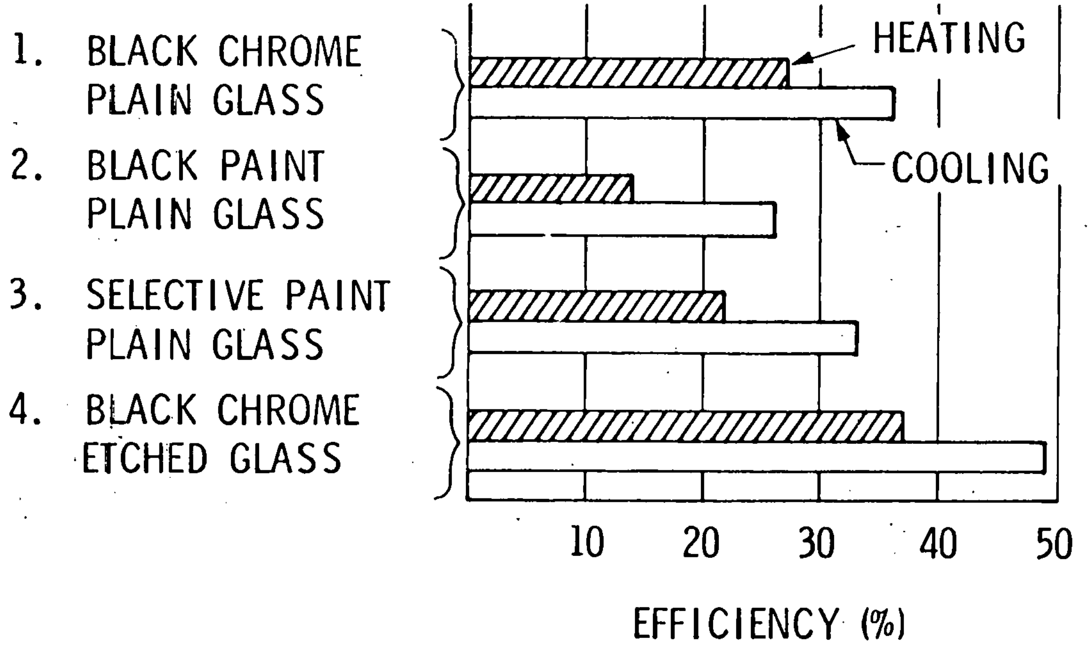
The types of specialized coatings used in solar collection systems are reviewed. The coatings can be divided into three classes: selective absorbers, anti-reflection coated windows, and heat reflecting windows. The ideal spectral behavior for selective surfaces are discussed, including the influence of solar concentration and collection temperature. Performance of collector systems with and without these special coatings are discussed and their cost effectiveness is pointed out.

The pioneering steps in the implementation of solar coatings are reviewed from the early efforts of Tabor, Hottel, Hass, and Duffie and others through some of the more novel recent approaches. The basic physical phenomena at work in achieving selectivity are reviewed. Accurate optical property measurements were a key factor in the early development of selective surfaces.

IDEAL SOLAR ABSORBERS FOR OPERATION AT 00°C, 300°C and 550°C



SOLAR COLLECTOR EFFICIENCY



HEATING: CHICAGO, NOV.-MAR., 943 BTU / DAY AVERAGE

COOLING: ATLANTA, JUNE- SEPT., 1709 BTU / DAY AVERAGE

Tabor, 1955, First Reference on Solar Application of Selectivity

Black Ni, Half-Silvered Mirrors

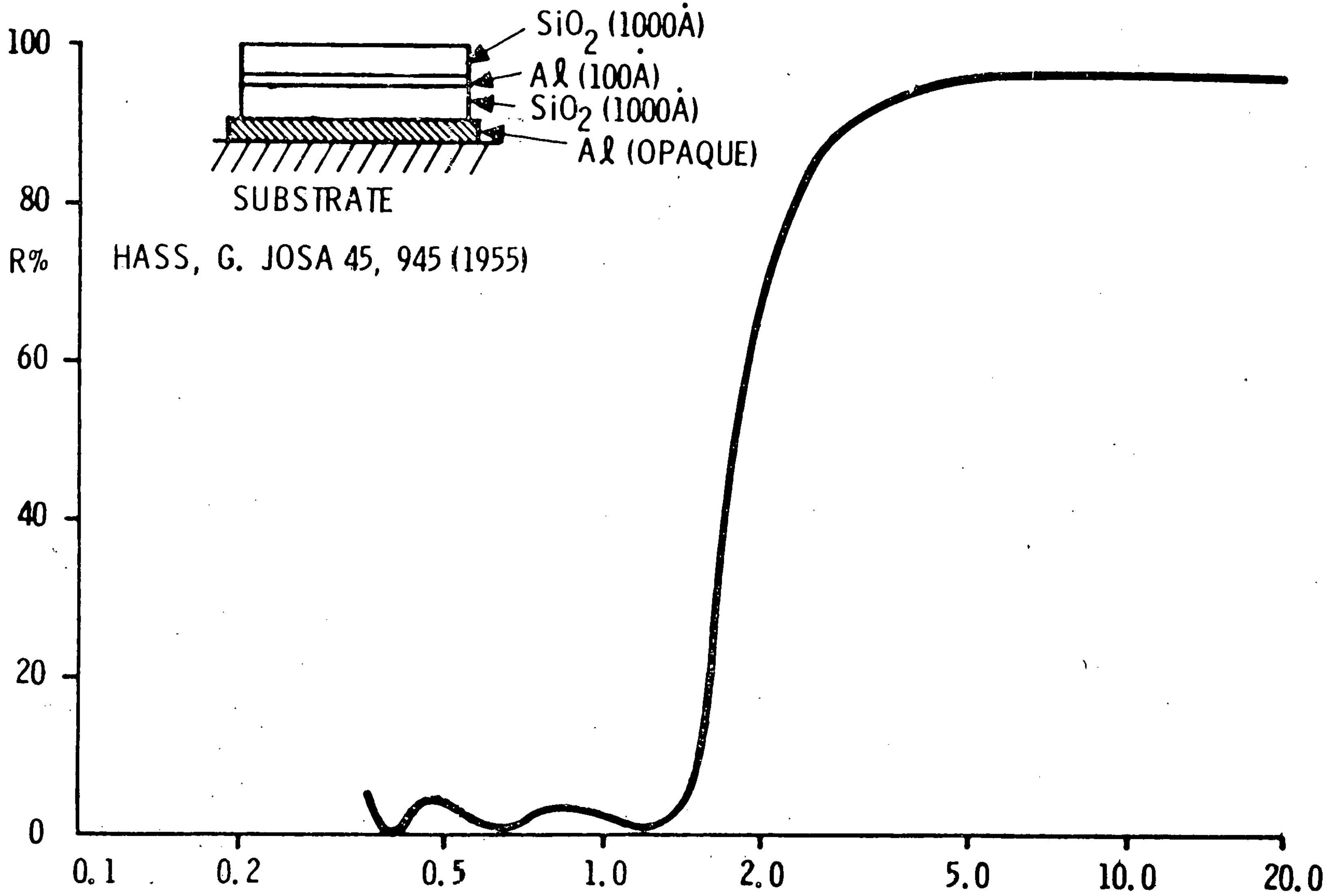
Selective Absorbers

Vacuum Evaporated Selective Absorbers

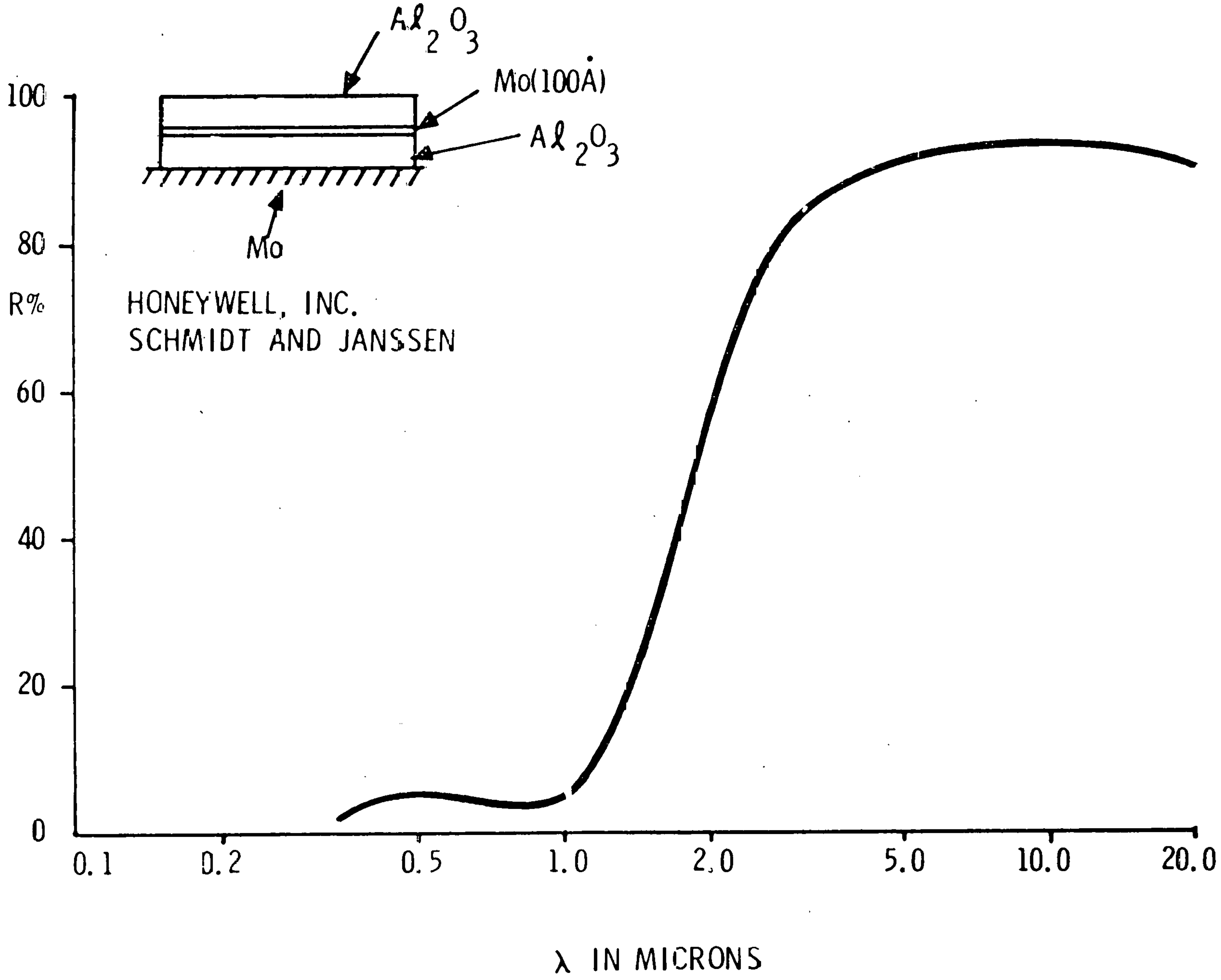
- Hass et al., 1953, SiO_2-Cr-SiO_2 on Al
- Schmidt, R.N. and Janssen, J.E., 1964
  MgF_2-Mo-CeO_2 on Mo
- Ramsey, J. and Peterson, R.E., 1975,
  Al_2O_3-Mo-Al_2O_3 on Mo

Plated Selective Absorbers

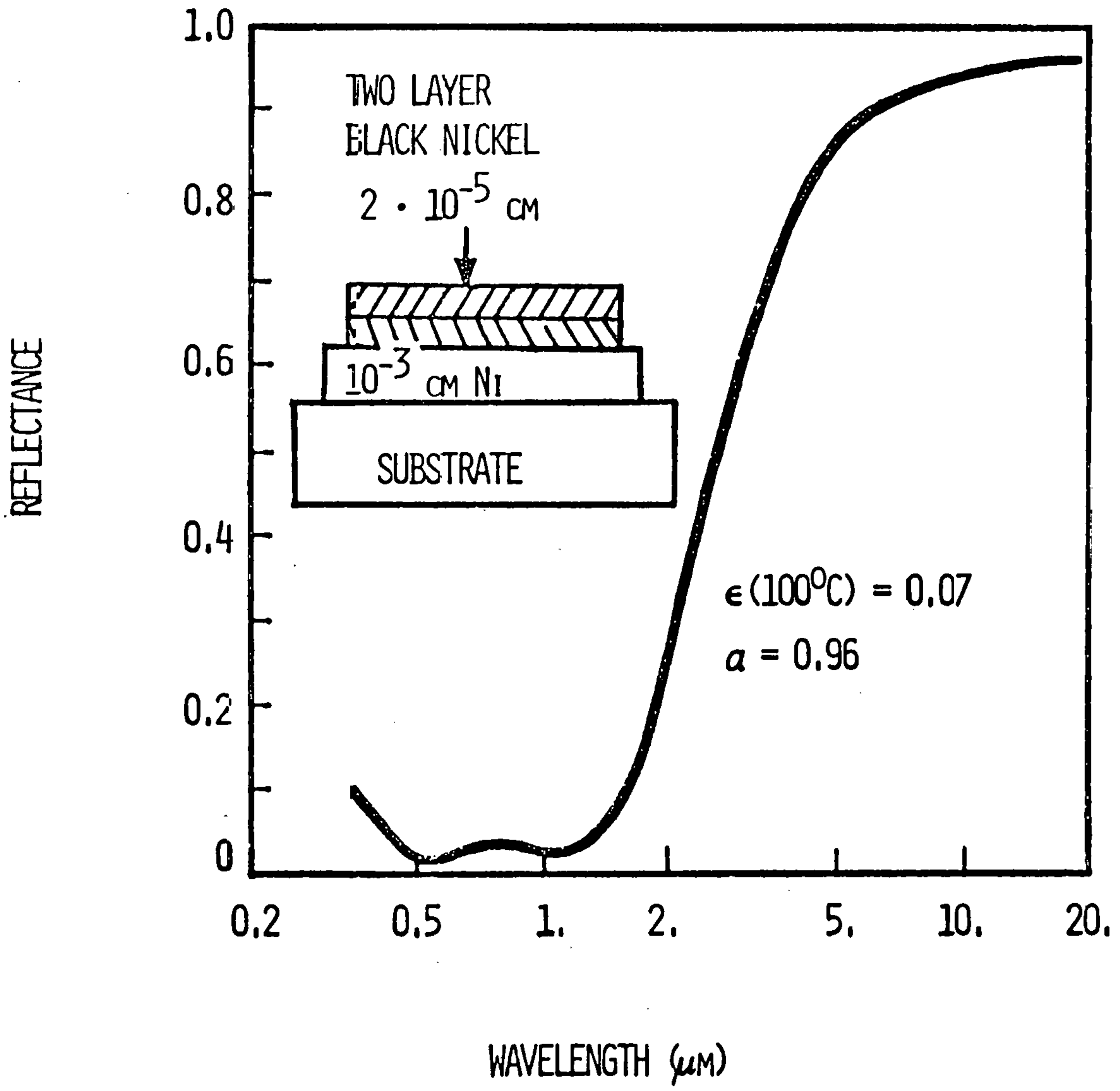
- Hottel, H.C. and Unger, T.A., 1959
  Copper Oxide on Al
- McDonald, G.E., 1974, Black Chrome
- Peterson, R.E., 1974
  Double Layer Black Ni
- Lin, R.J.H. and Peterson, R.E., 1976
  Improved Black Ni
- Pettit, R.B., Sowell, R.R. and Mattox, D.M., 1975-1976
  Black Chrome
- Lin, R.J.H., Mar, H., and Peterson, R.E., 1974-1977
  Black Chrome, Black Iron



HASS, G. JOSA 45, 945 (1955)



Al_2O_3
Mo(100Å)
Al_2O_3
Mo
HONEYWELL, INC.
SCHMIDT AND JANSSEN
R%
100
80
60
40
20
0
0.1
0.2
0.5
1.0
2.0
5.0
10.0
20.0
λ IN MICRONS


TWO LAYER
BLACK NICKEL
2 · 10^{-5} CM
10^{-3} CM NI
SUBSTRATE
ε(100°C) = 0.07
a = 0.96
REFLECTANCE
1.0
0.8
0.6
0.4
0.2
0
0.2
0.5
1.
2.
5.
10.
20.
WAVELENGTH (μM)

Chemical Vapor Deposited Selective Absorbers

- Gurev, H.S., Hahn, R.E., Masterson, K.D., and Seraphin, B.O., 1975, Si-Ag Tandem

Surface Structure Selective Absorbers

- Irhine, T.F., et al, 1958
  Stainless Steel Mesh. $\alpha = 0.73$, $\epsilon = 0.26$
- Woodall, J., 1975
  Tungsten Dendrite. $\alpha = 0.96$, $\epsilon = 0.26$ (500^0C)
- Berg, R.S., and Kominiak, G., 1976
  Sputter Etched Cu. $\alpha = 0.97$, $\epsilon = 0.30$ (158^0C)

Selective Paints

- William, D.A., 1963
  PbS in Silicone. $\alpha = 0.84$, $\epsilon = 0.19$
- Mar, H., et al, 1975
  Metal Oxide in EPDM. $\alpha = 0.90$, $\epsilon = 0.24$
- Lin, R.J.H., and Zimmer, P.B., 1977
  Metal Oxide in Silicone. $\alpha = 0.92$, $\epsilon = 0.13$

Selective Reflectors or Heat Mirrors

- Sheklein, A., et al, 1966

  Doped Tin Oxide. Ts = 0.75, R_{IR} = 0.80
- Fan, J., Bachner, F.J., Foley, G.H., and Zavracky, P.M., 1976

  TiO_2-Ag-TiO_2. T_s = 0.80, R (10 μ) = 0.98

AR Coatings

- Nicoll, F.H., 1942

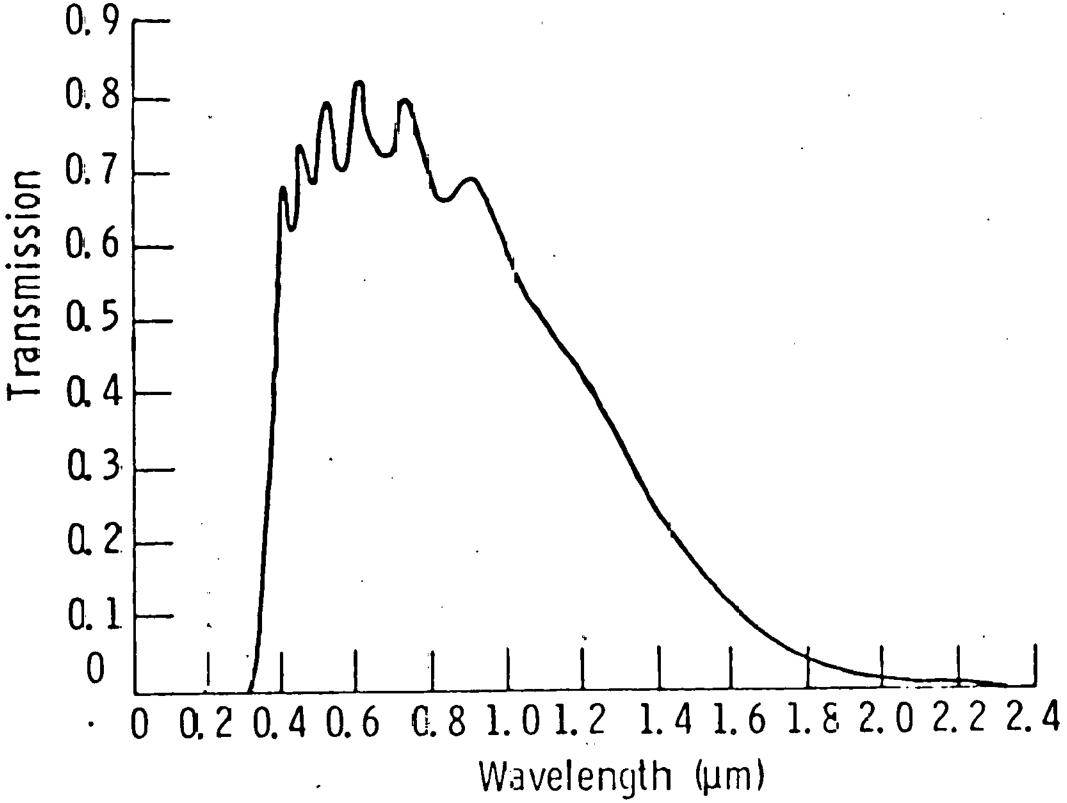
  First Chemical Etch Method
- Hsieh, C.K., and Coldewey, R.W., 1974

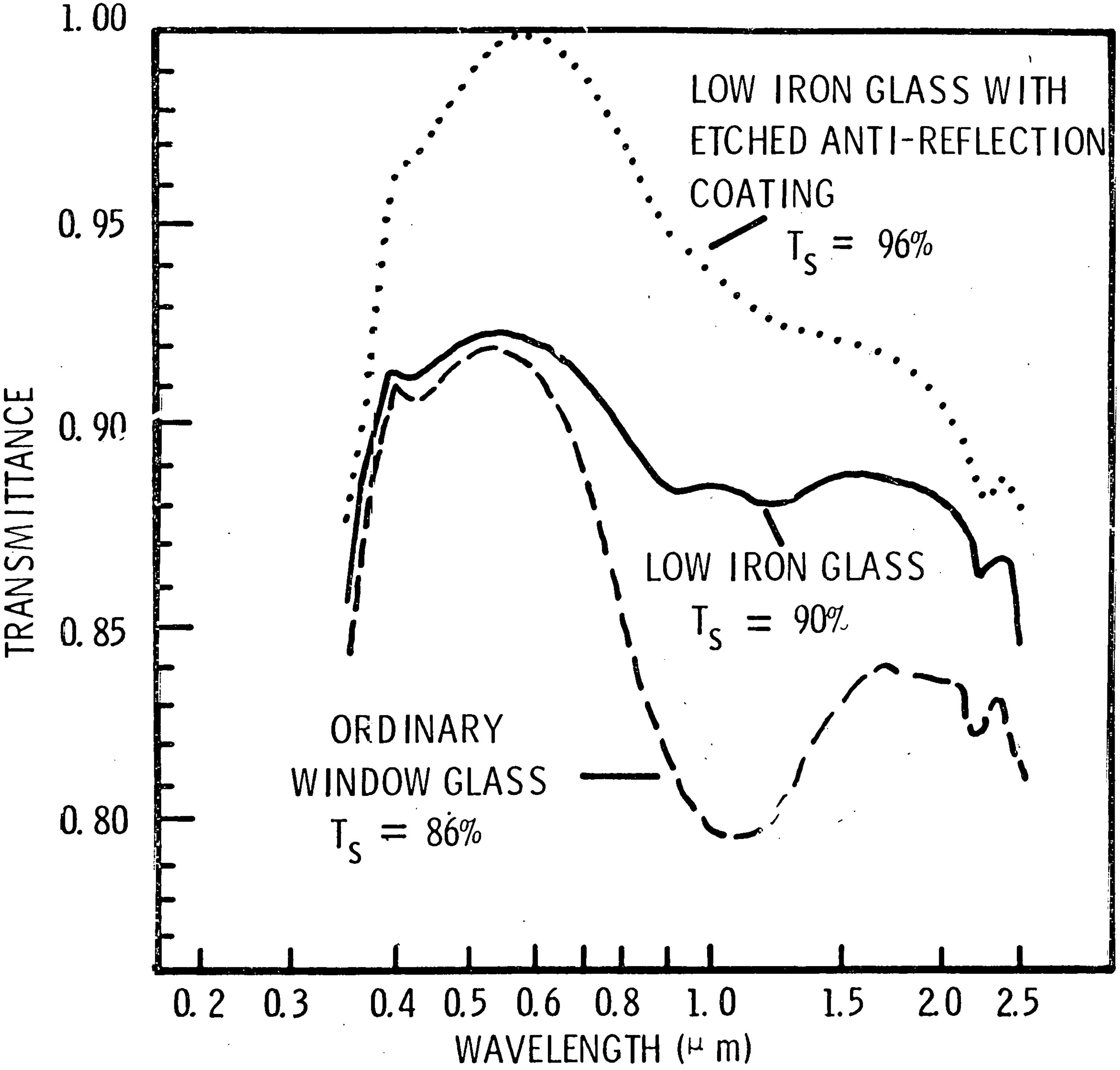
  Evaluation of Vacuum Deposited MgF_2 on Single and Double Glazing
- Lin, R.J.H., 1975

  Etched AR Glass, R_s = 0.8%
- Minot, M.J., 1976

  AR Etching of Phase-Separated Borosilicate Glass (e.g., Pyrex)

TRANSMISSION OF AN ITO FILM DEPOSITED IN ARGON ATMOSPHERE




1.00
0.95
0.90
0.85
0.80
TRANSMITTANCE
0.2
0.3
0.4
0.5
0.6
0.8
1.0
1.5
2.0
2.5
WAVELENGTH (μ m)
LOW IRON GLASS WITH ETCHED ANTI-REFLECTION COATING
T_S = 96%
LOW IRON GLASS
T_S = 90%
ORDINARY WINDOW GLASS
T_S = 86%

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Optical Measurements of Selective Solar Absorber Coatings

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I. Introduction

The efficiency of a solar collector may be defined as the fraction of the solar energy incident upon it that is transferred as heat to the heat transfer fluid. Losses from the collector fall into three categories: (1) incident solar flux that is reflected from the collector; (2) heat loss from the collector by reradiation to the surroundings; and (3) heat lost from the collector by convection and conduction. This paper will discuss ways of evaluating heat losses by the first two of these categories.

II. Reflection Losses

The collector is optically opaque, hence all incident solar flux that is not absorbed will be reflected. The measurement problem is to evaluate the fraction of incident solar flux that is reflected. The measurement of reflectance involves two aspects, geometrical and spectral.

The geometrical aspects of reflectance are the direction and solid angles of the incident beam and of the reflected beam accepted for measurement. Obviously all of the reflected flux should be measured. The standard way of doing this is with an integrating sphere which measures all of the reflected flux except the small fraction lost out of the entrance and detector ports. Ideally the geometry of the incident beam should be the same as that of the incident solar flux on the collector when in use. Unfortunately, integrating sphere reflectometers generally irradiate the sample undirectionally, or nearly so, that is, over a small solid angle about a single direction, or, the sample is irradiated over a hemisphere, and the reflected flux is collected for measurement over a small solid angle about a single direction. Reflectance varies with angle of incidence, measured from the normal to the surface, for most materials, but not with azimuth direction of incidence for isotropic materials, which includes most solar collector coatings. The best solution is to measure directional-hemispherical reflectance as a function of angle of incidence from near normal to at least 60° from normal. For most diffusely reflecting materials the reflectance is not a strong function of angle of incidence, and measurements at 10° or 15° intervals may be sufficient.

The reflectance of all materials varies with the wavelength. For the measured reflectance to simulate that of a reflector for solar flux, it is necessary that the combination of the spectral distribution of the incident beam, the spectral reflectance of the sphere wall and the spectral response of the detector match the spectral distribution of the solar flux reaching the surface of the earth. This is very difficult to do, because of the strong absorption bands due primarily to water vapor and carbon dioxide in the atmosphere. What is normally done is to measure the reflectance spectrally over the wavelength range of solar energy, usually from about 300 to 2500 nm, and then compute the weighted average spectral reflectance, in which the spectral distribution of the incident solar flux is used as the weighting function. Unfortunately, different laboratories are using different spectral solar distributions, and different methods of making the computation, which probably accounts for a major portion of the discrepancies in values reported. We recommend that a standard solar spectral distribution and method of computation be adopted for use by all laboratories in computing solar absorptance values to be compared with those evaluated in other laboratories, or published in the open literature. It would be helpful to the reader to publish the spectral reflectance in addition to reporting the solar absorptance.

III. Reradiation Losses

The reradiation loss is computed as $\varepsilon \sigma T_0^4$, where ε is the total hemispherical emittance of the collector, σ is the Stefan-Boltzmann constant, and T_0 is the operating temperature of the collector.

Total hemispherical emittance is not normally evaluated radiometrically, because of the difficulty in collecting for measurement the flux emitted over a hemisphere. Unfortunately, the normal integrating sphere coatings have low reflectance beyond about 2.5 μm, from which emittance can be computed.

Probably the most accurate method of measuring total hemispherical emittance is calorimetrically. A sample coated on all sides with the solar absorber coating, is heated in some way, such as electrically, so that the rate of heat input H can be accurately measured, under conditions where all heat transfer from the sample to its surroundings is by radiation, and allowed to come to thermal equilibrium. The total hemispherical emittance is then computed from the temperature of the sample T_s, the temperature of its surroundings, T_1, and the sample area, A, as

$$\varepsilon = H/A\sigma(T_s^4 - T_1^4).$$

The evaluation of emittance optically involves measuring the spectral directional-hemispherical reflectance of the coating, over the wavelength range of about 2.5 to 22.5 μm. Such measurements usually involve use of a paraboloidal, ellipsoidal or hemispherical mirror to collect the reflected flux, or use of a hohlraum reflectometer, in which a water cooled sample is inserted into a heated cavity, where it is irradiated by blackbody radiation from the hot cavity walls, and viewed directionally through a small hole in the cavity wall. The reflected flux is dispersed by a monochromator, and the sample and cavity wall are viewed alternately. The ratio of the relative spectral radiances of the sample and wall is the spectral directional-hemispherical reflectance at that wavelength. The total directional emittance is computed as one minus the weighted average of the spectral directional-hemispherical reflectance, in which the spectral distribution of a blackbody radiator at the operating temperature of the collector is the weighting function. This is empirically converted to total hemispherical emittance.

IV. Collector Efficiency

The optical efficiency of the selective abosrber coating, α_m, may be expressed as

$$\alpha_m = 1 - \rho_s - \varepsilon\theta^4$$

where ρ_s is the directional-hemispherical solar reflectance, ε is the total hemispherical emittance of the coating, and θ is dimensionless temperature where

$$\theta = T_o/T_e$$

where T_o is the operating temperature of the collector and T_e is computed as

$$T_e = (S/\sigma)^{1/4}$$

where S is the solar energy incident on the collector, in units of $W \cdot m^{-2}$, and is the equilibrium temperature that would be reached when no heat is being extracted from a collector with unit absorptance and emittance and no heat loss by convection and conduction.

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Evaluation of Solar Absorptance

by

Joseph C. Richmond

A major source of the differences in values of solar absorptance for supposedly identical materials reported by laboratories working on contracts for the Division of Solar Power of the Department of Energy appears to be the method used to convert spectral reflectance data to solar absorptance.

Before discussing the conversion, it may be relevant to discusss the measurement of directional hemispherical reflectance. This property is rarely measured as such. Direct measurement requires separate measurement of the incident and reflected flux, which presents experimental difficulties. Also, it is impossible to measure all of the reflected flux. The solid angles of the incident beam and that over which the reflected flux is collected for measurement are mutually exclusive. By making the solid angle of the incident beam very small, the solid angle of collection for the reflected flux can approach, but never equal, a complete hemisphere. There are also flux losses out the apertures in the sphere, and due to the absorptance of the sample.

Most commercial integrating sphere reflectometers measure reflectance factor, not reflectance. Reflectance factor is defined as the ratio of the flux reflected by a sample to that reflected by the ideal perfectly-reflecting isotropically-diffusing surface under identical conditions of irradiation and collection. While no real materials are either perfect reflectors or perfect isotropic diffusers, several materials come close in the solar spectral range, and corrections are made for the deviations of the reference standard from the ideal. In some cases, the wall of the integrating sphere is used as the reference. McNicholas [1][1] has shown that, if certain conditions are met, the sphere wall reference gives absolute reflectance values. This is further elaborated in [2]. In reflectance factor measurements the errors due to flux losses exactly compensate if the geometrical distribution of the flux reflected by sample and standard are identical, [3], and largely compensate if both are either diffuse or specular reflectors, even though not identically. In general, all integrating sphere reflectometers, if properly designed, calibrated and operated, measure spectral reflectance factor with small uncertainties, usually less than 2%. These measurements are not believed to be the major source of the observed variations in values reported. If directional-hemispherical reflectance factor, $R(\theta,\phi;2\Pi;\lambda)$[2] is known,

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[1] Figures in square brackets refer to references cited.

[2] Nomenclature and symbols are explained in [3]. θ & ϕ are the incident direction in polar coordinates; 2Π is the solid angle of the hemisphere over which the reflected flux is collected for measurement, and λ indicates a spectral quantity-when in parentheses it indicates that the quantity is a property, a dimensionless ratio at wavelength λ; when a subscript, it indicates a spectral concentration at wavelength λ, or in both cases it may also indicate the property or quantity as a function of wavelength. Once given in detail, the simpler notation of $\alpha(\lambda)$, $R(\lambda)$ and E_λ will be used.

the spectral directional-hemispherical absorptance, $\alpha(\theta,\phi;\lambda)$ is computed as $1 - R(\lambda)$. The directional solar absorptance, $\alpha(\theta,\phi;s)$ is then computed as the weighted average directional spectral absorptance, with the relative solar spectral irradiance, $E_{\lambda,s}$ as the weighting function. Expressed mathematically

$$\alpha(s) = \frac{\int_{\lambda_1}^{\lambda_2} \alpha(\lambda) E_{\lambda,s} d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\lambda,s}\, d\lambda} \tag{1}$$

where λ_1 and λ_2 are chosen to include nearly all incident solar radiation. Generally the limits are about 0.3μm to 2.5μm.

The differences in the procedures used in different laboratories to perform the computation indicated in equation (1) arise from two sources: the method of performing the integration and the particular $E_{\lambda,s}$ distribution used. The spectral distribution and computational methods specified in ASTM Standard E-424-71[4] have been adopted as standard for use in evaluating α_s for solar heating and cooling applications.

Since neither $R(\lambda)$ or E_λ is known as an algebraic function, the integration must be approximated by a summation. There are three methods in general use, (1) the weighted ordinate method, (2) the selected ordinate method, and (3) the distorted graph-planimeter method.

In the weighted ordinate method values of E_λ are taken at convenient wavelength intervals, $\Delta\lambda$, at which the value E_λ applies, and multiplied by $\alpha(\lambda)$ at the same wavelength and by $\Delta\lambda$. These products are summed, and the sum is divided by the sum of the products of E_λ and $\Delta\lambda$ at the same wavelengths. Expressed mathematically

$$\alpha_s = \frac{\sum_{\lambda_1}^{\lambda_2} E_\lambda \, \alpha(\lambda)\Delta\lambda}{\sum_{\lambda_1}^{\lambda_2} E_\lambda \Delta\lambda} . \qquad (2)$$

If the wavelength intervals are all equal, the n $\Delta\lambda$'s come outside the summation sign in both numerator and denominator and cancel, and the equation becomes

$$\alpha_s = \frac{\sum_{\lambda_1}^{\lambda_2} E_\lambda \alpha(\lambda)}{\sum_{\lambda_1}^{\lambda_2} E_\lambda} . \qquad (3)$$

The above procedure simplifies the computation, but may result in errors if $\Delta\lambda$ is large, because of the several rather sharp absorption peaks in the terrestrial solar irradiance curve.

Values for use in equation (2) are given by Thekaekara [9,10] for air mass values of 0, 1, 4, 7 and 10 for O_3 thickness of 3.4 mm, precipitable water thickness of 20mm, and for particulate matter parameters of $\alpha = 1.3$, $\beta = 0.02$; $\alpha = 1.3$, $\beta = 0.04$; $\alpha = 0.66$, $\beta = 0.085$; and $\alpha = 0.66$ and $\beta = 0.170$.

Values for use in equation (3) are given in ASTM Method E-424-71 [4], with $\Delta\lambda = 50$ nm.

In the selected ordinate method the area under the E_λ curve is divided into n equal areas A_i by vertical lines. An average λ_i is selected for each A_i. Then α_s is computed as 1/n times the sum of the $\alpha_{s,i}$ values at the n λ_i values. Expressed mathematically

$$\alpha_s = 1/n \sum_{i=1}^{i=n} \alpha_{s,i} \; . \tag{4}$$

Reference [4] gives 20 selected ordinates for use in equation (4), based on Parry Moon's terrestrial solar irradiance curve for AM2 [5]. Better accuracy would be obtained if 100 selected ordinates were used, and it is believed that terrestrial solar absorptance curves based on more recent aircraft and rocket measurements are probably more nearly correct then the Parry Moon curve. No reference giving 100 selective ordinates based on the ASTM E 490 curve [6] and AM 2 atmospheric absorption are known to the writer.

In the distorted scale - planimeter method [7] solar absorptance is plotted as a function of wavelength on special graph paper in which the wavelength scale is distorted so that the selected ordinates referred to above are uniformly spaced, and equal areas represent equal amounts of incident solar energy. To compute solar absorptance, the area under the plotted curve is measured with a planimeter, and the measured area is divided by the area under a similar curve with spectral absorptance of

1.0 at all wavelengths. The distorted graph paper prepared by Hass [7] is based on the Parry Moon extraterrestrial solar spectral irradiance curve. The wavelength scale on a similar special graph paper prepared for an AM 2 terrestrial solar irradiance would be distorted to a much greater extent because of the several rather sharp absorption peaks in the AM 2 atmospheric absorption curve, and no such distorted scale has been found in the literature. Use of the Hass distorted scale - planimeter method with the original Hass distorted graph is not recommened for evaluation of terrestrial solar absorptance.

In most cases the directional-hemispherical reflectance factor R(λ) is not measured beyond 2.5μm. There is a small, but significant, amount of solar irradiance at wavelengths beyond 2.5μm.[3/] A correction can be made for the unknown error introduced by the lack of knowledge of the spectral absorptance at wavelengths beyond 2.5μm. Three methods have been used to make such corrections: (1) extrapolate the spectral absorptance curve to the longer wavelengths on the basis of the shape of the curve in the 2.3 to 2.5μm range; (2)assume that the spectral absorptance at wavelengths longer than 2.5μm is the same as that at 2.5μm; or (3) assume that the spectral absorptance at wavelengths beyond 2.5μm is the same as the weighted average spectral absorptance at wavelengths below

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[3/] Robinson [8] reports 5.8% beyond 2.00 μm at AM0, 6.3% at AM1 and 6.8% at AM2 . Thekaekara[9,10] shows about 4% beyond 2.5 μm at AM0. Moon [5] shows no solar irradiance beyond 2.3 at AM 2. Schulze [11] shows 1.3% beyond 2.5 μm at AM 1.

2.5μm, so that no correction is required. There is no basis for selecting one of these procedures in preference to another if nothing is known about the spectral absorptance beyond 2.5μm. For non-selective solar absorber coatings, in which the solar absorptance is high at all wavelengths, any one of the three methods of correction will probably give little residual error. For selective solar absorber coatings, where the spectral absorptance is uniformly low at the longer wavelengths, procedure (3) can lead to significant error, but procedure (1) or (2) should give adequate correction for the error.

The selection of the particular solar spectral irradiance curve to be used for computation of solar absorptance is somewhat arbitrary. There are a number of extraterrestrial solar spectral distribution curves in general use, that generally agree over most of the range, but which may disagree by 20 to 30% in certain wavelength regions, particularly in the near ultraviolet. Differences in the different curves are shown in [9], [10], [12], [13], and [14]. There are at least five extraterrestrial solar spectral irradiance curves in use at the present time.

The major variations in terrestrial spectral irradiance are due to variations in atmospheric attenuation. In the absence of clouds the atmospheric attenuation is due primarily to absorption by ozone, water vapor and carbon dioxide and scattering by molecules and aerosols (particulate matter) present in the atmosphere, with some minor effects due to other constituents. The general subject of atmospheric attenuation is well covered in [8]. While there is some variation in the amount of absorbing and scattering materials in the atmosphere from place to place and from time to time, the major changes in atmospheric absorption are due to changes in the path length, through the atmosphere, of the solar radiant energy. This path length is usually expressed as an air mass value, as AM1, AM2, etc. Air mass 1 corresponds to the path length through the atmosphere at a point at sea level (atmospheric pressure 1 bar) when the sum is directly overhead (declination of the sun is zero). The air mass value is a function of the altitude (barometric pressure in bars) and the secant of the angle of declination of the sun. The angle of declination of the sun is the angle between the sun's rays and a true vertical line at the point of measurement, and is a function of latitude and both time of year and time of day, and can be computed for any latitude, day and time from standard astronomical tables. For locations outside of the tropic zone, the minimum declination of the sun occurs at meridian, or noon local sun time, and will have a maximum value equal to the latitude plus the angle of declination of the Earth's axis, 23° 27' 8.2", the angle between the plane of the equator and the plane of the ecliptic. This maximum value of declination at meridian occurs at the winter solstice, about December 22. The minimum value of the declination of the sun at meridian will be equal to the latitude minus the declination of the Earth's axis, and will occur at the summer solstice, or about June 22. For latitudes of about 45°, the range of the declination of the sun at meridan is thus about 21.5° to 68.5°. The angle of declination at sunrise and sunset is determined by the local terrain - mountains or structures that may shade the location at sunrise or sunset. At sea, or on a large level plane, it becomes 90°.

At AM10, which is for an angle of declination of about 85°, the solar transmittance of the atmosphere is only about 23% of that at AM0, while at AM1 the transmittance is about 70%. For a level surface, the solar irradiance is further reduced by the cosine of the angle of declination of the sun.

It is recommended that for the present all values of solar absorptance included in reports to DoE or published in the literature be computed by one of the two methods described in ASTM method E424-71, and that in addition the spectral reflectance factor data from which the values are computed also be included in reports or publications.

The discrepancies in the published data indicate the need for additional measurements of spectral solar irradiance, both terrestrial and extraterrestrial, at wavelengths beyond 2.0 μm, and particularly beyond 2.5 μm.

The data published by Thekaekara [9], give solar spectral irradiances only for AM0, 1, 4 and 10. Arrangements are being made to obtain values for AM 0.5, 1.5, 2, 2.5 and 3 in addition. When such values are available, serious consideration should be given to adopting these values at AM 2 and the weighted ordinate method for computing terrestrial solar absorptance values of selective solar absorber coatings to be included in reports or publications. This subject will be discussed at the Seminar on Testing Solar Energy Materials and Systems to be held at the National Bureau of Standards, May 22-24, 1978.

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Surface Film Analysis and Profiling Techniques

Grant: COO-2953
to be presented at Absorber Coatings Workshop
Golden, Colorado
December 6, 1977

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The major accomplishments under this grant are summarized as follows:

a. The papers "Characterization of Selective Solar Absorber Coatings" and "Interdiffusion in Mo-covered Stainless Steels Studied by Auger Electron Spectroscopy" were presented at the 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces in Vienna, Austria and published in the conference proceedings.

b. Short (15 min) heat treatment of stainless steel in air at 900°C produces a dense Cr_2O_3 coating which is an excellent diffusion barrier. We demonstrated with Auger thin-film composition-depth profiling analysis that this simple-to-produce coating increases the operating temperature of an AMA-Mo-SS 304 solar thermal absorber coating (1 hr in vacuum) from less than 500°C to about 900°C without noticeable deterioration. The diffusion of C from SS 304 and the stainless steel constituents Fe, Cr, Ni into the sputter-deposited IR Mo reflection film is so effectively stopped by this layer that the absorber coating on a SS substrate can be operated as if it were deposited instead on a Mo substrate. At 1000°C the Cr_2O_3 barrier finally breaks down completely and then no difference exists between Cr_2O_3 coated and uncoated stainless steel. Air oxidation of the stainless steel at less than 750°C creates a mixture of Fe- and Cr-oxides which is a much less efficient diffusion barrier than is the pure Cr_2O_3 layer.

c. Sputter deposition of Mo (5000 Å) on SS in a clean low gas pressure (10^{-1} Pa) Ar triode discharge resulted in well-adhering Mo films which show with Auger analysis only negligible traces (less than 0.5%) of C or O.

d. Auger composition depth profiles of a Mo coating on SS or Cr_2O_3-coated SS show a rather pronounced Mo tail extending far into the SS substrate. We were able to show that this is an artifact caused by the knock-in of Mo into the SS during sputter microsectioning under the argon ion bombardment.

e. Replacing the Mo film on air-oxidized SS by a sputter-deposited W coating resulted (surprisingly) in a noticeably poorer diffusion barrier performance of the Cr_2O_3 layer. This result is still tentative and needs to be repeated because the W film was not of good quality.

f. The Cr_2O_3 layer on SS provides an excellent diffusion barrier for preventing not only the outward movement of stainless steel constituents but also the inward movement of constituents from other surface coatings.

A Au film, for instance, begins to move into uncoated SS at temperatures as low as 300°C. With the Cr_2O_3 coating on the SS the Au stays on the surface at temperatures of up to 600°C and the depth profile shows that its inward movement was completely blocked.

g. Exploratory experiments with a Torus magnetron-enhanced ring-gap discharge for sputter coating the outside of tubing with solar absorber stacks and the screening of the literature for related efforts of others along this line have convinced us that it should be possible to coat rather economically by sputtering SS tubing with film stacks if the individual layers in the stack are in the thickness range of 1000's of Å and not in the mils range. Sputter coating instead of electrolytic coating gains more and more favor among environmentalists and in view of stricter OSHA regulations. We do not foresee any major obstacles for designing and building a coater which would sputter deposit 1000 Å of Mo, 600 Å of Al_2O_3, 300 Å of MoO_x, and 600 Å of Al_2O_3 on Mo on SS tubing at the rate of 4 km/month. In view of the fact that from here on the task would become more of an engineering project (which would be better suited for industry to pursue), we have (in agreement with the sponsor) shelved this project for the time being.

h. In support of other ERDA solar grant recipients, we have provided various, sometimes rather substantial, Auger and ESCA services.

Absorber Surfaces for High Temperature Alloys

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High temperature alloys are required for the absorber materials in large central receiver solar-thermal conversion systems. We have measured the optical properties of absorber surfaces prepared on samples of alloys that are candidate receiver materials. These include alloys of the Croloy, Inconel, Incoloy and stainless steel types. The absorbers consisted of native oxides grown in air in laboratory furnaces at temperatures of 500, 800 and 1000°C for times of 18 hours, 2 hours, 30 minutes respectively and a commercially available high temperature paint (Pyromark). Prior to oxidation the samples were either left as received or ground and optically polished in order to remove scale acquired during milling and to obtain optical specularity. Samples painted with Pyromark were sandblasted and then coated following the manufacturer's recommended procedure.

The samples were exposed in the White Sands Solar Furnace in order to test their durability under thermal stress and high flux conditions that they might experience during actual receiver operation. The thermal stress was achieved by cycling the samples, attached to a rotating wheel, into and out of the solar flux. Over 400 cycles, each approximately 45 sec, were completed on each of two principal test sets. Sample exposure was approximately 2 sec per cycle. Temperatures cycled between maxima and minima of approximately 600 and 300°C for samples with high absorptance and low heat capacity to between 400 and 300°C for samples with low absorptance.

Diffuse reflectance measurements were made on the samples before and after exposure at White Sands using an integrating sphere reflectometer. The results show that, in spite of a slight tendency to peel, the Pyromark paints low reflectance of 0.04 to 0.06 over the measured spectral region of 350 to 900 nm changed very little after solar exposure. X-ray diffraction studies indicate the silica binder in the paint had not completely vetrified leaving a crystalite structure, and that the coating did not prevent oxidation of the metal substrate. The oxide layers formed on Inconel and Incoloy by heating to 1000°C produced a very diffuse surface which was also optically and mechanically very stable. The reflectance over the measured spectral region for these surfaces was in the 0.10 to 0.15 range. The Inconel and Incoloy samples oxidized at 500 and 800°C had in general less favorable reflectances (greater than 0.15) which show

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*Present address: SERI. 1536 Cole Blvd., Golden, Colorado 80401 strong spectral dependences. Although the surfaces were structurally stable they often showed significant changes in reflectance. The oxides grown on the as received surfaces generally gave lower and more stable reflectance profiles.

The Croloy alloys arrived with a black scale that had a reflectance between 0.10 and 0.15. Croloy 1/2 was an exception with a reflectance of only 0.035 which remained stable during subsequent tests. In general the results were not systematic. Some oxides were quite stable. The Croloy 9 alloy with the higher chromium content formed the most stable oxides with least variation in spectral reflectance. The reflectance was however fairly high at about 0.15.

In a second phase of the White Sands tests we oxidized four cleaned and polished samples under steady state conditions. The flux levels were controlled to maintain constant temperatures of 600°C on a Croloy 1 1/4 alloys and 800°C on Inconel 617, 625 and x750 alloys for two hour periods. The diffuse reflectance of these samples was compared to that of a similarly prepared set which was oxidized in air in a laboratory furnace for the same time and temperatures. Only small differences in reflectance was observed except for the 617 alloy where the laboratory grown oxide was much less absorbing.

High temperature reflectance measurements were restricted to a few polished samples that maintained their specularity during oxidation. The results show very little reversible change in absorptance occurring at temperatures as high as 700°C. However, as in the solar furnace tests some permanent changes in absorptance were observed due to continued oxidation of the surface even though the test chamber was evacuated to 10^{-5} Torr.

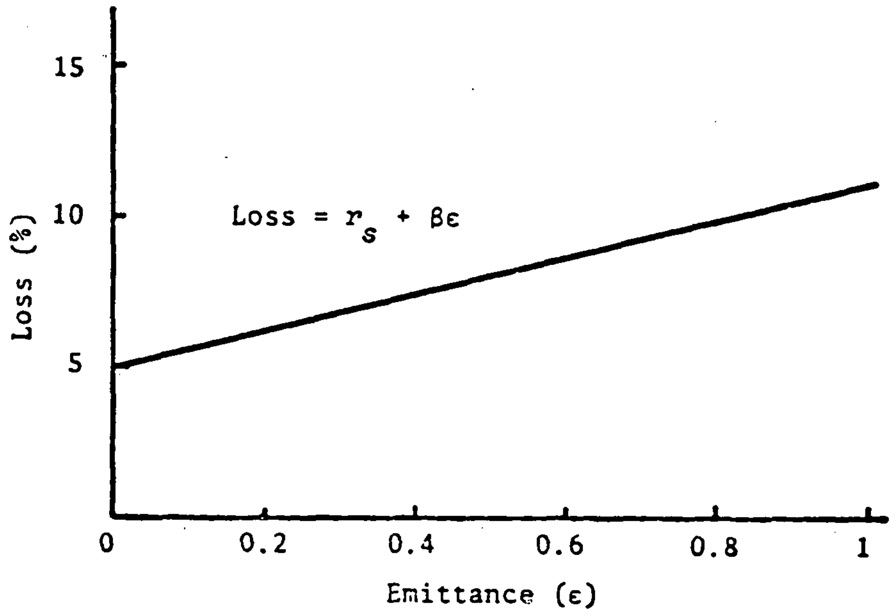


Fig. 1. Loss from absorber surface due to reflection (r_s) and emission ($\beta\varepsilon$) for central receiver. The coefficient β is approximately $\sigma T^4/\tau x\phi$, where the various quantities are listed below along with their typical numerical values for central receiver operation.

Symbols	Definitions	Values
σ	Stefan-Boltzmann constant	5.67×10^{-8} W/m^{2}K^4
ϕ	Solar flux at surface on earth	10^3 W/m^2
T	Temperature of absorber surface	800°K
X	Concentration ratio	500
τ	Transmittance through collector system	0.8

Alloys for Receiver Tube Applications

Alloy	Percent Cr - Ni	Max. Metal Temp. (°C)	Cost/Ft. 1/8" wall - 1" OD tube
(Cr,Mo,Fe)			
Croloy 1/2	1/2	550	0.90
" 1 1/4	1 1/4	565	to
" 2 1/4	2 1/4	607	
" 5	5	621	
" 7	7	635	
" 9	9	647	∿1.50
(Ni,Cr,Fe)			
Stainless 304	21 - 32	>700	6.00
Incology 800	19 - 10	760	4.50
(Ni,Cr)			
Inconel 600	15.5-76	>700	11.00
" 617	22 - 54	"	"
" 625	21.5-61	"	"
x 750	15.5-73	"	12.00

Fig. 2. List of alloys tested and their important characteristics.

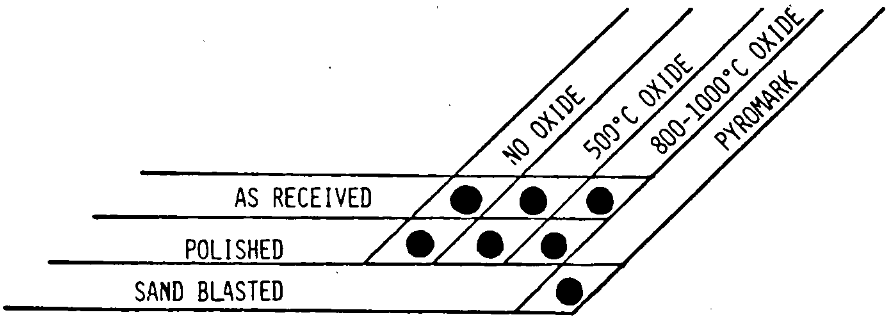


Fig. 3. Matrix showing various surface preparations used for samples cycled in White Sands Solar Furnace (WSSF).

SAMPLE SET	I	II	III
CYCLES	65	490	408
TIME IN FLUX/CYCLE (SEC)	6.3	1	1.4
TOTAL TIME (MIN)	270	277	353
FLUX LEVELS (W/cm^2)	100 - 150		
TEMP MAX (°C)	400 - 600		
TEMP. MIN (°C)	300 - 400		

Fig. 4. Exposure parameters for WSSF tests.

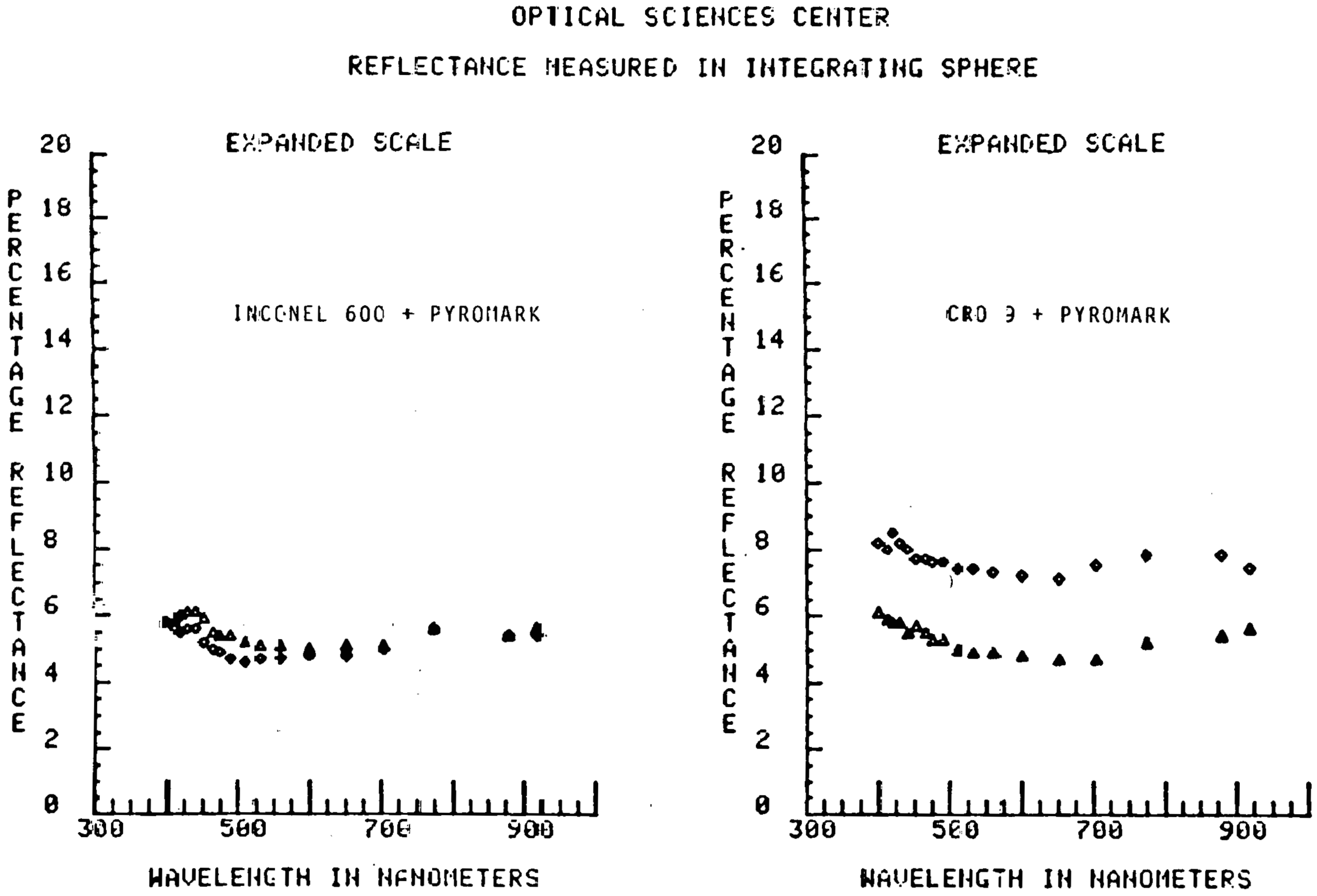


Fig. 5. Diffuse reflectance of samples coated with Pyromark Paint. The triangles show the reflectance before cycling at WSSF while the diamonds give the reflectance after cycling.

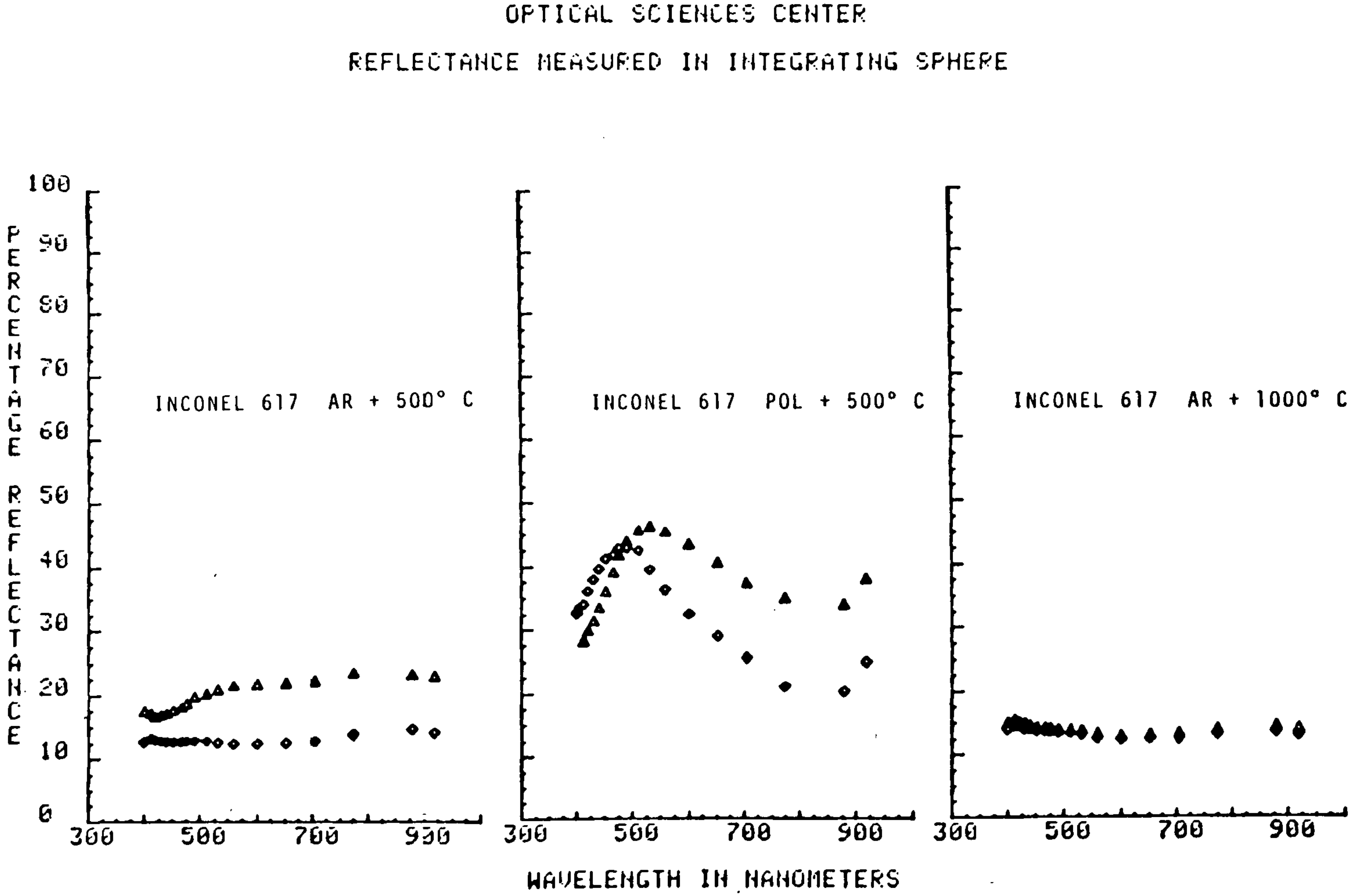


Fig. 6. Diffuse reflectance of Inconel 617 alloy with various surface treatments and oxidation temperatures before (triangles) and after (diamonds) WSSF tests. AR = as received, POL = polished.

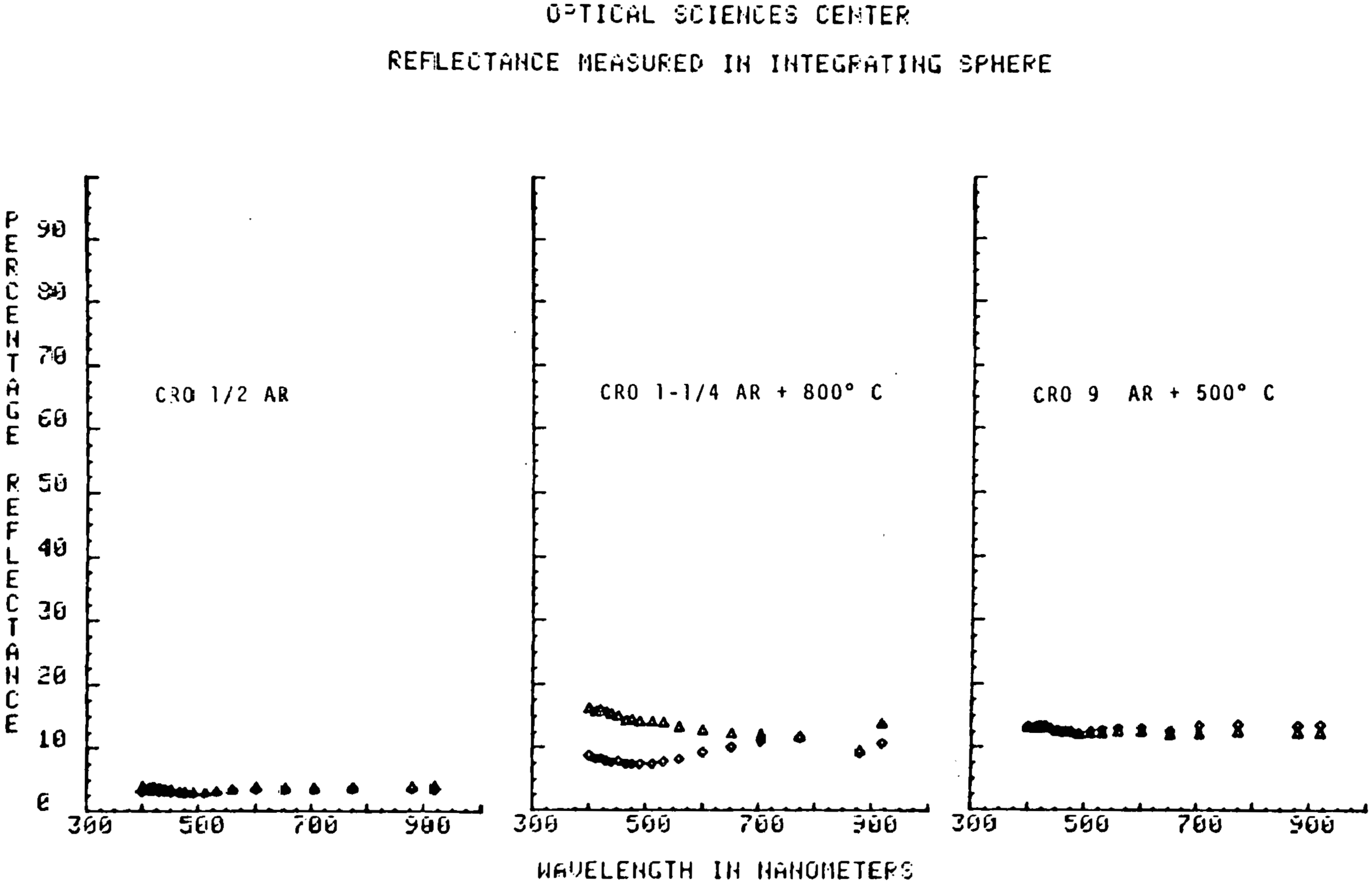


Fig. 7. Diffuse reflectance before (triangles) and after (diamonds) WSSF tests of as-received (AR) samples of various Croloy alloys with different pretest oxidations.

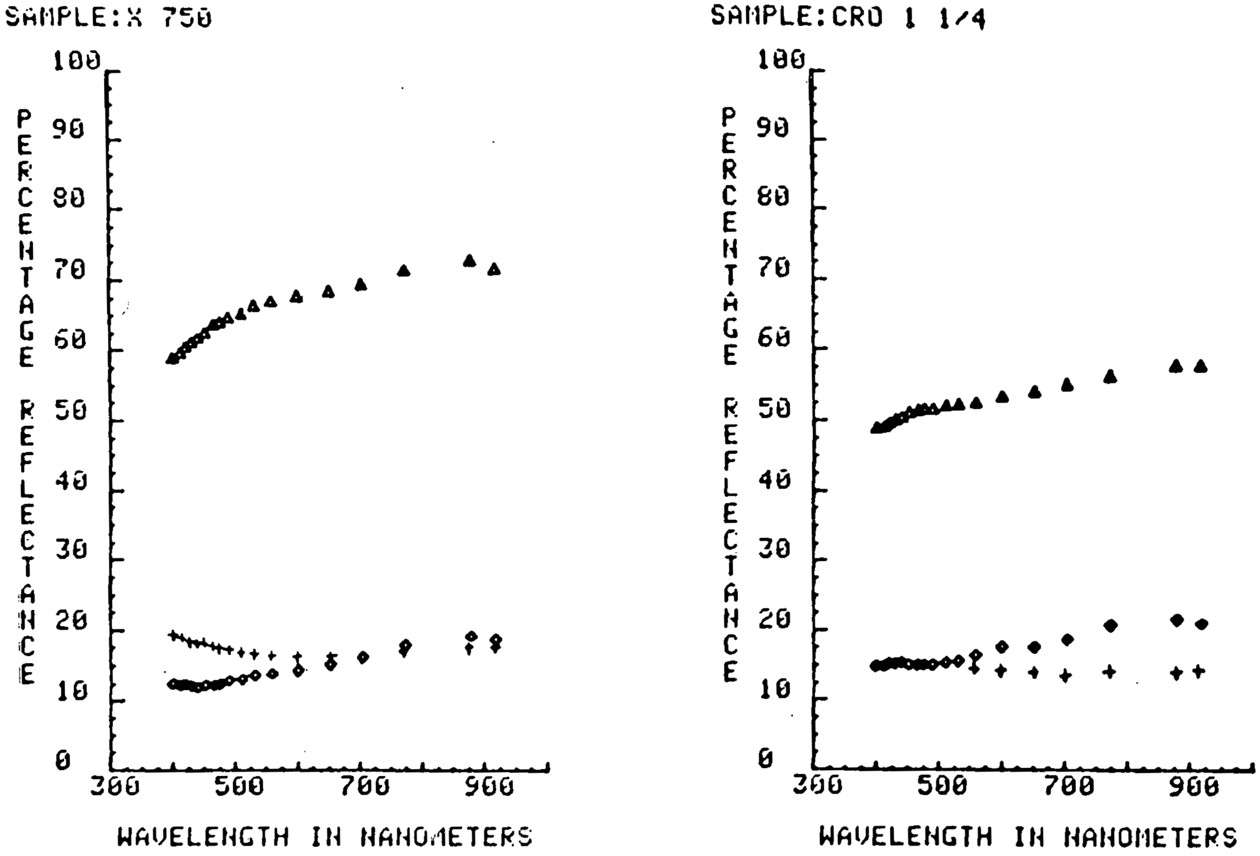
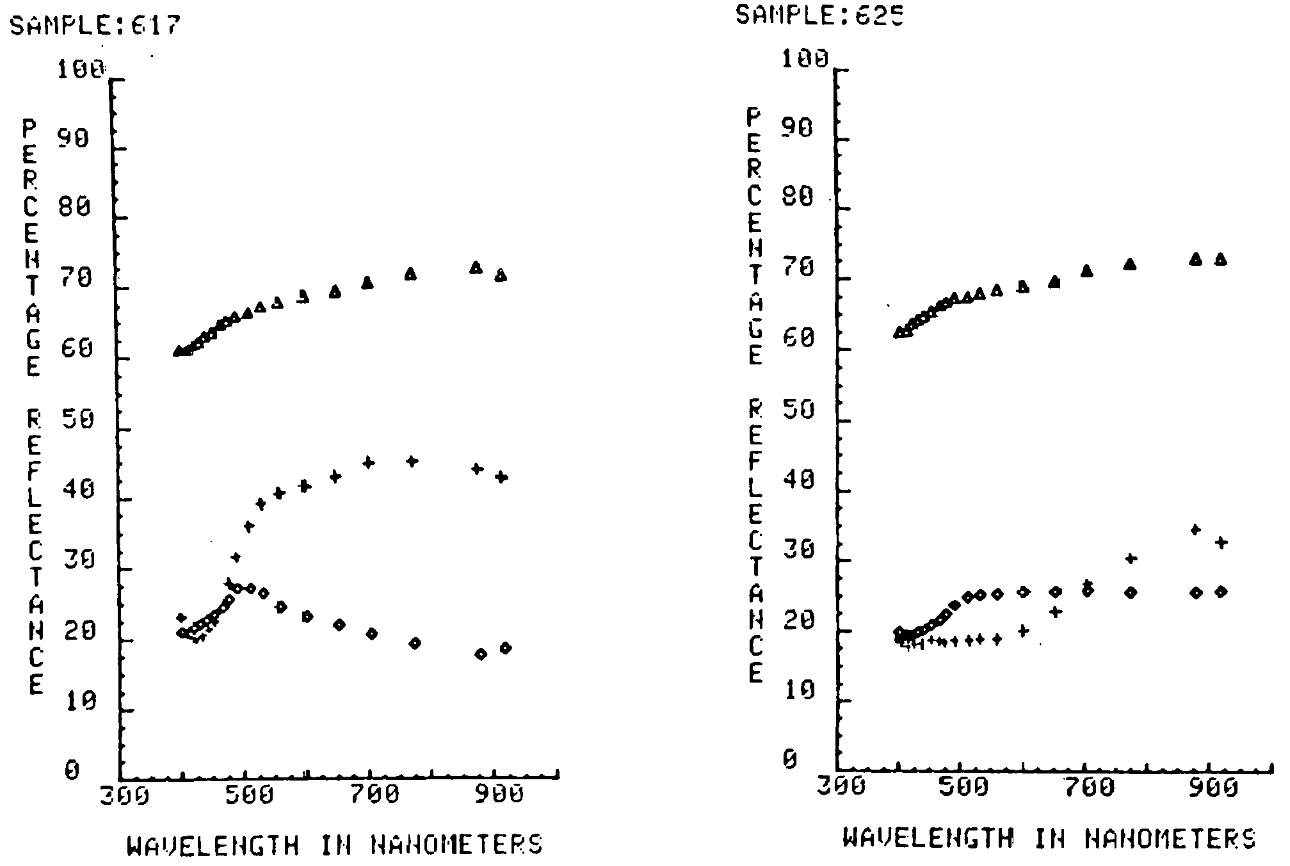


Fig. 8. Diffuse reflectance of polished Inconel x750 and Croloy 1 1/4 alloys prior to oxidation (triangles) and after oxidation for two hours in the WSSF (crosses) or laboratory furnace (diamonds). The Inconel was oxidized at 800°C and the Croloy at 600°C.


SAMPLE:617

SAMPLE:625

Fig. 9. Diffuse reflectance of polished Inconel 617 and Inconel 625 alloys prior to oxidation (triangles) and after oxidation at 800°C for two hours in the WSSF (crosses) or laboratory furnace (diamonds).

MR. MUENKER: When you were talking about the pyromark, did I understand correctly that you referred to a silicate binder?

CHAIRMAN MASTERSON: I believe it has a silica binder, yes.

MR. MUENKER: It is my understanding that it has a silicone binder, there is a difference there.

MR. SOWELL: I think I can answer that, it is a silicone binder. But when you take it up to 350 or 400 degrees C, it converts to an oxide which --

CHAIRMAN MASTERSON: Which is a silicate, yes.

MR. SIEVERS: Do you have any explanation for the big change in the absorptivity of your alloys?

CHAIRMAN MASTERSON: No, I don't really at this point. Primarily there was a large change, on only one sample, there was a small change in the others, but I can't attribute that right now. Except for this unknown X phase in which, you might well think the solar flux photons are promoting a chemical reaction because of a resonance phenomenon where the actual energy in the photon is going into generating electronic states which then settle back into particular oxide phases.

MR. SEIVERS: I think that is a point that I have heard boiler people talk about for years. No research was needed in this area because boilers were well understood, and I think the confusion was that boilers were well understood when they were contacting a spectrum which was a 500 C, a 1000 C spectrum. The difference here is that it is in contact with a 6000 C spectrum, that is not an equilibrium situation, and you can have photon-assisted diffusion and photon-assisted chemical reactions, and none of this has been studied.

CHAIRMAN MASTERSON: Right, and on top of that, the obvious thing is, of course, that in a boiler, I think primarily you are in a reducing atmosphere. In the solar reservoirs, you would be in an oxidizing atmosphere so there are some differences there.

MR. SCHWARTZ: I think your measurements at temperature would be high, I don't know how much higher the absorptance is because if you get scattering out of the cone of detectors, diffuse rather than specular, your values are going to be high. How high are they, that's the question.

CHAIRMAN MASTERSON: Most of the curves here are integrated sphere measurements.

MR. SCHWARTZ: I am not talking about the ones at room temperature, I am talking about the ones at high temperature.

CHAIRMAN MASTERSON: The measurement at elevated temperatures is specular. How high the measurement is depends on the specularity of the sample, and that is, of course, a difficult thing to assess. What we do is take a sample that we know is specular and measure it at different temperatures. Then, we can tell from that particular sample, of course, what's going on.

In the diffuse sample, the only alternative we have is to measure the diffuse reflectance at room temperature in one instrument, take it out, put it in the high temperature reflectometer, if we can get enough signal to run, to measure the reflectance. Then we look at it at room temperature again.

So, one can say there is a difference between the diffuse and specular components.

Now, if the specularity is changing with temperature, then that's --

MR. SCHWARTZ: Yeah, at the low reflectance or high absorptance, the thing that you are interested in, the thing that happens is that the specimens move from specular to diffuse. If they move towards diffuse, then you are unsure of what your value is.

CHAIRMAN MASTERSON: That's true. If it is changing in its specularity from becoming a specular to diffuse surface and back again in a process, then you are unsure of it.

MR. SCHWARTZ: Now, your room temperature measurements, I notice you only take it out to 900 nanometers, you have got like another 40 percent of energy.

CHAIRMAN MASTERSON: We are instrumenting the sphere with a lead sulphide detector, but we haven't got that all finished yet.

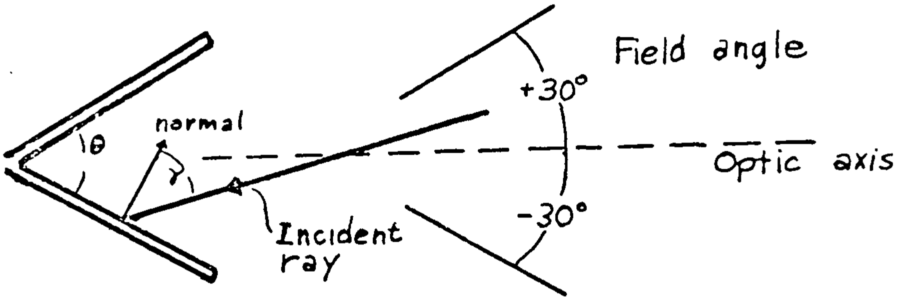
MR. SCHWARTZ: The values that you got up to 900 nanometers, have you compared that with other workers in the field?

CHAIRMAN MASTERSON: Yes, they are pretty comparable, and I guess if you want any absolute numbers, a couple of croloys had very good absorptance, but it is questionable whether they will be of service at the operating temperatures, and the pyromark paint seems to be very serviceable if applied correctly.

Performance of A Shallow Cavity Receiver

Keith Masterson, SERI

The use of a shallow cavity to reduce the losses from a solar receiver has been analyzed with respect to specular versus diffuse and selective versus non-selective surfaces. The particular cavity geometry is shown below and was chosen to approximate a 12-vaned receiver in an early power tower design[1]. It is also appropriate for a linear trough collector with a rim angle of 30° and concentration ratio of approximately 50.



The following assumptions are made: (1) incoming flux is distributed uniformly over the ±30° aperture; (2) absorptance is independent of the angle of incidence; (3) reflectance of the diffuse surface and the emittance of all surfaces[2] follow the Lambertian cosine distribution; (4) the cavity walls are isothermal.

The analysis for the enhanced absorption a_e was made by determining the percentages absorbed, reflected, and lost by scattering each time a ray was incident. Repeated application as the rays reflect about the cavity results in a geometrical series that, for a specular surface, truncates after a few reflections if the ray exits the aperture, and for a diffuse surface is summed to infinity.

For specular walls it can be shown that

$$1 - \alpha_e = (1 - \alpha)^n \qquad \text{specular (1)}$$

where α is the absorptance of the flat surface and n is the number of times the ray undergoes reflection before exiting the aperture. For the geometry above one-half the incident flux undergoes two reflections and one-half has three reflections.

For diffuse walls a fraction, F, of the reflected light is lost out the aperture upon each reflection. For the simple geometry chosen it can be shown[3] that $F = \sin \theta/2 = 0.5$ and that the enhanced absorption is

$$\alpha_e = \frac{\alpha}{1 - (1 - \alpha)(1 - F)} \qquad \text{diffuse (2)}$$

with α as defined above.

To calculate the effective emittance ε_e one substitutes ε for α in (2) above[2].

The fraction, L, of the incident energy that is lost due to reflectance and reradiation from the absorber surface is given by

$$L = (1 - \alpha) + \beta\varepsilon \qquad \text{where } \beta = \frac{\sigma T^4}{\tau X \phi} \qquad (3)$$

with the parameters defined and assigned values appropriate to the linear trough collector as given immediately below:

σ = Stefan-Boltzmann constant = 5.67×10^{-8} W/m^2K^4
ϕ = Solar flux at surface on earth = 10^3 W/m^2
T = Temperature of absorber surface = 623°K = 350°C
X = Concentration ratio = 50
τ = Transmittance through collector system = 0.8

For these parameters $\beta = 0.17$. The results of the calculations for effective absorption and emittance and the optical losses associated with these parameters are summarized below:

Flat Surface	Cavity with Specular Walls	Cavity with Diffuse Walls
$\alpha=\varepsilon= 0.9$	$\alpha_e= 0.995$, $\varepsilon_e= 0.95$	$\alpha_e=\varepsilon_e=0.95$
L = 0.25	L = 0.17	L = 0.21
$\alpha=0.9$, $\varepsilon=0.15$	$\alpha_e=0.995$, $\varepsilon_e=0.26$	$\alpha_e=0.95$, $\varepsilon_e=0.26$
L = 0.13	L = 0.05	L = 0.09

Under the assumptions made above the lowest loss occurs for a cavity receiver with a specularly selective surface.

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[1] L. Vant-Hull et al., "Solar Thermal Power Systems Based on Optical Transmission", presented at Solar Thermal Workshop, University of Houston, May 1975.
[2] R. Siegel and J.R. Howell, Thermal Radiation Heat Transfer (McGraw-Hill, 1972, New York), p. 166.
[3] Ibid, p. 190.

Thermal Aging of Electrodeposited Black Chrome*

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Evaluation of selective absorbing coatings for Sandia's Solar Total Energy Test Facility included electrodeposited black nickel, multilayer interference coatings and Harshaw's electrodeposited black chrome (ChromOnyx).[1] Black nickel coatings, although having acceptable optical properties, were unstable at the operating temperature of the facility (~ 310°C) in air and at lower temperatures in the combined presence of heat and moisture. Multilayer interference coatings were expensive and difficult to apply to tubular geometries. There was also a question about long-term degredation of these coatings at 300°C that might result from diffusion between the evaporated layers. Electrodeposited black chrome was selected as the most suitable selective coating for our application. With proper substrate and plating control, acceptable optical properties (solar absorptance, α_s, ≥ 0.95 and emittance, ϵ, at 300°C ≤ 0.25) could be obtained with relative ease and at reasonable cost.

In our initial studies,[1] coatings plated in our laboratory and at Bendix, Kansas City Division, exhibited little or no degradation in optical properties after 1000 hours at 350°C in air. The maximum decrease in α_s was on the order of 2% or less. There was a considerable decrease observed in α_s after 70 hours at 400°C in air. These results are essentially

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*Work supported by U.S. Department of Energy.

consistent with results reported by Honeywell that black chrome was stable to ~ 425°C after only one hour tests in air.[2]

After approximately two years in our facility, the visual appearance of some receiver tubes had changed. (It should be noted that the actual time at operating conditions was considerably less than two years.) One tube, which had been located near the outlet and thus had been located near the maximum fluid temperature of ~ 310°C, was removed for examination. Optical measurements were made on the black chrome surface which had faced the parabolic trough using Gier-Dunkle instrumentation.[3] The average of solar absorptance measurements from seven locations on the tube was 0.85 while the average emittance at 300°C was 0.19. Optical measurements made prior to initial installation showed $\alpha_s \geq 0.94$ for all receiver tubes in the facility. The observed decrease in α_s was, therefore, in contrast to our earlier thermal aging studies.

Because of this discrepancy, flat panels that were plated at the same time as the receiver tubes were tested in the laboratory at 250, 300, 350, and 400°C in air. In addition, samples from Olympic Plating, Canton, Ohio, Highland Plating, Los Angeles, California, and Harshaw Chemical Co., Cleveland, Ohio, were exposed to the same thermal aging tests.

All coatings tested showed no significant change in α_s after several hundred hours at 250°C. At 300°C and 350°C, α_s of some coatings decreased by 6 - 10% after only 25 - 50 hours while for other samples, α_s remained unchanged after several hundred hours which agrees with our earlier results. It was observed that coatings which were stable at 300°C were also stable at 350°C. After the initial decrease in α_s for the unstable coatings, the solar absorptance remained essentially constant after continued testing.

The behavior of a stable coating is shown in Fig. 1 where α_s did not change at 300°C and 350°C for the 150 hours plotted. The tests were extended to the times shown at the right of the figure so that after 470 hours at 300°C and 800 hours at 350°C, α_s was still ~ 0.96. At 400°C, α_s initially drops rapidly and appears to continue decreasing slowly so that after 620 hours, it was below 0.90.

The behavior of α_s for an unstable coating is shown in Fig. 2. A very slight decrease in α_s occurred at 250°C, but after 25 hours, the curve was flat. At 300°C and 350°C, α_s dropped below 0.90 after 50 hours. The reason for the different thermal stability is not known. Differences in the plating process and resulting variations in the deposited coating composition, thickness, and morphology are being studied. In addition, coating-substrate interactions are being investigated.

It should be mentioned that the only coatings found to be stable at 350°C in air were obtained from Bendix, Kansas City Division. However, some of the coatings obtained from Bendix are unstable. Coatings obtained from Olympic, Highland, and Harshaw have all been unstable.

As a first effort to determine differences between stable and unstable coatings, the film composition was examined by sputter-Auger-profiling. The profile of Fig. 3 is typical of all black chrome coatings before heat aging. The oxygen/chromium (O/Cr) ratio established on single crystal

Cr_2O_3 is 2.4. Progressing through the film, the Auger peak height as a function of sputtering time gives a fairly high O/Cr ratio at the surface but rapidly decreases, showing a gradation ranging from a value of 0.9 to 0.5 near the interface with the underlying nickel.

The composition as a function of sputtering time shown in Fig. 4 is typical of all coatings heated in air at 300°C or 350°C. Near the surface, the O/Cr ratio approaches that of Cr_2O_3 but decreases to ~ 1.2 near the nickel-black chrome interface. The oxygen peak height remains higher than that of Cr throughout the film. After heating at 250°C, the sputter-Auger profiles show a considerable amount of oxidation but less than those after the 300°C and 350°C heat treatments.

These results do not reveal any significant composition difference between stable and unstable coatings. Both coatings oxidize and there is no evidence that diffusion is occurring between the nickel substrate and the coatings, at least for the time studied.

Scanning electron microscopy studies indicate that no detectable change in surface morphology occurs after heat aging for both stable and unstable coatings. Preliminary transmission electron microscopy and diffraction studies have detected no significant difference between stable and unstable coatings. Process records of bath composition, temperature and plating time maintained during the plating of the receiver tubes and control panels do not offer any clues to differences between the coatings. Although bath composition varied, there is no obvious correlation with coating behavior.

Because large scale projects that require the black chrome coating are planned for the near future, the stability problem must be resolved. Questions that need to be answered are:

(1) How do stable and unstable coatings differ?

(2) Can the differences be related to the plating parameters so that consistent coatings may be obtained?

(3) What are the mechanisms of degradation under both short and long term environmental exposure?

To answer these questions, a study of the plating process variables is being made to establish a process which consistently produces stable black chrome coatings. It appears that process control limits which are adequate for decorative black chrome are not sufficient for solar applications. We are also continuing our studies to determine the difference in composition, thickness, structure, and/or morphology between stable and unstable coatings. One objective of these studies will be to document the findings in a handbook format for commercial electroplaters.

Thus, we presently do not know how to specify the plating process in order to obtain a stable black chrome coating. Auger sputter profiles have shown no significant composition differences between stable and unstable coatings and that both coatings oxidize upon heating in air. We are currently obtaining additional samples from Bendix, Olympic, Highland, and Harshaw for further testing.

References

1. R. B. Pettit and R. R. Sowell, "Solar Absorptance and Emittance Properties of Several Solar Coatings," J. Vac. Sci. Technol. 13, 596 (1976).
2. H. Y. B. Mar, et al., "Optical Coatings for Flat Plate Solar Collectors," Final Report 16 September 1974 to 16 September 1975, COO/2625-7511, Contract No. NSF-C-957.
3. R. B. Pettit, "Evaluation of Portable Optical Property Measurement Equipment for Solar Selective Surfaces," presented at the Winter Annual Meeting, ASME, Atlanta, GA, November 27-December 2, 1977 (Paper 77-WA/SOL-1).

Figure Captions

Fig. 1 - The solar absorptance as a function of time at temperatures of 300, 350, and 400°C for a stable black chrome coating.

Fig. 2 - The solar absorptance as a function of time at temperatures of 250, 300, and 350°C for an unstable black chrome coating.

Fig. 3 - Auger peak height as a function of sputtering time for a typical black chrome coating as plated. Sputtering was done at 5 kV and 25 mA.

Fig. 4 - Auger peak height as a function of sputtering time for a black chrome coating after heating in air at 300°C or 350°C. Sputtering was done at 5 kV and 25 mA.

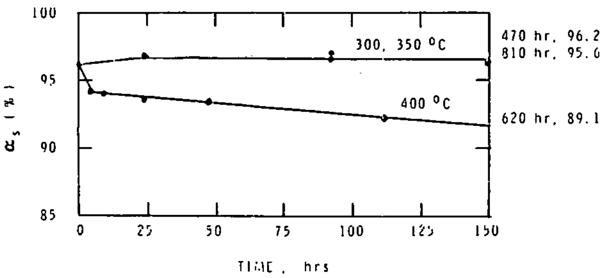

Figure 1

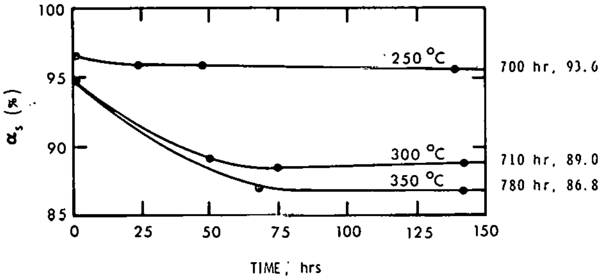

Figure 2

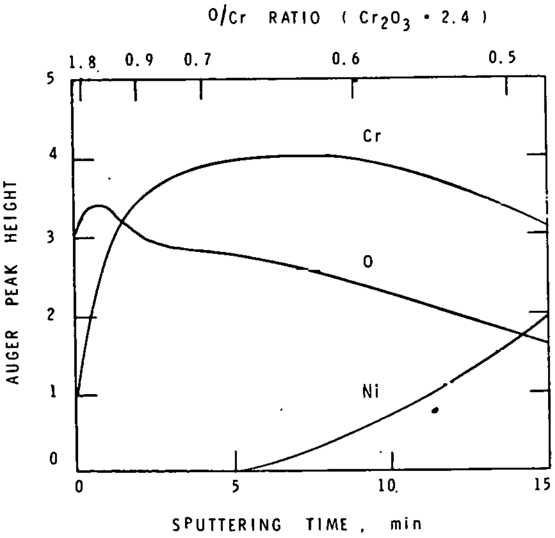

Figure 3

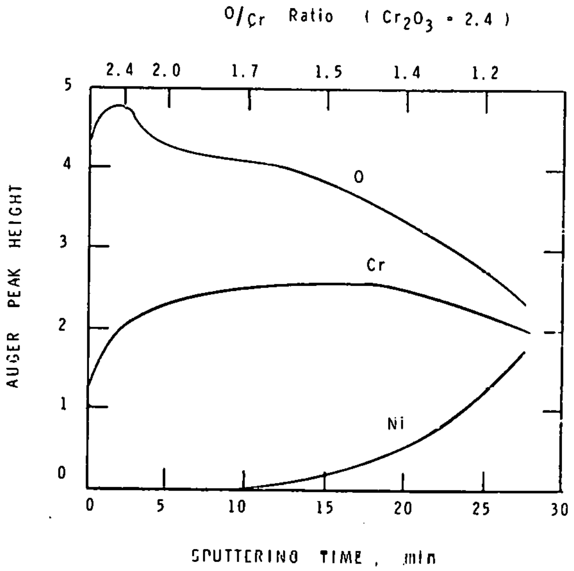

Figure 4

MR. BLICKENSDERFER: One of the areas for great potential use of reflective surfaces has been evacuated systems, I was wondering what the stability of black chrome is under vacuum?

MR. SOWELL: It is early on in the program. In our evaluation, it was stable in air. We also ran it sealed in quart tubes where we evacuated to about 10-6 Torr, and the stability was very good. I don't know that that means anything.

As I say, it is oxidizing, but that may not be the only or the prime mechanism for degradation on optical properties.

Also, as Jim Leonard mentioned this morning, we had a partial vacuum there. Actually, it is an oxidizing atmosphere, and you are talking in terms of years of cycling. Forget it, we don't have a vacuum.

MR. RICHMOND: Perhaps this question should be better asked of Chairman Masterson, but in this work has any attention been paid to the activity of the metal previous to the application of the coating or previous to oxidation?

CHAIRMAN MASTERSON: In terms of working the substrate, you mean, rolling, or in terms of surface treatment prior to --

MR. RICHMOND: Passivation. In some experiments that we did at the Bureau of Standards on oxidation of alloys, we found that the state of activity of the metal before you put it in the treatment has a very significant effect. For instance, if you passivate one of these high temperature alloys by a short treatment with nitric acid, the oxidation rate is about one-tenth of what it is if you have activity by sand blasting and the character of oxide is different.

We didn't look into the exact morphology of it, but it is very different in character, and the composition of the oxide layer is different.

In both cases, the ratio of the metals in the oxides is different than it is in the base metal. When you have a very active metal, you get more of the chrome in the oxide than when you have a passivated one.

CHAIRMAN MASTERSON: We had initially wanted to explore some of the possibilities, pickling techniques, but it turned out to be a bigger job than we had money for, so we did not do any of that. The high temperature heating is a method of passivating the substrate as far as making a diffusion barrier between some of the coatings especially those interference-type coatings where you have to maintain sharp interfaces.

MR. SOWELL: I think with the electrodeposited coatings, a certain amount of surface oxide is tolerable. But, if enough oxide is there, the adhesion is very poor. We don't have a lot of latitude with the surface condition.

On the steel substrate we have looked at sand blasting, and we have looked at a number of different nickel platings ranging from bright nickel which has one crystal structure to sulfamate and other nickel coatings which are rough on a micro scale.

MR. NELSON: As you know, our concentrator uses Olympic black chrome and our collector people tell me that we get discoloration in as little as four hours at temperatures as low as 500 F down to 400 F.

We have no actual experimental data to show exactly what kind of a drop that corresponds to in absorptance or emittance, or if it does at all. Are you saying you don't think it is an effect there? I mean you might get discoloration, and yet not get an actual drop in --

MR. SOWELL: I think that is true, because the eye can be very misleading. We did look at some Acurex receivers, they were spares that went into that irrigation project, but they were put on bright nickel, not a satin or mat-finish nickel. But, I believe the absorptance looked pretty good. As a matter of fact, we did some heat aging studies on those, but we were at temperatures above your operating temperature because some of those got overheated, if you recall.

MR. NELSON: Right. Even those that did get overheated, we thought showed some kind of significant discoloration. Apparently, there is no problem with that?

MR. SOWELL: Well, yeah, there are a lot of different colors there. Some that we looked at looked fairly non-uniform to the eye, I think were fairly uniform. Dick Pettit may be able to give us some numbers on that. What is your recollection, Dick?

MR. PETTIT: I think there was some nonuniformity in some of the coated tubes that we looked at. The nonuniformity was more apparent after heating than before heating. Typically though, at 250 C in the air, they were relatively stable. There are cases in the first couple of hours of heating, you do see changes of maybe two or three percent, from there on stable.

MR. SIEVERS: I just want to ask along this line of testing at 350 C, is this a thermal test or is this actually using a simulated solar spectrum so that the heating comes about using standard photons?

MR. SOWELL: This is in a furnace.

MR. SIEVERS: That's really not the complete test, is it?

MR. SOWELL: No, this is not a simulated surface that comes further on down the line, and right now, I don't feel smart enough to design a simulated surface test. If we start throwing in concentrated sunlight, a little moisture, that's going a little faster than I want to go right now.

MR. SCHWARTZ: You may be in very good shape with your measurements. I noticed one went up at .95, and then down to about .87. Now, if you use that black chrome even with the .87 in the cavity, you have got a pretty good cavity, and most of the applications I design, you are using a cavity, your absorptivity instead of being .87 is as high as, it would be about a .98.

So, if you take a look for the change in your alpha, what the change in alpha effective is, it could be insignificant. It is like one percent, one-and-a-half percent. Aren't we worried about something that we shouldn't be worried about, because the key thing is that it has flattened out already.

MR. CZANDERNA: I was wondering if any attempt has been made to study the oxide thickness at these various stages, and also at the various stages of degradation, if any attempt with the scanning electron microscopy has been made to look at the surfaces?

MR. SOWELL: Yes, we have looked with the scanning electron microscope. We haven't made a concentrated effort in looking at thickness.

As far as the microstructure is concerned, there doesn't seem to be a noticeable difference on either of the stable or the unstable coatings.

MR. CZANDERNA: Is there any correlation between the topography and the rate of degradation of the sample?

MR. SOWELL: We haven't seen that, but I wouldn't rule that out. I don't think we have looked at those sort of times enough to be able to say.

MR. SIEVERS: I would like to make a comment about black chrome and cavities, as soon as you use a cavity, the emissivity goes up. One of the reasons for using black chrome was because it is selective. You are destroying the selectivity when you start mixing cavities and black chrome together.

MR. LEONARD: Another comment on the cavities, for low concentrating designs such as the ∿ 50 X line focusing systems use, I haven't seen a cavity designed to make sense yet, but the cross sections I showed this morning would be called at best quasi-cavities. For a low concentrating collector, one must work hard to get a sharp image and to allow that to pass through an aperture into a cavity receiver is just spoiling the quality and destroying your ability to achieve high temperatures. So, we very reluctantly give away the sharpness of our image on the relatively low concentration collectors.

Black Chrome Surface Morphology

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The surface morphology or microstructure of electro-deposited black chrome and inert-gas chrome have been studied within a mean field or continuum model. Previous work with the gold black system has shown the applicability of this model for dispersed metallic particles in a dielectric medium. The particles are assumed to have varying spheroidal shapes, e.g., various semimajor-to-semiminor-axis ratios with the distribution of these shapes being a significant factor determining the optical absorption of the blacks. This spheroidal-particle distribution can be extracted for a given black by comparing the experimentally determined absorption coefficient to that predicted by the Spheroid Model.

For inert-gas chrome black, specimens were prepared by evaporation of pure chromium from a tungsten-filament-heated carbon crucible in an atmosphere of 2 torr helium. The black was deposited on glass-cover slip substrates, and integrated spectral transmittance measurements were made for wavelengths between 0.35 μ and 2.40 μ, using an integrating sphere spectrophotometer. This determined the absorption coefficient of the black, and comparison with the spheroid model yielded a log-normal distribution of spheroidal particles (Fig. 1). This log-normal distribution is equivalent to that found for gold black, and its occurrence for inert-gas-evaporated samples is expected.

A significant point that can be drawn from the Spheriod Model applies to the tailoring of the microstructure of an absorber to achieve selectivity and increased solar absorptance. Figure 2 shows comparison between several model calculations for inert-gas-evaporated chrome black deposits on a reflective-metal substrate. A deposit of spheres of size less than the wavelength of light and 1 μ thick shows little selectivity and poor optical absorptance, whereas a similar deposit 10 μ thick shows high optical absorptance and selectivity. Changing the microstructure from spheres to spheroids of semimajor-to-semiminor-axis ratio of 5 and a film thickness of only 1 μ yields a reflectance almost equivalent to that of the 10 μ thick sphere deposit.

The important and significant point to note from the evaporated-chrome study is that there is a major dependence of the optical properties of a solar absorber on its microscopic structure.

The Spheroid Model has been applied to electro-deposited black chrome coatings to deduce their microscopic structure so that changes in the optical properties of black chrome upon heating, exposure to air, and exposure to high solar fluxes can be in the future related to possible changes in its microstructure. Black chrome was deposited on highly polished pure nickel substrates using Harshaw Chemical Co. Chromonyx plating solution with a current density of 200 mA per cm^2. Pure nickel was chosen for the substrate because a pure metal with known optical constants is required for the determination of the absorption of the black chrome coating via measurement of its reflectance in the integrating sphere spectrophotometer. Nickel has also been the most widely used base for black chrome deposits since it provides a diffusion barrier.

Application of the Spheroid Model to black chrome assuming that black chrome consists of small metallic chromium spheres (dia. $< \lambda$) embedded in a Cr_2O_3 dielectric matrix has yielded poor agreement with experiment for the spectral integrated reflectance. The poor agreement indicates that the assumed structural model is probably incorrect. To clarify the films structure, a study has been undertaken by scanning electron microscopy (SEM). High-resolution SEM has indicated that the black chrome films (between 0.1 μ and 0.4 μ thickness, as determined by SEM) consist of a top layer of loosely packed 200 Å to 300 Å dia. particles which, when removed by inert-gas-ion etching, revealed one or two sublayers of larger (1000 Å to 2000 Å) particles on the nickel substrate. The larger particles are not far from being spherical, however, they are quite loosely packed with voids between the particles (Fig. 3).

ESCA-XPS depth-profiling measurements of the black chrome films have indicated that the top 200 Å to 300 Å are primarily Cr_2O_3 with only 10 to 15% of the chromium present in the metallic state (Fig. 4). The remainder of the film is primarily metallic chromium in the Cr^{+3} oxidized state, and a small amount of oxygen in a binding state equivalent to that found in Cr_2O_3, i.e., little Cr_2O_3 in the bulk of the film as compared to the top-surface layer.

The conclusion from the SEM/ESCA studies of black chrome are the following:

(1) The top surface of black chrome is a 200 A to 300 Å thick layer of loosely packed particles of Cr_2O_3.

(2) The remainder of the film is at most several layers of loosely packed but uniformly dispersed 1000 Å to 2000 Å dia. chromium particles.

(3) There is little Cr_2O_3 (10 to 15% of the amount in the top layer) in the bulk of the film, and it is probably found as a thin oxide on the chromium particles, indicating that the chromium particles are separated by voids in the film, making the film quite porous.

A more realistic model of the black chrome films structure can now be utilized in the application of the Spheroid Model to black chrome to more fully understand the role that the film microstructure plays in determining its optical properties. In addition, now that the microstructure of as-deposited black chrome is known, the detrimental effects on the optical properties observed upon heating in air can be related to possible changes in the film microstructure and chemical composition (e.g., possible oxidation of the film's loosely packed chromium particles converting the whole film to Cr_2O_3). Once the bases for the detrimental effects are identified, attempts can be made at rectifying the problems.

The effects of furnace heating in air for short and prolonged periods as well as the possibility of solar heating in air are now being studied with respect to changes in the black chrome microstructure and chemical composition.

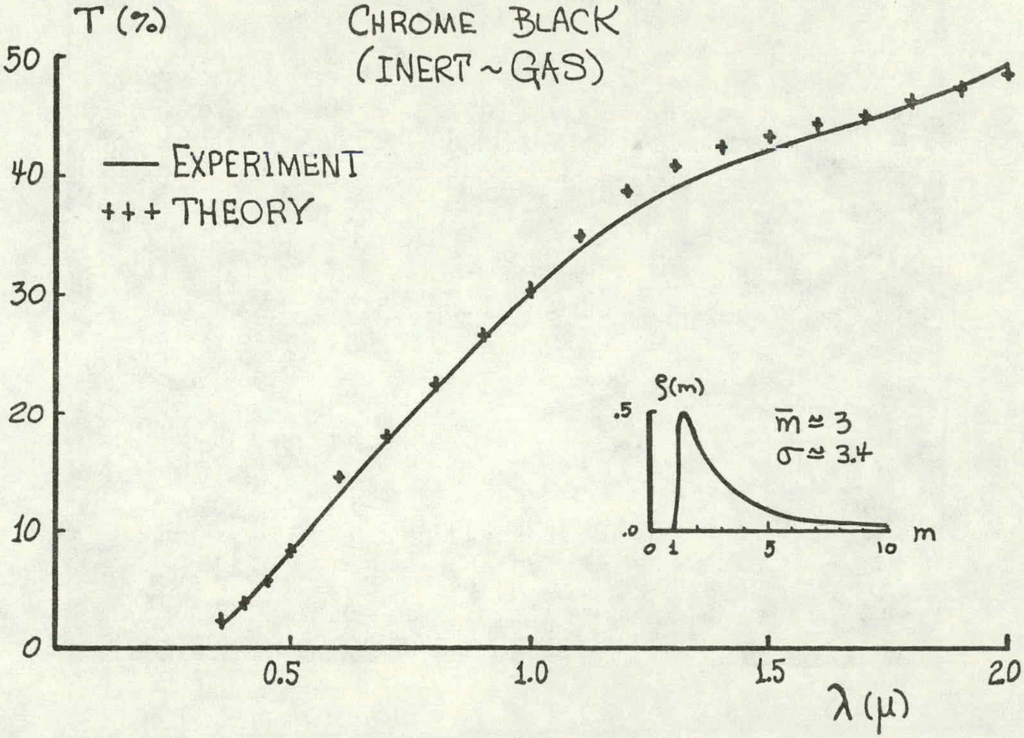

Figure 1. Integrated transmittance of Inert-gas evaporated chrome black. Insert shows log-normal distribution of spheroids used in calculation.

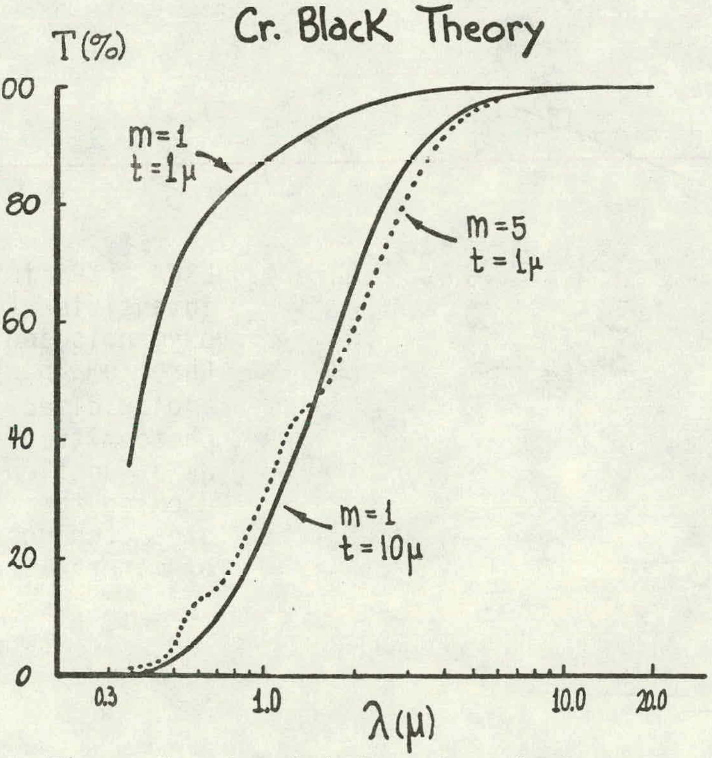

Figure 2. Sensitivity of optical properties on microstructure of a particulate solar absorber.

3b
1 Etch +50Å
35K
45°

Same Area as 0 etch

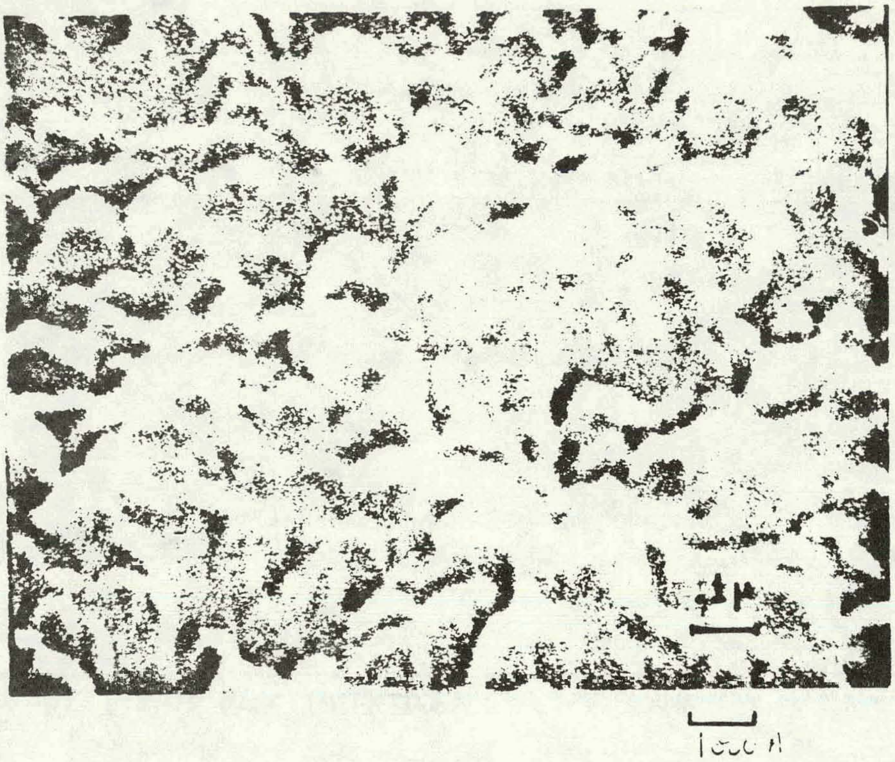

Figure 3. SEM micrograph of electrodeposited black chrome after an ion etch removing approximately the first 300 Å of the film. Note particulate nature.

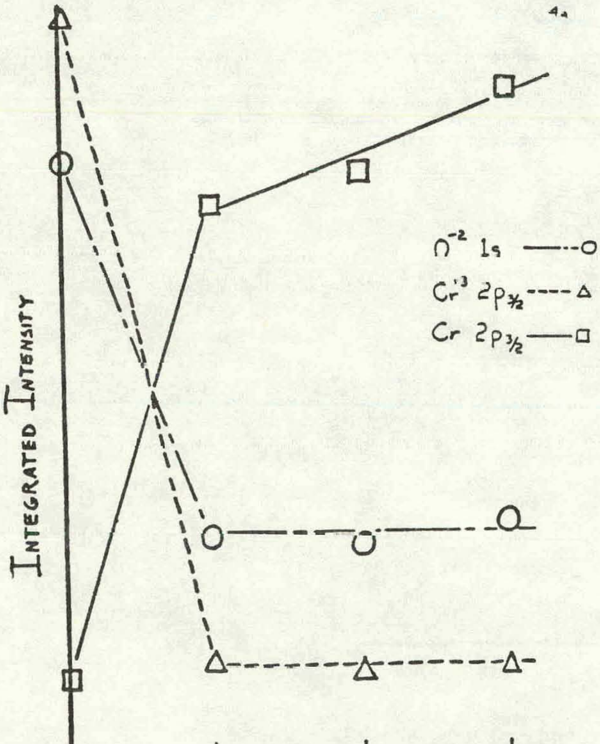

Figure 4. ESCA - XPS integrated intensities for the oxygen 1s and the Chromium $2p_{3/2}$ (metallic and oxidized states) photoemitted electrons as a function of ion etching time (20 minutes etching ≃ 300 Å of material removed).

MR. SIEVERS: Back in the beginning of your talk where you showed your spheroid model, you have the electric field along the long axis of the spheroid. Now that only accounts for one polarization, what about the other polarization that looks at the narrow axis?

MR. IGNATIEV: Both are accounted for in that. In fact, we assume ellipsoids oriented along all three possible directions, and we assume normal and parallel electric fields. The depolarization factors are for both normal and parallel fields in the direction for

MR. SIEVERS: How many parameters do you have in fitting that curve in --

MR. IGNATIEV: We need information on the dielectric constant of the chrome particles. We need to know the electron collision time in the chrome particles that has changed by the fact they are small. We need to know things like possible changes in the electron band structure in the material, and then what we end up doing is we generate the distribution of ellipsoids to give us the best comparison to experiment.

When we do that, we find that our distribution is essentially a log normal distribution. Once we have assumed that all we need is the median and the deviational distribution, those are the two parameters to fit that curve, in other words, we are assuming a log normal distribution. We feel that it is physically significant that that's the case. We have to know the median particle size for any distribution and a standard deviation of distribution itself.

MR. SIEVERS: What about the thickness?

MR. IGNATIEV: That's measured, as is the density of the material.

CHAIRMAN MASTERSON: When you speak of distribution, you mean size distribution or distribution of the ellipsivities?

MR. IGNATIEV: The distribution is in the ellipsivities. The size is assumed to be less than the wavelength of light, we need to have that assumption for the theory to work or to be at least applicable.

MR. VOSSEN: You have gone through quite a few gyrations to get the sputtering artifacts out of your depth profile, I might suggest to you that it is a very convenient thing to do both Auger and SIMS. Look at what's left after sputtering, and look at what is coming off due to sputtering. Put the two of them together, then it makes a great deal more sense with a lot less hassle.

MR. IGNATIEV: That is correct. We just got our SIMS flying.

MR. VOSSEN: I would also like to suggest that it is a waste of time to try to sputter profile an oxide using XPS because you are basically looking for bonding information which by definition you are destroying in the sputtering process.

MR. IGNATIEV: That is not totally correct. There has been a significant amount of information done on XPS and measurements of sputtering and oxide reduction by XPS measurements, that's the only way you can measure oxide reductions is by XPS. And in fact, sputtering, you are locally damaging a surface, that's point number one. You could be locally changing the concentration, but by and large, you are sputtering off pieces of materials. SIMS has shown that things come off, in fact, in a number of oxides in the composition of the oxide within the material. You get suboxides coming off also under SIMS.

However, the damage involved in changing the chemical constituency near the damage point is something which does not overshadow the chemical analysis.

MR. VOSSEN: That depends very much on the escape depth at the energy levels you are dealing with. At low energy, that is not true anymore.

MR. CALL: Have you taken into account the possibility of alignment of the ellipses in the layer that you are talking about?

MR. IGNATIEV: In terms of the vacuum evaporated chrome blacks, no, because we feel there is no preferential alignment. In terms of the electrodeposited coating, we haven't gone the next step yet as to saying look, our particles really aren't spherical.

We look at the SEM, the particles are just not spherical, they really are quite distorted and inhomogeneous in size.

So, we want to include that, although one could classify it as a parameter, want to include that next, and therefore, we have to worry about orientations of these with respect to the incident beam.

Low Temperature Solar Coatings

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Solar coatings have a significant effect on the performance of solar collection systems, especially the flat plate collectors. The improvement of collector efficiency by using different types of coatings is illustrated in Figure 1. Through the use of selective absorbers and antireflection (AR) coated glass windows an efficiency increase of ~ 50% can be obtained at a cost increase of less than 10%.

Honeywell has recently completed Phase II of the solar coating program for ERDA begun in 1974. The objective of the program was to investigate coatings which would enhance the performance and economic feasibility of flat plate collectors. Coatings investigated included selective absorbing plated and paint coatings (Figures 2, 3, 4), and AR coatings for window materials (Figure 5).

Key requirements for a practical solar coating are optical efficiency, durability and low cost. Table 1 summarizes the key features of several of the most promising solar coatings developed to date. Life expectancy of these coatings is a preliminary estimation based on the results of accelerated humidity tests and 2½-year outdoor exposure of black nickel coatings in actual collectors. The selective paint was formulated using an iron-manganese-copper oxide pigment in a silicone or urethane binder. The selective paint has good optical properties ($\alpha = 0.92$, $\varepsilon = 0.13$) and good environmental stability. It is particularly attractive for its low cost. Black chrome and black nickel have the best optical properties of the selective solar absorber coatings. They also are relatively low cost coatings. Black chrome appears to have the good durability required for flat plate collectors. Black nickel may also meet the durability requirements but additional long term outdoor life tests must be made to assure its reliability. Etching in a silica saturated fluosilicic acid solution has been developed which reduce the two-surface solar reflection loss of glass from the original 8% to less than 2%. A Teflon coating on glass has also been made which increases the solar transmission of glass by ~ 5%. The cost of Teflon coating is even lower than that of etched AR glass.

FIGURE 1. **COLLECTOR PERFORMANCE COMPARISON**

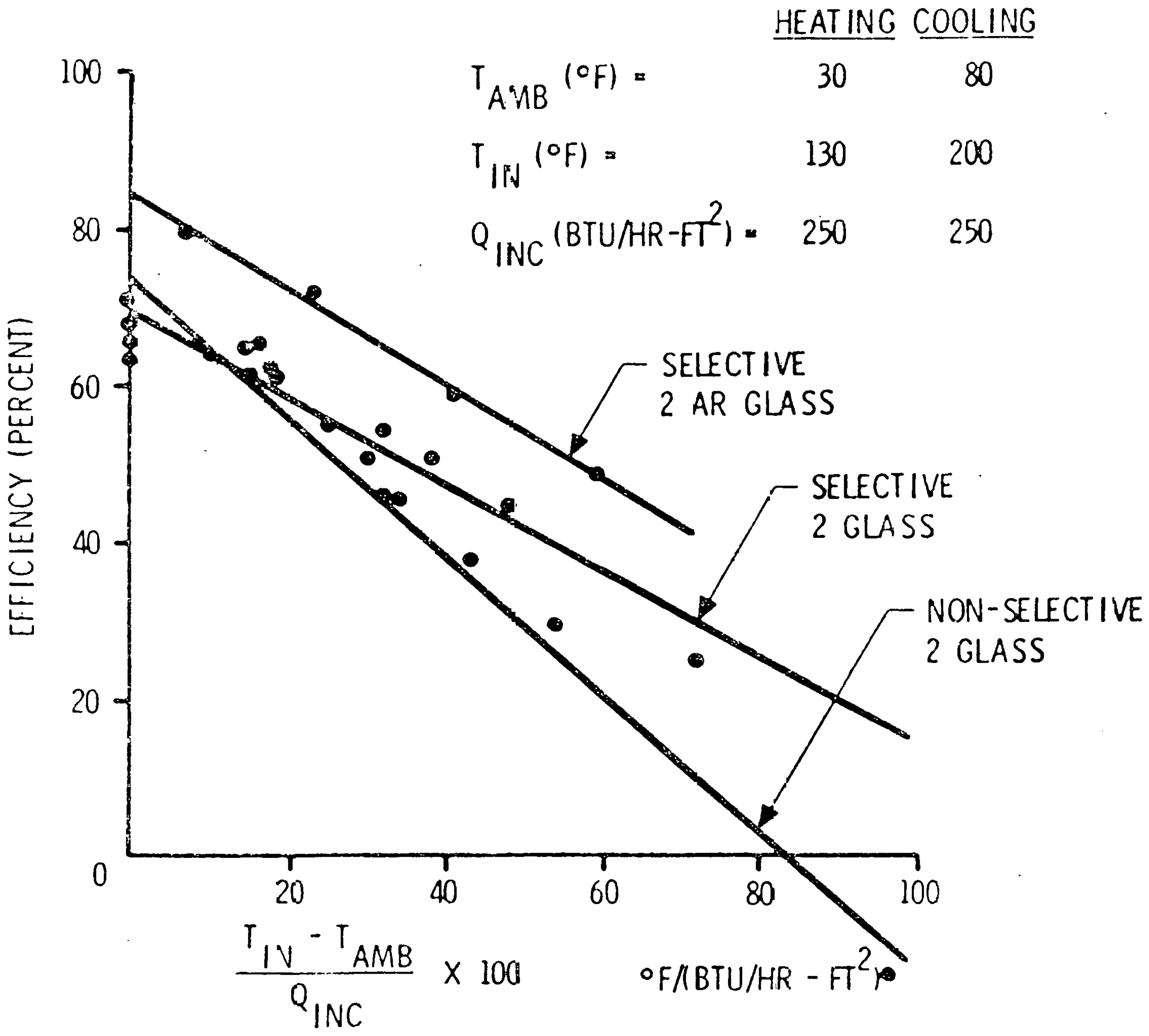

FIGURE 2. **SELECTIVE SOLAR PAINT**

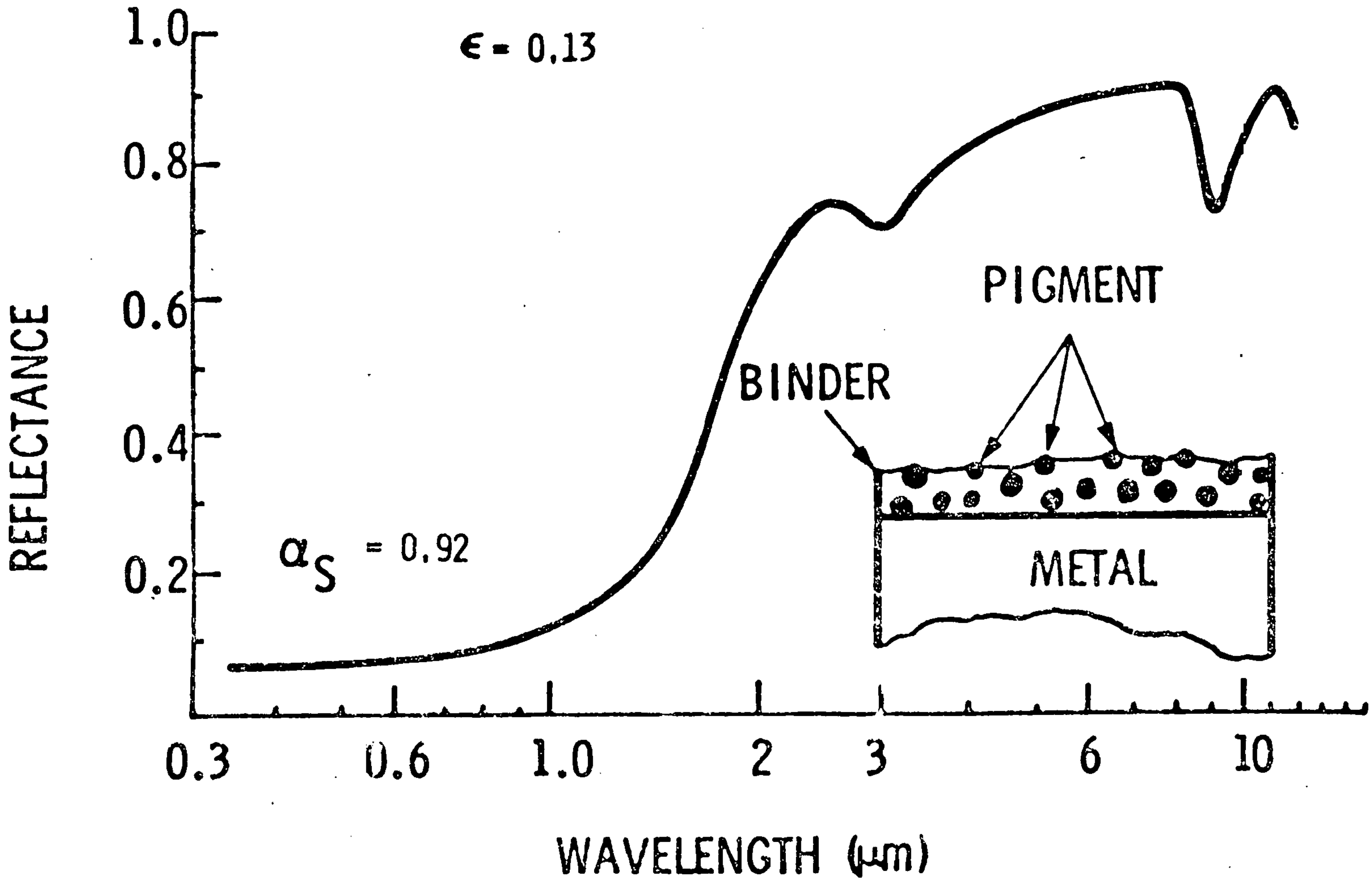

FIGURE 3. **BLACK CHROME SOLAR ABSORBER**

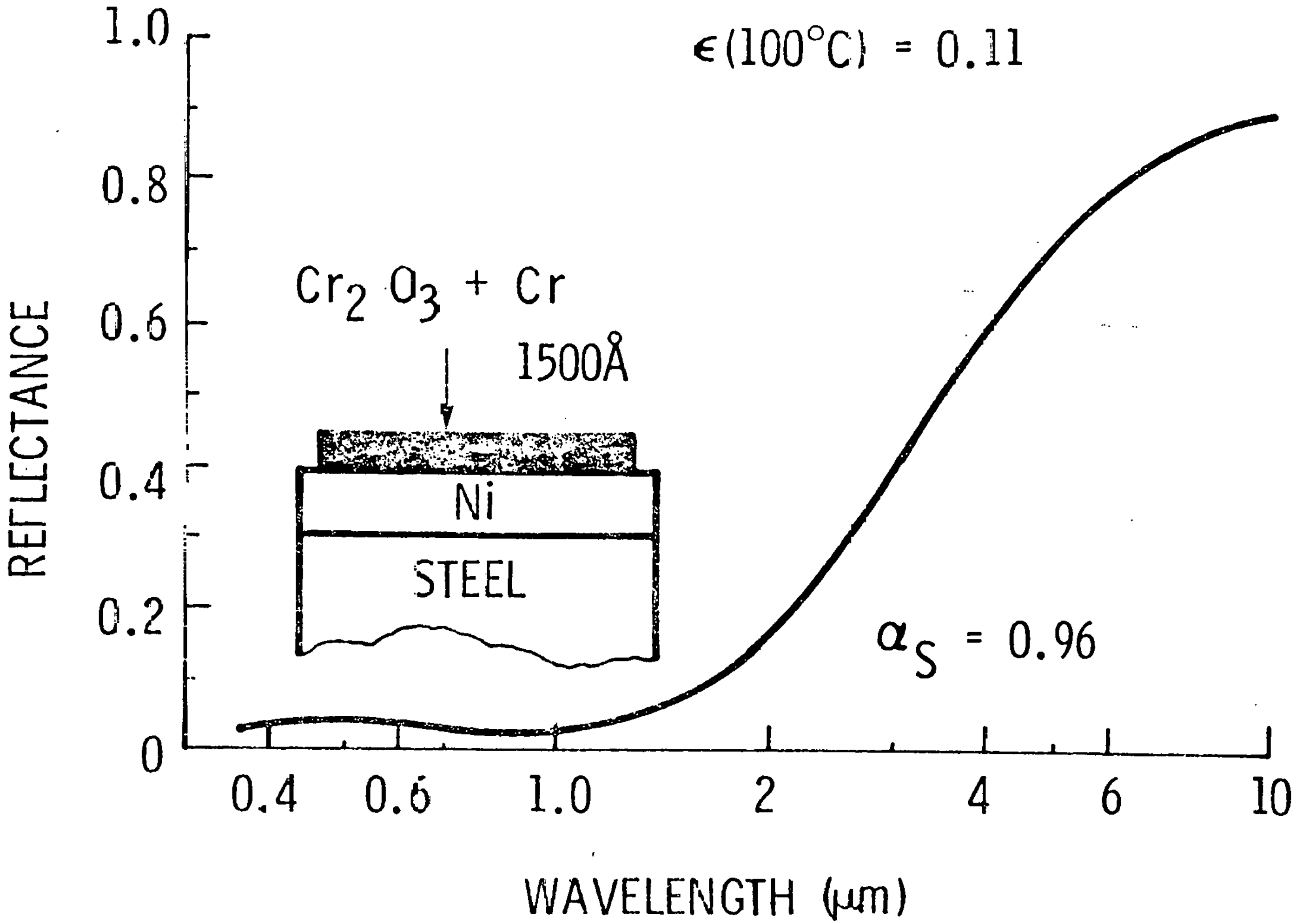

FIGURE 4. DOUBLE LAYER BLACK NICKEL

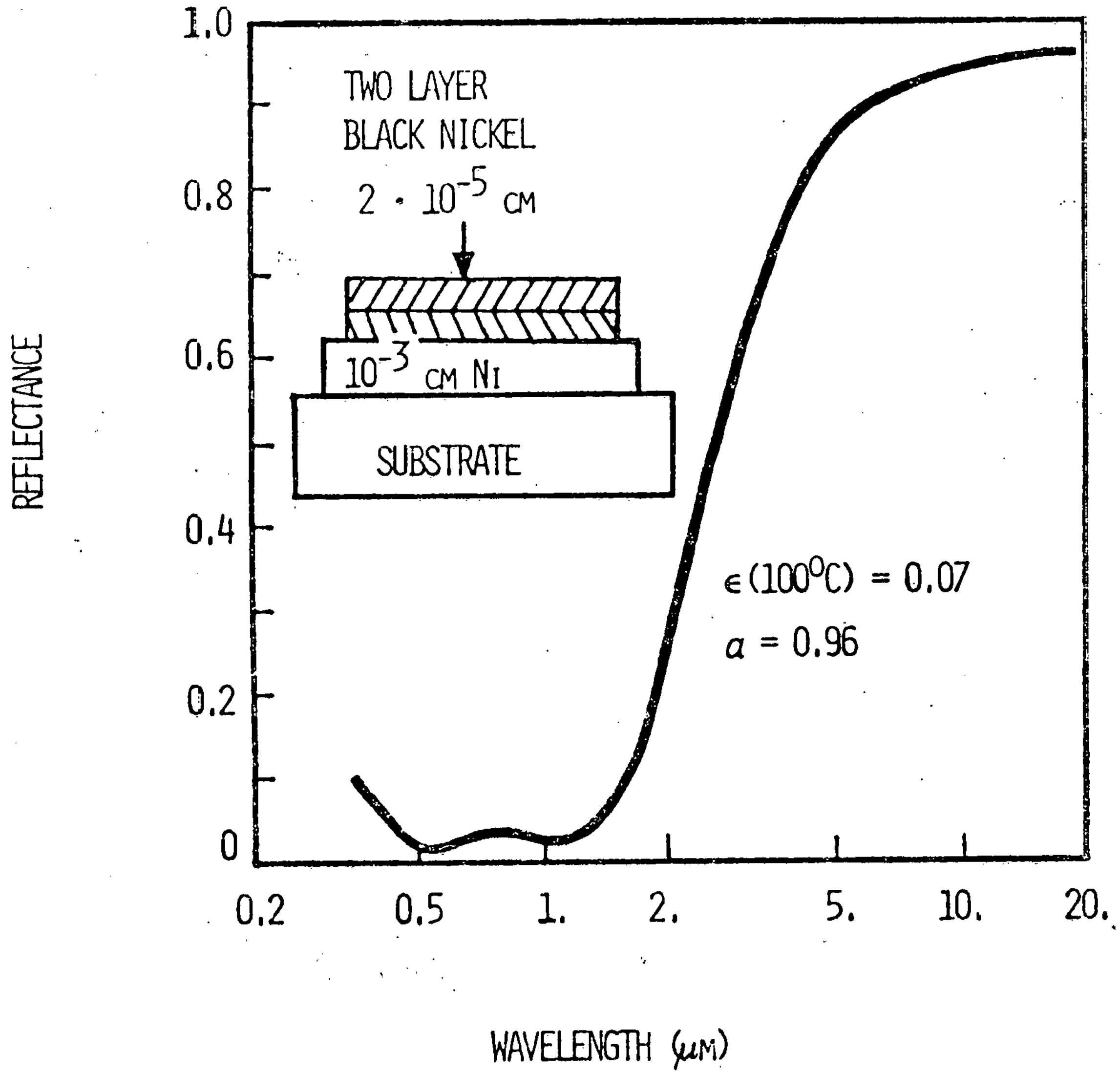

FIGURE 5. ETCHED AR COATINGS

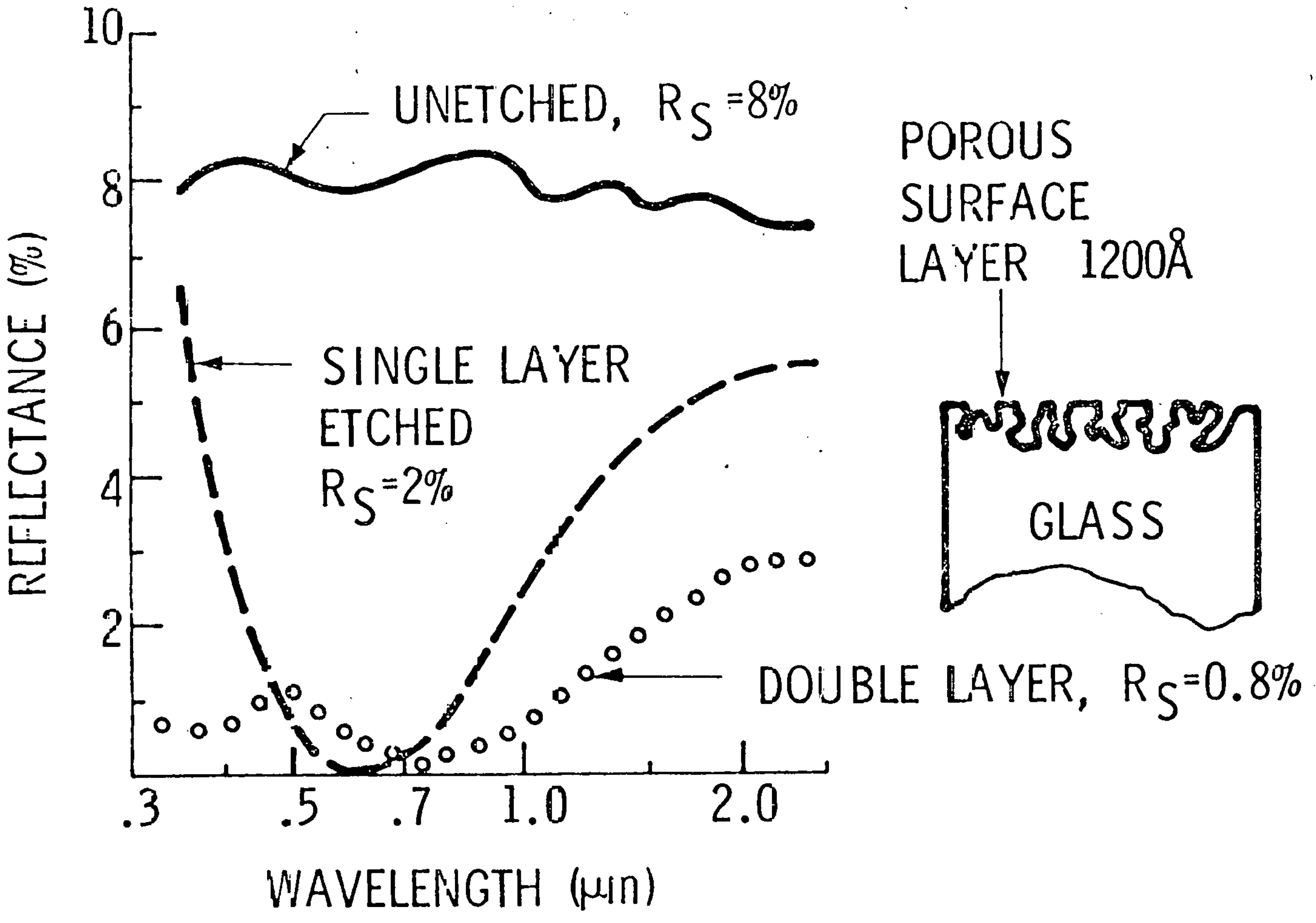

TABLE 1. PROPERTIES OF SELECTED SOLAR COATINGS

COATING	SUBSTRATE	OPTICAL PROPERTIES		ESTIMATED MANUFACTURED COST ($\$/FT^2$)	ESTIMATED LIFE (YRS)
		α	ϵ (100^0C)		
SELECTIVE PAINT	ALUMINUM	0.92	0.13	0.05	>20
BLACK CHROME	STEEL/NICKEL (1/2 MIL)	0.95	0.09	0.50	>30
BLACK CHROME	STEEL/NICKEL (1/4 MIL)	0.95	0.09	0.35	>15-20
BLACK NICKEL	STEEL/NICKEL (1/2 MIL)	0.96	0.07	0.50	> 2
ETCHED AR GLASS	--	R = 0.02		0.10	>15
TEFLON AR COATING	GLASS	R = 0.03		0.05	--

MR. RICHMOND: Have you made any tests or do you have any information on the effect of surface etching on the cleanibility of the glass?

MR. LIN: Well, we did some durability tests--four outdoor tests for six months--and while it does collect a little bit of dirt, you can clean it just by water and you can insure a high transmission.

One case when we measured a transmission after we put it on a roof for three months, and only two or three days after a rain it appears to have been washed by itself, and it gave a reasonable high transmission.

MR. RAY: What thickness is the selective paint?

MR. LIN: It is less than five microns. The particle size of the organic pigment is in the neighborhood of about four to five microns.

MR. GILLIGAN: You mentioned hemispherical transmittance, that's what you are quoting; is that right? You didn't measure the normal transmittance?

MR. LIN: Well, for the air tests, we measured a normal transmittance.

MR. RICHMOND: For a flat plate collector, it doesn't make too much difference.

MR. GILLIGAN: It isn't whether they are usable, the point I was trying to make was the fact of the normal versus the hemispherical transmittance can be and usually is farily big for the AR.

MR. LIN: Here I would like to point out on the teflon-coated glass, we used the hemispherical equipment because the surface is kind of diffuse, and we did find a five percent difference with the normal transmission equipment. But for the ordinary glass, it is not that diffuse, it doesn't matter much.

MR. MUENKER: How do you control your thickness on selective paints to five microns?

MR. LIN: We use the two different application techniques. One is by spray coating. We did not get 88 percent absorptance and 17 percent emissivity.

Then, we switched to dipping, and it turns out we get a better control over the surface by the dipping technique, and that's where we come up with 92 percent absorptance.

MR. MUENKER: In other words, you control your viscosity, your concentration of the pigment in the binder?

MR. LIN: Yes, there are a lot of factors, but it is thickness that is one of the major factors determining emissivity because the absorptance binders absorbs the infrared.

MR. CARROLL: How did you measure the emittance of the selective paint?

MR. LIN: We used the Gier-Dunkel portable machine

MR. MUENKER: I have never seen a paint with an organic binder with emittance that low.

MR. LIN: We did check that result with directly-measured emissivity. We measured the emissivity in a cavity, heated it up to 100 degrees centigrade, and we measured the selective paint with the Gier-Dunkel, and we compared results, and it was probably one or two percent different.

MR. GILLIGAN: What was it painted on?

MR. LIN: Aluminum. Selective paint doesn't protect the steel very well, that's why we put it on aluminum because you put it on in a very thin layer --

MR. GILLIGAN: I think you are seeing more aluminum than you are pigment.

MR. LIN: More and more people are using aluminum. There is one person who compared the cost against the conductivity, and it turns out the cost of aluminum was only about 20 percent more expensive than steel, and the conductivity was twice better than the steel. So actually, if you use aluminum, it is cost effective.

CHAIRMAN MASTERSON: Have you put your selective paint on glass to look at the transmission?

MR. LIN: No. We haven't tried it.

MR. RAY: I think in the first phase of this work, you reported that you saw little effect on the selective properties by the pigment concentration, was that also observed in the second phase of the selective paints?

MR. LIN: Well, it does show some difference, but not very much. Between 30 PVC, and say, 50 PVC, there is not much difference. Two percent, four, five percent emissivity. It has more affect on emissivity than absorption.

Summary of Discussion

CHAIRMAN MASTERSON: A discussion is in order now of everything we have touched on this afternoon trying to keep primarily to optical and compositional characterization of the solar absorber materials and things that we need to think of, I guess, primarily not so much materials themselves, but in fact, the characterization methodology.

One question that we wanted to discuss is if there is any use or need for a dedicated facility which would view optical measurements, morphology measurements, SEM, and compositional measurements for the solar coatings program, or are the facilities that are presently available and distributed throughout the country equipped for that?

MR. RICHMOND: I would like to add one other question to what has been proposed, and that is, we would very much like to know at the Bureau of Standards if you need any standards in this area. Frequently, if you can get calibrated standards to be used in the various laboratories to check the equipment, it will perhaps be almost as effective as having a dedicated laboratory, and I think we ought to consider that as an alternative.

MR. SIEVERS: While I guess I am a little confused with that question because if you have got enough money, it would seem that you would always want to have everything in one place. What is the real question here? Is it that there is not enough money, so can't you use different instruments at different parts of the country, or is there a lot of money, and are you trying to decide best how to spend it, or what?

CHAIRMAN MASTERSON: I think, though it is my own personal feeling, money aside, that you need both. You need tremendous capability in one place where you can couple the optical and the morphological compositional characteristics altogether. It turns out, I think it is just a matter of working convenience and productivity. If you have to shift things around to different places to get the measurements, then productivity perhaps goes down. It would be nice to have everything in one place for that reason, but that's sort of like putting all of your eggs in one basket.

I think there is a tremendous need to have interlaboratory comparisons in order to make sure we are all measuring the same kinds of numbers and reliable results.

MR. RICHMOND: I might comment on what has been said. To me it doesn't make sense to send all the samples in your screening tests and so forth to a central facility for measurement. You are likely to find if you have a dedicated lab, that it might take you six months turnaround to get your results back.

I think it does make good sense to have a dedicated facility where after you have done your screening and you think you have the best you can get by your own procedures, where you can send them and get a really definitive value.

Generally, measurements made in any laboratory are very likely to be satisfactory for ratings of coatings. It can tell that one is better than the other, but they can't tell how good either one is.

But, a dedicated lab should be able to give you results with very small uncertainties.

On the other hand, you have got to remember that to make measurements with very small uncertainties takes a great deal more time than it does to make measurements for screening purposes, and the cost is going to be considerably higher.

MR. SCHWARTZ: I think I would have to disagree with having a central facility. I think an illustration of a field of endeavor that I was involved with for a number of years is the space effort. I can't think of any effort that warranted a central facility more as far as optical properties were concerned than the space effort, and I think the space effort made it. I don't think it made it by the skin of its teeth. I think there were a lot of good laboratories that were around to make the measurements, like TRW.

I think the thing that could eliminate the need for a central facility is such a thing as standards. I think there is something even simplier than that, and a lot of people don't like to do it, and it is done in the space effort, a round robin.

There is another issue, and that is how warranted is a coatings program. So far, what I have heard today, I can see one regime in which you are interested in it. I can see very considerable use of just native materials, construction materials, that are oxidized.

I think the ability to characterize the materials may be more involved with the research phase than with the final quality control issue, and I think characteristically, research has been done by a whole group of organizations, and they all have had access to scientific instruments, various types of instruments, measurement instruments, and I think it can make it. And I think it would be an unnecessary expense to have this type of central facility.

MR. CALL: You indicated in a discussion earlier where we decided that there were no facilities for making the measurements we needed at the temperatures --

MR. SCHWARTZ: This is a very unique case that we are talking about here. This measurement of alpha at temperature is one of many types of measurements, and it is probably one of 20, 50 different types of measurements in this optics field. This thing could be very readily done. This capability may even exist either at TRW or at Minneapolis-Honeywell. There are a lot of places. We are going to have to canvas it.

I have asked the people to submit to Elliott writeups describing the instruments. After we have looked at that, then we can come to a conclusion. But I don't think you can draw any conclusion at all from the fact that we apparently can't determine a hot alpha. I don't think that's a crucial issue at all.

I think to build that type of an instrument is not complicated. Measurements of alpha, at temperature, have to be done. I have done it. I have done it up to about 250-300 F in a Cary 21. You just have to go to different types of instruments. But, that's no reason to set up a central facility.

MR. CARROLL: We identified a need this morning, I think it is a real need to measure alpha at temperature. I would like to make a plea to this group, don't everybody go out and build that equipment because I think it is going to be very rare if you have a material that is going to be temperature sensitive. What you need is one place where you can go to find out if your particular system is temperature sensitive. From there on, you can make the measurement at room temperature once you have determined that it is not temperature sensitive.

The kinds of effects that you are going to find in and on solar absorptance are no where near what we heard this morning, 0.95 to 0.65. There may be a 0.05 kind of effect, maybe a 0.1 kind of effect for certain systems. But, I would be very surprised if there was anything at all where the alpha would change more than 0.05.

I have been fooled before, and I think we need a facility to check that.

MR. GUTSTEIN: As one of the many participants in this organization, I want to second what has just been said as to people going out and building a whole bunch of instrumentation.

MR. SERAPHIN: Keith Masterson has shown curves of reflectance changes of the materials involved in the CR project by 15 percent, and we wimply don't have any information available that could back up your claim that optical materials or engineering materials don't change alpha. But, any predictions about what optical or engineering materials are doing at elevated temperatures are not known, and we have to realize that.

We are making predictions about efficiencies of multi-million dollar facilities without even having measured what they are going to do at the operational temperatures.

CHAIRMAN MASTERSON: I think it depends a lot on the kinds of materials that you are working with. The semi-conductor coatings, for instance, that we worked with in Arizona inherently are more temperature sensitive than the refractories of nonconductor-type materials.

MR. SIEVERS: This business with alpha and the photon-assisted processes was mentioned a couple of years ago, and a few universities since then have tried to put together some temperature-dependent-type measuring systems. On the other hand, I feel that if there had been a dedicated facility at that time, really directed to this problem, they would have jumped on this thing and done it much faster and put a lot more money into that aspect because they would have felt under the gun.

So, I still come back to a central facility as having some purpose in solving our problems in a small amount of time.

CHAIRMAN MASTERSON: May I ask, does the National Bureau of Standards serve that capability at the present time to a degree that is satisfactory in any way to the coatings program?

MR. RICHMOND: It depends on what measurements you are talking about. The present philosophy at the National Bureau of Standards is they don't want to make routine measurements. They will calibrate standards, they will help other laboratories to obtain the capability of making measurements, but we don't want to get into the mode of making a lot of routine measurements. We think we have more important things to do.

One of the things that we do, and why I made my plea before, is that we do prepare and calibrate standards for any products for which there is a demonstrated demand.

MR. SERAPHIN: I would like to add one point where either NBS or SERI could be very helpful if there is not going to be a central facility, and this is simply the setting of standards even the agreement on a certain nomenclature or test procedure and so on.

NBS or SERI could be very helpful in setting the standards here and prescribing procedures.

CHAIRMAN MASTERSON: I think there is another purpose for a facility somewhere in the country whether it is SERI's obligation or NBS, but somebody needs to verify coating performance independently for the manufacturers. A lot of research goes on in the universities, it would be nice to have an independent verification of those results.

MR. RICHMOND: If you are going to publish any experimental results and expect anybody else to believe them or use them, you have to first characterize the sample so that somebody else can reproduce your sample, and second, you have to give enough information about the measurement procedure used so that somebody else can duplicate your measurements. If those two things are not done in a publication or by reference, the publication is essentially worthless. I have been working in the field of nomenclature since the middle 1950s, and we have developed a nomenclature, I think, that is fairly widely accepted, and we do have lists of nomenclature.

If it would appear worthwhile here, we could come up with a glossary of terms with definitions.

I am the chairman of the technical committee TC 1.1 of the U. S. National Committee for the International Commission on Illumination, and we are presently working on the revision of the international lighting vocabulary, which is published by the International Commission on Illumination, and contains definitions of a very large number of terms that are concerned both with lighting and with radiant heat transfer, and these definitions are given in four different languages: English, French, Russian, and German, and the terms themselves, but not the definitions, are given in five different languages.

Nomenclature, when we got into this back in the 1950s was a real fouled up mess, and the reason is that the different disciplines have different nomenclatures for these various concepts.

With the group that I was working with up until about 1970, we had a kind of nomenclature, and we could talk to each other and understand each other. Most of the people who were engaged in that business at that time are no longer in it, and we are getting a new crop of people coming from various disciplines, and they need to learn the correct nomenclature, and not use that in their current discipline.

CHAIRMAN MASTERSON: I think that is clear. It is simply a matter that people need to be aware of what the nomenclature is, and perhaps there needs to be some sort of initiative taken to help people become aware of what the appropriate nomenclature is if they are not using it already.

MR. RICHMOND: There was a publication that has just come out on nomenclature and reflectance.

CHAIRMAN MASTERSON: Joe just handed me NBS Monograph 160 which is Geometric Consideration and Nomenclature for Reflectance. So, I think primarily the Bureau of Standards is the place to go if you have any questions at this point on nomenclature on these things. It certainly can help you.

MR. GILLIGAN: A couple of comments. One is that a couple of months back, I was chairman of a working session at the concentrating collector conference, and probably more than anything else what came out of the workshop was the fact that the terminology, nomenclatures, definitions, are all very poorly done. This was exemplified by people getting up and writing down numbers that looked okay. But the way they got them, the way the measurements were made and their description of those measurements was horrible. It was unbelievable.

There is a real need to get the standardized nomenclature out to the people so they know when they read a value of α_S that it is a hemispherical value and it is a total value. These kinds of things are very poorly known, specular and spectral are mixed up, normal and hemispherical are mixed up routinely.

I was going to make another comment. When you talk about a dedicated facility to do all kinds of things we are talking about composition, morphology, optical properties, that sort of thing, are we talking about these only with respect to selective coatings, or are we talking about all of the other materials that are used in collector systems?

CHAIRMAN MASTERSON: Any installation or facility that would be powerful would be obviously used for a lot more work than just the coatings, there is no doubt about that. The corrosion studies and all kinds of things that are important.

MR. IGNATIEV: Just listening to all of this, I would like to give my two cents worth, and that is that it looks like most of the people here are under the impression that simply a couple of tests are going to solve all of our problems. As soon as we know what happens at high temperatures, we have licked the problem, and that's not the case.

My personal opinion is that we really don't know what's going on. We don't know why these materials are absorbing, we don't know how to make them any more or less absorbing. Okay, all we are doing is sitting here and measuring α and ε or whatever it is, and saying well, this is what it is now, we will make some more and test them again.

In reference to all of that, my feeling is that we really are going to have to point our intention more to what's really happening at the solar receiver. The fact that it is going to be sitting out there in air, in water vapor, at high temperatures, in high solar flux. Okay; again, things that have been mentioned two years ago and that now almost preclude the fact that you have to have some sort of facility to do that. You can't go and build a high temperature furnace, hemispherical emittance, a monitor in your laboratory, because it doesn't mean anything. It is maybe a direction, it may show you some direction on what is happening at high temperatures, but it doesn't tell you what is going to be happening in actual field conditions. In actual field conditions means that you have to get out there and have some sort of collector somewhere of relatively large size with support facilities, and again, something like a central facility.

You really need operational tests. I think one should worry a bit more than simply about the tests. One should worry about understanding why and how, in addition to how to make things better and bigger.

MR. SIEVERS: Well, do you want that in a central facility as to the why and how, or do you want that spread over the country?

MR. IGNATIEV: The why and how would almost have to be in a central facility because there is no other way to measure it.

MR. SCHWARTZ: Measure what?

MR. IGNATIEV: Measure high temperature, high photon flux, total hemispherical emittance, or absorptance.

MR. SCHWARTZ: You say a central facility, the way it originally was proposed, not only do you make the measurements, you do the morphology. The point I was making is that you don't want that, you don't need it.

The capability exists in very many places in the country.

MR. IGNATIEV: Then you are going to have to give every place a concentrator if you really want to worry about 400-500 C and high photon fluxes. You are not going to do it with a furnace.

The radiation is absorbed in the top several microns of the metal, not all the way through. You are going to have temperature differentials across the system.

There are a large number of aspects which people are not looking at currently which have to be carefully attacked, and you can't simply do that by saying I have got a furnace in my lab, I am going to do everything I want to do in the furnace.

CHAIRMAN MASTERSON: I might second that with the two oxidation studies that we did showing the oxidation in the furnace and in the laboratory which turned out to be considerably different reflectance properties.

MR. JURISSON: We have built up an expensive, in-house facility for routine testing of samples, also in situ measuring.

Now, whether there is a need for a central facility, I can see that only if I want to really reference my coatings or my devices against something, and I think this needs some kind of permanent receiver which can do these kinds of measurements. I think these are two separate functions.

MR. SCHWARTZ: You can come up with a standard that is appropriate, or another possibility which is used very extensively, and I think Carroll will verify that was the round robin. You didn't have a standard.

MR. CARROLL: Let's not do that again.

MR. SCHWARTZ: The standard, I think, would suffice, and would be very useful because then everybody could check their instruments. I don't see anything wrong with that.

I think the thing that you have today is a lot of people who have left the field since the pulling back of the space activity, I think you have a lot of capability and measurements still in the field, and I think you can continue that very effectively.

MR. SIEVERS: I phoned around the country last spring when I was going to take my sabbatical to see if there was any place that actually did high temperature measurements, optical properties, and solids, and I wasn't able to find a place that I could go to, whether I tried a big solar energy place or some place that didn't work in solar energy.

I excluded Seraphin from this --

MR. SERAPHIN: You didn't call me.

MR. SIEVERS: I excluded him because I knew all about his work, and I was trying to find something completely different.

So, the statement you are making that there are a lot of places around the country is not clear to me.

MR. SCHWARTZ: I think the thing is that a lot of these instruments exist, but they are probably not being used right now because of the de-emphasis in the space era. Like, I think, if you went to Bevins, if you went to Rockwell International, and places like that, they did do a heck of a lot of high temperature radiation property measurements.

As best I know, a lot of that capability still exists, and it is dormant because there hasn't been a requirement for it.

CHAIRMAN MASTERSON: I think we ought to spend a little bit of time talking about what the equipment is.

We have talked about making measurements, whether the facilities are necessary, but maybe it would illuminate things a little bit to find out what kind of equipment is really necessary to make those measurements, and that would determined then whether some of the necessary pieces of equipment are already existing.

MR. SCHWARTZ: As far as I know, Joe, isn't that your charter. This is what you are supposed to be doing. First of all, determine hopefully what the requirements are, and then to see what is in the field to match those requirements? Isn't that what you are doing right now?

MR. RICHMOND: It is one of the things that we are looking into.

MR. SCHWARTZ: Now, as far as I know, Joe, back in '66 you did a survey of what was the measurement capability in the country. I think that we need, after the requirements have been determined for the solar area, is an update of such a report that you put out in '66. I would hope that would come out of this workshop.

MR. RICHMOND: They have made it rather difficult to do anything like that. In order to send out a questionnaire to more than 10 people, you have got to get direct approval from the Office of Management and Budget, and that takes about six to nine months usually to get through.

MR. CALL: Does your area of interest go past optical measurements into the service characterization and stress characterization as well?

MR. RICHMOND: Not currently.

MR. CALL: That might be part of a bigger program--standardized stressing and environmental aging.

MR. SCHWARTZ: Well again, I think the thing that has to be nailed down is how important is that to the program.

I don't know the measurement and the various environmental tests. I heard the university feelings, however you may not have to go any further and know the whys and wherefors. I say you may not, but it would be very nice from a research standpoint.

I would like to see that work continue, that type of work. You may not need to do that, you may not have to, as I say, characterize the material or define the material much better than it has been. I think the thing that is very important obviously is the measurements as Dr. Seraphin has pointed out.

To think of building a Barstow plant of $120-million without knowing the hot alpha, frankly, that is why I was asking some very specific questions to you, that's what I thought the purpose of your program was at the University of Arizona. I thought that was going to be an answer, and it wasn't an answer.

CHAIRMAN MASTERSON: Those samples are very diffuse, and I think we need a hot diffuse reflector, and that comes out of the program.

MR. SCHWARTZ: My understanding, my very frank understanding was that you were going to build the instrument to do exactly that.

MR. SKINROOD: I want to not build Barstow unless we know what we are doing, to make sure you are going to make some kind of measurements to verify the performance. We still have a year and a half to do the detailed design and not that long before it is submitted, and I want to make sure it doesn't get out of hand.

MR. SERAPHIN: I think the problem is even more severe. This morning, we heard all of the very ambitious projects which in their efficiency really rely on input versus loss, and what it really boils down to is absorptance versus rejection by emittance again, and we better know these values before we make any statements about what amounts really to a key parameter in the efficiency of these plants, and namely, the ratio of what's being trapped to what's being lost either by reflectance or by re-emission.

So, what we are really after is the trapping of power and the re-radiative or reflective power loss.

Now, if you look at all of the things that we have talked about this afternoon, you will find that there is a rather loose connection between this power equilibrium, this power balance and what's being measured. This is what I propose first, and that doesn't enter into the debate over a dedicated facility.

Let's agree on what we mean by emittance, and how it relates to this power balance, and how we go about measuring something that can be done in an instrument of reasonable size and as close as possible to this power balance.

If you look at the emittance, for example, you can go about measuring the emittance in a variety of ways. It has come out this afternoon that you can go about it calorimetrically or you can go about it in a spectral manner.

Well, let me tell you that, for instance, if you take 1-R and even 1-R hemispherical, you are really dealing with an ideal surface, and if you cover this surface with a film, not to speak of a coating, then all bets are off, and you don't know how E normal relates to the total power loss, is that true? There are things like the "Brewster" angle, and so on, which represented terrific power drain from a surface which may have a normal emittance as low as six or seven percent, but you really don't know the power loss from the surface.

Of course, these things are all very well described in books and proceedings of which Joe Richmond has been the program chairman and so on.

But, the point is that they are not being used in the practice of the measurement, and I would suggest that we agree on simple and reasonable measurement procedures that carry certain names so that we know what we are talking about and that somehow relate to this power balance. I think this is a very necessary step that we should look at.

MR. JURISSON: If you look into the possession of the measuring instruments today, it is primarily large aerospace corporations. Whereas, if you look at the black nickel coating, black chrome, and glass etching, that is something that any small electroplating shop can do if they have access to these type of measurements. It is important from that point that we have some sort of a centrally known location where we can get measurements and make a comparison which is not available today.

MR. SCHWARTZ: Why can't they contract that out to the facilities that presently exist?

MR. JURISSON: One of the problems as I see it, having done measurements with people from the outside, we have felt rather reluctant to do that. The manpower they have available, we have even reluctantly reactivated some of the equipment which we used about 10 years ago.

MR. SCHWARTZ: But, there may be other groups that may not be reluctant to do that. I know one group on the West Coast that does a lot of business, and they are highly reputable.

MR. JURISSON: That's true, but that's only one.

MR. SCHWARTZ: I only know one, I said there may be quite a few others.

MR. JURISSON: It is a large aerospace corporation, and there is not anything commercially available, I guess that's what I am talking about.

MR. GILLIGAN: I keep hearing all these things, but I think one of the things that bugs me most and bugs me on our program we have at DOE, and that is what are the appropriate measurements to make, and once you have decided what is appropriate to measure or what it is you want to learn, then you can go to Joe Richmond's books or some of these other standards, and you can find out the name of that thing if you want to do that.

But the point is that you need to know what it is you want to measure. Then when you set it down in plain and simple English, we want to know the hemispherical emittance of things, and we want to know the specular or spectral absorptance of things, and you want angle and temperature and things like that, and what are the equipment available for doing those. I think you run into real severe problems in trying to go to a central lab because not all of these things exists in any one lab.

The expertise for getting them to work doesn't exist in any one place. I know, because we have had serious problems putting together rush equipment. If you want to do it right, you do have to have pretty high powered talent, and that talent doesn't exist across the country in great big bundles.

CHAIRMAN MASTERSON: The kinds of properties that you want to measure even vary from application to application. There is no consistent set or subset.

MR. GILLIGAN: This is what we propose, and we are doing measurements which we have argued out amongst ourselves and our consultants.

We are very certain that there are going to be some assumptions to the directional properties of things here that may, unless you know something about them particularly at high temperature, you may be in serious troubles. You may measure the alpha in a sphere at 700 C or whatever, and then be way off because you don't know what the directional properties are. We know the selectives are going to be very sensitive directionally, we know that already.

CHAIRMAN MASTERSON: Right. Another point which has been made before, but sort of comes to light in a different aspect, is that, for instance, measurement of emissivity can be done a few ways, and the most direct way and easiest is to calorimetrically measure --

MR. GILLIGAN: It is not the easiest.

CHAIRMAN MASTERSON: Well, it is not the easiest, okay. But it gives you the total emissivity hemispherical, everything you want. But, if you are going into a development program, it really doesn't tell you much about what the optical profile of the reflectance or emittance. The spectral emittance will help you in a developmental program to make changes.

MR. SIEVERS: One of the sort of flavors that I get is that we can farm some of this stuff out, and I sort of attach that with the feeling that these problems are not long-range problems. I think solar energy will be going on for 30 years.

I think you want to develop something that is kind of going to pick up momentum and develop new techniques over that kind of a time scale because this isn't a short-term problem that we can confine to one area and finish it off, it is a very long-term problem.

For example, in the spectroscopy business, interferometers have been developed in the last 10 years that the people who were in the space program and making measurements didn't have access to. These are machines for cranking out data very fast, and now such things are available. If you go into the space program, maybe you are not going to find them. I think there are some developments, a lot of surface physics in the last five years, new techniques there, and I think the things have changed so much that you are not going to be able to do it piecemeal. You are going to have to take the big view and thrust ahead for 30 years, look at it in that term.

MR. RICHMOND: It is not going to be cheap.

CHAIRMAN MASTERSON: It is not going to be cheap and that was one question we want to address--what kind of money is involved? People who have had experience building some instruments have ideas, and I wonder if we could get some comments back on, for instance, what would be a cost estimate of a diffuse reflectance interferometer that operates in the infrared? I know how you can do when you go out and you buy the interferometer from somebody, but the interfacing which you can't buy, the necessary interfacing which mostly you can't buy off the shelves, in terms of manpower cost, labor costs, do you have any idea of what it would be?

MR. SIEVERS: I would say about $100-thousand for the cheapest system you could put together to do that. But, I can imagine even better systems as things progress. Research in that area would develop something, and you couldn't go out and buy it.

MR. RICHMOND: It would probably take three-man years in addition to that $100 K.

CHAIRMAN MASTERSON: I think the point may be that there is one instrument that is working or will work in this regime, one instrument I don't think is enough, and for the number of measurements that we would want to make, are you going to supply every university or every aerospace company with a $100 K instrument for their own use? Where is the tradeoff there?

MR. CARROLL: That's one instrument. To set up a laboratory to make the kind of measurements necessary, you are talking about a half a million dollars per university or contractor.

MEMBER OF THE AUDIENCE: More.

MR. RICHMOND: That's the set-up cost. It would cost you another $150-thousand a year to run it.

When you are setting up a new lab, you have a very high capital cost as has been indicated, but unless you can get experienced people and there are very few of them available today, if you are getting new Ph.D.'s right out of college with some background in the area, it is going to take them a learning period of two, three, maybe even five years before they begin to put out really good data. It takes that long to find out what you are doing in this field.

You can't buy a piece of equipment and turn it over to somebody just out of college and expect to get good data.

MR. SCHWARTZ: I think the aerospace people found in the space effort that it took a minimum of three years to get any decent data.

CHAIRMAN MASTERSON: I guess we ought to ask the question then very pertinently, maybe the equipment is sitting around, but how about the people to run it. Either they have moved into management or no longer have their hands on it, or they got laid off in the '70s.

MR. IGNATIEV: Keith, on that point, I guess a little off that point, but I want to reiterate what Al Sievers said. You can't come back and say, "Geez, I let this horse out to pasture four years ago, I am going to ride him in a race today." Most of that stuff, I am not familiar with it, but it is probably so out of date to try to revitalize it, spending an extra two or three years getting it going and running again, you are going to be out of date so far.

This is supposed to be a new, moving, interesting field, and we are going to try and go back 10 years and see what people did then, and try to revitalize it, it doesn't follow.

MR. SCHWARTZ: You are not revitalizing it.

MR. RICHMOND: I agree with you 100 percent. There have been tremendous developments in the field of thermal radiation measurements within the last 5 to 10 years that have really revolutionized the whole field. Primarily, in the field of Fourier Transform Spectroscopy which has tremendous advantages when you are working with very small amounts of energy, and also the development of the pyroelectric detector which gives us tremendously increased sensitivity with many other advantages compared to the detectors that were available 10 years ago.

These two developments really revolutionized the whole field of thermal radiation measurements. You can do much better work today than you could 10 years ago.

But still, unless you have that somebody who knows what they are doing, they are going to have to go through this learning process even with the improved equipment that is available.

MR. DICKSON: Engelhard is new to the game of selective coatings and I am certain we would have been happy to have a central facility. I think that Henry Marvin was saying today, to determine what we need to meet the goals of in '85. There is no question that whatever has to be done should be done to meet that need.

What needs to be done with a central facility, is not necessarily what needs to be done in determining the morphology because I don't think we can find out in time to make an impact on anything in '85.

I think what we have to do is evaluate what we have available today, and be ready to go for things in '85, and then I think as far as coming up with a central facility for later than that, I think that's something that has to be done based on what is available right now.

MR. IGNATIEV: Let me argue that a bit. What I have listened to mostly today, I have listened to a lot of things that don't work. I haven't seen anything that really does work. You are not going to solve these problems by saying, "well, let's put it in a hotter furnace and see if it works better in a hotter furnace or a different spectrometer or whatever." I mean, you really have to get down to it and find out why it doesn't work, and how you are going to change it so it does work.

You can't do that by simply saying, "well, maybe it will all pass. We will just try and run it through real quick not knowing any more than we know right now, and not worrying about any other details."

MR. JURISSON: It seems like SERI has a pretty important function to look into which is nobody elses except SERI's, is that a valid conclusion? It is the agency responsible for doing research and development and standardization, I think that should be one of the jobs of maybe getting a bigger interest and role in this area.

MR. IGNATIEV: I second that motion.

MR. WEHNER: We are not concerned with alpha and epsilon, but we offered our services for Auger and thin film analysis many, many years ago in all those workshops which we had. Many of you might remember them. I always made a pitch, here you get service, you have experienced people who know what they are doing.

I think those we have helped, I think they were satisfied with our services, but I must say, I was very disappointed.

Although Glenn McDonald sent out 17 letters to all those who might be interested, and the number of customers, although I thought I had made it sufficiently clear and considered myself as a central facility for determining thin film profiles, the response was very meager, and it puzzles me, and I can only say what I have said in my talk, people are reluctant to give their coatings to others. Maybe they don't want to have the full truth.

I don't think that a central facility would do the job.

MR. SCHWARTZ: I think you need the directional spectral absorptivity for the various applications, particularly for the Barstow plant. You have got to have that.

Okay; now, with regard to the epsilon, it of course would be nice to have the directional spectral emittance, it would be nice to have that, and as Joe says, at the turn of the century, some fine fellow was making those measurements, I have never seen it. I am not that old yet.

Now, I think from an engineering standpoint, we don't need epsilon normal or the epsilon hemispherical. I think if you have the epsilon total hemispherical, I think that may be sufficient. But, I think the thing that we need to do is to think that one over a little more carefully.

We have a number of choices there, you can get $\varepsilon(\lambda)$ normal, you can get ε normal, you can get $\varepsilon(\lambda)$ total hemispherical, you get a whole bunch of these.

My own feeling on the matter is again, I kind of draw it from the space business. I think it will be sufficient if we get the total hemispherical emittance, and this is one that is commonly used.

Now, the reason I think that would be sufficient is I think we have an isotropic or lambertian type of emitter. In most cases -- now if you don't have that, there is a directional aspect to it, you could get in some trouble. But, I think this group, this workshop ought to think about this very carefully as to what we need, because the measurements are not going to come unless we set forth the requirements. This, I think, we all agree with that we want the spectral absorptivity.

MR. GILLIGAN: That's not all that simple.

MR. SCHWARTZ: It usually is quite easy to measure.

MR. RICHMOND: There is only one piece of equipment made in this country that will do it though, I think. That is the Gier-Dunkel sphere.

MR. GILLIGAN: That wouldn't be a sphere measurement at all. First of all, you want to know the directional characteristics of the function of angle. So that you have two things up there, theta A and theta I. That's the more appropriate measurement to make.

MR. SCHWARTZ: Without getting into the details, I think we are on the same spectral wavelength. The thing that I think we ought to try to establish at this meeting is what we need from an engineering standpoint. Unless we are doing that, there aren't going to be any right measurements made because everything is going to be crazy. So, let's try to establish at least in this workshop what our requirements are in these measurements.

Up until now, I think the thing that we have been getting is the $\alpha(\lambda,\theta)$ without knowing what the outgoing radiation is, a lot of instruments at room temperature exist that can do that. This one here, as I said, epsilon total hemispherical, that's very common, and in the space business, that's all that was ever done.

Now, the question we have to ask ourselves, do we have any firmer or stronger requirements than what we have in the past?

MR. GILLIGAN: Let me answer you this way, let me tell you some of the measurements that we make, and we make an awful lot of them, and I would be very much interested if we are going to change the ballgame to more appropriate measurements than the one we are making, then I would like to know that.

But, we measure an absolute spectral hemispherical reflectance, we can measure it from 190 nanometers out to 1600 nanometers. The standard measurement is from 325 to 2600, it is a spectral hemispherical reflectance value, and it is what Joe refers to as a directional hemispherical. It is the incidence direction, and it is roughly seven degrees off normal. That is a standard measurement in all the samples.

We measure that both internal to the sphere and external to the sphere, and you can get a normal measurement or a hemispherical measurement depending on whatever you put that in the beam path.

So, we measure transmittance of all the materials with exactly the same thing. We do not do that as a function of angle, again, it is seven degrees off normal.

We also do directional measurements on selective coatings and on black coatings and on certain reflective coatings, highly reflective coatings, and these we do, we do two measurements. We call one a ρ_b with bistatic, and a ρ_n, normal measurement. In the normal measurement, you are using a laser at 4880Å. You illuminate the sample, take a normal incidence, and then scan the reflected radiation.

Bistatic is where you look at the specular reflectance as a function of angle so that you maintain theta I and theta R equal and opposite as a function of angle. That has a hell of a lot of relevance to selectivity because it tells you what angle the reflectance starts to go way up, and that gives you a figure of merit on how good a performer that particular coating is, how much of the day is it going to absorb, and there are some pretty big differences on some of these coatings.

What I am saying is that from an engineering point of view, they may sound like highly sophisticated measurements and they probably are, but from the point of view of a guy wanting to know how long that thing is going to have an alpha of .92, you better know that, because if it is only six hours a day, it is one thing, and if it is .92 for eight hours, that is a hell of a lot better than .92 for six hours.

MR. SCHWARTZ: It is going to come back to establishing some engineering requirements for the use standpoint, and once we do that, then I think we can ask ourselves, well, can we make those measurements that the user would like to have. Now, if we can come up with that and after we establish those two things, then with the measuring capability that Joe Richmond is assessing we have something.

MR. ELLIOTT: I sat through a discussion that covered most of these same topics from a somewhat different viewpoint, from an engineering and an integrated total energy viewpoint, a couple of months ago and these parameters and these requirements are built in and will be refined. I don't think we have terminology problems. They will be built into the specifications and the procurement of materials and the verification of performance. Of course, the ultimate test is going to be 10 megawatts electrical, 50 megawatts thermal, with sunlight falling on a large calorimeter on the roof. That's going to be the beginning in one sense and the end of another in experimentation.

MR. RICHMOND: I have one comment with regard to what Herman Schwartz was saying about the need for that bidirectional spectral reflectance, do you know what you are asking for?

We did some of that. If you are going to measure with intervals of five degrees over a hemisphere and do it for all possible combinations of angles of incidence and angles of reflectance, you have got over 20-thousand measurements for each sample.

MR. GILLIGAN: You can make a continuous scan. You don't dot the machine from one point to the next.

MR. PETTIT: In addition, nobody can use the data in a real collector.

MR. RICHMOND: You have got to use a computer to do anything with it.

MR. SCHWARTZ: Well, bidirectional, you can do the $\alpha(\lambda,\Theta)$ without finding out what the reflectance is, what are the outgoing rays, in other words, how they disperse, I think you can do that very readily.

MR. RICHMOND: Well, that's directional hemispherical. That is really what you want, that is what you need?

MR. SCHWARTZ: Right.

MR. RICHMOND: And most materials are sufficiently isotropic, that you need measure only one plane of incidence. You don't need to measure at the various azimuth angles. And if you do that, something on the order of five or six measurements are probably enough to give you a pretty good idea.

MR. SCHWARTZ: Well, that's all we ever do is about six.

MR. RICHMOND: And you can do it at 10 or 15 degree intervals because it changes rather slow. If you find it is changing rapidly, you can go back and do a couple more intermediate values.

MR. IGNATIEV: Let me get into this engineering discussion, I would like to throw a monkey wrench into that. Whatever happened to the great talk about doing all this at elevated temperatures? Whatever happened to the fact that wouldn't one want to do that in a controlled atmosphere? Wouldn't one want to do that under a situation where you really have incidence of solar radiation heating the sample and not a furnace? I mean, all of those things, and the answer is that there isn't anything like that around. I am not going to do it, and probably you aren't either, but somebody is going to have to worry about generating a half million dollars to put something like this together when somebody knows how to do it.

MR. SCHWARTZ: You may want to do that, but you don't want to necessarily put a number of those exotic things in one place.

MR. IGNATIEV: But, we don't even have one, and starting with one it has got to be available to a large number of people.

MR. SCHWARTZ: Okay; I am not disputing that. If it is very speical, as Bill Carroll says, that's all you need. But, you may not want to put every new device in one central facility, that's the point I am making. You may not want that.

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HIGH TEMPERATURE SPECTRALLY SELECTIVE COATINGS FABRICATED BY CHEMICAL VAPOR DEPOSITION

Summary of a Presentation by

B. O. Seraphin *
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at the

ERDA Workshop on Selective Absorber Coatings

held at the

Solar Energy Research Institute
Golden, Colorado

on December 6, 7 and 8, 1977

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SUMMARY OF PRESENTATION AND VISUAL AIDS USED

During the last four years, our group at the Optical Sciences Center of the University of Arizona has developed, under NSF/RANN and ERDA support, a novel technology for the deposition of optical multilayer stacks of the spectral selectivity required for high temperature photothermal conversion. The work demonstrated the feasibility of fabricating converters of intermediate selectivity (a/e = 12 at 500 C, with a = 0.80), long-term survival at elevated temperatures (several thousand temperature cycles to 500 C, several hours at 700 C), and in a manner that can readily be expanded to economically attractive large-scale manufacture.

The program aims can be summarized as follows:

PROGRAM AIMS

Develop Techniques for Depositing Coatings:

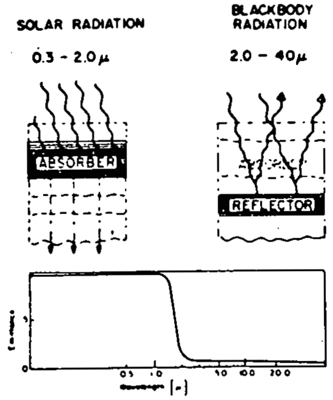
a) On long pipes in a continuous economic
mode of fabrication

b) Of sufficient spectral selectivity at
temperatures in excess of 300 C

c) That withstand longterm operation at these
temperatures without deterioration.

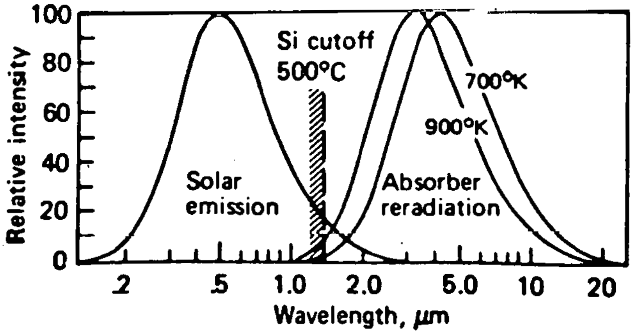
Our approach is characterized by the following three features:

FIRST CHARACTERISTIC FEATURE



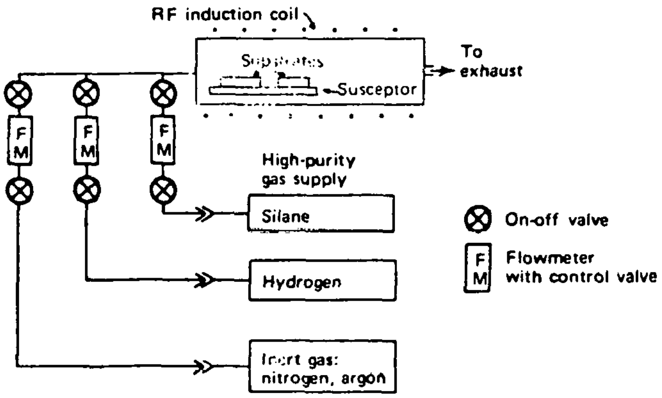
The spectral profile of an ideal solar energy convertor is approximated by the tandem action of an absorber overlaid onto a reflector, each operating in the proper wavelength range.

SECOND CHARACTERISTIC FEATURE



The absorber consists of a semiconductor with an absorption edge near 1.5μ, such as silicon. The reflector consists of a thin metal film deposited underneath. Both components act in an 'intrinsic' mode, meaning that about one electron per atom takes part in the optical function.

THIRD CHARACTERISTIC FEATURE



All components of the absorber-reflector stack are deposited successively by chemical vapor deposition.

The most prominent feature among the three - and the one that establishes the novelty of the technology - is the use of Chemical Vapor Deposition for the fabrication of optical multilayer elements such as spectrally selective coatings In the method, the stainless-steel substrate to be coated with silicon is placed into the hot zone (>700 C) of a furnace and exposed to a silane/carrier gas mixture. If all parameters are properly chosen, the silane breaks up through the transfer of thermal energy at the surface of the hot substrate, leaving behind a thin layer of the silicon absorber. If repeated through different reaction zones under different conditions, a sequence of successive layers of different materials and functions can be deposited in a similar fashion, and a multilayer stack results at the end of the line.

CVD techniques are well under control for specific applications in semiconductor device technology, corrosion resistant coatings, and specific coatings for use in the atomic energy field. In all of these areas, little or no attention has been paid to the optical properties of the resulting layers and their dependence on the CVD process parameters. Hence, with respect to optical applications, our work had to re-open existing technology at a fundamental level.

The resulting transfer of CVD methods to the fabrication of optical multilayer elements signals the availability of a novel technology for large-area optical applications operating at elevated temperatures, such as photothermal solar energy conversion.

The advantages of CVD fabrication can be summerized as follows:

CVD FABRICATION OF OPTICAL MULTILAYER ELEMENTS

Advantages

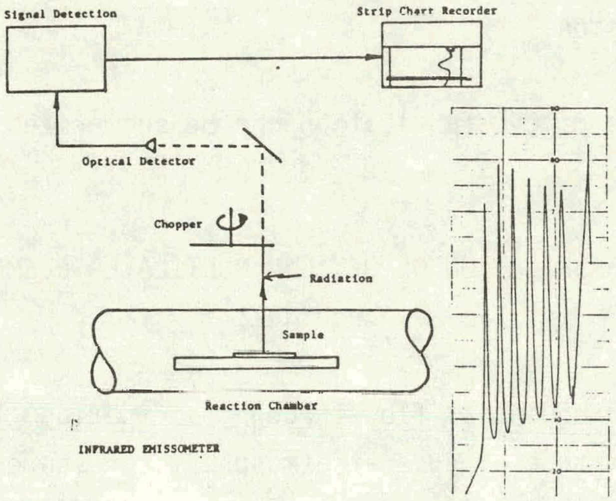
Sequential flow-through fabrication
Open-tube process at atmospheric pressures
Fabrication at temperatures > 650 C
Economic availability of starting materials

The following disadvantages of the method have been overcome by our work of the last four years:

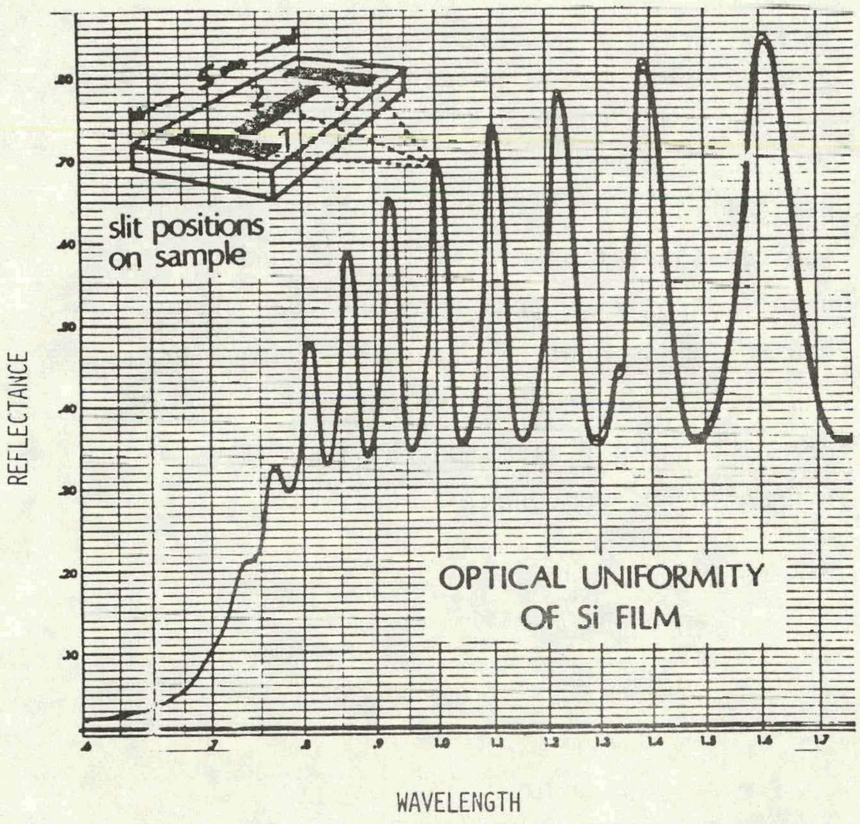
Disadvantages of the Concept

Chemical vapor deposition of optical elements requires adaptation of existing technology.
Uniform deposition from turbulent gas phase requires close control of process parameters.
High deposition temperature poses problems of thermal expansion mismatch, agglomeration and interaction of component layers, etc.

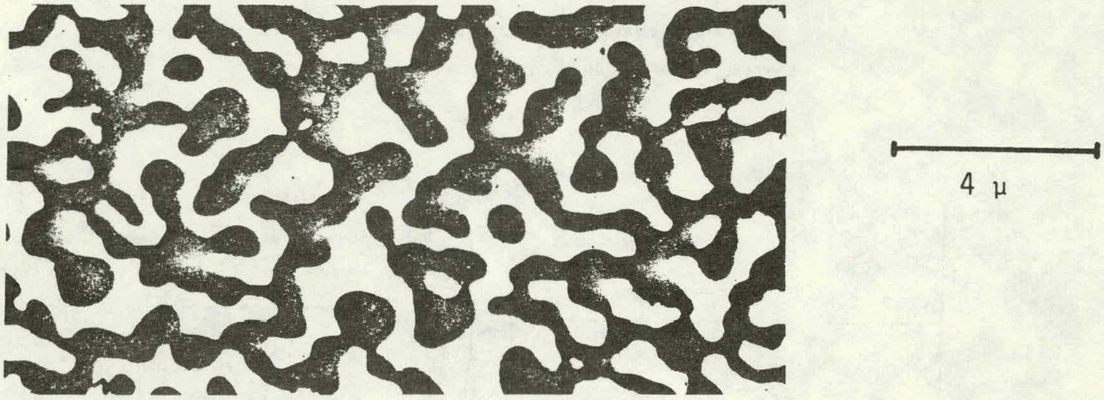
We monitor the emittance of the growing film at a wavelength of 2 µm, as shown in the diagram below:



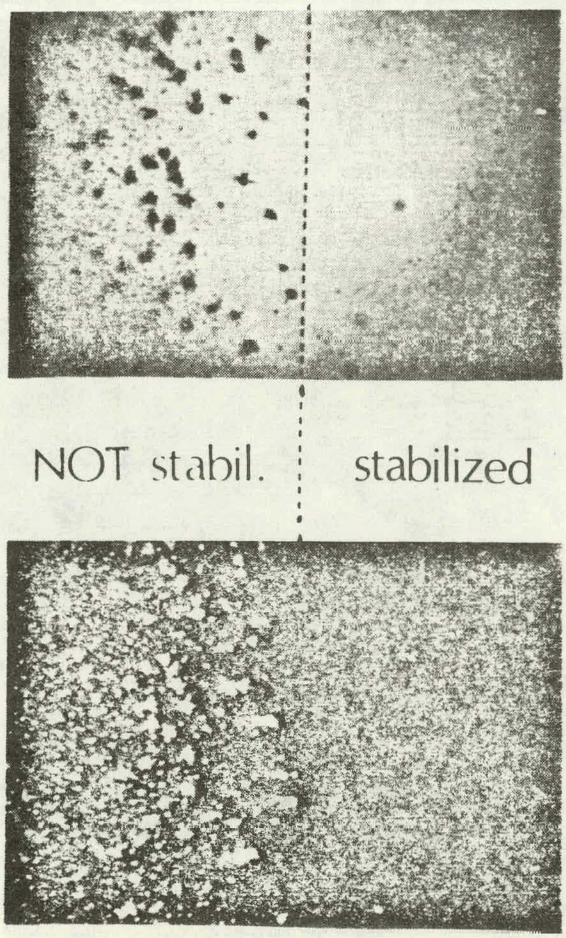
The close in-situ emittance monitoring results in a close control of the film thickness. The uniformity of the films compete favorable with that of films deposited by conventional vacuum deposition, as evidenced by the diagram below.



The agglomeration of the thin silver reflector at the temperature of the CVD process presented a serious problem. A thin silver film annealed to as low a temperature as 250 C agglomerates quickly, as shown in the SEM picture below.



We have investigated a number of materials such as Cr_2O_3, SiO_2, Al_2O_3, and Si_3N_4 that stabilize thin metal films against high-temperature agglomeration, as evidenced by the photo-micrograph of an interface between stabilized and unstabilized films, as shown below.



LIGHT FIELD 225x

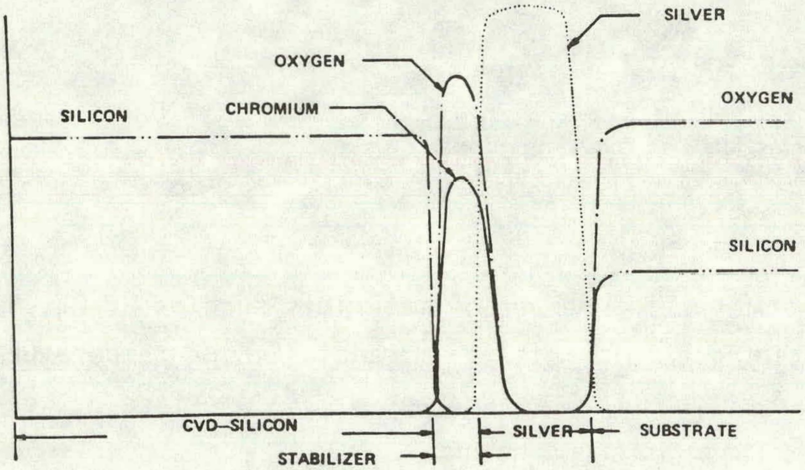
Stabilization of silver films

DARK FIELD 225x

The stabilizers act, at the same time, as diffusion barriers, as evidenced by the Auger profile of a stack that has been annealed for 150 hours at 540 C.

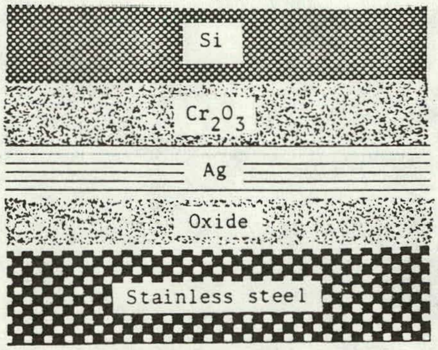
AUGER ANALYSIS OF SOLAR ABSORBER

SAMPLE: No. 399 HEAT CYCLED 150 HRS. AT 540 C



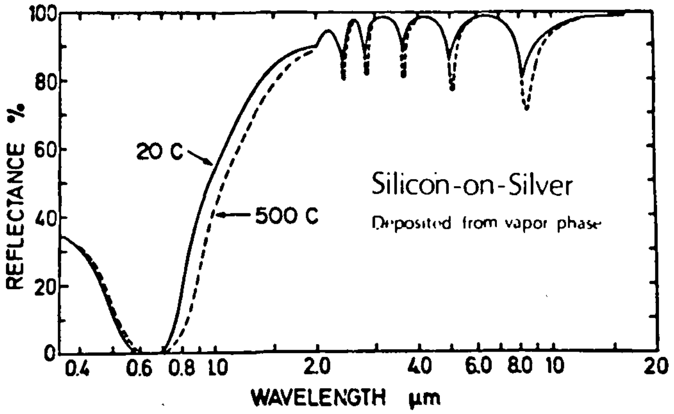
The performance and lifetime tests reported in the following are based on stacks of the cross section shown below:

CROSS SECTION OF THE CONVERTER STACK



Function	Material	Thickness (µ)
AR layer	Si_3N_4	λ/4 at 0.5 µm
Absorber	Si	1.5 - 1.6
Diff.barr. Stabilizer	Cr_2O_3	≈ 0.02
Reflector	Ag	≈ 0.1
Diff.barr. Exp. buffer	Oxide	≈ 0.03
Substrate	Stainless steel	massive

Their near-normal reflectance is routinely measured at room temperature and at 500 C in our high-temperature reflectometer. Traces such as the one shown below are planimetrically evaluated with respect to *a* and *e*.



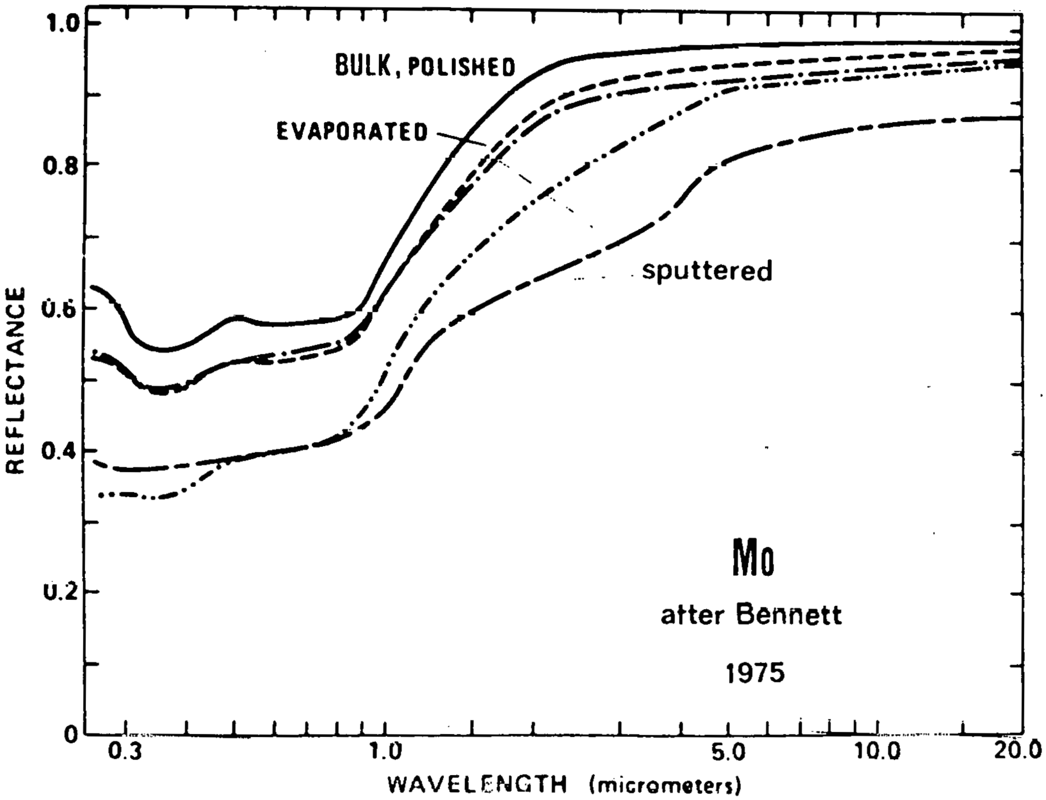
Proving the feasibility of the process on the laboratory level, the development program has resulted in the following state-of-the-art as of the end of 1976:

1. *The spectral profile of the reflectance, if integrated numerically in the usual manner, gives a spectral selectivity a/e = 15 at room temperature.*

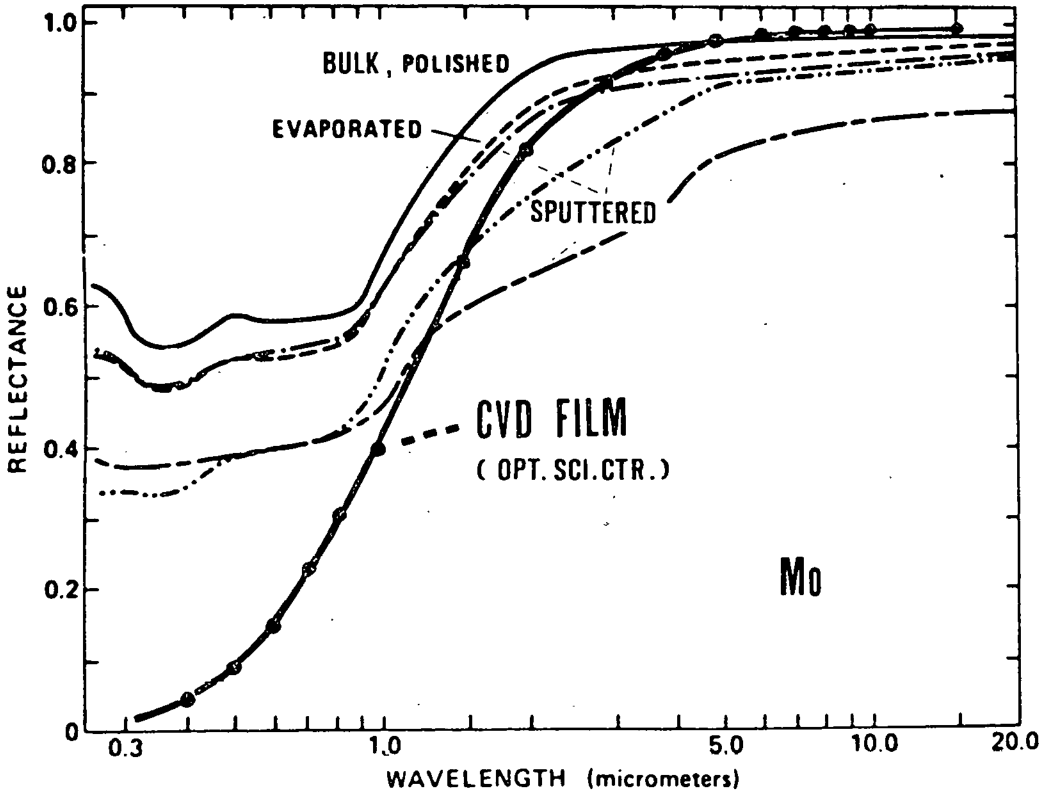
2. *Reflectance measurements actually performed at 500 C result in a/e = 12-14. This slight reduction in a/e at 500 C, compared to the room temperature, is typical for a semiconductor/absorber, and sets it aside from other converter types.*

3. *Stacks cycled several thousand times to 500 C did not degrade in their optical performance. Sample sets annealed at 700 C for several hours resulted in changes of their infrared reflectance of less than 2.5%. The same result is obtained for a one-hour anneal in open air at 800 C. Degradation of the performance does begin after anneal in open air at 900 C.*

Work in progress attempts first to eliminate the need for the complex stabilization of the silver reflector presently used in the absorber-reflector tandem. Refractory metals are more stable than the noble ones, and do not need a stabilizer. Unfortunately, the refractory metals, such as molybdenum and tungsten, are prohibitively expensive in bulk form, and must be disqualified for large-scale applications. If evaporated or sputtered as thin layers, however, their strong gettering action and/or structural modifications give the films a considerably lower reflectance, as shown in the following diagram compiled by Bennett:

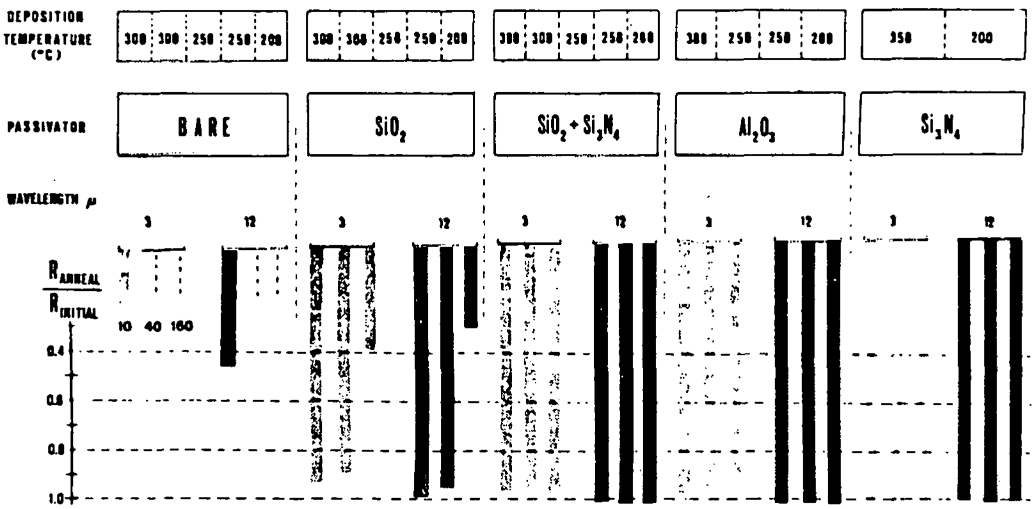


If, in contrast, the metal is deposited in the highly-reducing atmosphere of the chemical vapor deposition process, a film results with a reflectance close to that of the bulk metal. This development introduces the refractory metals to thin-film technology.



High temperature applications are possible, since molybdenum films can be passivated against oxidation. Without degradation of their infrared reflectance, such Mo-films have been exposed to open air at 550 C for several hours, after they had previously been protected by a number of passivator layers, with the results shown in the diagram below.

CVD SAMPLE SET



EXPOSURE TO AIR AT 500 C FOR 10, 40, 160 min.

We employ presently two different methods of depositing molybdenum from the vapor phase:

CHEMICAL VAPOR DEPOSITION OF MOLYBDENUM

Hydrogen Reduction of Pentachloride

$2\ MoCl_5 + 5\ H_2 \rightarrow 2\ Mo + 10\ HCl$

Side reactions: Mo - oxychlorides

Advantages: Films of high IR reflectance 95 %

Disadvantages: High deposition temperature 600-800 C
Reactant and product corrosive

Pyrolytic Decomposition of Carbonyl

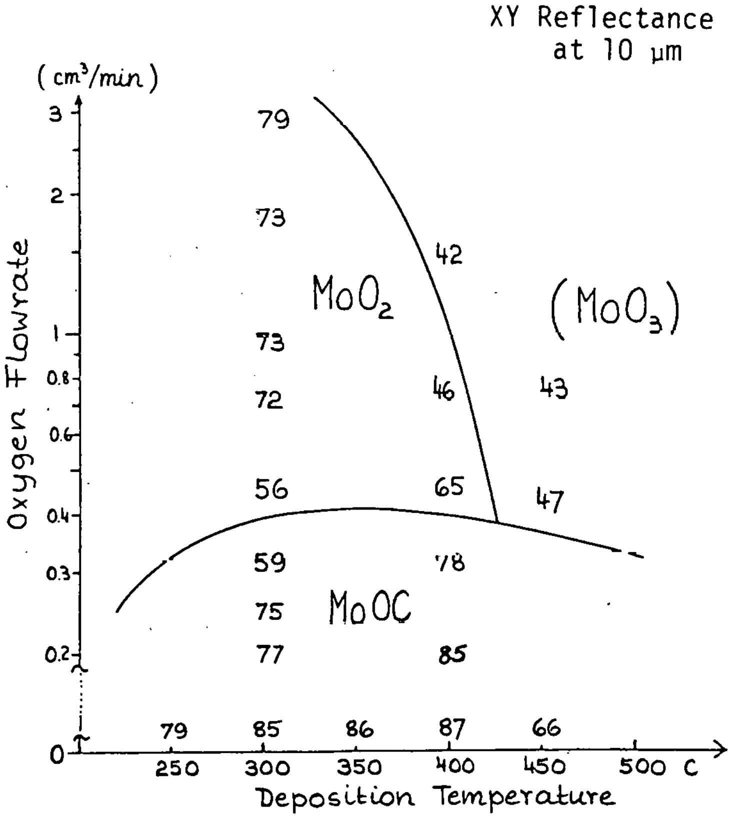
$Mo(CO)_6 \rightarrow Mo. + 6\ CO$

Side reactions: Mo-oxides and carbides

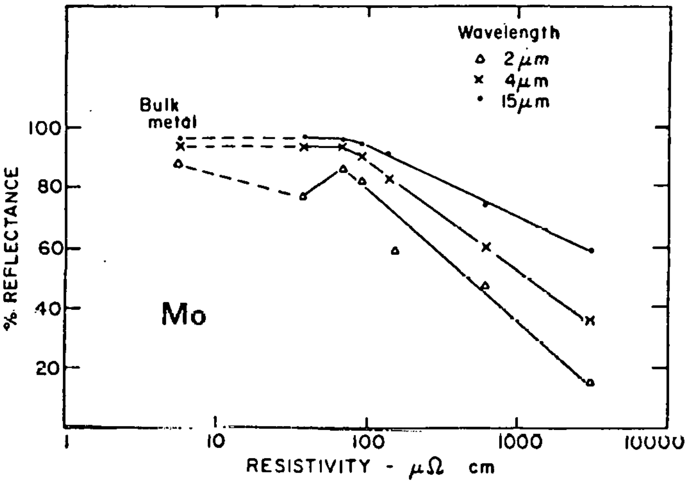
Advantages: Low deposition temperature 200-300 C
Neither reactant nor product corrosive

Disadvantage: IR reflectance presently 87 % only

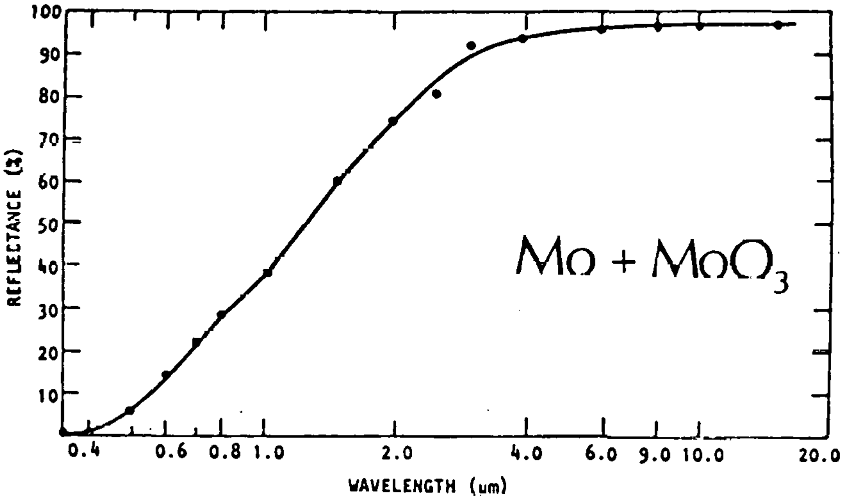
Our studies so far indicate that traces of impurities - oxides, carbides, oxychlorides of molybdenum - are responsible for the optical performance of the films, presumably even enhancing the reflectance of the pure metal under certain circumstances. We are presently scanning the range of conditions of deposition, monitoring simultaneously the presence of these impurities and the reflectance, as shown in the diagram below:



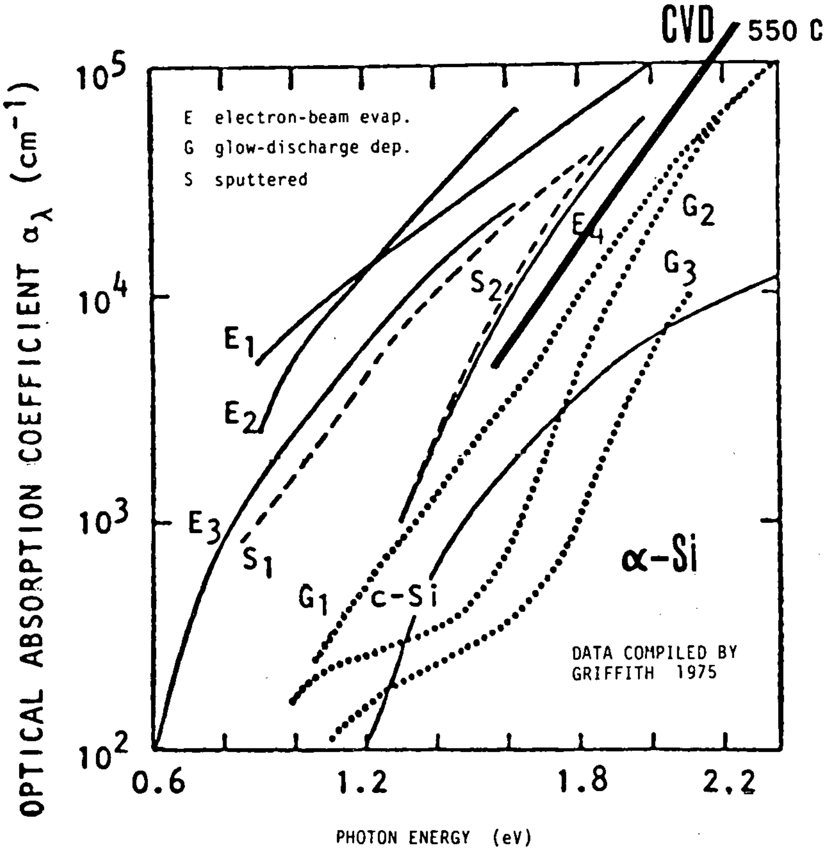
We try to interpret the variations of the reflectance in terms of the electrical conductivity, since both phenomena are based on the scattering of the metal electrons. The correlation is apparent in the diagram below.



By proper choice of the impurity, it may even be possible to have a single, doped layer of molybdenum perform as a solar converter all by itself, as shown below in the reflectance spectrum of a molybdenum film containing MoO_3.

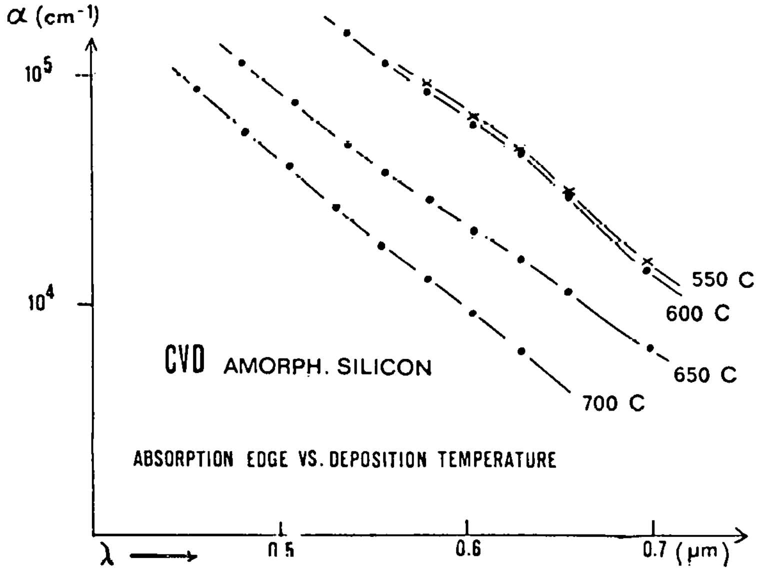


In a second development underway, the moderate solar absorptance of the stacks is improved by replacing the crystalline silicon absorber with a layer of amorphous silicon. Although recognized early by our group in its potential for increased absorptance, amorphous silicon was known to crystallize above 500 C, rendering it unsuitable for high-temperature application. However, fabrication by CVD produces a material that is more stable and still has the favorable infrared absorption of amorphous silicon deposited at low temperature and under the restrictions of vacuum-based methods.



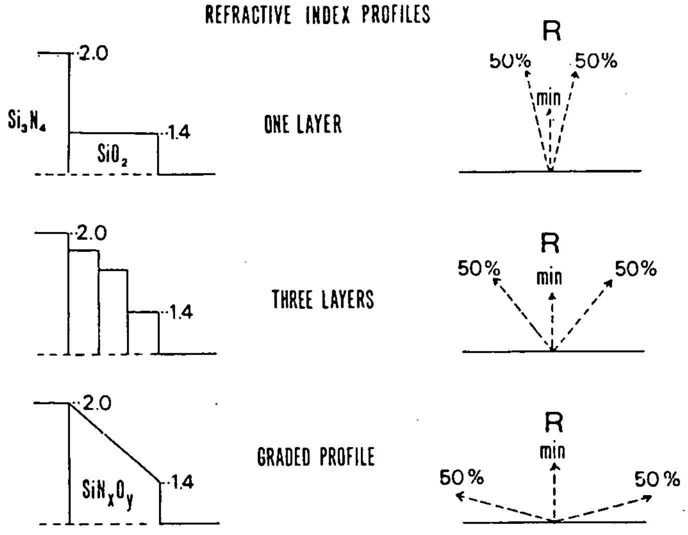
In addition to the increased solar absorptance, amorphous silicon deposited by CVD is temperature-stable to 600 C, and can potentially be fabricated at atmospheric pressure in a flow-through operation.

The optical absorption of the amorphous silicon deposited by CVD depends upon the temperature of the substrate, as shown in the following diagram. Above 650 C, the film is deposited as a polycrystalline layer.

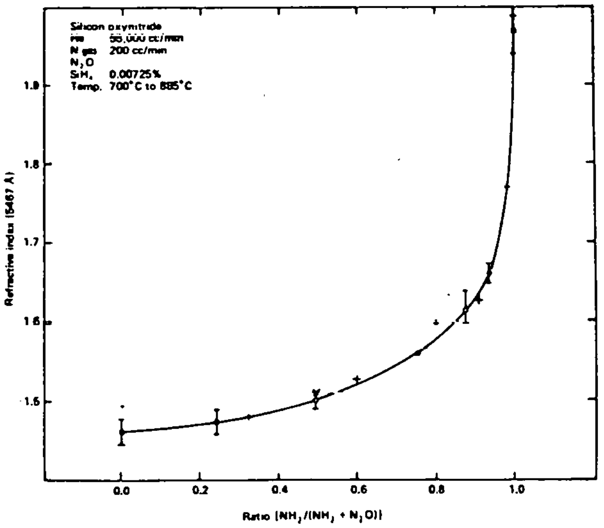


Turning finally to pending projects, we point out that besides the attraction of potentially continuous fabrication at atmospheric pressure, chemical vapor deposition of multilayer stacks provides a particularly elegant feature. By changing the composition of the carrier gas as the film grows, the nature of the deposit can be altered in a continuous manner, resulting in a preprogrammed profile of the refractive index. We have shown, for instance, that by gradually changing the fractional composition of the gas stream, the deposition can go through the sequence silicon-silicon nitride-silicon oxynitride-silicon dioxide. Such graded-index profiles antireflect over a large angular field of view, giving the resulting stack superior performance in concentrating collectors of large optical acceptance angles.

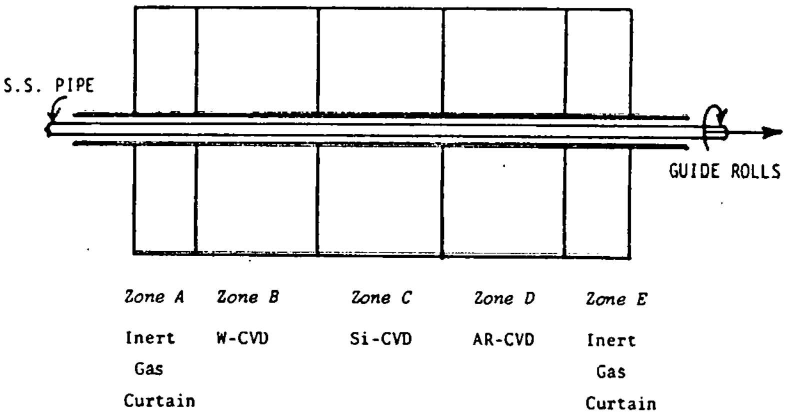
ACCEPTANCE ANGLE VS.
REFRACTIVE INDEX PROFILES



We have experimentally realized such graded profiles by simply changing the composition of the gas phase in the CVD process, as shown in the diagram below.



We are waiting for a decision of the sponsor on the realization of the flow-through, continuous fabrication of solar converter stacks. Such an economically attractive mode of large-scale fabrication of pipe profiles is, in principle, possible in CVD, and has been tried in device manufacture. For our process, it will be realized in a sequence of heater stations, as shown below:



CONTINUOUS COATING OF
SOLAR ABSORBER ON S.S. PIPE

We see in the successful transfer of CVD technology to the fabrication of spectrally selective surfaces a promising addition to solar conversion technology. The two features under development - greater solar absorptance through the use of CVD amorphous silicon, and simplified fabrication through incorporation of CVD refractory-metal reflectors - will increase this potential. If finally developed into the continuous, flow-through mode of operation, the method will provide an attractive technique for economic large-scale deposition of photothermal converters of high-temperature resistance.

REFERENCES TO OUR WORK

1. B. O. Seraphin, Principal Investigator, *Research Applied to Chemical Vapor Deposition of Solar Energy Convertors*, Annual Progress Report, NSF/RANN Grant SE-GI-36731X (1973 through 1975).

2. H. S. Gurev, B. O. Seraphin, Principal Investigators, *Chemical Vapor Deposition of Refractory Metal Reflectors for Spectrally Selective Solar Absorbers*, Annual Report, ERDA Contract E(29-2)3709, June 28, 1977.

3. B. O. Seraphin, Proc. 6th Int. Conf. Solid State Devices, Tokyo 1974, J. Japan. Soc. Appl. Phys. 44, 11 (1975).

4. R. E. Hahn and B. O. Seraphin, J. Vac. Sci. Technol. 12, 905 (1975).

5. H. S. Gurev and B. O. Seraphin, P. 667, *Chemical Vapor Deposition, Fifth International Conference*, (The Electrochemical Society, 1975).

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8. H. S. Gurev, G. E. Carver and B. O. Seraphin, P. 36, in Solar Energy, (The Electrochemical Society, 1976).

9. K. D. Masterson, J. Solid State Chemistry 22, 41-49 (1977).

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10. R. W. Griffith, *Sharing the Sun -- Solar Technology in the Seventies*, Winnipeg, Canada, 15-20, August 1975, International Solar Energy Society, Vol. 6, P. 205, 1976.

11. H. E. Bennett, Semi-Annual Report No. 6, ARPA Order 2175, Michelson Laboratory, NWC China Lake, California, P. 9, May 1975.

MR. MELAMED: If you compare the amorphous silicon to the crystalline silicon, how much more net absorptance will the amorphous silicon give compared to crystal silicon in your original stack concept. In other words, you mentioned an 80 percent absorptance for crystal silicon. What is your estimate of the increase in that value in going to amorphous silicon assuming that you could stop degradation.

CHAIRMAN SERAPHIN: I don't have to rely on estimates. I can just cite projections that Rich Griffith has made and that he is probably going to talk about at the close. The estimates of absorptance values are in excess of 90 percent.

MR. GRIFFITH: That's right, but one has to be very careful when dealing with amorphous silicon because amorphous silicon are "alloys." That is very important.

CHAIRMAN SERAPHIN: Okay. So, you will hear more about it. The absorption curve runs typically one order of magnitude above the other and a 90 percent estimate seems to be justified.

MR. GUTSTEIN: Okay, so has Arizona made some estimates on amorphous silicon?

CHAIRMAN SERAPHIN: Well, you have seen some curves here, yes, we have. We have the absorptance curves of amorphous silicon deposited by chemical vapor deposition. It's in the handout there.

It's very early work and you have in there the absorptance curves which of course have to be planimetered in order to give you the absorption, but we have not yet put antireflective coatings on the amorphous films. This will come out if we are in a position to continue this.

MR. VOSSEN: Most of the amorphous silicon work that I am familiar with is for photovoltaics. And, the problem with it is that you start getting hydrogen evolution out of the film at about 300 C. Now, I don't think I understood fully. I think you were saying that your films could operate up to 600 or 700 C?

CHAIRMAN SERAPHIN: They change at between 640 and 650 C.

MR. VOSSEN: But, what about the hydrogen evolution at lower temperatures? You should be able to --

CHAIRMAN SERAPHIN: Right. The photovoltaic people, in particular Brodsky at IBM, have found that the hydrogen that goes originally into the amorphous silicon from 10 to 30 percent escapes in two steps. First the 300 C figure that you referred to is a true excess hydrogen. There is a second step that is in the neighborhood of 600 C where the SiH bonds are being broken that makes the material perform the way it does.

We think what we have in our process is of course an equilibrium that has shifted way into the direction of turning the hydrogen loose again. You see what you do here is you have that silane molecule that the photovoltaic people break up by RF assistance. We break it up by KT, but the basic process is of course the same and the "nascent" hydrogen is available for incorporation into the lattice at that temperature in the form of SiH bonds. Of course at 600 or 550 C, the lattice is shaking violently and turning a certain fraction of the hydrogen loose again. We have done annealing studies already that I haven't referred to here that show that the temperature is the essential state variable that determines this hydrogen incorporation. Undoubtedly we have much less hydrogen in there than the photovoltaic people.

MR. SARGENT: Steve Sargent, Department of Energy. Can you give any kind of cost estimates for this continuous process?

CHAIRMAN SERAPHIN: Oh, yes. I can give you a very rough one. We have looked at the direct cost. That means that we have assumed that the factory and the cafeteria and the air conditioning has been paid for. We just looked at the direct costs that go into continuing coating, and we found that it is in the order of twenty to twenty-five percent of the cost of the substrate. Whatever you do, you have to start with the substrate, so our direct costs in coating are between twenty and twenty-five percent of the costs of a polished boiler steel tube of two-inches diameter.

MR. WEHNER: I have to put in a good word for sputtering because sputter deposited molybdenum did not look so good and I think the sputtering was done the wrong way. If you do it the right way, namely, high deposition rate, good vacuum and if you in addition positively bias your substrate so that you remove any oxygen which gets deposited there, I

CHAIRMAN SERAPHIN: I agree that films can be better than the bulk. I'm looking forward to it being shown for the case of molybdenum. I have taken this diagram from Bennett and you can usually have much confidence in what Bennett publishes. I know of one result by Roger Schmidt and I'm glad you mentioned this. Roger has prepared molybdenum with ten to twelve hours of pre-sputtering plus pre-deposition treatment which raises his curve considerably above the one that Bennett reports.

MR. SIEVERS: I would expect that any dielectric that has hydrogen in it as an alloy would be a very high emitter, have you looked into that at all? You may be increasing absorption, but I think because of the hydrogen vibrational modes that you are going to get very high emittance.

CHAIRMAN SERAPHIN: Yes, of course. We have the stretch band modes that you are probably referring to however due to the thinness of the films--you get by with 1-1.5 of this material--the emittance is proportional to thickness and we are below the critical value.

Tauc has made a prediction about the infrared absorptance of amorphous silicon--you know the paper probably. It was presented in Rome last year where he arrives at a negative evaluation of amorphous silicon. As much as I hate to say anything negative about Tauc, this prediction is wrong because it was based on a transmittance measurement that would never permit him to make a statement about in the order between 50 and 100cm. We are going to publish a comment on this because we think it is very important to realize that this does not apply to amorphous silicon. So, this can be kept under control due to the thinness of the film.

MR. SIEVERS: I'm surprised that in one micron you don't see any vibration.

CHAIRMAN SERAPHIN: In what wavelengths range would that be?

MR. SIEVERS: Three microns.

CHAIRMAN SERAPHIN: Yes, well, we get of course the SiO band and the SiN bands, but they are not strong. You can see it, I agree, and it leads to the fringes that you have seen here.

MR. SIEVERS: No, with the hydrogen--what with the hydrogen alloys?

CHAIRMAN SERAPHIN: Well, we have much less hydrogen in this because we deposit at a temperature where probably the hydrogen is two orders of magnitude less than what the photovoltaic material uses.

MR. NELSON: I have three questions and I'll try to be quick about it. First of all, following up what Steve said on cost, what is the basis of that cost projection--is it mass production? How close are you or how close is the process to manufacturing?

CHAIRMAN SERAPHIN: I would rather not elaborate on this. We are all physicists and metallurgists and we know very little about how to make a realistic cost estimate. I think the only thing that you can take me up on is that the direct cost of the deposition is smaller than the cost of the substrate. Philip Baumeister has stated repeatedly that CVD equipment is much less cost intensive with respect to the initial capital investment than regular vacuum based equipment.

MR. NELSON: Do you feel this is close to being manufacturable? A year or five years or something like that?

CHAIRMAN SERAPHIN: I would very much like to pull this through the feasibility proof of continuous fabrication.

MR. SCHWARTZ: The CVD coatings are primarily used in vacuum, as I understand them, am I right or wrong?

CHAIRMAN SERAPHIN: Wrong.

MR. SCHWARTZ: In other words you can use them in air also.

CHAIRMAN SERAPHIN: Well, on the diagrams were several test exposures to open air up to 700 C. A part of my lifetime testing slide said exposure to open air up to temperatures of 900 C. At 900 C they seem to come apart. At 800 C we can keep them for one hour. At 700 C we can keep them for reasonable test times. This was done in open air.

MR. SCHWARTZ: The point I am making is, though, in continuous use, in the normal use, the normal use is in vacuum, isn't it?

CHAIRMAN SERAPHIN: This is up to the designer I would say.

MR. SCHWARTZ: Well, if you are talking about a few hours, a few hours is nothing for an application.

CHAIRMAN SERAPHIN: Right.

MR. SCHWARTZ: How many hours in air can you use this type of stack? That's the question.

CHAIRMAN SERAPHIN: This is something that my discussion with Martin Gutstein has stimulated. We will keep the stacks for longer periods of time. We have so far test times in the order of two or three thousand hours. That's when we stopped.

MR. SCHWARTZ: Now, two or three thousand hours in air or in vacuum?

CHAIRMAN SERAPHIN: This was done in vacuum.

MR. SCHWARTZ: Okay. Now, let's go one step further. If you take a look at the oxidation protection of moly or any of the refractories, the state of the art after--and I think Mr. McCreight agrees twenty years of effort, fifty to one hundred million dollars worth of work, I would be giving them the benefit of the doubt if I said they were able to achieve three to four hundred hours. The National Academy report out on this thing and very reputable people have been on this who have been looking at it, and that is the state of the art. It is pitiful. And, these were very top level people,

excellent metallurgy, coatings people and materials people that worked in this field, and it's nowhere and they started in the fifties and went to the seventies. After twenty years and fifty million dollars and upwards of work, they're at two to three hundred hours. We can't use two to three hundred hours in this type of application. The thing that we need are hundreds of thousands of hours. Now, any oxidation protection on moly other than the silicides or aluminides or what have you I don't think is going to work. The reason I don't think it's going to work is that you're going to get defects or cracks, and the minute you get a crack, you're finished. The reason they went to the silicides and the aluminides is that they are self healing type of things. So, the point I'm really making here is that if you anticipate using moly in an air application--I'm not talking about a vacuum--I think you've got a helluva problem. Now, what's your opinion?

MR. McCREIGHT: That would be my guess.

MR. RICHMOND: Catastrophic oxidation.

MR. SCHWARTZ: Yes, it is catastrophic. Get MoO_3 or MoO_2 or --

CHAIRMAN SERAPHIN: What you're making is a suggestion. The next thing I am going to do when I go home is to put the tests back in air in the furnace. I'll report back to you.

UNIDENTIFIED SPEAKER: What substrate?

CHAIRMAN SERAPHIN: Stainless steel. And, we were--Martin Gutstein's original comments addressed the accidental failure of enclosures and so on, and we thought that 25 hours would be a good time --

MR. SCHWARTZ: The thing that I would be looking for if you intend to use this type of stack even with a vacuum, is what happens if you lose vacuum and you're at temperature.

I think that there is another thing that you ought to be kind of contemplating and that is that during the thermal cycling in vacuum, you're going to get cracks. The cracks are going to form. If they don't, I'll be absolutely amazed. And, when they do form what happens when you then expose it for a period of time, hours. If you just go up once and say, well, you're not going to have any cracks and then you expose it to air, that is a different type of test than thermal cycling.

CHAIRMAN SERAPHIN: There is one thing that I have to add here, the stacks here were bare molybdenum protected by as little as 250 angstrom of the passivator and the air had access just to these 250 angstroms of passivator. In the real stack, we will have the passivator plus the micron and a half of silicon, a very efficient oxygen trap, plus about ten times the thickness of the passivator as an anti-reflection coating.

MR. SCHWARTZ: I would still be amazed --

CHAIRMAN SERAPHIN: So, we will do it. Of course you cannot predict 100,000 hour test results.

MR. SCHWARTZ: I think the major factor is not the number of hours, I think it is the thermal cycling. It's not the number of hours. If you don't get any cracks through the thermal cycling, I'm not afraid of the diffusion through the stacks. That's not going to happen.

CHAIRMAN SERAPHIN: And, you think that thermal cycling through a vacuum is more of a test than in the air?

MR. SCHWARTZ: No, it's the same. It's --

CHAIRMAN SERAPHIN: We have finished these other cycling tests. The solar tests have "withstood" 4,000 cycles and then we stopped, for a small unit --

MR. SCHWARTZ: Did you get any crack?

CHAIRMAN SERAPHIN: No, we didn't get any cracks.

MR. SCHWARTZ: Did you look for the cracks?

CHAIRMAN SERAPHIN: We looked for the cracks. We didn't get any cracks. After 4,000 hours, we stopped, so we can be reproached for having stopped after 4,000 cycles, but we rent the facilities and we're not industry --

UNIDENTIFIED SPEAKER: What was the substrate of those tests?

CHAIRMAN SERAPHIN: Also stainless steel. We have for three years now consistently used stainless steel because this is the only substrate that is compatible with the possibly aggressive heat transfer fluid behind it.

MR. CARROLL: If I recall your report, your tests with the protective coatings on moly were done on glass--if I understand the report correctly?

CHAIRMAN SERAPHIN: No. we have worked half on glass. Many things are easier and better to do on fused quartz because you get smooth surfaces, but the tests were always done on a half inclusion of stainless steel substrate.

MR. CARROLL: The other point I want to make is that accidental breakage of the tube is not necessarily the only oxidizing condition you are going to see. Economically viable vacuum systems for these things are going to have very high partial pressures of oxygen, so you are going to be continuously exposed to oxygen.

CHAIRMAN SERAPHIN: Right, and the 4,000 cycle continuous exposure was done in the vacuum that approximately resembles the atmosphere that Bill is making reference to. I'm still a little bit curious about your plans to run high temperature, high concentration designs in open air. You're thinking of the outside walls of central receivers apparently. Is that right? Because, all of the dispersed systems probably have evacuated collectors.

MR. LEONARD: The dispersed systems will at best probably have roughing pump type kind of vacuums. But, many, many very attractive designs have no vacuum at all around the receiver. We recently tested a collector by Hexcel which did not have a vacuum and is doing very nicely in performance tests.

UNIDENTIFIED VOICE: It doesn't appear to be a cost effective tradeoff to go to a vacuum system. It doesn't appear that what you pay for buys you that much in performance.

MR. RICHMOND: Thicker films are more likely to crack than thin films.

CHAIRMAN SERAPHIN: Well, the films here, are the same that we put on the silver films and they didn't crack.

MR. SCHWARTZ: Well, that's heartening that the silver didn't. Now again, you've got quite a difference in expansion--

CHAIRMAN SERAPHIN: That's worse for silver. Don't forget, that's worse for silver. Silver has about three times the expansion. Moly is the ideal material if you have trouble with expansion because it has an extremely low expansion.

MR. SCHWARTZ: Well, it depends what the relative values are.

CHAIRMAN SERAPHIN: This is why all semiconductor electronics is riding on moly substrate.

MR. SCHWARTZ: Well, if you did sectioning and you have not found in the silver stack any crack at four thousand cycles, that is very encouraging, but again the thing I want to point out is that if you get a crack and you had elevated temperature, you're going to get oxidizing in a moly. You're going to lose it.

CVD has a problem in terms of repair. There is nothing nicer than taking a can of spray paint and then allowing it to cure, but if you take a receiver and if it is of a moderately large size, and you CVD the tubes and then you assemble let's say the receiver to the boiler inside, and then all of a sudden something happens and you want to repair that, the thing that you literally have to do is build a new boiler or build a whole new receiver. You can't do the type of repair that you can do with a "pyromark" which you grit-blast off the remaining pyromark maybe do another gritblasting if you wanted to and then you can easily paint it on and then bake it. CVD doesn't lend itself to repairing. That is what is bothering me about CVD. Now, what's your answer to that?

CHAIRMAN SERAPHIN: Well, of course, we have been dreaming about mobile units that run along a distributor collector system repairing any defective units in the field, but whether it can beat pyromark, I don't know.

MR. IGNATIEV: Coming to that question. I'm taking a totally opposite approach. If your point is that you didn't want to make a paint and to paint it on for three cents a square foot or whatever it is, then that should be the thrust of the work. There is too much talk about 900 C when we haven't got a paint to do that so if we have to start at ground zero, we try to find a system that is adequate.

MR. SCHWARTZ: Well, no, the thing I'm saying is that in the central tower application, if you have a choice between a CVD coating that is spectrally selective of the type he's mentioning versus let's say pyromark which is a flat one, and let's say that this is somewhat superior, which I don't think it is from an α and ε standpoint, but let's presume it were, I think the thing that may be a factor may be the repairability. The repairability is a thing that you've got to consider in anything that you build.

MR. IGNATIEV: But, it is coupled with lifetime.

MR. SCHWARTZ: Of course it is. That's obvious.

MR. IGNATIEV: And the lifetime question still hasn't been answered.

MR. SCHWARTZ: That's another issue; I'm talking just about repairability. How do you put a coating on if you have to put another coating on, and that is a very practical issue.

MR. IGNATIEV: My point of view is that if you have to repair it because it dies, because it has died, then I'm saying that is a lifetime effect. If you are confident that the original coating is going to last for 400,000 hours, I am not going to worry about repairing it after three hours.

MR. MASTERSON: I just wanted to comment that perhaps repairability is important, but that is something that should be looked into--how many actual field tests have you done on repairability of pyromark? Perhaps some of the people should take a look at this and take a tube and sand-blast it in the field and see if they survive. There may be some question about repairability.

MR. SCHWARTZ: If you have to work on a boiler, which you probably have to do in one form or another to replace a boiler tube and stuff like that, you have to have that capability.

CHAIRMAN SERAPHIN: Most of the present coatings don't qualify under this point of view. I think a more important reason is to look at the temperature transients and maybe we can avoid the need to replace an entire unit by giving enough margin in the high temperature coating that it can survive the shutdown period.

MR. RICHMOND: Is there any possibility of shoving that absorption edge out another half micron or micron? You'd get a much better coating if you could get it out a little farther.

CHAIRMAN SERAPHIN: This is what we try to accomplish with the amorphous work.

MR. RICHMOND: Is there any chance of going beyond what you do with amorphous silicon?

CHAIRMAN SERAPHIN: You can go beyond by using germanium, but germanium has a number of unpleasant features which you can't get around. It is a narrower gap material which, of course, gives you the shifted edge, but at the same time you have the free carrier absorption in the infrared. I don't think that germanium is a good high temperature coating. Secondly, germanium oxides are not stable, so you don't have that elegant feature here of protecting the layer with a sequence of silicon oxynitrides, but there'a always ways to do it.

MR. TOBIN: In commenting on the solar tower and repairing it or replacing the coating, right now the pilot plant is 24 sets of panels, so conceivably if the coating would decay or be destroyed, the panel could be removed overnight, a new one put up, and presumably if it was necessary you could reprocess this panel surface at some central location assuming that you have such a facility, so I wouldn't say that it is unrealistic.

MR. CALL: Would you say that you would follow the same procedure with pyromark?

MR. TOBIN: You could do that on site. Basically with our test tubes and test panels if we have had a spot where essentially the stuff is coming off, we would just--well, essentially in this case a guy would hand sand it off and spray it back on and it normally would survive, so I don't have any doubts really about the refurbishment of the paint. It is a fairly standard technique. They use this paint on helicopters for example. My point is these panels can be removed and replated or whatever the process is, so I wouldn't want to preclude using that.

MR. PETTIT: I would like to ask, on the oxidation studies of moly that were mentioned at what temperature range was the problem found? Was it a very high temperature problem or was it a problem in the 300 - 500 C region?

MR. SCHWARTZ: Most of the investigations of oxidation protection of moly were at the higher temperatures. The ranges that they were interested in started, oh, at about 1100 C, just because those were the ranges that were looked at. You see they were thinking obviously of the refractory metals rather than the super alloys, and I would say from some of the looks that I have had on moly oxidation, probably extends down--just take a guess-five to six hundred C and could be of significance in that range.

UNIDENTIFIED SPEAKER: I think the oxide melts at 800, doesn't it?

CHAIRMAN SERAPHIN: 792 C or something, that is right.

MR. BUTLER: I think what is happening here is we are getting lost in the difference between research and product development. The kinds of coatings that we're talking about are the kinds that would be made available and unless you do research, you won't have new available candidates, and then you have to do the product development to see how you can apply those to a boiler. I think the argument that you can take a panel down and refurbish it, reprocess it is an extremely good one. If we could guarantee, for example, that this coating-we're talking about durability--if this coating would perform for the expected life with no degradation, no loss in performance or guaranteed losses in absorptivity, then we wouldn't worry about refurbishing the panels, we would give them a useful life and we would replace. I mean, this is what Alex was getting at. Now, if we don't do something in the line of research, then we won't have any alternatives to select from, and I think that is the point that is being made.

MR. SCHWARTZ: Well, it's another issue here. If you have to repair a boiler for various reasons replacing boiler tubes or what have you and during the process that you are doing the repair you injure the coating, then the next thing that you've got to start thinking about which would be quite expensive, is how do you repair it?

MR. BUTLER: Well, Herman, I agree that repair is important, don't get me wrong, but that comes down the line. Are we looking at putting these coatings in place in two years, in five years, or ten years? Now, that's the question. If you're looking at two years ahead, then we have to know refurbishment because DOE doesn't want a large mistake sitting out there that they have to keep replacing.

MR. SCHWARTZ: I think if you are doing research, the thing you should be doing is anticipating the practical problems such as repair. It's no sense doing a research job, a very good one obviously, and then later on you find that after you are finished with it, you can't do any repair work when repair work is obviously necessary. You shouldn't have done the work to begin with, so I think that the thing that you ought to be doing is anticipating the ability of repairability.

MR. CARROLL: Well, I think the critical issue on oxidation protection of moly for high temperatures is the temperature at which it forms a volatile oxide. That's why it is so catastrophic. If you are operating below that, you could potentially be on good ground.

MR. SCHWARTZ: Well, the point I'm making is that you form, I believe, a volatile oxide around 500 - 600 C.

CHAIRMAN SERAPHIN: It's 800 C.

UNIDENTIFIED SPEAKER: That is the problem that the industry has faced. You don't use moly if you go above that temperature.

MR. IGNATIEV: In totally unrelated work we have worked with molybdenum from a surface physics point of view and have in fact looked at oxygen absorption and oxidation of molybdenum below 450 C and all we get--all one observes at that point is you get a chemisorbed oxygen layer on molybdenum and not multilayer oxide growth below 450 C.

MR. WEHNER: Did you ever treat your stainless steel? We are all talking here about what happens on the surface of the molybdenum. What I still am concerned about is the interface between the stainless steel and the molybdenum.

Did you do any oxidation at 900 C before you deposited your molybdenum?

CHAIRMAN SERAPHIN: No, and you are the one to know best because you told us what the oxide consists of. We seal off our stainless steel substrates simply by exposing them to open air at about 600 C or something like that. That is mainly a "depletion" of the stainless steel in the formation of chrome oxide essentially.

MR. WEHNER: But, I want to emphasize here the fact that if you really want to have the good diffusion barrier, do it fifteen minutes at 900 C.

MR. NELSON: Have you applied your surface, your coating, to tubes at all?

CHAIRMAN SERAPHIN: No, I have not yet applied it to tubes, but since we work in quartz tubes with the flow-through geometry of the reactant, we expect to have less trouble than on the flat substrates. The flat substrate is really something that isn't well adapted to our field geometry. This is part of the continuous CVD proposal that I hope to have accepted.

MR. NELSON: Okay, question two. You mentioned the absorptance at, room temperature, 25 C and 600 C, what is it in between there. Does it tend to drop off very quickly, or is it reasonably linear between them?

CHAIRMAN SERAPHIN: That's a linear shift from the room temperature to 600 C.

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Amorphous Semiconductor Thin Films in Solar Thermal Conversion

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Summary of Presentation

Under the auspices of the Thermal Power Systems Branch, we recently carried out an initial technical feasibility study on the possible use of amorphous silicon (a-Si) thin films, and those of related materials, as the basis of the primary absorber in a selective absorber coating. The study consisted of a theoretical investigation, and a modest experimental component to probe and test areas of especial interest. Our findings include the following:

i) Near the center of the solar irradiance spectrum (where wavelength $\lambda \simeq 0.48$ μm for AM2 sunlight), the a-Si absorption coefficient is at least an order-of-magnitude greater than that of the crystalline phase. This statement pertains to a-Si that is prepared by any major technique: evaporation, sputtering, and rf glow-discharge decomposition of silane. (a-Si prepared by chemical vapor deposition from silane also satisfies this criterion). Hereafter in this discussion, films produced by these major techniques will be referred to as E, S, and G films, respectively.

ii) The absorption edges of a-Si at room temperature generally lie at more favorable positions for solar absorption than does the edge of crystal silicon (c-Si). However, as a function of increasing anneal temperature T_a, the absorption profiles for (unhydrogenated) E and S films, <u>relatively</u> degrade and approximately converge on the position of the profile for G films at high substrate temperature T_s. At film temperatures T that are above room temperature--as would be relevant for the coating of a solar collector-- <u>a red shift</u> of the amorphous profile improves the solar absorptance. This red shift, or translation to longer wavelengths λ, does not completely compensate for the anneal effect in long-lived E and S films of a-Si.

iii) Free-carrier absorption in a-Si that could have increased the infrared emissivity of a thin-film solar coating at high temperature T appears to be quite negligible.

iv) The addition to silicon of another common material, namely boron (B), is found to stabilize anneal behavior. Indeed, thin G films of the alloy $a\text{-}Si_{1-x}B_x$ (with incorporated hydrogen) have been produced that are anneal-stable up to at least T_a = 770°C. The position of the alloy absorption profile is adjustable over a large range of wavelengths as a function of composition x, and exhibits enhanced optical absorption. These profiles can further be enhanced by the aforementioned red shift at elevated temperatures. Figure 1 illustrates both the adjustable profile at $x \simeq 0.20$ and the red shift for $\Delta T = 400°C$. This behavior is contrasted with the crystal profile.

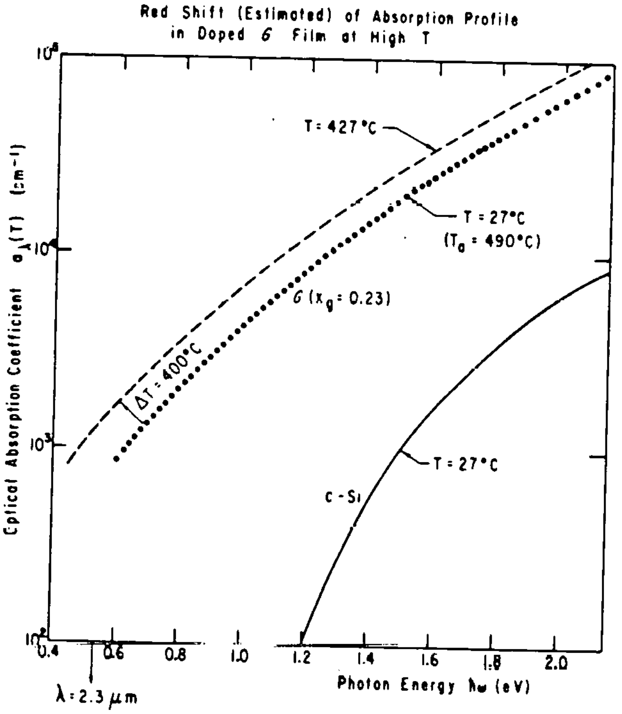


Figure 1

At infrared (IR) wavelengths, residual impurity absorption occurs in these films especially due to Si-H and B-H stretching modes. But the level of this absorption and its effect upon the IR emittance can be reduced by annealing. Free-carrier absorption in this amorphous alloy at high T is expected to be small, but this point should further be tested. Such alloy films may find application as the primary absorber in a selective-absorber/concentrating-collector system for conversion at medium-high temperatures and perhaps even at high temperatures.

v) The amorphous state is time-dependent as a function of film (collector) temperature, but this "metastable" state can be long-lived at temperatures of interest in solar thermal conversion. It appears that a 20-year lifetime may be expected for a-Si at medium-high temperatures, with longer lifetimes or higher temperatures applicable to certain compositions $x > 0$ for the alloy discussed in iv).

vi) The index of refraction of semiconductor materials is sizeable ($\eta \simeq 3.1$-3.6 for a-Si). Therefore, the high solar reflectivity of the primary absorber must be reduced by the use of anti-reflection coatings, surface morphology techniques (texturization), or even dispersions or granular composites. Other, more novel, techniques may eventually be called for.

We note that the maximum theoretical solar absorptance $\tilde{a}_s$ can be estimated at $T = 427°C$ for the alloy in Figure 1. For this purpose, let the film overlay a perfect mirror, and assume the solar reflectivity to be effectively suppressed. Then, for a film only 1 μm thick as the sole absorber in the tandem, $\tilde{a}_s(427°C) \simeq 0.91$ in AM2 sunlight. Conservatively assuming a minimum IR value $\alpha\lambda = 400\ \text{cm}^{-1}$ still gives $\ell \leq 0.09$. Such an absorber would be a candidate for a concentrating collector, with medium values $X \sim 10$-30, that compensate for a somewhat shallow fundamental profile. Of course, in order to realize in practice the above theoretical value for the solar absorptance, the solar reflectivity must be reduced to zero for the solar absorptance, the solar reflectivity must be reduced to zero. Even larger (theoretical) solar absorptances are possible at medium-high temperatures if one is willing to sacrifice somewhat the emissivity. (In the low-temperature regime of photothermal conversion, $T \simeq 100$-$200°C$, this compromise is not really necessary.)

On the basis of the above findings, we conclude with the following comments. Amorphous-semiconductor thin films, comprised of common materials, appear to be promising candidates for the primary absorber of a selective-absorber coating that is intended for solar thermal conversion at elevated temperatures. Applications could include photothermal/electric conversion as well as the production of non-electric process heat. Further R&D in this area of advanced materials would be desirable, especially with regard to exploring a whole range of common semiconductor materials that lend to: a) novel and effective ways of reducing the solar reflectivity, and b) compatibility with inexpensive substrates at high temperatures.

Amorphous-Semiconductor Solar Energy Program

(in development)

Initiating a major materials program to explore the optical, electrical, and structural properties of a-semiconductor thin films tailored for solar energy conversion.

Examples of such materials will include Si, C, B, P in various doped or alloyed compositional mixes.

Supportive Tasks

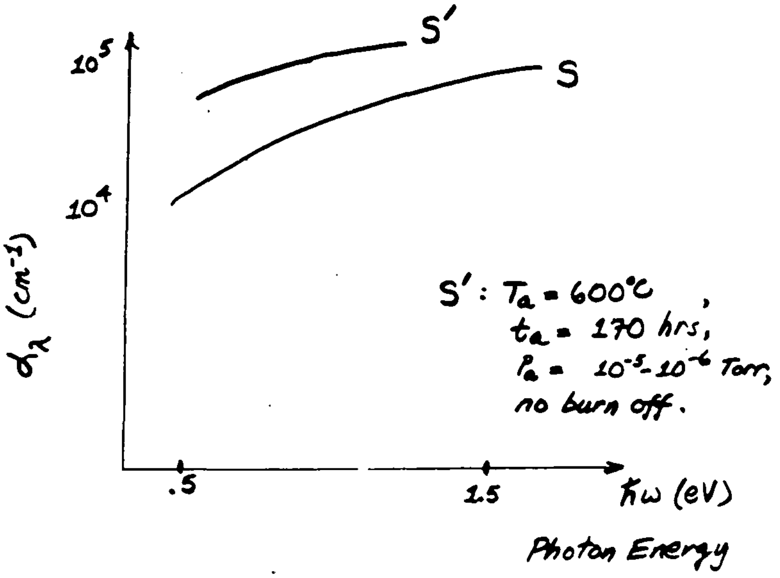
1) Novel and effective ways of reducing the high semiconductor solar reflectance.

- AR coatings.
- Texturization (cones, nodules, etc.)
  - --cannot have irreversible changes at high T
  - --cannot have anisotropy such that $e_{total,H} >> e_N$
- Dispersions, granular composites

2) Compatibility at high temperatures of the absorber with inexpensive, high-reflectivity substrates.

- An example of a study at present is the preliminary investigation of the optical and stability properties of a-C films that have been prepared by rf sputtering, arc-evaporation, e-gun evaporation, and aqua-dag dipping (!).

By contrast with other films of elemental valence IV materials, films of a-C, depending upon the state of anneal, have an admixture of two kinds of bonds: diamond (sp^3) and graphite bonds (sp^2)

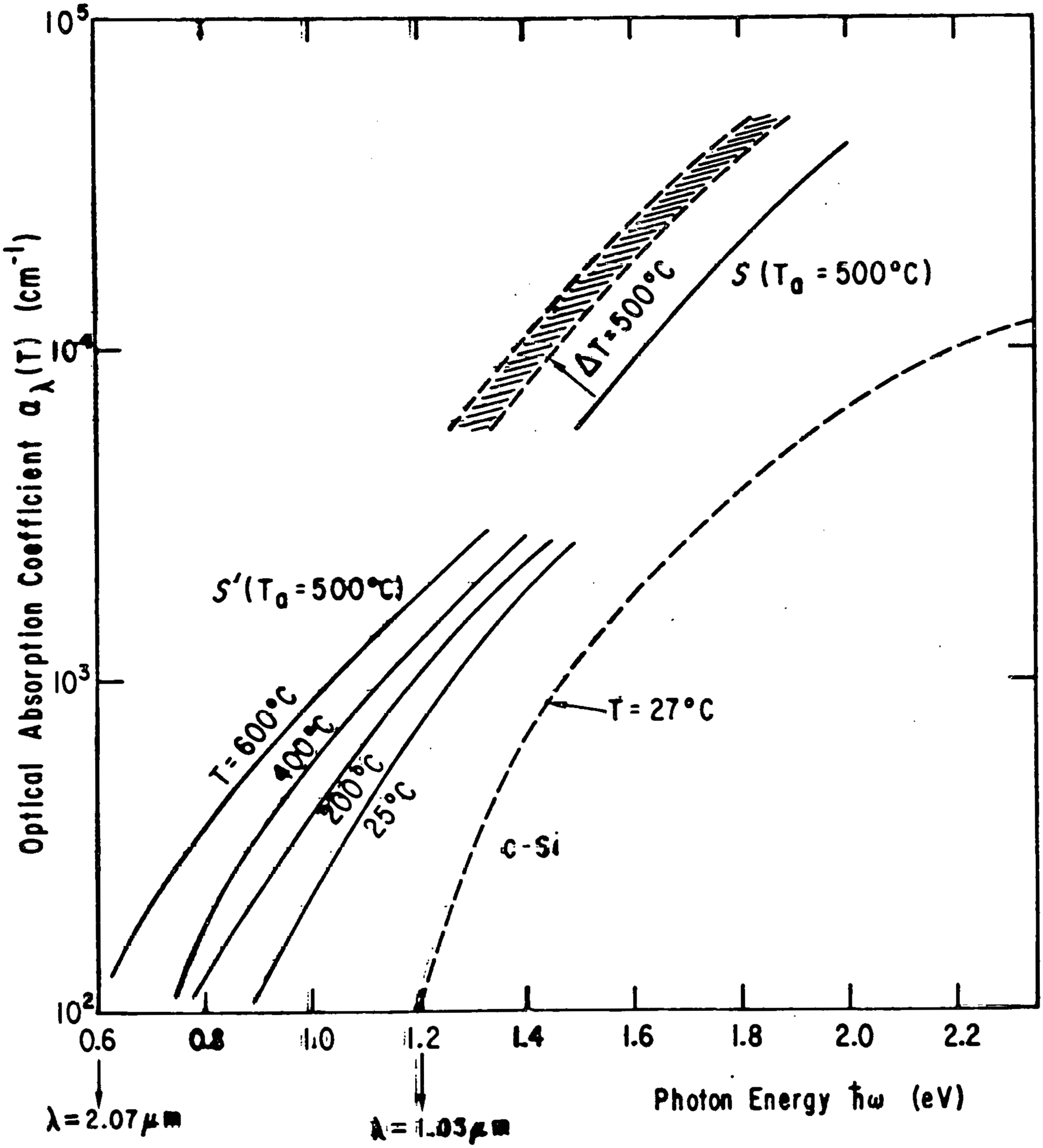


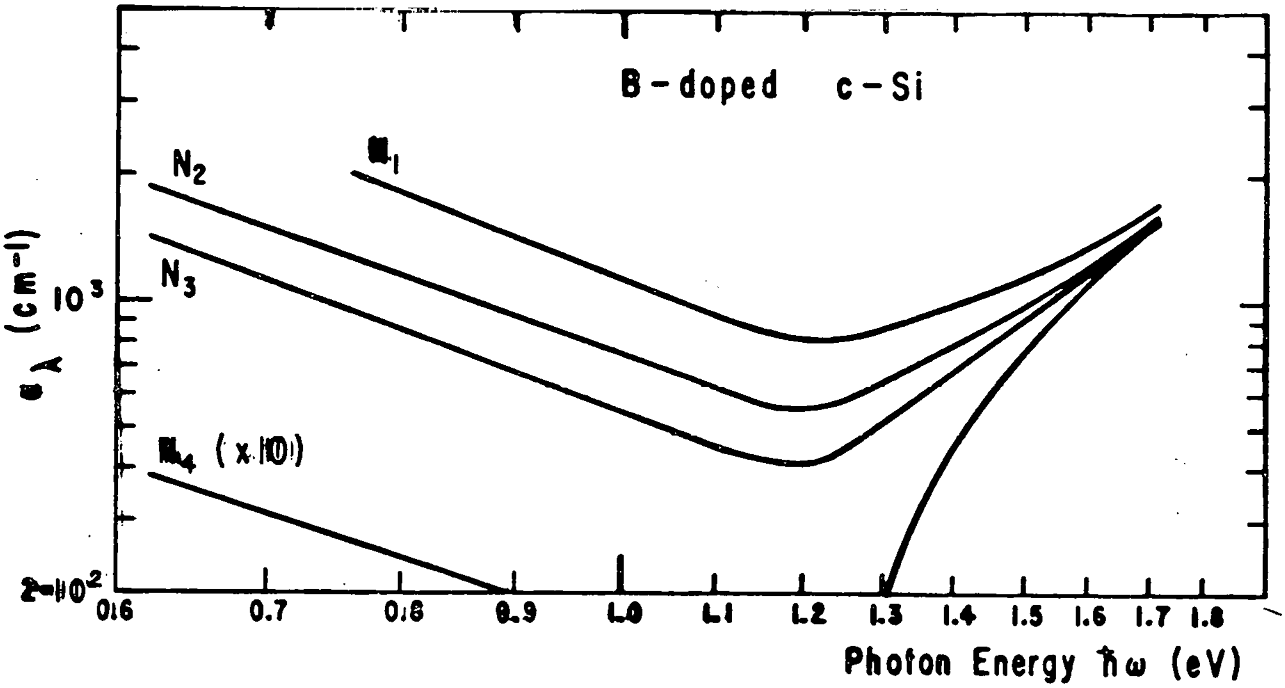
Some current acitivities in developing the Amorphous-Semiconductor Solar Program:

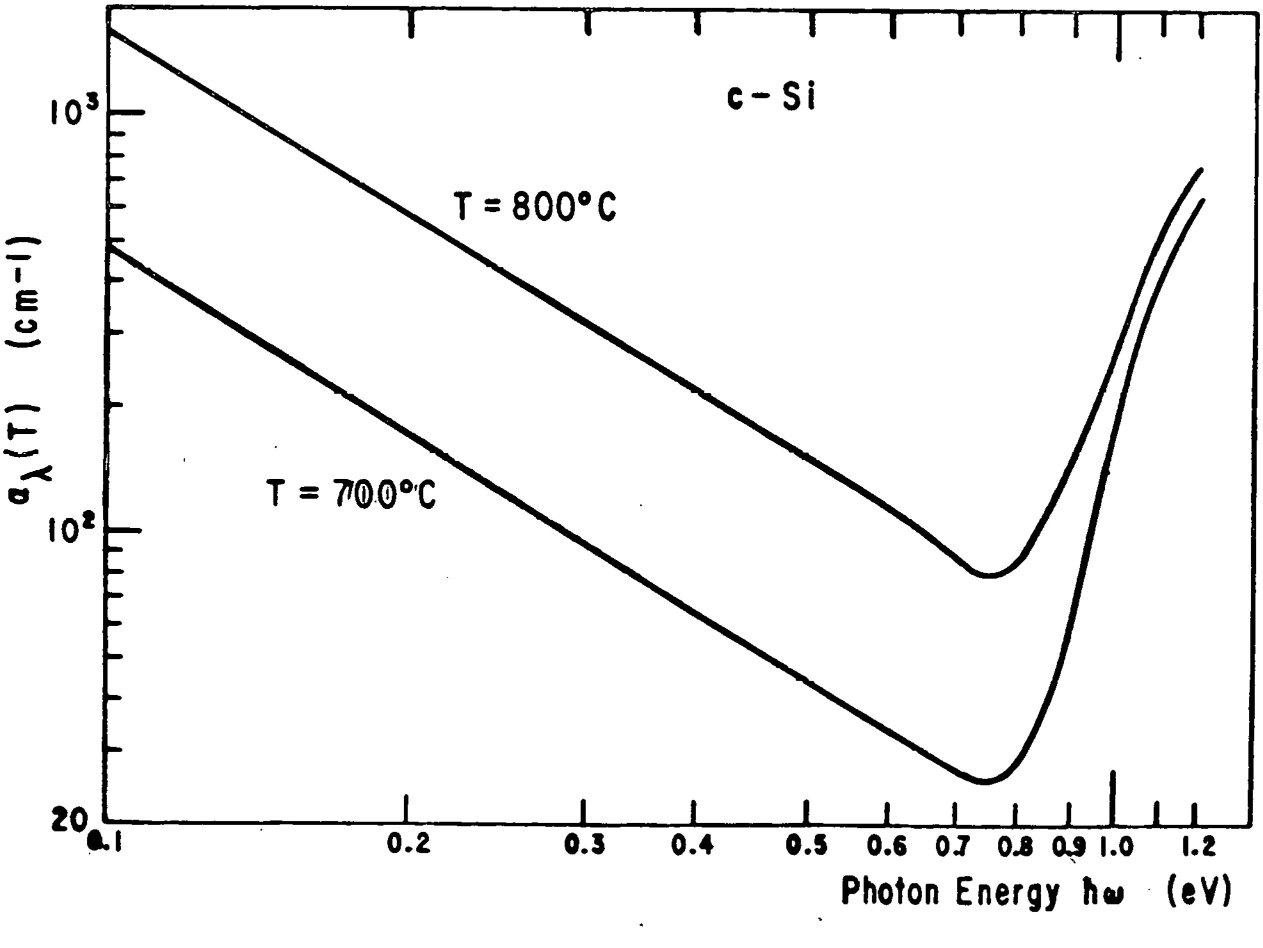
- We are in various stages of setting up a solar materials lab for optical measurements such as:
    i) R and T measurements over $\lambda = 0.3 - 15$ μm.
    ii) Temperature-dependent Spectral Emissivity
- We are building a reactor to produce compositionally-mixed films, e.g., a-$Si_{1-x}B_x$ alloys, by plasma decomposition of hydrides.

The reactor will use capacitively-coupled rf power with a controlled dc bias between electrodes.

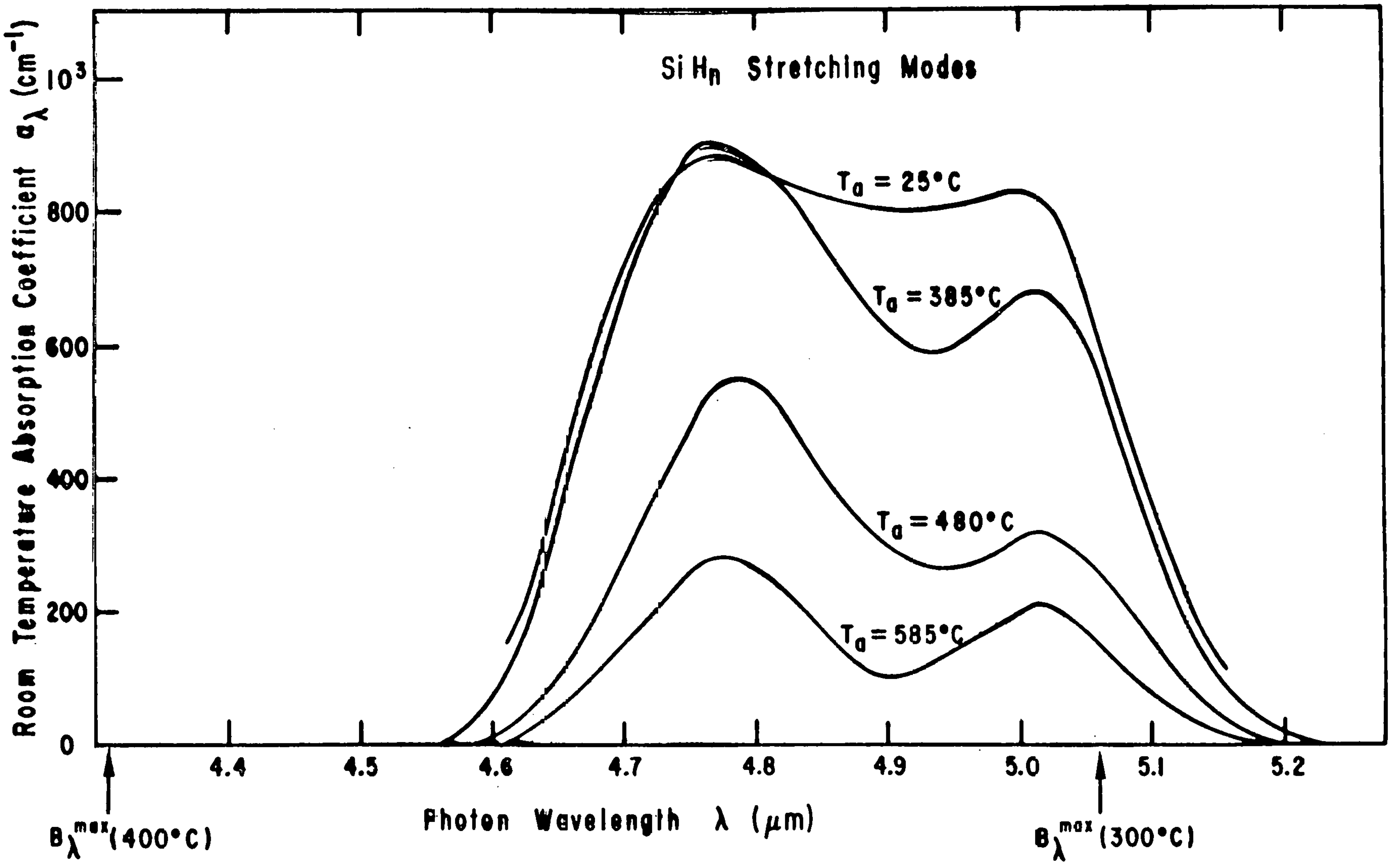
Red Shift of a-Si Absorption Profile
at Elevated Temperatures



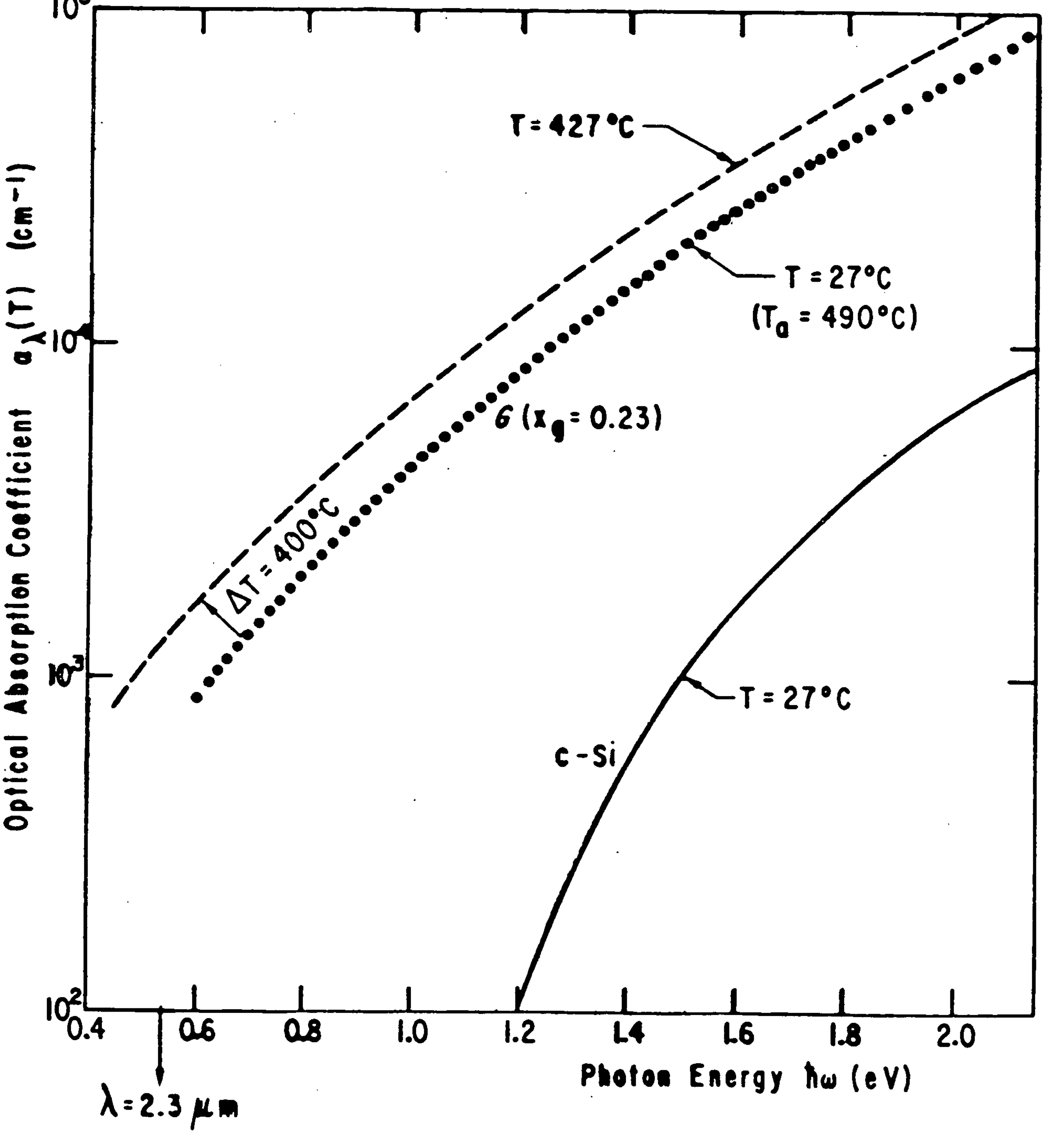

B-doped c-Si
N1
N2
N3
N4 (x10)
αλ (cm-1)
10³
2×10²
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
Photon Energy ħω (eV)


c-Si
T = 800°C
T = 700°C
αλ(T) (cm-1)
10³
10²
20
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.2
Photon Energy ħω (eV)

Anneal Behavior of Infrared Absorption for Undoped *G* Film

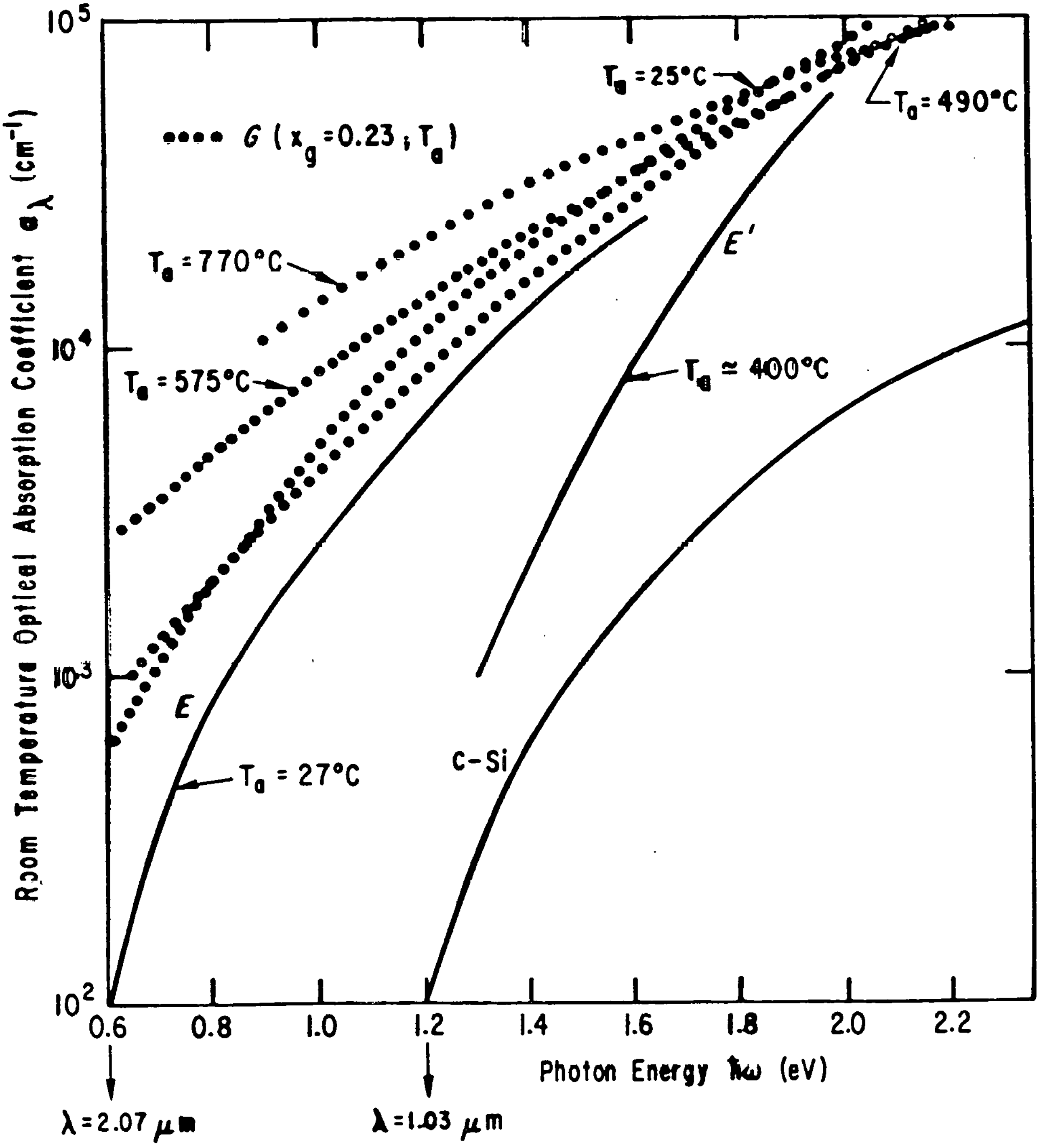


$\tilde{a}_s(427°C) \simeq 0.91$



Red Shift (Estimated) of Absorption Profile in Doped 6 Film at High T

Anneal Stability of
Alloy G Film Prepared on Hot Substrate
(T_s = 267°C)



MR. SIEVERS: In your silicon boride alloys that you've shown here, it looks to me like if you want a 56 percent absorption you need a 10μm thick film, not a 1 μm thick film that you mentioned.

MR. GRIFFITH: You have to remember where the center of the solar irradiance spectrum lies.

MR. SIEVERS: You've got to remember where the edge of it lies, too, and that's at 2μm

MR. GRIFFITH: I took that absorption coefficient, the so-called fundamental edge. I took a reasonable level in the infrared. I made an extrapolation of the edge as you saw it down to the level of the infrared. Then I calculated the solar absorptivity.

MR. RICHMOND: It wasn't entirely clear to me when you were talking about this crystallization, the heating at 600 C and then at 400 C. Was this a case of nucleation at 600 C and then when you heat it at 400 C that you would get much more rapid crystallization at that temperature or were you talking about continued heating at 600 C?

MR. GRIFFITH: The comparison I was making was a continuous anneal of two different temperatures, 600 C and I chose 467--let's say 500 C. It is a thermally activated process.

In fact, well, I can show you the formula if you like later.

MR. RICHMOND: You can with some materials get a nucleation by heating at high temperatures for short periods and very greatly accelerate the crystallization.

MR. GRIFFITH: Oh, right. Absolutely.

UNIDENTIFIED SPEAKER: Have you noticed any tendency of that type in these amorphous silicons?

MR. GRIFFITH: I don't think that has been adequately explored, but I can tell you that we do know this, if you take one of these low discharge type films and you anneal it for only a half hour between 720 and 780 C, that is sufficient to crystallize it. It's like using the upper end of the activation curve. Now, you're saying suppose you take 650 C, well, just let's say 700 for a half hour, you don't crystallize it, now you put it back in the oven and heat it up at 500, will it crystallize faster? The answer is probably yes.

CHAIRMAN SERAPHIN: Just adding to this, in the paper that I passed out to you there are some experimental results on annealing amorphous films where we studied this type of thing and in general it turns out that a film that has been deposited at a low temperature and then annealed to a higher temperature has the same optical properties that a film that has been deposited at the higher temperature.

MR. SCHWARTZ: I have another question, and I'm not going to ask you about repairability. I have a general question for both of you. After you apply these coatings to stainless steel, say to a tube, that's the beginning. You then have to shape it in order to manufacture the final item. In the shaping, what is the ability of either one, particularly the stack, to accept shaping such as bending and what have you without cracking because you're not going to have just straight runs of tubing. That is very unlikely particularly in a boiler. You take a look at any of the boiler designs and you'll find there are a lot of bends there. You don't have straight runs of tubing. Now, how amenable is the process that you're using, the way of putting it on, to shaping? It's a very practical question in building a boiler.

MR. GRIFFITH: Well, I can plead ignorance, but I could say that that is a good thing to try.

CHAIRMAN SERAPHIN: I think your question can be answered on two levels. You should not bend these thin films nor should you bend any other thin film to the point where they crack and peel off. Within these limits, you can bend the finished product. There is one difference, too, in photothermal coatings with respect to photovoltaic coatings, we are not in the optical properties depending upon lifetime conservation like the photovoltaic people are. Photovoltaic devices are very sensitive to the stresses as they are even produced by cooling or annealing, not to speak of bending. You don't bend photocells, but the photocell coating, of course, is not dependent upon the film stresses so this gives a certain tolerance, but I don't see any reason why you shouldn't start out making up your mind what kind of configuration you want and then coat it.

MR. SCHWARTZ: Except that you may have difficulty in coating it in the apparatus you show which is a straight run type of device. I don't know if you can go around bends and whether it is amenable to that, I don't know.

MR. VOSSEN: I can answer that question on two levels also. First of all, these amorphous films produced by glow discharge deposition are generally in compressive stress, very large amounts of compressive stress; therefore, bending the thing with the film side out actually acts to relieve that stress and in fact helps the situation a great deal.

The second point is that virtually any deposition process if you want to take the trouble to do it can be used to coat any shape that you want to talk about. So, if you do want to shape a part, it is not a big problem. It really isn't.

MR. HAHN: Have you seen any indications of recrystallization due to contact with metal. There has been some work reported, I think, a couple or three years ago with amorphous films that suggested they would tend to recrystallize at much lower temperatures.

MR. GRIFFITH: Yes, that is an extremely important point and for example if you have silicon, amorphous silicon in contact with aluminum there is "mass" transfer, dissolution, and resulting crystallinity at very low temperatures for example 200 to 300 C; therefore, aluminum--I should say amorphous silicon on top of aluminum without any barrier in between would be a bad possibility. I think the situation is much better with stainless steel, but aluminum seems to be especially bad.

UNIDENTIFIED SPEAKER: Just a related question. When you calculated emittance of these films, was this essentially just a 1 μm thick film?

MR. GRIFFITH: Right, thin film.

UNIDENTIFIED SPEAKER: Did you take any interference effects into account in this calculation?

MR. GRIFFITH: No, I assumed, considering what I knew to be the impurity absorption and what I could estimate for the free-carrier absorption. I thought I was being overly conservative.

UNIDENTIFIED SPEAKER: As a suggestion, I might just recommend that when you do this typically these films are placed on top of a highly "reflective" substrate and when you get interference minima, a little bit of absorption in the film often will significantly enhance the reflectance dip at those wavelengths. Sometimes you can get fooled because it is possible to even enhance the absorptance that you get in an unsupported film. In some cases it makes a big difference and in other cases it doesn't. So, it's just a caution.

MR. RICHMOND: In your emissivity calculations, did you calculate them for one thickness or double thickness film? If it is applied to substrate, you would get the effect of a double thickness.

MR. GRIFFITH: Double thickness.

By the way, to answer your question also, and to add to and reinforce some of the things that were said, if you were to deposit an 18 μm thick amorphous silicon film, you can be sure at low temperature it will crack and indeed when you deposit thinner films, they are more elastic and particularly if you increase the substrate temperature, there is a kind of healing that goes on in the films against the stresses and strains, although it was pointed out that might actually help you. At any rate, there are fewer stresses and strains that are formed as you raise the temperature. And, I'm really talking about films that might be produced at say 400 C or 500 C and this is very much different from those that are as deposited and could crack if too thick.

Composite Dielectrics

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Summary of Presentation

Recently we have begun a program to study the utility of dispersions of Si and Ge in transparent insulators as selective absorbers for the photothermal conversion of solar energy. Si and Ge are nearly ideal selective absorbers for high temperature, low concentration factor photothermal conversion. Because of the well defined energy gap, they exhibit high absorbtance in the visible and low emittance in the infrared and a very sharp transition from one behavior to the other. However, their high index of refraction results in a large fraction of solar radiation being reflected rather than absorbed.

Co-sputtering of Si (or Ge) with a transparent, low index of refraction insulator produces a fine dispersion of Si grains in a transparent matrix. The optical properties of such a composite is similar to that of a semiconductor with an energy gap the same as that of Si (with a somewhat reduced extinction coefficient) but with a lower index of refraction. Thus a single sputtering process results in a film which exhibits an appreciably smaller reflection loss than pure Si and hence eliminates the need for additional processing required by the application of antireflection coatings.

Measurements of reflectance from films of Si-CaF_2 and Ge-CaF_2 on Al and Au mirrors have shown the following properties which are essential for efficient photothermal conversion of solar radiation at high operating temperatures and low solar concentration factors:

1) High absorptance (low reflectance) in the visible part of the spectrum, to 1 or 1.5 μm depending on the choice of semiconductor.

2) A rapid transition to low emittance (high reflectance) in the range 1-2 μm

There is an additional requirement which is extremely important for efficient high temperature conversion. The absorber material must not have absorption bands at IR wavelengths less than about 20 μm Even a small amount of absorption at shorter wavelengths can result in a severe loss in efficiency at, say, 500°C. Unfortunately both Si and Ge composites have exhibited absorption bands near 12 μm, indicating that some chemical reaction between the semiconductor and the CaF_2 is taking place.

Currently our work is centered on determining the optimum concentration of Si, Ge and a Si-Ge alloy in CaF_2 by determining the variation of index of refraction and extinction coefficient as a function of composition and wavelength. In the future serious consideration will be given to the minimization or elimination of chemical reaction.

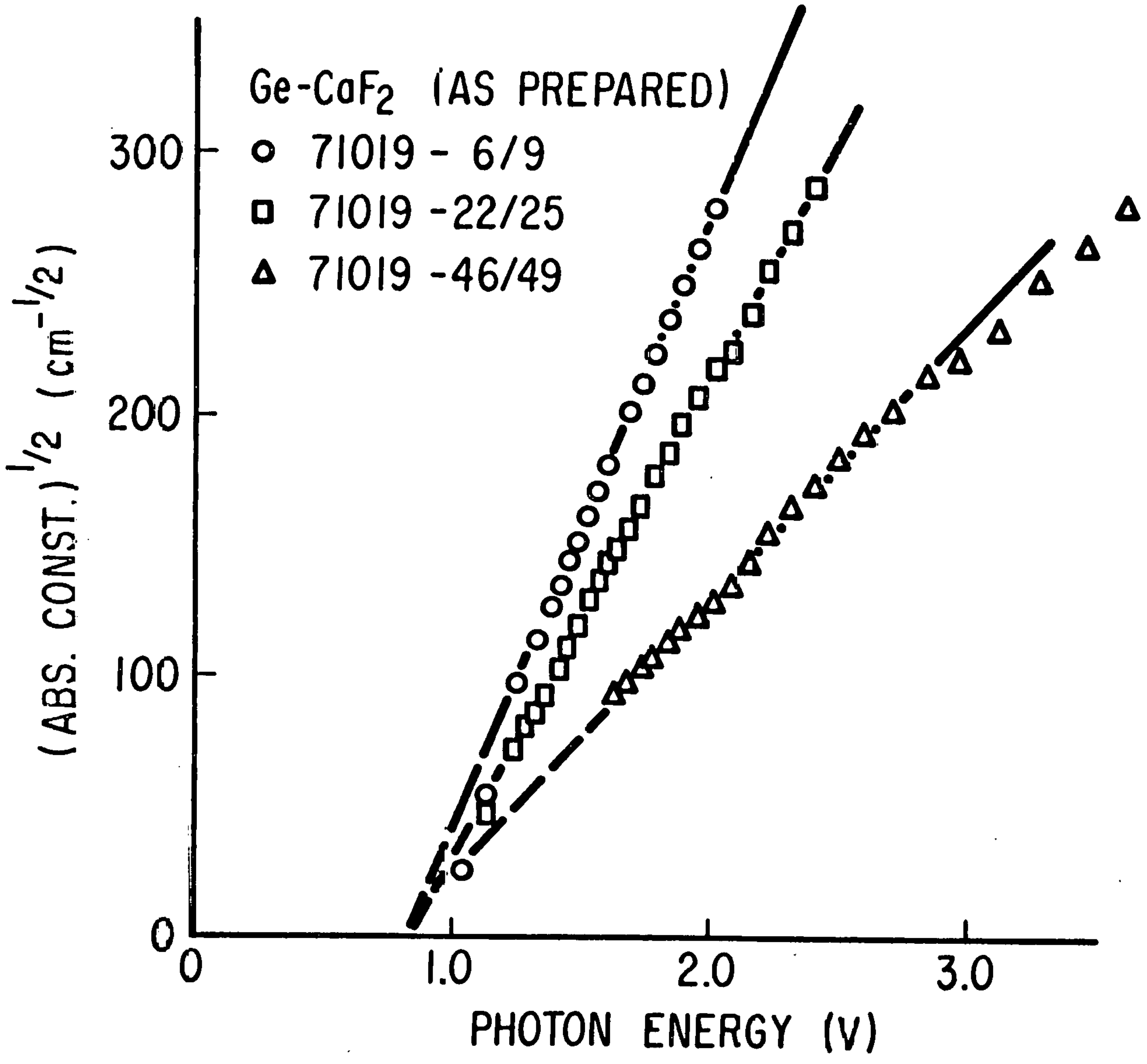

Figure 1. Square root of absorption constant vs. photon energy for three Ge-CaF_2 composites.

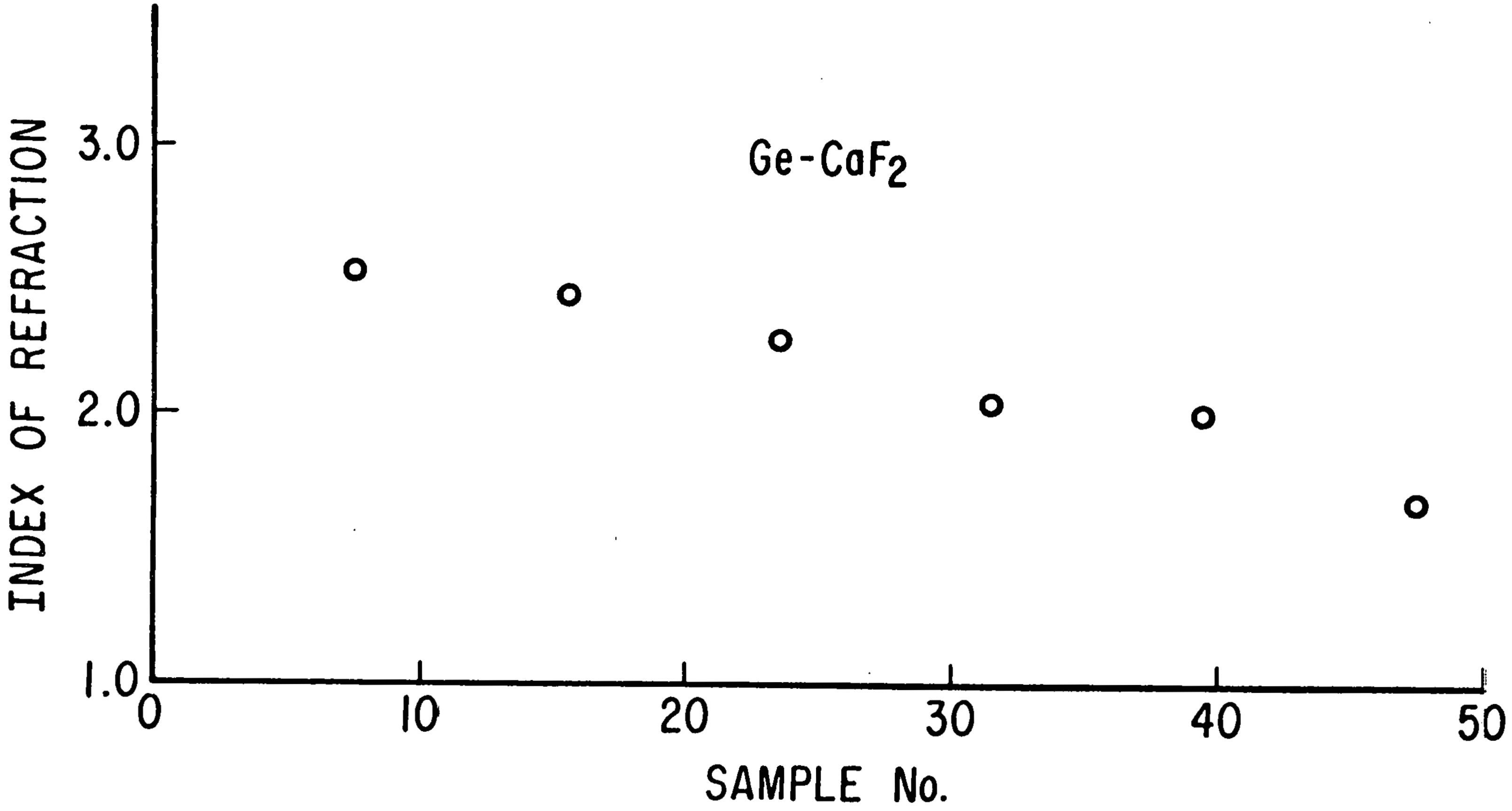

Figure 2. Index of refraction vs. sample number for a set of Ge-CaF_2 composites.

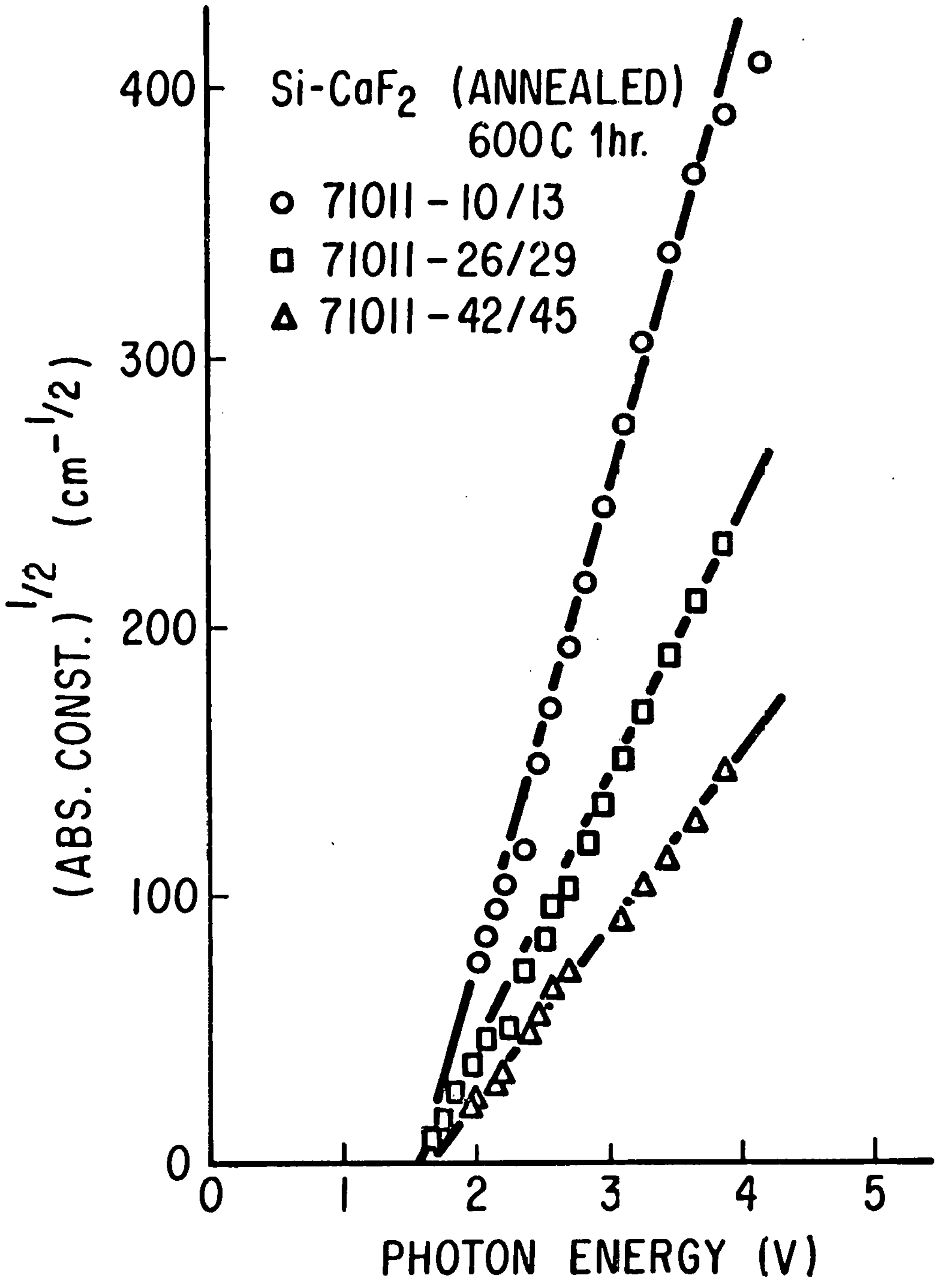

Figure 3. Same as Figure 1 but for Si-CaF$_2$.

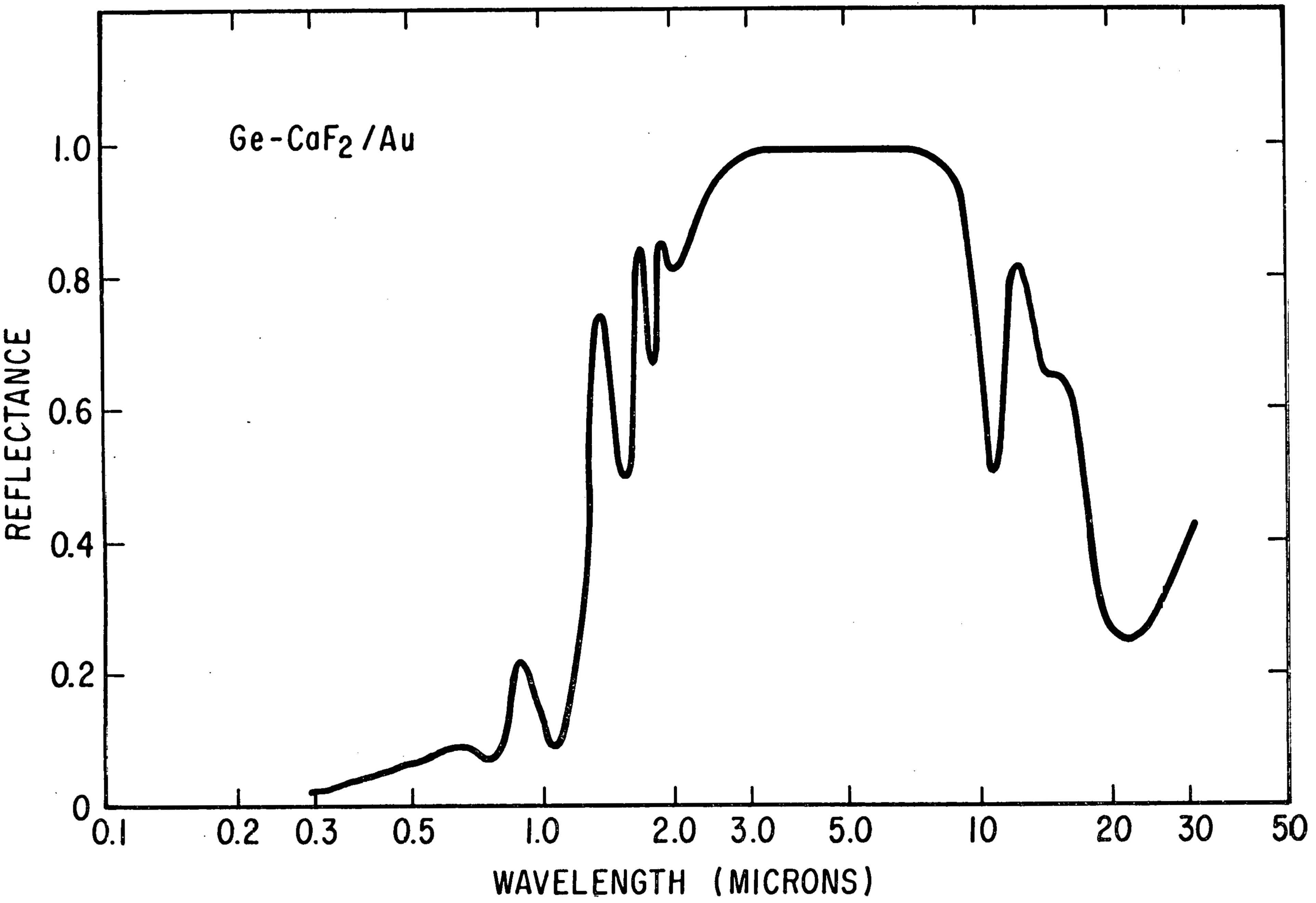

Figure 4. Reflectance vs. wavelength for a Ge-CaF_2 composite film on a gold mirror. Main features: sharp rise in reflectance (accompanied by interference) between 1 and 2 μm and an anomalous absorption at about 12 μm.

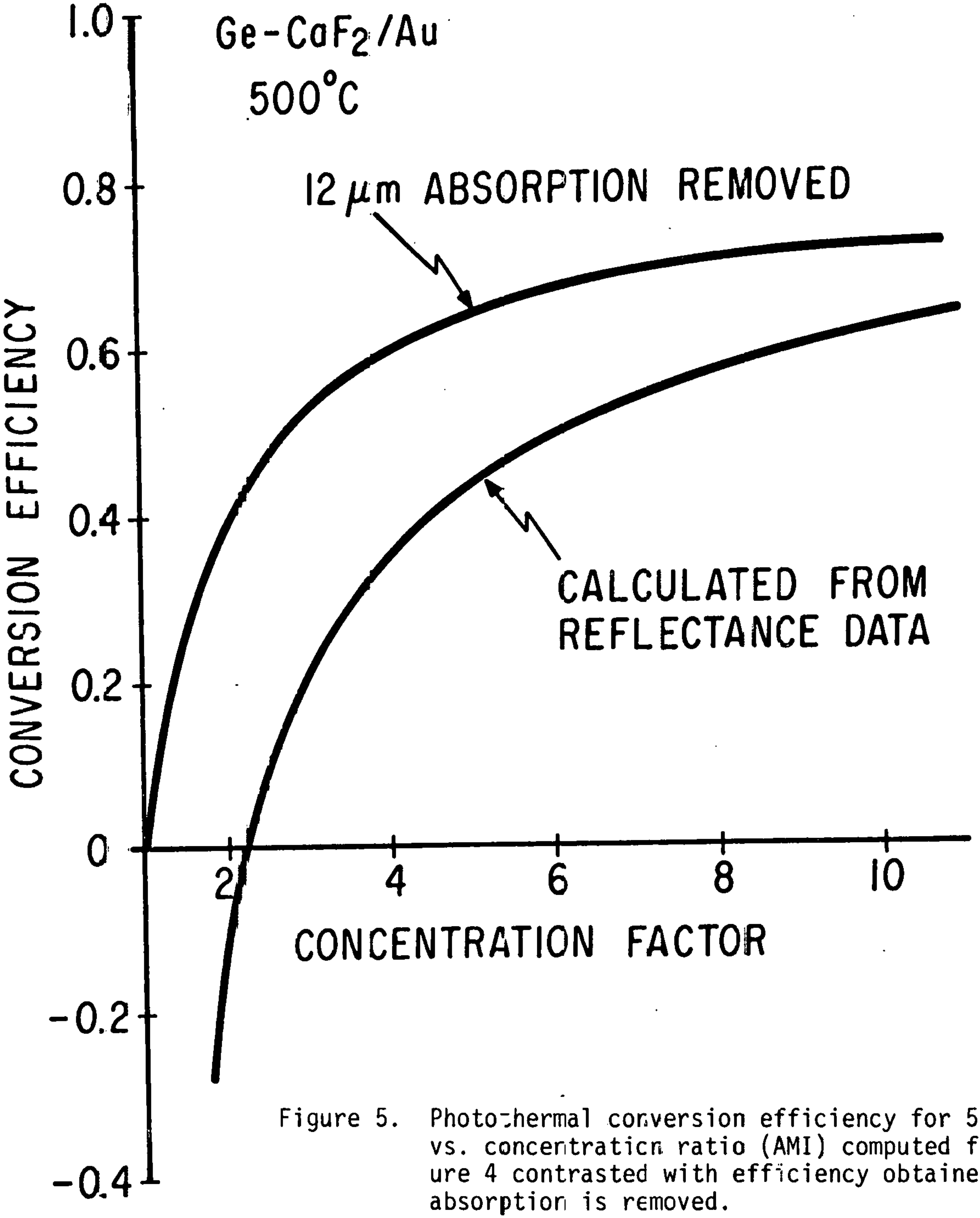

Figure 5. Photothermal conversion efficiency for 500°C operation vs. concentration ratio (AMI) computed from data in Figure 4 contrasted with efficiency obtained if the 12 μm absorption is removed.

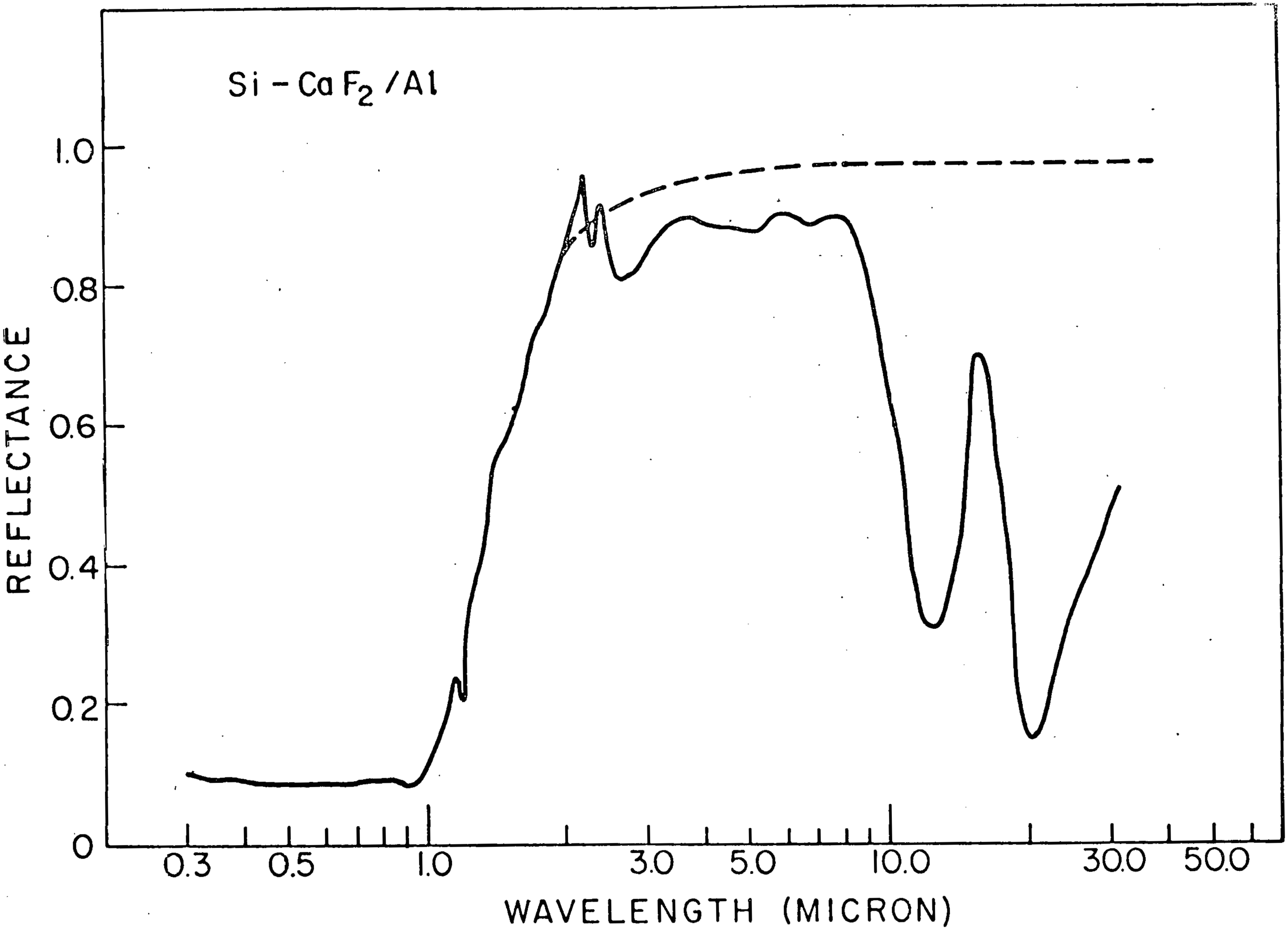

Figure 6. Same as Figure 4 for a Si-CaF$_2$ composite.

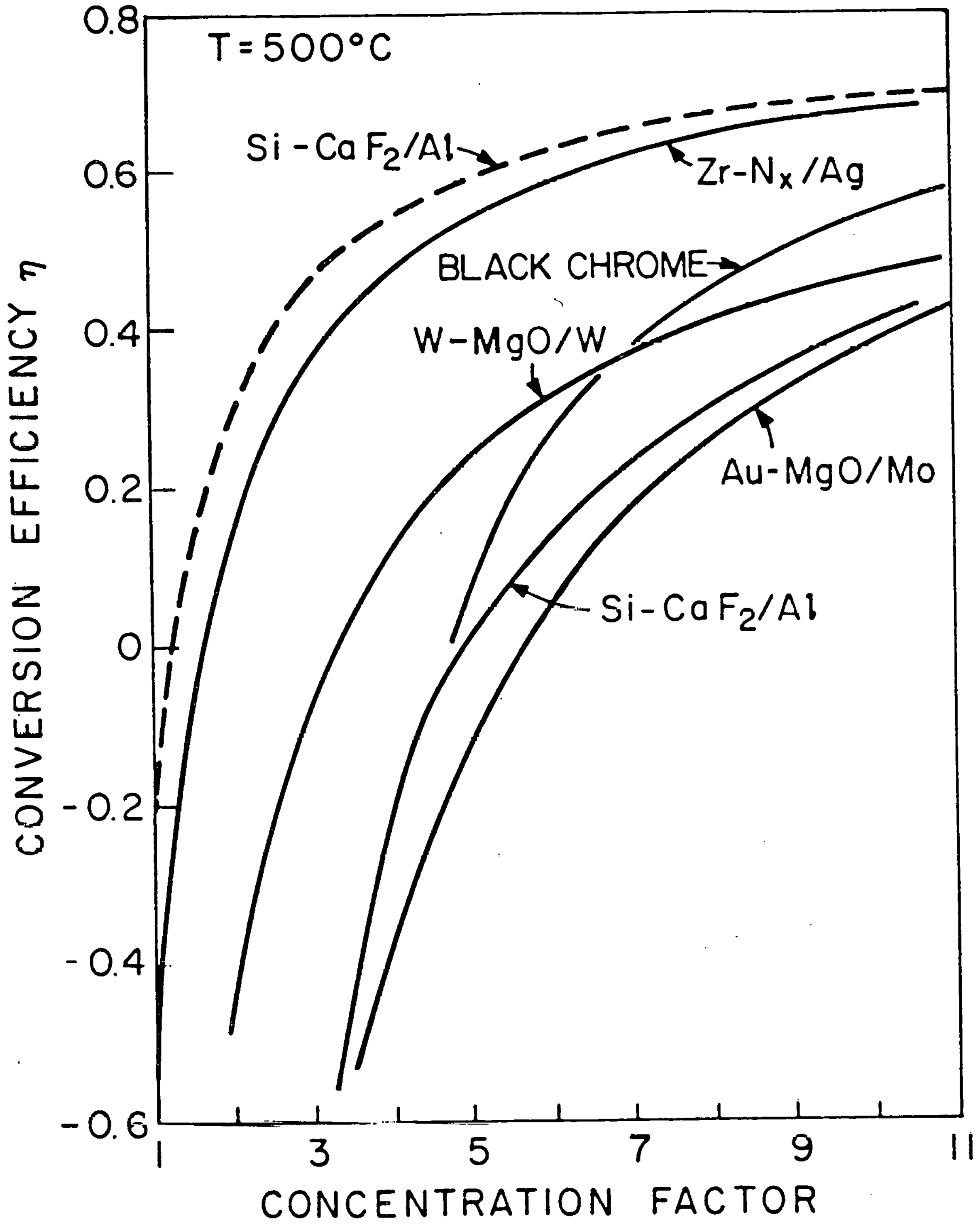

Figure 7. Same as Figure 5 for a Si-CaF_2 composite. Hypothetical efficiencies computed from published reflectance data given for comparison purposes.

MR. MELAMED: I presume, John, that the thrust of your program was to, by using the technique of graded index of refraction achieve or defeat the otherwise high Fresnel surface reflection losses which are associated with any semi-conductor film. You didn't state this clearly. Has this diminished in your program or is this still an objective of your program?

MR. GITTLEMAN: No, no. It's still an objective.

MR. MELAMED: I'm a little concerned about that because this is the thrust that I thought was unique to your program.

MR. GITTLEMAN: Well, as you can see, the indices are appreciably lower. The index of refraction for germanium is about four and here we can achieve indices of less than two.

MR. WEHNER: You didn't say much about the deposition conditions for these cermets. I think that the substrate temperature and the deposition rate are very important parameters for determining the grain size of your product.

MR. GITTLEMAN: That's quite so. The deposition rates are measured in fact on the order of a thousand angstroms per hour, on that order. I'm not sure exactly because I didn't bring that with me. The starting pressures were about 10-8 Torr.

MR. CARROLL: If I recall correctly some data from Naval Weapons Laboratory in Corona several years ago, germanium has a very strongly temperature dependent infrared absorption coefficient so much so that it has been considered as a solid state louver for spacecraft temperature. Have you looked at that?

MR. GITTLEMAN: Not yet, no.

MR. CARROLL: Maybe it's a contamination or doping effect, I don't know for sure, but you had better take a look at that because it is double the emittance in about 150 C. It has a very strong effect.

CHAIRMAN SERAPHIN: Have you made temperature measurements on these composites?

MR. GITTLEMAN: Not yet, no.

MR. IGNATIEV: These are not graded. You are showing us singular, uniform films in depth?

MR. GITTLEMAN: Yes. Each specimen is of uniform composition. The composition varies with the sample number. The target configuation here is a calcium fluoride target with a triangular wedge of say silicon overlay so that the location of the substrate beneath the sputtering target determines composition.

MR. IGNATIEV: And you haven't done TEM work?

MR. GITTLEMAN: No, it is not trivial because in brightfield the contrast ratio is very small and the grains are too small to do much darkfield, so we are trying to, anneal the films to be used in the TEM.

MR. DICKSON: The last slide you showed had a comparison of efficiency and you had black chrome in there at a temperature of 500 C. What sort of calculations were they based on?

MR. GITTLEMAN: They were all based on the same thing just for comparison purposes. I didn't want to presume that any of these materials could survive at 500 C. I merely calculated all of these conversion efficiencies on the same bases; that is, their room temperature reflectance data that was available.

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OPTICAL PROPERTIES OF METALLIC SURFACES, SMALL PARTICLES AND COMPOSITE COATINGS FOR SOLAR ENERGY CONVERSION APPLICATIONS

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Objective:

A theoretical and experimental investigation of the optical and physical properties of metals, alloys, and composite coatings.

Thumbnail sketch of program:

I. Theoretical work on composite media

II. Experimental work on metal dispersions

  1. Optical Instrumentation
  2. Metal Smokes
  3. Ceramic Rich Cermets

III. Status

IV. Future

I. Theoretical

Question: Isolated ultrafine metal particles have an electronic resonance in the visible but what happens to this resonance when the particles interact with each other?

Maxwell-Garnett answer (1904)

$$\bar{\varepsilon} = \epsilon_h \frac{[2\epsilon_h+\epsilon_b+(2f)(\epsilon_b-\epsilon_h)]}{[2\epsilon_h+\epsilon_b-(f)(\epsilon_b-\epsilon_h)]}$$

Bruggeman answer (1935)

$$\frac{3f}{2+\frac{\epsilon_b}{\epsilon}} + \frac{3(1-f)}{2+\frac{\epsilon_h}{\epsilon}} = 1$$

Cornell Multiple Scattering Theory Approach (1977)

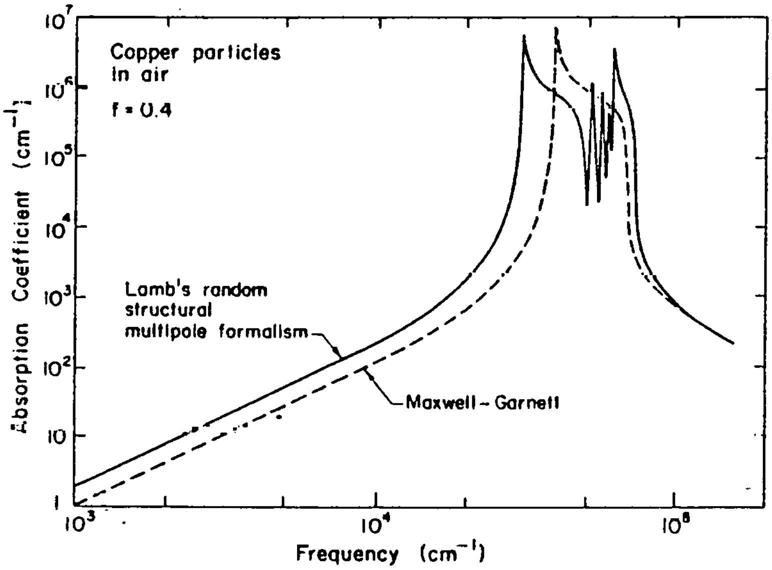
$$\bar{\epsilon} = \epsilon_h \frac{[2\epsilon_h+\epsilon_b+(2f-\Delta)(\epsilon_b-\epsilon_h)]}{[2\epsilon_h+\epsilon_b-(f+\Delta)(\epsilon_b-\epsilon_h)]}$$

where Δ contains structural multipole information,

Cornell expression → Maxwell-Garnett as $\Delta \to 0$.

Local inhomogenieties in composite takes absorption strength from the visible and moves it to the infrared.

Resonance is weaker and broader than given by Maxwell-Garnett formalism.



II. Experimental

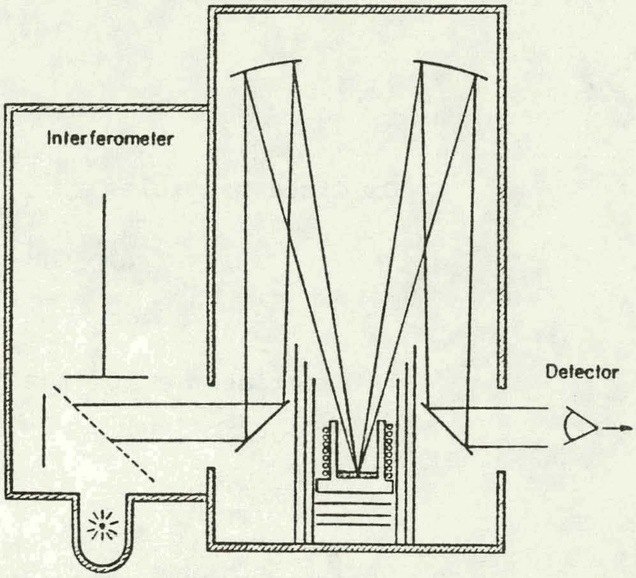
1. Optical instrumentation

a. Hemispherical emittance calorimeter for coated or clean metal surfaces. (room T → 1000°C).

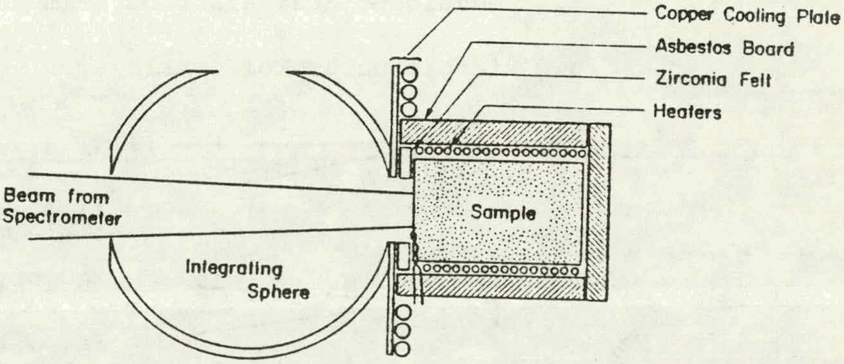
b. Fourier transform spectrometers 1000 microns → 1 micron. Specular reflectance from room T → 400°C.

c. Cary spectrophotometer plus integrateing sphere. 2.5 microns through visible hemispherical reflectance room T → 300°C.

(b) IR interferometer plus high temperature specular reflection attachment. Spectral range 1 → 8 microns temperature range room T → 400°C.



Integrating sphere plus high temperature sample attachment.



Spectral range: 2.5 microns → visible

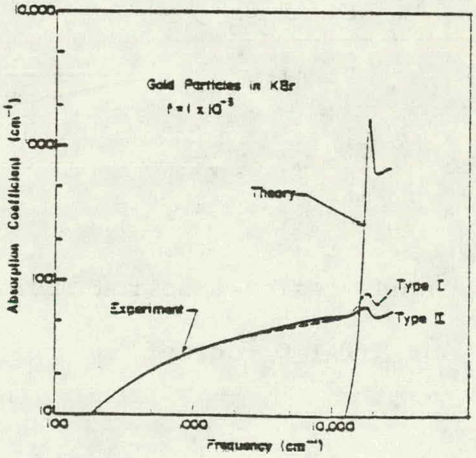
Temperature range: room T → 300°C

II. Experimental

2. Metal Smokes

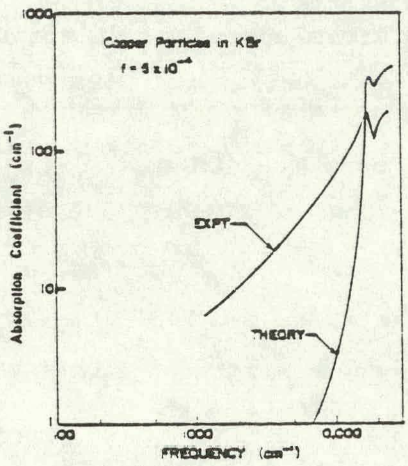
unoxidized particles

IR experiment ≈ 10^3 theory



Oxidized particles

IR experiment ≈ 10^2 theory



3. Ceramic rich cermets

   a. Technique: dual electron beam evaporation

   b. Microstructure of coatings

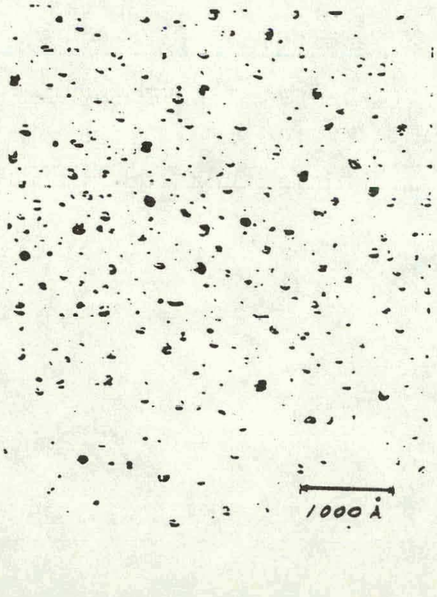
Ni/Al_2O_3 — Ni crystals; Al_2O_3 amorphous

V/MgO, Fe/MgO — MgO crystals; Fe, V highly dispersed

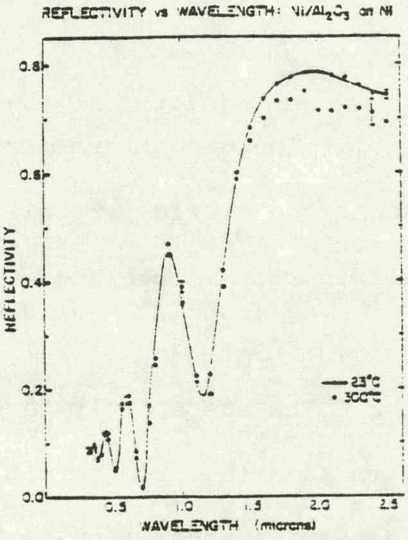
V/SiO_2, Fe/Al_2O_3 — Metal highly dispersed; Insulator amorphous

Pt/Al_2O_3 — Pt Crystals; Al_2O_3 amorphous

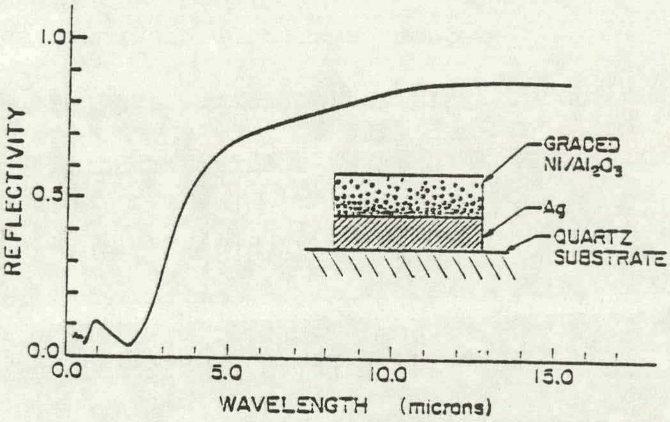
Transmission electron micrograph
of Ni/Al_2O_3 cermet



1. Reflectivity is temperature independent over solar spectrum.
2. Reflectivity is temperature stable to 500°C. Test:500°C for 26 days.

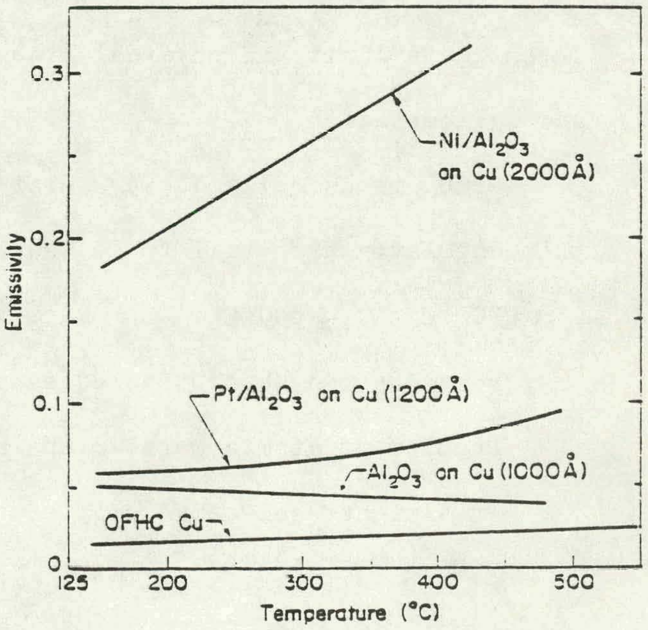


1. Grade Ni/Al$_2$O$_3$ to improve absorptivity ($\alpha_S = 0.94$).
2. Hemispherical ε(100°C) ≈ 0.16.



1. Amorphous Al$_2$O$_3$ O.K.
2. Note: low emissivity of Pt/Al$_2$O$_3$ in contrast with high emissivity of Ni/Al$_2$O$_3$.

High emissivity due to dispersed Ni.



III. Status

1. The nonuniform distribution of particles in composite coatings broadens the single particle sphere mode resonance. The absorption is weaker in the visible and stronger in the infrared than predicted by the Maxwell-Garnett theory.

2. The anomalously large infrared absorption in metal smoke composites appears to arise from particle clumping. The precise loss mechanism is not yet determined but it my be associated with photon assisted electron hopping between particles.

3. Some ceramic rich cermets such as Ni/Al_2O_3 appear to be stable at 500°C. This graded cermet absorbs 94% of the air mass - 2 solar spectrum. The structure has a large emissivity because some Ni atoms remain dispersed in the amorphous Al_2O_3.

IV. Future

Theory: Explore properties of "Δ" the structural multipole correction to Maxwell-Garnet theory.

Investigate optical properties of multi-component systems.

Experiment: $T > 500°C$

Investigate limits of physical stability. Problems of adhesion, oxidation and agglomeration.

Problems associated with solar photon assisted diffusion and also with photochemistry are still to be tackled.

$300°C < T < 500°C$

Must sharpen absorption edges and decrease ε. What controls ε?

Problem of atomic metal dispersion in cermet must be faced.

Investigate selective emitters for solar energy transformer applications.

MR. IGNATIEV: In the gold smokes the usual classical comment is that they are there because of additional oxides or whatever you are evaporating them from. Are you doing this exclusively?

MR. SIEVERS: The gold smokes on the write-up are labeled type one and type two. One of those is the standard sort of tungsten oxide or something like that, and the other is the old technique of trying to make thermocoupled blacks.

MR. IGNATIEV: Also, in addition, in your emissivity increase in nickel, did you see that in a number of other systems?

MR. SIEVERS: No, it wasn't there in platinum; and when you say a number of other systems, we haven't done all of the other systems that are listed here because they didn't get strong absorption in the visible. They were dispersed already. You couldn't even see metal particles.

MR. IGNATIEV: Okay, but things like gold and platinum and silver like to puddle, like to pool when you start "growing" them in thin films. They make islands whereas nickel is not as extensive in that respect and that is maybe why you are getting more dispersion in nickel.

MR. PETTIT: Does the theory tell you when delta should go to zero, in other words as the particles become farther and farther apart, does the theory say two, three, five, ten diameters that delta goes to zero.

MR. SIEVERS: The theory says that delta goes to zero just because it does depend on the filling factor, but the details of how it goes to zero depend on what you are putting in as the important physical mechanism that is going on. So far the only thing that we've put in was the volume exclusion, you can't have one particle on top of another particle and already that had an effect.

MR. IGNATIEV: Along that same line, did you see a change in the infrared absorption as function of filling factor?

MR. SIEVERS: Yes, it varied linearly with filling factor. As you increase the filling factor, the infrared absorption increases.

MR. IGNATIEV: That couldn't be that you have clumping of particles as you increase the filling factor, in other words you have no longer singular particles, but clumps of smaller particles --

MR. SIEVERS: We are talking about the gold and that sort of stuff, right, no matter what level we looked at, what filling factor level, we found what we would have to say was clumping whether we were working at 20 percent or whether we were looking at a tenth of a percent.

MR. SIEVERS: Gold looks like chrome looks like nickel, they all look the same.

MR. CZANDERNA: I think if you would subject these particles to a long test in a higher temperature that you might be forming a nickel spinel and it is something to be concerned about for the future. For example if you would heat this at 800 C, I think your particle size and your distribution would change.

MR. SIEVERS: I agree with you completely. We are trying to follow that line up that it would go into spinel. In fact if we heat at 800 C, the whole thing disappears into dispersed nickel, so when I gave you the 500 C mark, that was in the same sense as people giving you 350 C for black chrome. You know, you're right on the edge of everything falling apart.

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Summary of Discussion

CHAIRMAN SERAPHIN: You have heard about four different advanced approaches to the manufacture of coatings and we may try in this structured discussion to relate the usefulness of these approaches or the usefulness of research and development in coatings in general to the needs of the users.

And, let me just quickly run through four points that I thought we all have learned yesterday from the presentations of the users. We hadn't realized the strong importance of a maximum solar absorptance for, the central receiver project as well as for the dispersed power systems. We have realized that we must know this absorptance value at the temperature of operation, that we do not know this at present, and that there is a strong need to measure this. The point was brought up that the absorptance that is so important for the efficiency of these plants is probably limited at these high temperatures. We were told that a gain in absorptance can be also provided by a suppression of the emittance and it was said that we are facing the option to suppress the emittance in the face of not being able to raise the absorptance further.

The necessity to look into the time/temperature characteristic of the deterioration of coatings as they may happen in transient temperature shocks due to loss of cooling was emphasized. We have to plan for a certain margin in these coatings. That is particularly important for the low and intermediate temperatures where we have to face the temperature limitation of black chrome. This seems to be in the neighborhood of 300 C leaving very little margin for temperature shocks.

The necessity to have a directional optical characterization is particularly important for the high concentration concepts.

Let us ask the question: What are the requirements and the constraints that we have to put on research in coatings with respect to the user's needs and may I open the discussion on this? Let me give you a very simple example of a constraint that is very real. Any design of a coating that is based on gold, for instance, I think is unrealistic to pursue because we can show that if you go to the areas that you will need in order to make an impact, you are going to use up the gold reserves that are available in this country even in layers on the order of a few thousand angstroms thickness, so--I know, Jim (Dickson), you are going to give me an argument on that--but even at a few thousand angstroms you are running into the limitation of the supplies. Someone else brought up the critical supply situation with respect to chrome, that we have to import from a country that we're supposed to boycott. So, these are just viewpoints, Jim, and I know that you are going to correct me this afternoon on this. I was just giving it as a demonstration of a constraint on research that we must realize. May I open the discussion along these lines.

MR. SCHWARTZ: I think from Leonard's discussion yesterday I feel convinced that at the 300 C level particularly at the low concentration factor, selective coatings are needed. The thing that I wonder about is the higher temperatures. As I see the higher temperatures, particularly at the higher concentration factors and also going to the cavity designs, it is hard for me to see from my vantage point as an engineer, what the need for this work is, but again maybe I haven't explored all the parameters. In my work the only thing that I would accede to at this point is that at the 300 C if the black chrome can cut it, I don't see another need for a selective coating. Now, there is such a thing as a backup, if you will, to the black chrome. As you go to much higher temperatures I think you are going to have to go to high concentration factors and when you start doing that, I think you are going to start going to cavities and when you start going to cavities I just don't see selective coatings giving you very much value.

MR. DICKSON: I'd like to make one point in defense of the selective absorbers. For people out in the great southwest in the sun belt in a low population density, maybe you are willing to put a lot of heliostats in. I think the rule for the people back in the northeast with the crowded situation is "selective absorbers buy a smaller heliostat field," I think we've got an advantage there because the price for property is high.

MR. SCHWARTZ: I don't see it. I don't see selectivity. I think you can get away with oxide surfaces or you can get away with a flat black or flat gray surface and that's all that's needed.

I'll go one step further, I don't think you need a high α as you start going to the higher temperatures, particularly if you are going to a cavity with $\alpha = 0.9$ in a cavity that goes to 0.98. So you really don't possibly need much higher than 0.85-0.9 from an engineering standpoint for α

MR. SKINROOD: I think some qualitative arguments are being made that may not be correct. I would like to also make some comments on the Barstow plant. The percentage loss for a receiver is dependent on the incident flux. We are currently uncertain what flux we can achieve, so the percentage loss due to re-radiation is still uncertain. However, even if we achieve the higher fluxes we still have a couple of percent of re-radiation going on, maybe two, maybe three percent with the open receiver. If we don't achieve the higher fluxes, the re-radiation is more like four or five percent. That is the margin you have to play with and that is what you have to work on with selective coatings so I think it is probably not correct to say that there is no role for selective coatings as long as you have a few percent to work on. Now, heliostats cost the same regardless of what part of the country you're from, and so we are looking for a couple of percent improvement in the southwest just as much as we are for the rest of the country.

Heliostats cost a lot of money, so that couple of percent is worthwhile working on for open receivers.

One other thing to consider and that is that as the temperatures go up, the re-radiation is also going up as T^4 so it's not totally clear that you don't still need to worry about re-radiation at higher temperatures. It is also not totally clear that you ought not to go to cavity type receivers. The jury is still out on open versus closed receivers. Barstow was selected for a specific design point and we shouldn't generalize to say that there are answers to be inferred from whatever was chosen for Barstow.

MR. MELAMED: I would like to make a rather general comment on an argument I've heard frequently expressed. The implication of the previous discussion is that we should guide the system designer by insisting that since we believe that a cavity is a coating insensitive approach and that every system should employ a cavity, this is like the tail leading the dog. I think the appropriate role we should take is to make as many options available to systems designers whether they be designers of low concentration/low temperature total energy systems or higher temperature/higher concentration systems or anything in between or anything beyond. We should make available to the engineering community the options so that their hands will not be bound. I think this is a prime requirement and an accepted prime function of DOE to further research which will give designers the opportunity to go as far as their imagination will permit, rather than to limit them in the first place, and I am strongly against limiting the options that a designer will have.

MR. SKINROOD: The Barstow plant was chosen because of its long range potential and was chosen not because it was optimized in the 10 MW(e) size, but because it had the potential to go to larger sizes and therefore we feel that the open receiver has that potential with that particular operating temperature and that particular operating fluid. The open receiver is the way to go because of cost and performance tradeoffs, they are not going to go away as long as we have water/steam systems.

MR. GUTSTEIN: If you were to raise the temperature of the central receiver say to 1500 F or more would you feel that the open receiver or the cavity receiver would be the more appropriate way to go?

MR. SKINROOD: It's a different tradeoff. I suspect we would end up with a cavity, but I don't know.

MR. GUTSTEIN: Well, you should know from the basis of convective losses as a function of operating temperature whether you feel that the open receiver has any chance whatsoever at those temperature levels.

MR. SKINROOD: There have not been detailed studies done in the higher temperatures. There is no current design that has been carried all the way through of a receiver operating at higher temperatures. The advanced receiver people are being asked to do that work right now, starting now.

MR. GUTSTEIN: How about the EPRI receivers? Are they open or are they cavity type?

MR. SKINROOD: They did not do a thorough tradeoff study. Right now they are closed, but they did not do a thorough tradeoff study and that is what we are insisting that the current contractors do. General Electric is being directed to do that. Boeing is being directed to go back and look at their choice, and then the other two contractors are also being directed to take a detailed look before they settle on a configuration.

MR. GUTSTEIN: It is very nice for technologists to provide an infinite selection, an infinite number of choices, but there just isn't that kind of money in the federal budget to provide those kinds of choices, and we've got to be restrictive. We have to identify priorities. One question is: What's the priority of the coatings area relative to other areas? Some of the things are a couple of percent effects and there are certain other components where effects may be twenty percent. Wouldn't you put your priorities on twenty percent effects and not the two percent effects?

MR. MELAMED: There is no question if you have limited funding or if we have two potential approaches on saving money on the system and one offers twenty percent improvement and the other offers a three percent improvement, with limited funding you want to go to the twenty percent. But the issue really is what are you spending for the twenty percent improvement and what are you spending for the three percent improvement? If you have a three percent additional investment cost to achieve a three percent improvement or a twenty percent investment cost in R&D to achieve a 20 percent improvement, you're at about the same level. So, really what we have to examine here is what is the cost from DOE's point of view and what is the potential payoff rather than just the magnitude of the improvement that is anticipated.

High Temperature Absorber Paints

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Summary of Presentation

A 10 month program to develop low cost, high solar absorptive paints to accelerate solar-thermal electricity technology was initiated on July 15, 1977. Analysis of the energy balance (i.e. absorbed solar energy vs. reradiation loses) shows that for a Central Receiver operating at or above 500°C and concentration ratios of 500X to 2000X, maximizing the solar absorptance of the receiver coating is more beneficial from a standpoint of net energy gain than minimizing IR emissivity. System studies consistently demonstrate that the heliostat field represents about one half of projected solar power plant capital costs and that system performance directly relates to receiver absorptivity. In general, as the concentration ratio increases, system efficiency becomes less dependent on emissivity. The objective of this program is to develop a stable high temperature solar absorber paint with $\alpha \geq 0.95$ that can be applied by conventional paint spraying techniques. By sacrificing low emissivity and emphasizing maximum absorptance, the development of low cost, high temperature stable inorganic solar absorber paints becomes a realistic goal. Eliminating the criterion of selectivity, i.e. abandoning the requirement of low ε while maintaining the criterion of high α, also obviates the need for close control of thin film thickness, since the success of selectivity is always intimately tied to maintaining very thin coating thickness.

Under previous Air Force sponsored programs at Exxon Research on low reflectance coatings at microwave and infrared frequencies, coating formulations containing selected spinel metal oxides had been identified to have low reflectance in the infrared and to be thermally stable at high temperatures. Subsequent reflectance measurements in the solar spectrum have shown that coating formulations containing these metal oxide pigments exhibit even lower reflectance in the solar spectrum, hence high solar absorptance, albeit low IR reflectance and hence high IR emittance.

Candidate coatings being developed for solar applications comprise dispersions of selected black pigments in two binder systems. Our prime binder candidate is an organo-polysilicate prepolymer which cures by hydrolysis to yield a completely inorganic coating. In addition, selected silicones are being evaluated as coating vehicles. Both binder systems exhibit thermal stability above 500°C.

Our initial task involves the selection of thermally stable black pigments which when formulated as coatings in the above silicate and silicone binders exhibit minimum solar absorptances of 0.95. Initial selection criteria include measurements of solar absorptance after 24 hour treatment in air at 500°C. Coatings showing optical degradation after this treatment are eliminated from the program. Seven inorganic pigments have been identified to date which yield solar absorptances from 0.95 to 0.98 when formulated in silicate and silicone matrices: CoO, $CoO \cdot Co_2O_3$, FeMn-CuOx, Co-CuOx and three mixed oxides of Cu-CrOx. They also show no evidence of degradation after 24 hour treatment in air at 700°C. These pigments are commercially available at less than $5/lb.

TEMPERATURE REGIMES OF INTEREST

- DISTRIBUTED COLLECTOR —

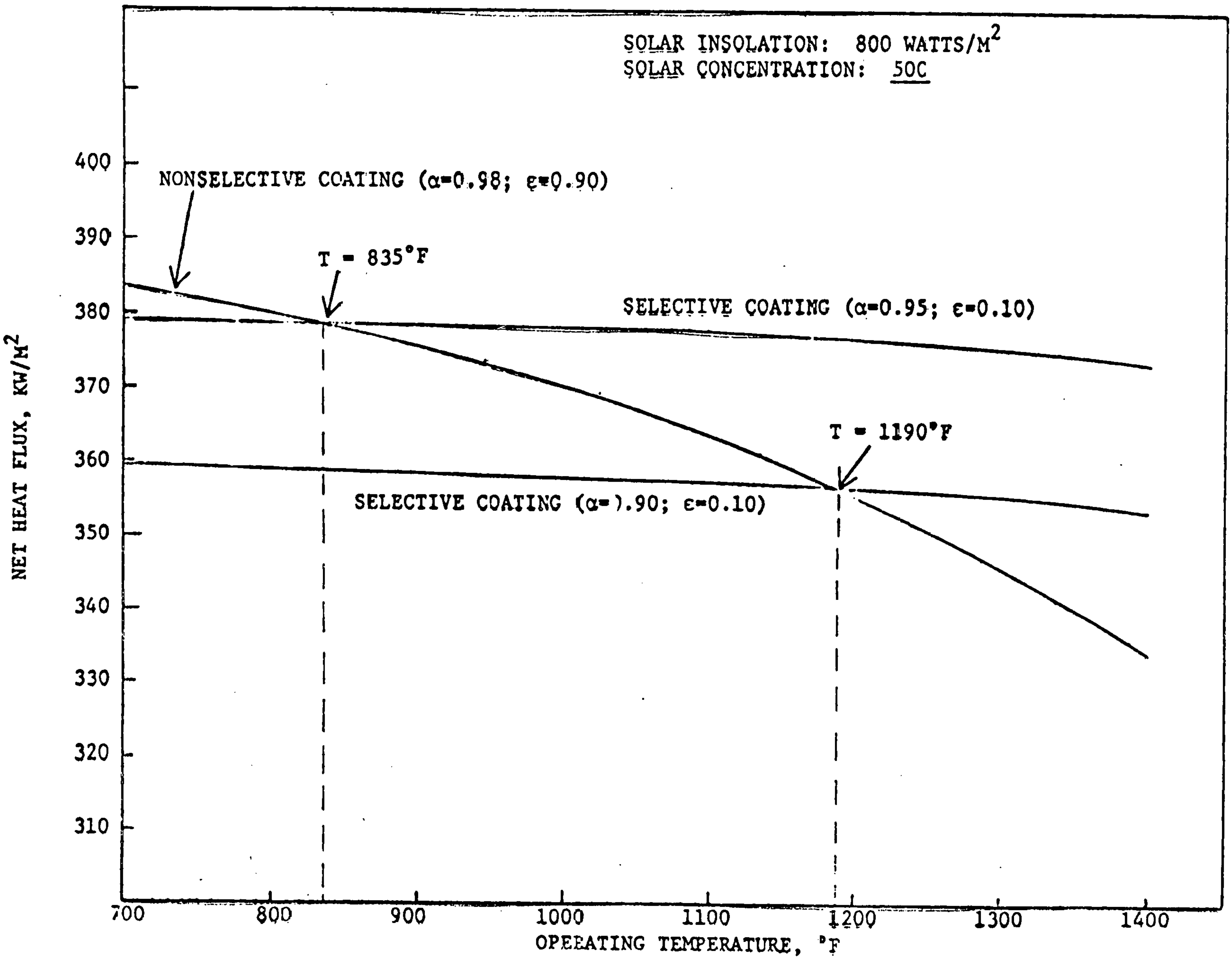
  TEMPERATURE REGIME: 500 TO 600°F
  SOLAR CONCENTRATION: 40:1

- CENTRAL RECEIVER —

  TEMPERATURE REGIME: 900-1000°F
  SOLAR CONCENTRATION: 200:1 TO 1500:1

- ADVANCED CONCEPTS —

  TEMPERATURE REGIME: 1300-1600°F
  SOLAR CONCENTRATION: 1500:1 TO 2000:1



NET HEAT FLUX: SELECTIVE VS. NONSELECTIVE COATINGS

SELECTIVE VS. NONSELECTIVE COATINGS

BASIS FOR COMPARISON:

SOLAR INSOLATION: 800 WATTS/M^2

SOLAR CONCENTRATION:
- 500:1 TO 2000:1
- 40:1 (DISTRIBUTE
  COLLECTOR)

NONSELECTIVE COATINGS

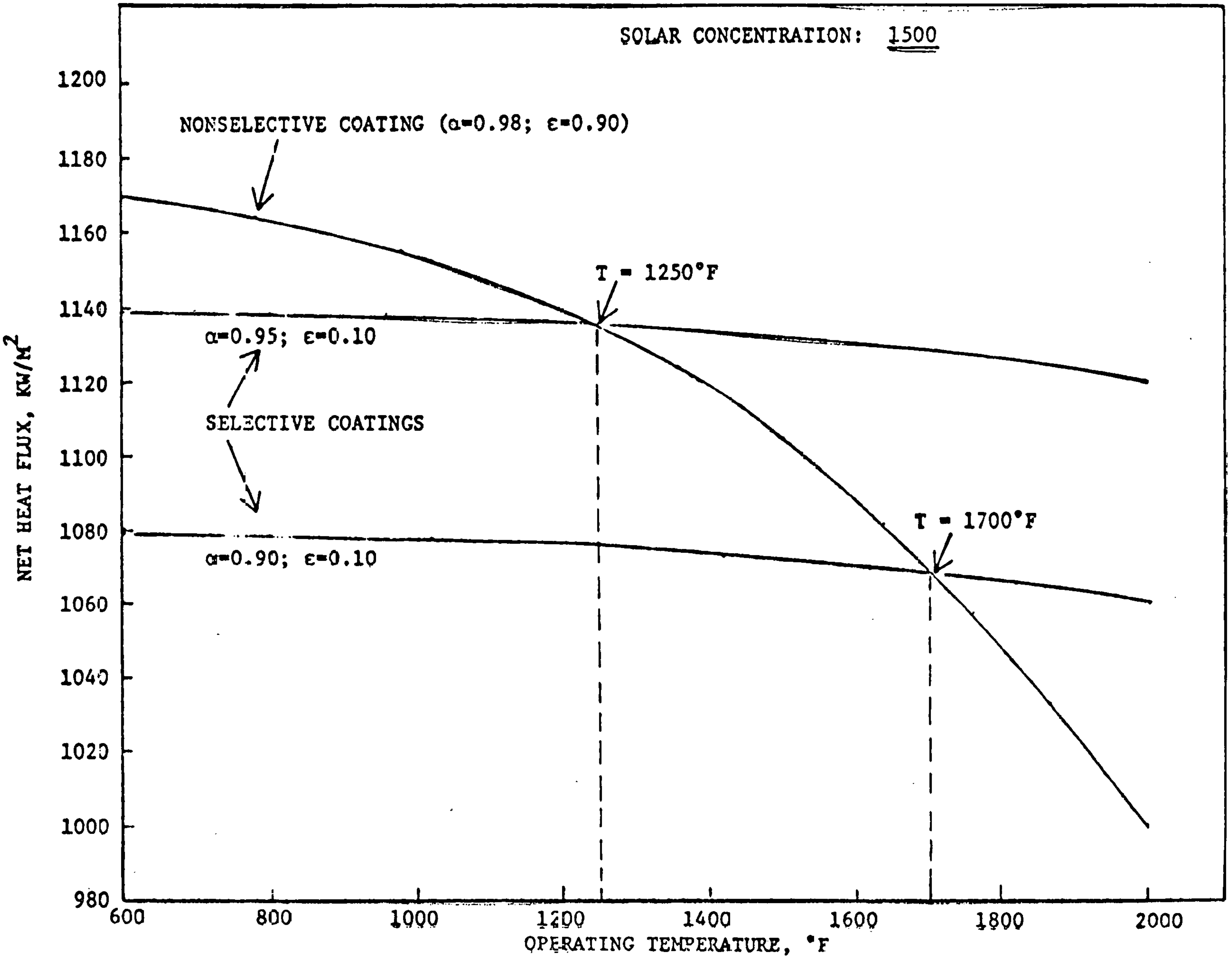
$\alpha = 0.98$
$\varepsilon = 0.90$

SELECTIVE COATINGS

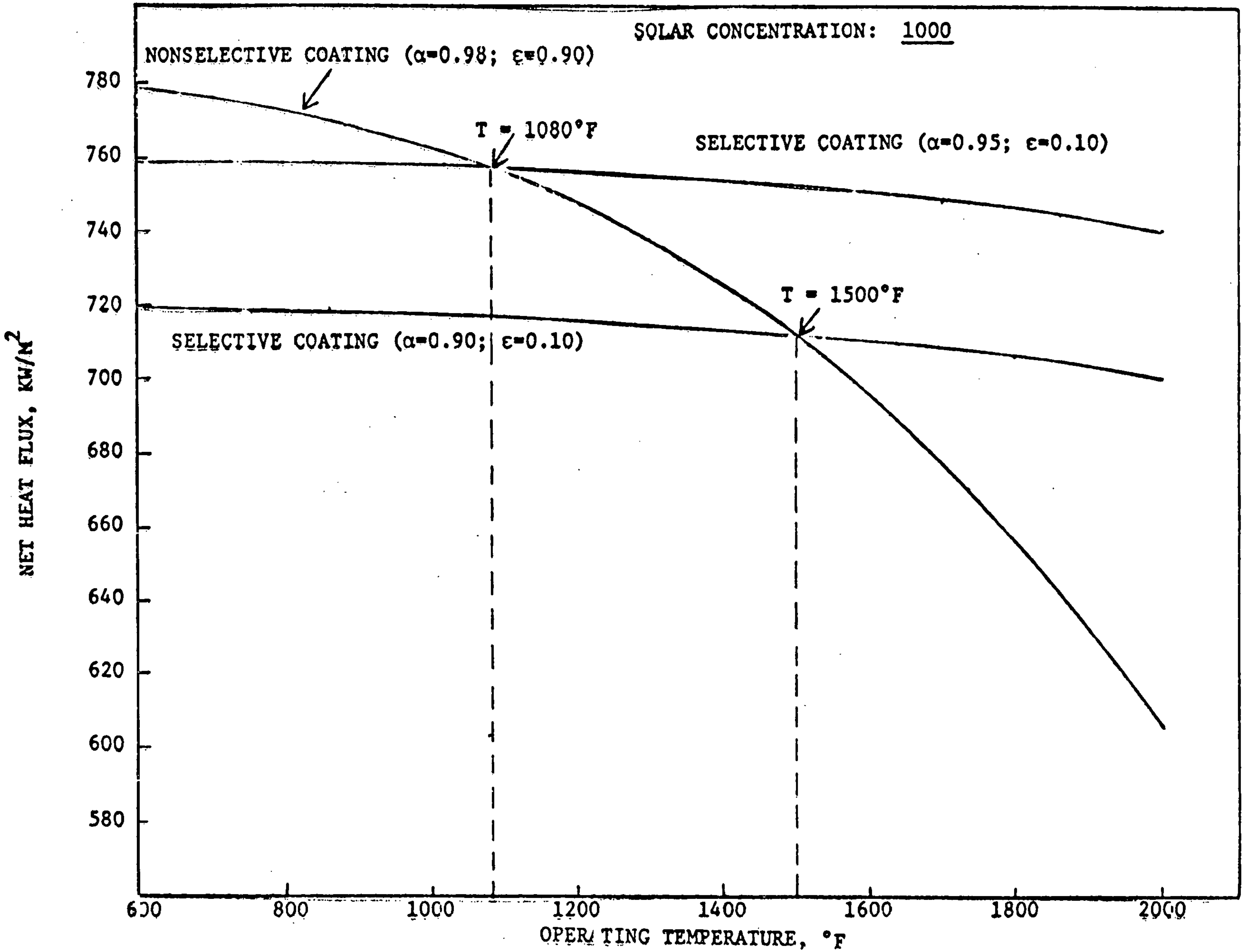
(1)
$\alpha = 0.95$
$\varepsilon = 0.10$

(2)
$\alpha = 0.90$
$\varepsilon = 0.10$

(3) BLACK CHROME
$\alpha = 0.96$
$\varepsilon = 0.06$



NET HEAT FLUX: SELECTIVE VS. NONSELECTIVE COATINGS



NET HEAT FLUX: SELECTIVE VS. NONSELECTIVE COATINGS

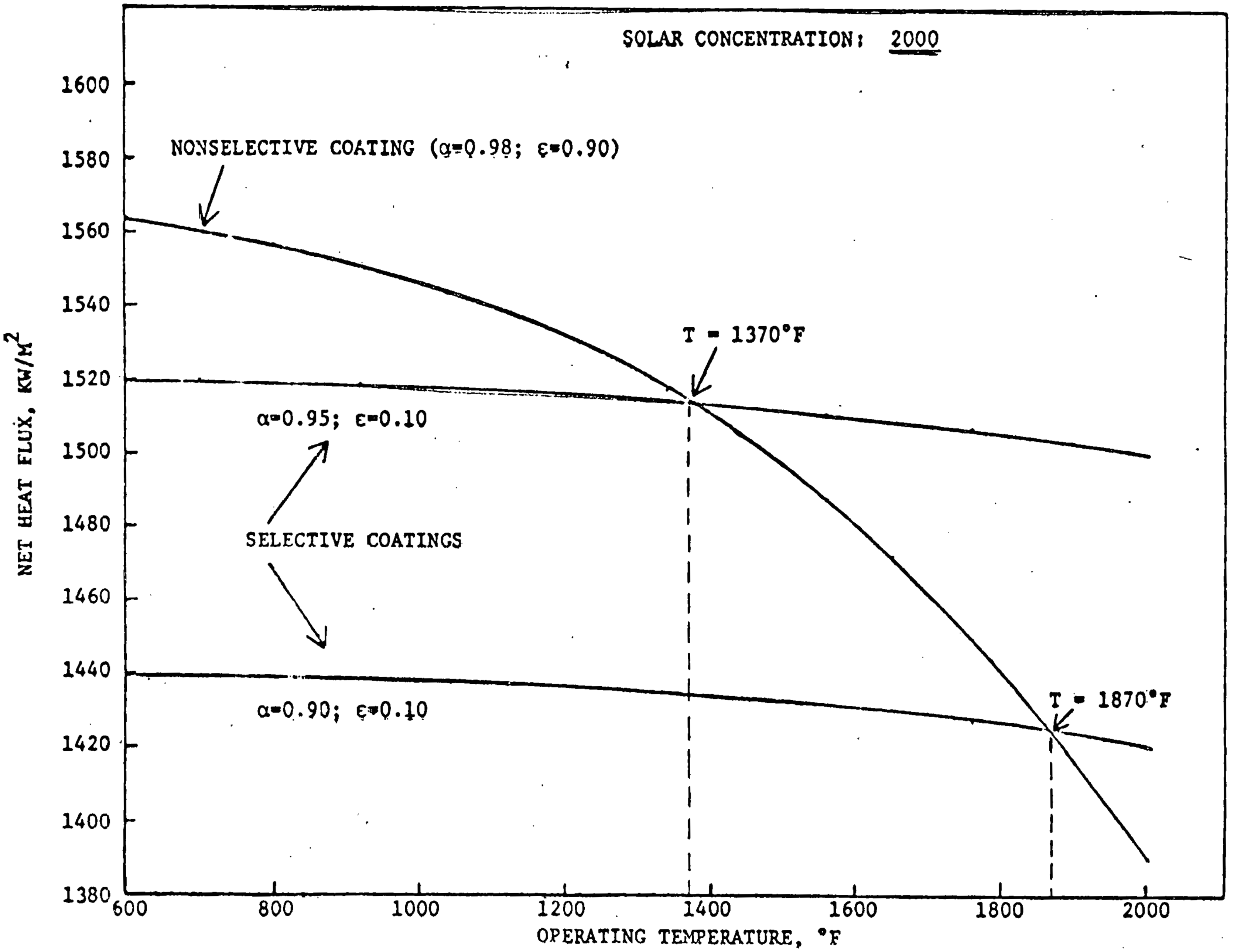
PROGRAM OBJECTIVES

- DEVELOP LOW COST, STABLE HIGH TEMPERATURE, HIGH SOLAR ABSORPTIVE COATINGS TO ACCELERATE SOLAR-THERMAL ELECTRICITY TECHNOLOGY.

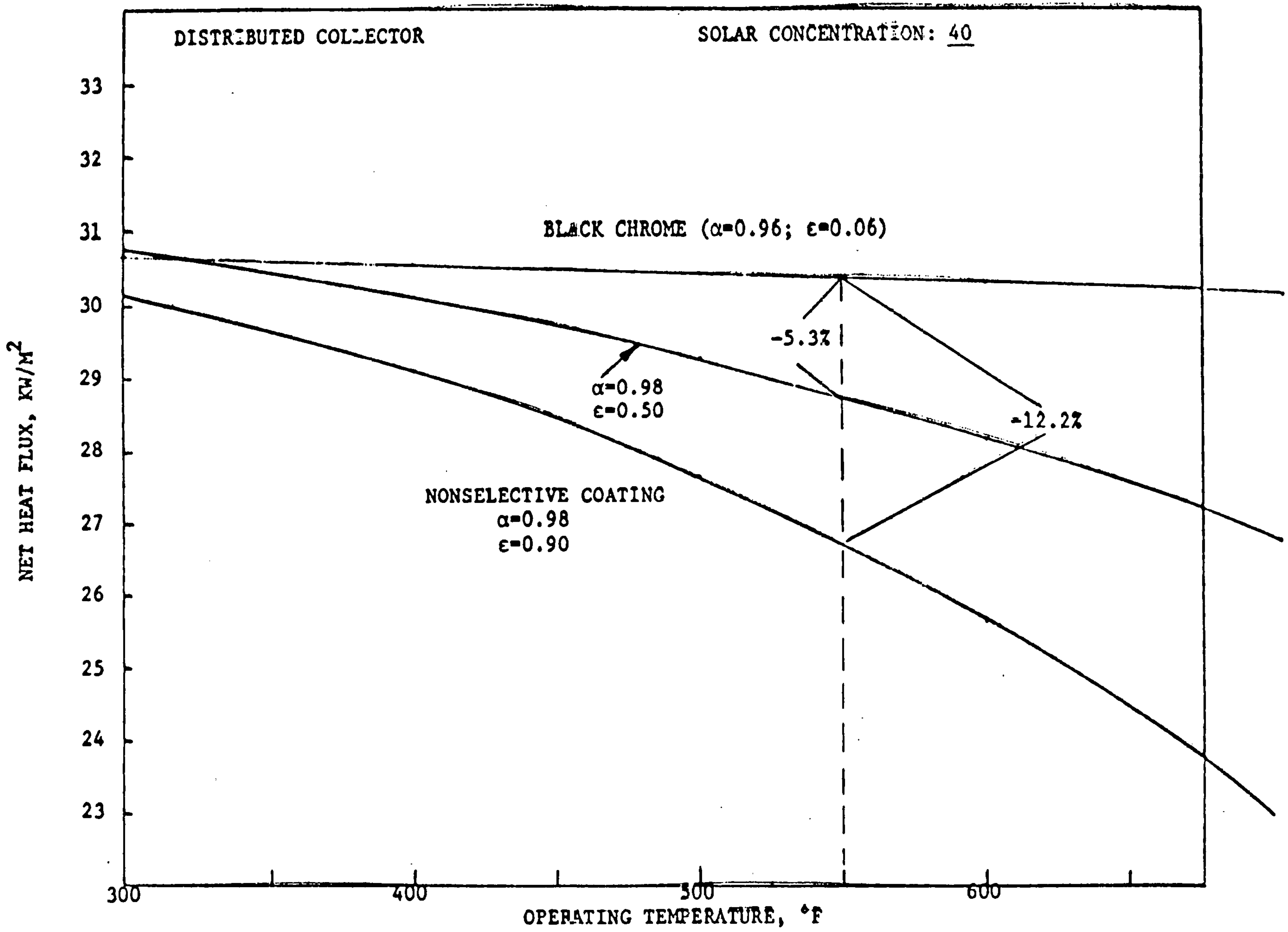
- MAXIMIZE SOLAR ABSORPTANCE TO $\alpha \geqq 0.95$
  - SACRIFICE LOW EMITTANCE
  - ELIMINATING THE CRITERION OF SELECTIVITY, I.E. ABANDONING THE REQUIREMENT OF LOW ϵ WHILE MAINTAINING THE CRITERION OF HIGH α, ALSO OBVIATES THE NEED FOR CLOSE CONTROL OF FILM THICKNESS.

- HIGH TEMPERATURE OPTICAL AND MECHANICAL STABILITY (T=1000 TO 1600°F).

- COATING TO BE APPLIED BY CONVENTIONAL PAINT SPRAYING TECHNIQUES.



NET HEAT FLUX: SELECTIVE VS. NONSELECTIVE COATINGS



NET HEAT FLUX: SELECTIVE VS. NONSELECTIVE COATINGS

ADVANTAGES OF HIGH TEMPERATURE NONSELECTIVE ABSORBER PAINTS

- COATINGS ARE APPLIED BY CONVENTIONAL SPRAY PAINTING TECHNIQUES

- COATINGS "CURE" AT OR NEAR ROOM TEMPERATURE
  - USING A SILICATE BINDER RESULTS IN A COMPLETELY INORGANIC COATING

- NO NEED FOR CONTROL OF COATING THICKNESS
  - SELECTIVE COATINGS REQUIRE CLOSE CONTROL OF ABSORBER THICKNESS
  - α AND ε VARY WITH COATING THICKNESS

- VERY HIGH ABSORPTANCES ARE ATTAINABLE ($\alpha = 0.98$)

- COATINGS ARE AMENABLE TO "IN-PLACE" REPAIR

- AT HIGH SOLAR CONCENTRATIONS THEY MAY EXHIBIT HIGHER EFFICIENCIES THAN SELECTIVE COATINGS OF LOW EMITTANCE ($\varepsilon = 0.10$) AND ONLY SLIGHTLY LOWER ABSORPTANCE

STUDY PARAMETERS

- SELECTION OF SUITABLE BLACK PIGMENTS WITH HIGH TEMPERATURE OXIDATIVE STABILITY AND HIGH SOLAR ABSORPTANCE.
- PIGMENTS INVESTIGATED ARE ALL METAL OXIDES, CONTAINING ONE OR MORE METAL OXIDES, WITH THE METAL IN ONE OR TWO DIFFERENT OXIDATION STATES.
- PIGMENTS WILL PRIMARILY DETERMINE SOLAR ABSORPTANCE AND INFRARED EMITTANCE OF COATING.
- PIGMENT PARTICLE SIZE SHOULD HAVE NO SIGNIFICANT EFFECT ON OPTICAL PROPERTIES.
- PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION MAY AFFECT BONDING PROPERTIES.
- PARTICLE SHAPE MAY ALSO AFFECT BONDING AND OPTICAL PROPERTIES AND PIGMENT SETTLING RATE AND THEREFORE INFLUENCE SPRAYING PARAMETERS - OUTSIDE SCOPE OF PROGRAM.
- PARTICLE SIZE MAY ULTIMATELY AFFECT COST.

- BINDER CANDIDATES
  - SILICATE
  - SILICONES

- BINDER WILL HAVE MINIMAL EFFECT ON OPTICAL PROPERTIES
  - SiO_2 REFLECTION PEAKS OCCUR IN THE INFRARED BETWEEN 8 TO 10µ WHERE AT BEST THEY MAY HAVE A SMALL BENEFICIAL EFFECT ON THE TAIL END OF THE RERADIATION SPECTRUM THROUGH ITS EFFECT ON ε.

- PIGMENT/BINDER RATIO MAY AFFECT BOTH OPTICAL AND ADHESIVE PROPERTIES WITH THE MAJOR EFFECT ON ADHESIVE PROPERTIES.

- TOO LITTLE BINDER (SiO_2), I.E. HIGH PIGMENT/BINDER RATIOS WILL TEND TO PRODUCE CHALKING. REVERSELY, TOO MUCH BINDER (LOW PIGMENT/BINDER RATIO) MAY PRODUCE MUD CRACKING.

- OPTIMUM PIGMENT/BINDER RATIO MAY DIFFER BETWEEN PIGMENTS DUE TO DIFFERENCES IN PIGMENT DENSITY, PARTICLE SIZE DISTRIBUTION AND SHAPE.

- SUBSTRATE: HASTELLOY X
  - SURFACE PREPARATION: GRIT BLASTING

BINDER CANDIDATES

- SILICATES - TOTALLY INORGANIC AFTER CURE
- SILICONES - CONTAIN ORGANIC LIGAMENDS
  - LONG TERM STABILITY AT HIGH TEMPERATURES IS QUESTIONABLE
  - SHORT TERM STABILITY (DAYS) AT $T \sim 1600$°F HAS BEEN DEMONSTRATED

SILICATES

- AVAILABLE AS PREPOLYMERS SOLUBLE IN ORGANIC SOLVENTS

$$(H_5C_2O)_3\text{-SiO-}\left[(C_2H_5O)_2SiO\right]_x\text{-Si-}(OC_2H_5)_3$$

ETHYL POLYSILICATE PREPOLYMER

- CURE
  - SOLVENT EVAPORATION
  - HYDROLYSIS THROUGH MOISTURE ABSORPTION FROM AIR
  - CONDENSATION
  - UPON CURE A NETWORK OF $(SiO_2)_x$ IS FORMED
  - THE AMORPHOUS SILICA DEPOSITS ADHESIVELY AROUND THE PARTICULATE SOLID PIGMENT AND INTERLOCKS THESE PARTICLES TO FORM A TOTALLY INORGANIC COATING

- CURE SCHEDULE
  - 24 HOURS AT AMBIENT TEMPERATURE AND RELATIVE HUMIDITY >50%
  - BAKE-OUT STEP AT 300 TO 400°F (2-4 HOURS)

PIGMENTS EVALUATED IN HIGH TEMPERATURE SOLAR PAINTS

- $CoO \cdot Co_2O_3$ (Co_3O_4)
- CoO
- $Mn_{.9}Zn_{.1} \cdot Fe_2O_4$
- (Fe-Mn-Cu) Ox
- (Cu-Cr) Ox (4)

$FeO \cdot Fe_2O_3$ (Fe_3O_4)
PbS
CuO
$CuO \cdot V_2O_5$
$CuO \cdot WO_3$
$CoO \cdot WO_3$
$CoO \cdot Cr_2O_3$
$Co \cdot Fe_2O_4$
$CoO \cdot BaO \cdot 8Fe_2O_3$
$LiCoO_2$
$Ni_{.35}Zn_{.65}Fe_2O_4$
$(Li_{.5}Fe_{.5})_{.9}Zn_{.1}Fe_2O_4$
$SrO \cdot 6Fe_2O_3$

ACCEPTANCE CRITERIA

- $\alpha \geq 0.95$
- NO CHANGE IN α AFTER HEATING IN AIR AT 500°C FOR 24 HOURS

HIGH TEMPERATURE SOLAR COATINGS

		α		
PIGMENT	BINDER	AS PREPARED	AFTER 24 HRS AT 500°C	AFTER 24 HRS AT 700°C
$CoO \cdot Co_2O_3$	SILICATE	0.98	0.96	0.97
"	SILICONE	0.97	0.97	0.97
CoO	SILICATE	0.97	0.98	
"	SILICONE	0.97	0.97	0.96
$(Fe\text{-}Mn\text{-}Cu)O_x$	SILICATE	0.97	0.97	0.99
"	SILICONE	0.98	0.98	0.99
$(Cu\text{-}Cr)O_x$	SILICATE	0.96	0.97	0.96
"	SILICONE	0.97	0.97	0.97
$(Cr\text{-}Cu)O_x$	SILICATE	0.96	0.96	0.95
"	SILICONE	0.96	0.96	
$(Cu\text{-}Cr)O_x$	SILICATE	0.95		0.95
"	SILICONE	0.95	0.95	0.95
$(Cr\text{-}Cu)O_x$	SILICATE	0.97		0.96
"	SILICONE	0.96	0.94	0.94
$Mn_{.9}Zn_{.1}Fe_2O_4$	SILICONE	0.95	0.95	
$FeO \cdot Fe_2O_3$	SILICATE/SILICONE	0.97		0.91 (-200 mesh) 0.77 (5μ)

SOLAR ABSORPTANCE
MEASUREMENTS OF METAL SUBSTRATES

METAL SUBSTRATE	SUBSTRATE PREPARATION	THERMAL TREATMENT IN AIR	α
HASTELLOY X	SOLVENT CLEANED	NONE	0.54
"	GRIT BLASTED	"	0.62
"	"	24 HRS AT 700°C	0.88
"	"	1 1/2 HRS AT 900°C	0.89
"	"	24 HRS AT 900°C	0.90
"	SOLVENT CLEANED	1 1/2 HRS AT 900°C	0.78
"	"	24 HRS AT 900°C	0.88
RENÉ 41	SOLVENT CLEANED	NONE	0.53
"	GRIT BLASTED	"	0.60
"	"	24 HRS AT 700°C	0.88
"	"	24 HRS AT 900°C	0.87
"	SOLVENT CLEANED	24 HRS AT 900°C	0.84

COATING PROPERTIES OF INTEREST

- STABILITY OF OPTICAL PROPERTIES WITH TEMPERATURE AND TIME
  - OXIDATIVE STABILITY
  - MOISTURE STABILITY

- INTEGRITY OF COATING-SUBSTRATE BOND UNDER LONG TERM HIGH TEMPERATURE SERVICE CONDITIONS
  - TEMPERATURE CYCLING CAPABILITY
  - RESISTANCE TO THERMAL SHOCK

- INDEPENDENCE OF ABSORPTANCE ON ANGLE OF INCIDENCE

CONCLUSIONS

- IDENTIFIED EIGHT CANDIDATE PIGMENTS THAT YIELD COATINGS WITH $\alpha = 0.95$ TO 0.99 WHEN FORMULATED IN SILICATE AND SILICONE BINDERS.

- HIGH α, NONSELECTIVE COATINGS MAY EXHIBIT HIGHER EFFICIENCIES THAN SELECTIVE COATINGS OF ONLY SLIGHTLY LOWER ABSORPTANCE IN APPLICATIONS WHERE HIGH SOLAR CONCENTRATIONS ARE EMPLOYED.

- ABSORBER PAINTS ARE AMENABLE TO "IN-PLACE" REPAIR.

- NO NEED FOR CONTROL OF COATING THICKNESS.

MR. RICHMOND: I was curious why you didn't look at the nickel oxide mixed with oxides of cobalt, iron, and manganese.

MR. MUENKER: Well, we have manganese in there and I looked at nickel sometime ago under a different program and I was never able to get numbers that were in excess of 0.95. It doesn't mean that I have exhausted all possibilities with nickel.

MR. RICHMOND: It seems to me that in evaluating the binders you need to know both the adhesion to the substrate and the cohesion of the coating and that if you are going to try to evaluate them you should evaluate them separately. You said that there was no need for thickness control and I think that is somewhat of an oversimplification. There is no need for thickness control providing it is thick enough. You have to make sure it is thick enough.

MR. IGNATIEV: In terms of the thickness, have you worried about the thermal conductivity of the coatings?

MR. MUENKER: Well, you see there are concerns about not only the thermal conductivity, but coefficient of expansion. What you would like is a complete match and you won't get that. That is quite impossible. With the silicone maybe it isn't that important because silicones have some elasticity. The silicates do not. But, on the other hand, if you then suggest that the silicones once you go up to these high temperatures become silicates anyway, you are back again to the same thing. I would say that the bonding properties of the high temperature coatings are probably the most critical, not the high α so much. Of course I am making the assumption that the α I have seen here will be essentially the α at the operating temperature.

MR. IGNATIEV: In terms of thermal conductivity, of course you realize that in real operation you could conceivably generate significant temperate gradients between the back and the front of the film.

MR. MUENKER: Oh, yes. No question about it.

MR. IGNATIEV: Also particle size--how big? How small?

MR. MUENKER: Most of the products are in the order of 1 μm . There are some that are simply listed as -325 mesh which means that the particle size is smaller than 45μm but probably in most cases it is closer to 1 μm

MR. MELAMED: In a non-selective coating, it is obviously not significant and in fact we shouldn't bother to speak about what the is measured over in terms of wavelength. So when you speak of an of 0.98 and attempt to compare that to an of 0.95 in the selective coatings, to what extent are these numbers comparable?

MR. MUENKER: Yes. I would have to take that into consideration. It is a small difference, but it is nevertheless a difference.

MR. SIEVERS: How did you measure alpha?

MR. MUENKER: Beckman Recording Reflectometer and then we used the weighted averaged method to compute the α We are going to send all of these samples that are of interest out to independent laboratories so we get a check on them. Many of them show a reflectance that is just very, very flat and a slight increase as you go out to a higher wavelength.

MR. SCHWARTZ: What wavelength did you take it out to?

MR. MUENKER: 0.35 μm to 2.2 μm Some of them have a peak at around 1 μm only a few percent higher. In each case when we made the measurement we used the 3M coating, the velvet coating which has $\alpha = 0.98$. It is very flat, just a slow increase. It is below two percent and then goes up to a little bit above two percent.

MR. RICHMOND: How did you apply the 3M?

MR. MUENKER: The same way we applied the other coatings, by spray coating.

MR. RICHMOND: You get higher absorptance by spraying it than when you brush it?

MR. MUENKER: The brush marks may give you some trapping effects.

MR. RICHMOND: No, you get the higher absorptance on the spray coating.

MR. MUENKER: I must say I now recall I've seen that with other coatings as well between brushing and spraying there are small differences and I'm not sure they are always in the same direction. I think I have observed the opposite effect, that the brushed coating generally had a higher alpha than with the spray coatings which I interpret to mean that it affected the surface characteristic of the coating.

MR. RICHMOND: When the coating is sprayed you may get evaporation of some of the vehicle before it actually hits so that you have a coating with a much higher viscosity when it actually hits the surface and you don't get the smoothing out that you do with a brush coating, so you get a much rougher surface.

MR. MUENKER: Well, you see what you do is when you brush and when you spray you usually use different viscosities. In other words you have more solvent in there when you spray than when you brush.

Thin Film Absorber Coatings from Metallo-organic Solutions

James Dickson

Engelhard Industries Division,
Engelhard Minerals and Chemicals Corporation
Menlo Park, Edison, New Jersey

Summary of Presentation

This program explores the development of selectively absorbing films for the thermal conversion of solar energy at high temperatures prepared by the thermal decomposition of metallo-organic solutions. Initially the concept was directed toward films for power tower boiler uses at greater than 500°C. The program was based upon gold matrix films with 0.5α_s developed in 1962-63 by Engelhard Industries for use in space. The data for the first sixteen months of this two year program will be presented.

All films were prepared from metallo-organic compounds dissolved in suitable solvents after application by painting on surface of glass, quartz and metallic substrates, and air firing at 500-800°C. The films thus produced are 1000-2000 Å thick and consist of unique metal oxide systems. The compositions of the films are controlled by regulating the solution chemistry and composition. The methods for characterizing these films will be briefly described, including optical measurements, high temperature emittance measurements and scanning electron microscopy.

The advantages of thin films prepared by the Engelhard process are durability of the metal/oxide systems, the low cost and flexibility obtained through thickness control by application techniques (present technology), the ability for selected area applications, and the adaptability to mass production. These films are expected to be thermally stable and durable since they are air fired at 500-800°C.

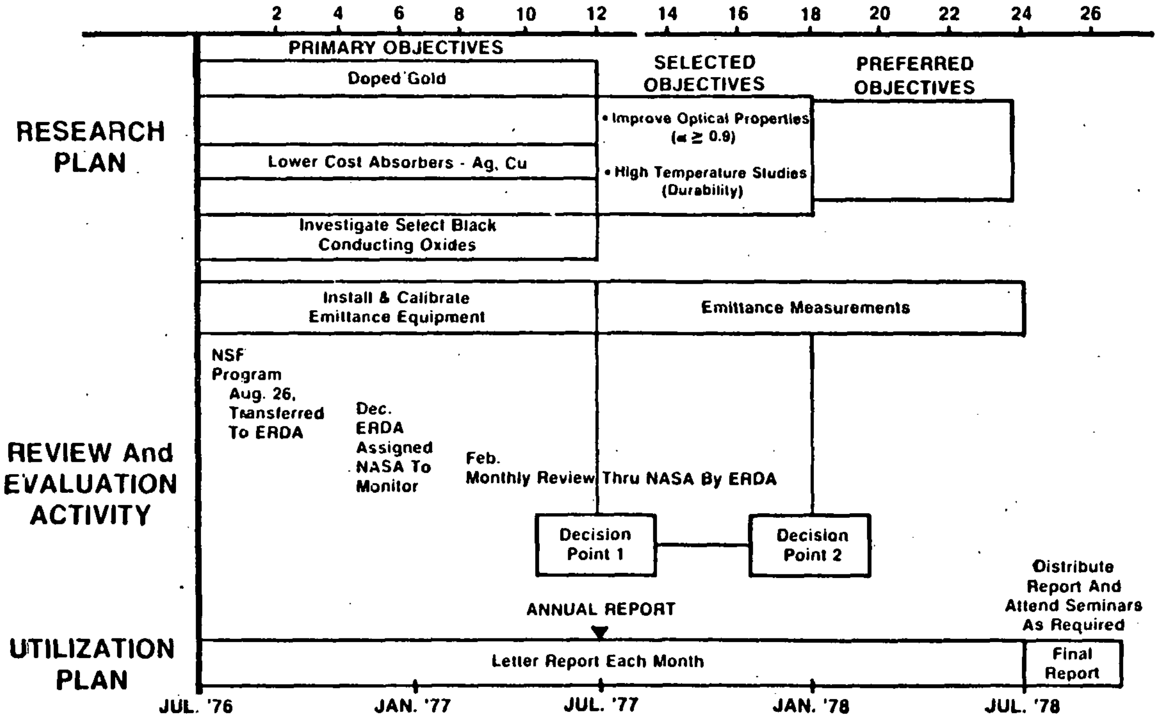
The data show an improvement of α_s from 0.5 to 0.8 in gold matrix material. The emissivity of these films has remained at less than 0.06 at 540°C.

In order to employ materials less expensive than gold, investigations were carried out in silver and copper matrices. A silver matrix copper oxide film on stainless steel substrates was developed with an absorptance of 0.9 and an emissivity of 0.06 at room temperature and 0.1-0.2 at 500°C. The upper temperature for use of this film has still to be determined. It appears it will be below 500°C.

Attempts were made to prepare films of other conductive, black oxides such as lead ruthenate and palladium cobaltate. Studies of these films indicated that they were unsuitable as selective absorber coatings.

Future work will be directed to improve the optical properties of the silver matrix/copper oxide thin films by investigating the film structure, the use of antireflecting coatings, and the effects of the characteristics of the substrate surface. In addition, the thermal stability and the emittance at high temperature of these films will be determined with a goal of $\alpha_s \geq 0.9$, ε_t of ≤ 0.1 and demonstrated long term stability in air and vacuum.

SCHEDULE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RESEARCH PLAN
PRIMARY OBJECTIVES
Doped Gold
Lower Cost Absorbers - Ag, Cu
Investigate Select Black Conducting Oxides
SELECTED OBJECTIVES
• Improve Optical Properties (α ≥ 0.9)
• High Temperature Studies (Durability)
PREFERRED OBJECTIVES
Install & Calibrate Emittance Equipment
Emittance Measurements
REVIEW And EVALUATION ACTIVITY
NSF Program Aug. 26, Transferred To ERDA
Dec. ERDA Assigned NASA To Monitor
Feb. Monthly Review Thru NASA By ERDA
Decision Point 1
Decision Point 2
UTILIZATION PLAN
ANNUAL REPORT
Letter Report Each Month
Distribute Report And Attend Seminars As Required
Final Report
JUL. '76
JAN. '77
JUL. '77
JAN. '78
JUL. '78

ADVANTAGES OF ENGELHARD THIN FILMS

1 Production of Unique Metal/Glass Systems by Solution Adjustment — (High α, Low ϵ and Durable).

2 Thickness Control by Application Technique — (Low Cost and Flexible).

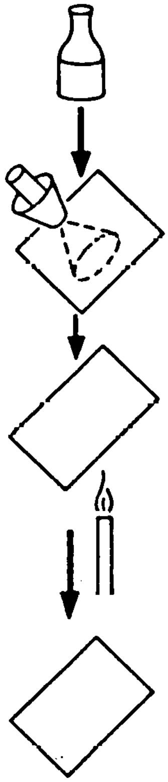
3 Selected Area Application — (Low Cost).

4 Uses Established Mass Production Techniques — (Low Cost).

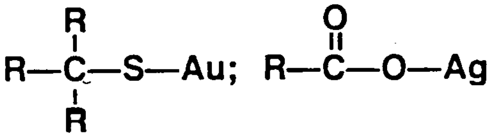
5 Applied With Air Firing At Up to 900°C (Thermally Stable and Durable).

ENGELHARD

FILM FABRICATION



METAL RESINATES :



$R{-}\overset{R}{\underset{R}{C}}{-}S{-}Au;\quad R{-}\overset{O}{\overset{\|}{C}}{-}O{-}Ag$

"PAINT" SOLUTION ON SUBSTRATE : Spray, Brush, Screen

AIR FIRE : 500°C — 800°C (Typical)

PROPERTIES : Thickness — 1000 A° — 2000 A°
Unique Metal/Glass Systems
Easy Composition Control

ENGELHARD

COATING GOALS

1. Absorptance (α_s) $\geqslant 0.9$
2. Emittance (ϵ_t) $\leqslant 0.1$
3. Demonstrate Long Term Thermal Stability In Air and Vacuum.

ENGELHARD

TECHNICAL SUMMARY; FIRST SIXTEEN MONTHS

1. Increased α_s From 0.5 To 0.8 For "Doped Gold" Coating, Retained ϵ_t of 0.06
2. Developed Ag/CuO Coating With $\alpha_s = 0.9$, $\epsilon_t < 0.1$
3. Poor ϵ_t For "Black Conducting Oxides"
4. Developed High Temperature Emittance Instrumentation

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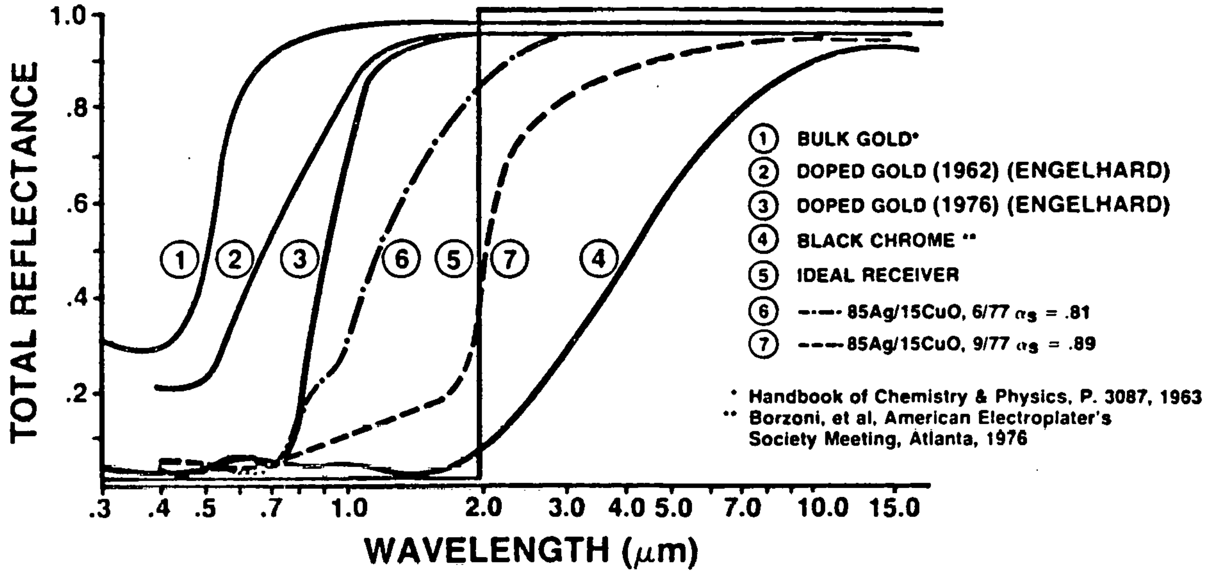
OPTICAL PROPERTIES OF SOLAR ABSORBERS



* Handbook of Chemistry & Physics, P. 3087, 1963

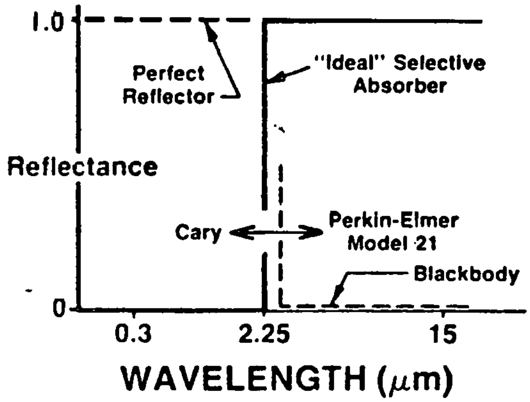
** Borzoni, et al, American Electroplater's Society Meeting, Atlanta, 1976

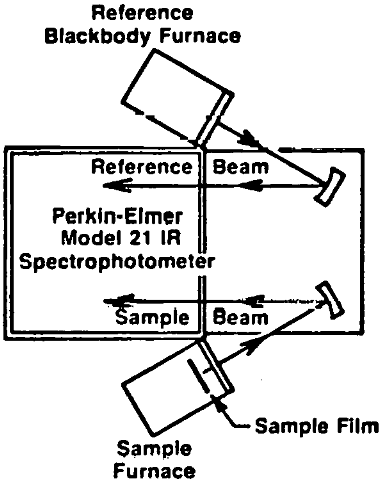
FILM CHARACTERIZATION

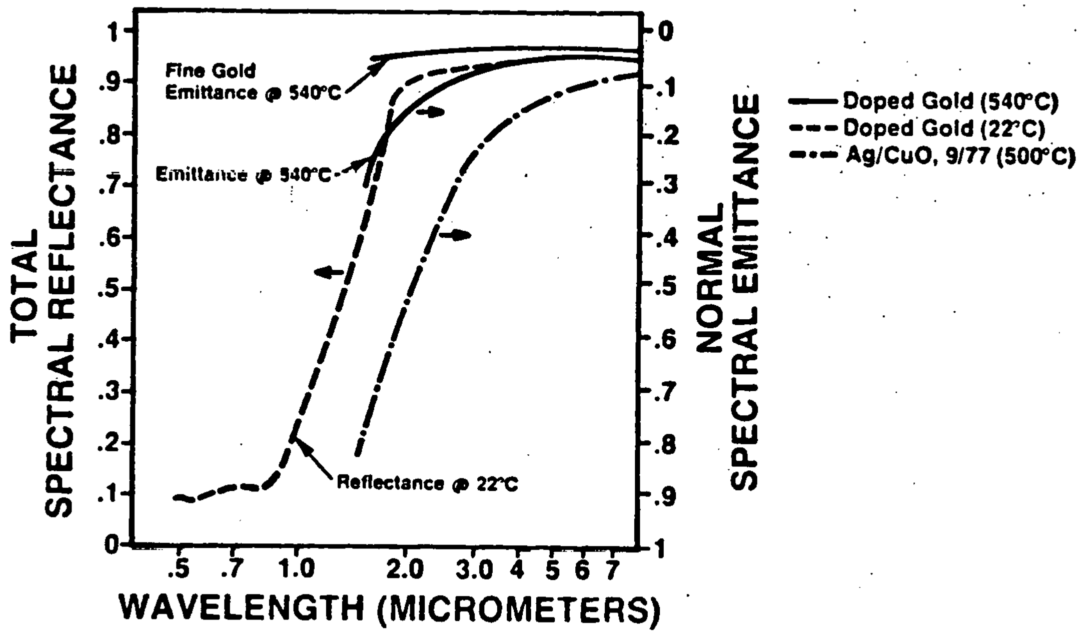
INSTRUMENTATION: Spectrophotometer Modified For Specular or Hemispherical Reflectance Measurements.

THEORY : For Opaque Samples: Absorbance = 1 - Reflectance

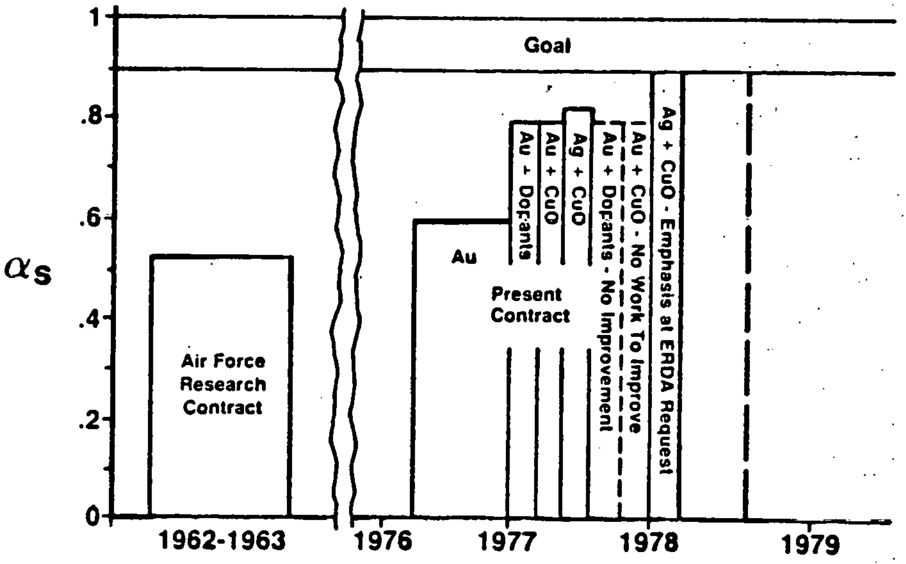
At Thermal Equilibrium: Emittance = Absorbance







IMPROVEMENTS IN ABSORPTANCE



PLANS FOR FUTURE WORK

1 Improve Optical Properties of Ag-CuO System
   - A. Film Structure
   - B. Anti-Reflection Coating
   - C. Substrate Surface Effects

2 High Temperature Studies of Primarily Ag-CuO System
   - A. Thermal Stability
   - B. High Temperature Emittance

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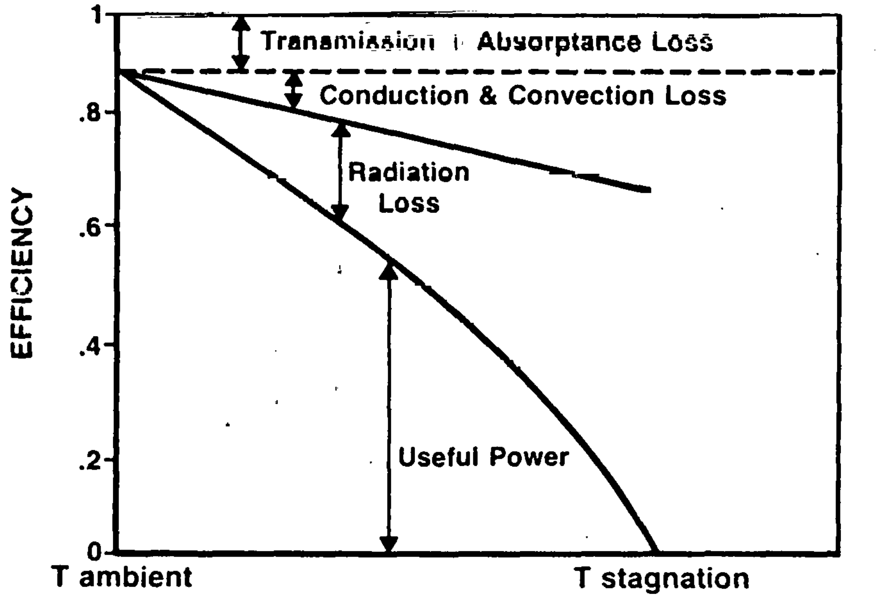
IMPACT OF ABSORBER COATING PROPERTIES (α, ϵ) ON SOLAR COLLECTOR EFFICIENCY

$$\text{Efficiency} = \frac{\text{Useful Power (To Process)}}{\text{Input Power (From Sun)}} \qquad \text{Efficiency} = -\frac{1}{HC}\left[R(T_1-T_2) + \overset{\epsilon\sigma}{\swarrow}(T_1^4 - T_2^4)\right]$$

GRAPHICAL BREAKDOWN OF COLLECTOR EFFICIENCY



AVERAGE TEMPERATURE OF COLLECTOR

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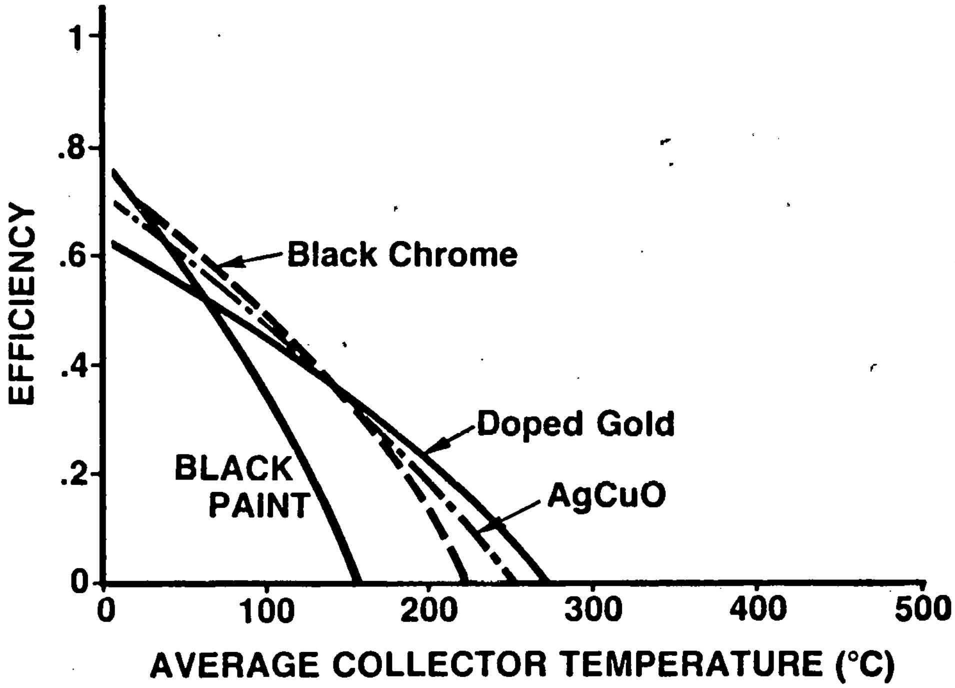
COMPARISON OF SOLAR COATINGS FOR DOUBLE GLAZED FLAT PLATE (1X)



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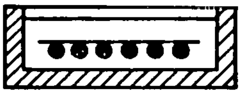
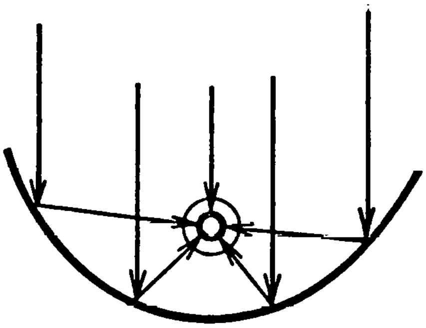
DESIGN CONSIDERATIONS

FLAT PLATE (1X)

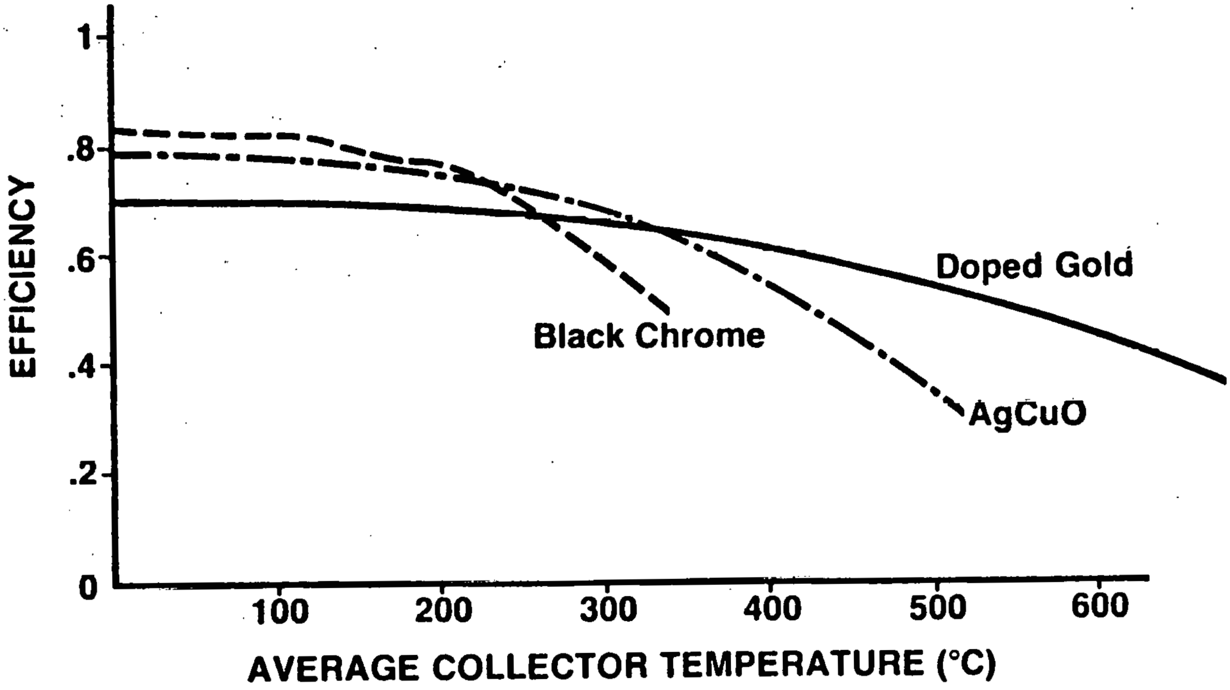


PARABOLIC TROUGH (10X)



ENGELHARD

COMPARISON OF SOLAR COATINGS FOR PARABOLIC TROUGH (10X) WITH SINGLE GLAZE AND AN EVACUATED LINEAR RECEIVER



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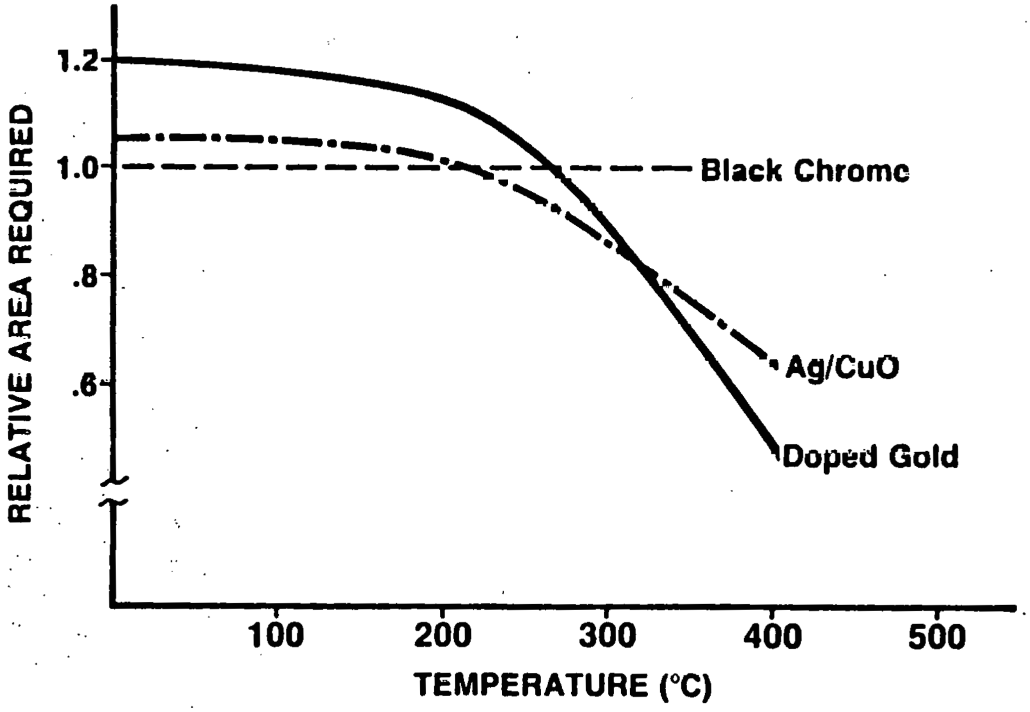
RELATIVE AREA (SOLAR WINDOW) REQUIRED TO PRODUCE THE SAME QUANTITY OF HEAT BASED ON THE NOMINAL EFFICIENCY OF BLACK CHROME AT THE GIVEN TEMPERATURE



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MR. LIN: Can you describe in a little more detail how you apply the coatings?

MR. DICKSON: We are using a spray paint technique like you see at the amusement park where you put a solution in and spray it. That's for consistency and also for the ability to be able to change the thickness of our film. We can put these films down with a brush or with a silkscreening and printing technique.

We have not gone into any detail, but there may be the possibility of using solar reflectors to repair the films in situ. We do not see significant degradation if we put on a multiple coating, so if we do overrun the actual repair section, the performance of the rest of the collector would not deteriorate. The curing temperature of silver was up to about 650 C, in the range of about six to thirty minutes in air. For gold we have done some films up to 800 and 900 C. Again, some of the firing has been for as short as five minutes and some has been as long as thirty minutes.

MR. VOSSEN: What's the gold doped with and to what extent?

MR. DICKSON: In the case of gold we are talking someplace about 80 to 85 percent gold. Copper is approximately 15 percent and the dopants contain silicates, barium, chrome, and rhodium. One of the things I need to bring up is that there definitely is the ability to use gold in these films. We are talking about material cost of under a dollar, 88 cents/ square foot for the gold. MR. PETTIT: Do you obtain the same selective properties for coatings that are a couple of microns thick?

MR. DICKSON: We are talking here about 1000 to 2000 angstroms. We have not investigated thicker coatings.

METAL OXYCARBONITRIDE SOLAR ABSORBERS

by

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Bureau of Mines
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Albany, OR 97321

GENERAL

A family of carbides, oxides, and nitrides of certain Group IV metals has been found to possess a high degree of spectral selectivity in the wavelength range of interest as solar absorbers. The compounds are of the general formular $MC_xO_yN_z$ where M is titanium, zirconium, or hafnium, and $x + y + z$ is less than 2. Thin films of the oxycarbonitrides of these elements were found absorptive in the solar spectrum while being very transparent in the longwave thermal spectrum. A reflective base, such as silver or aluminum, used beneath the absorptive film, controlled the longwave emittance of the substrate. The selectivity transition occurs, as in the usual thin film absorber, near the wavelength corresponding to the first interference minima of the transparent film. A high extinction coefficient in the shortwave spectrum suppresses the shortwave interference maxima.

SPECIMEN PREPARATION

The absorptive films were prepared by reactively sputtering the metal or the metal carbide in the presence of low pressure nitrogen, oxygen, carbon monoxide, or their mixtures. Because the partial pressure affects the metal-gas reaction, a wide range of compositions from pure metal M to stoichiometric MC, MN, MO_2, or a combination of any could be prepared. A second method for achieving absorptive films was by heating a thin metal film of zirconium in air to produce ZrO_xN_y. More information on experimental procedure is given in reference 1.

The solar absorptance and thermal emittance could be varied over a wide range by adjusting the composition and thickness of the film. By sacrificing absorptance, it was easy to achieve very low longwave emittance and very high values of $\alpha(s)/\epsilon(T)$, (over 40 at 327° C). However, considerable effort was directed toward maximizing solar absorptance because of its great importance.

Solar absorptance and thermal emittance were calculated by numerical integration of the normal reflectance data. The solar distribution of Moon for AM2 was used.

RESULTS

The resulting solar absorptance and the emittance at 327° C for selected specimens of the types developed are summarized in table 1. Among all the compositions studied, substoichiometric compounds of TiN_x, ZrN_x, and ZrC_xN_y (on silver) were found to possess the best overall combination of high solar absorptance, and low thermal emittance. Normal spectral reflectance curves for typical specimens are shown in figure 1. Calculated values of solar absorptance were 0.86 to 0.88, and for thermal emittance, 0.034 to 0.065 at 327° C. The optical properties of TiN_x and ZrN_x were nearly identical, but HfN_x had neither as high a solar absorptance nor as low a longwave emittance as the former two. The suboxide films, TiO_x and ZrO_x also had less solar absorptance, 0.72-0.80, with longwave emittance up to 0.42. The best pure carbide film, ZrC, had solar absorptance of 0.81 and longwave emittance of 0.075 at 327° C. A carbon addition to the zirconium nitride film to form ZrC_xN_y was beneficial as it tended to increase solar absorptance by several points. The substitution of oxygen in the nitrides or carbonitrides to form ZrO_xN_y or $ZrC_xO_yN_z$, generally decreased solar absorptance and increased longwave emittance. A notable exception was the type of absorptive film produced by oxidation of a Zr film which resulted in solar absorptance up to 0.93. The normal spectral reflectance curves for two of these oxidized specimens are shown in figure 2. Additional results are in reference 2.

Attempts to increase the solar absorptance were made by altering the morphology of the interfaces. One scheme, an aluminum reflective film with a preferred orientation of growth, increased absorptance by 0.05 (table 1, No. 451). A second scheme, a thin amorphous AlO_x film about 300A thick over the absorptive film increased the absorptance 0.03 to 0.14 (table 1, No. 412C and 413C).

The effects of composition on the reflectance of the $MC_xO_yN_z$-reflector system can be partially generalized. Beginning with the pure metals, as the quantity $(x + y + z)$ increases from zero the reflectance decreases over the shortwave spectrum and increases over the longwave spectrum. At certain compositions, the spectral selectivity becomes marked and the longwave reflectance approaches that of the reflective film. The transition wavelength can be adjusted by choosing the proper film thickness to satisfy interference requirements. As the quantity $(x + y + z)$ approaches stoichiometric values (especially for oxygen), a pronounced interference pattern develops in the shortwave region of the spectrum indicating increasing transparency of the $MC_xO_yN_z$ film.

ELEVATED TEMPERATURE PROPERTIES

Calculated absorptance and emittance values were confirmed by measurements carried out at elevated temperature. Normal spectral reflectance measurements at a temperature of 500° C in vacuum by Masterson and Seraphin (3) showed only a slight dependence of reflectance on temperature. The normal spectral reflectance curves for specimen 422 (table 2), presented in figure 3, indicate no appreciable difference in reflectance between room temperature and 600° C. At 700° C the reflectance decreased irreversibly because of deterioration of the reflective film. Most of the other specimens tested had a slightly lower reflectance in the solar spectrum at 400°-500° C than at room temperature (reversible) while the longwave reflectance was unchanged. This corresponded to an increase in solar absorptance of about 0.02 while the emittance would be the same as that calculated from room temperature data.

Normal total emittance measurements were also carried out on a number of specimens to temperatures of at least 500° C. The emittance data for three typical stabilized specimens are plotted in figure 4. Values of emittance calculated at 327° C from the reflectance data for these specimens agreed very well with these emittance data at 327° C. The relatively large rate of increase in emittance with temperature is typical of a highly selective surface such as these specimens possess.

STABILITY

The stability of tandem absorptive-reflective films was also evaluated. Free energy differences favor the oxidation of the absorptive $MC_xO_yN_z$ film to MO_2 at any pressure from atmospheric to below 10^{-10} Torr. The kinetics, however, are very slow at room temperature. Specimens stored in air at room temperature have remained stable to the present (up to 3 years). The early specimens were not stable and began losing several percent of solar absorptance at temperatures above 125° C in air. By adding a thin film (300A) of aluminum oxide to act as a diffusion barrier, the stability in air was increased to about 175° C. Under "vacuum" in a sealed tube, the absorptive films were relatively stable at high temperature. Several absorptive films survived cumulative heating periods of 500 hours to the maximum test temperature, 700° C. Under these conditions, the films changed composition slightly as equilibrium with the gas phase was approached. The stability test data for four specimens are given in table 2. Note that heating the specimen in "vacuum" in some instances produced an increase in solar absorptance. The substitution of carbon for nitrogen in ZrN_x seemed to improve the high temperature stability.

The stability of the tandem films at high temperature in vacuum was limited by the agglomeration of the silver film. Initially limited to about 350° C, stability was increased by the method of Seraphin, namely, addition of a film of chromium oxide beneath the silver. A number of other oxides were also found to stabilize silver, and even a substrate of oxidized pure iron was discovered to be satisfactory. The limit of silver stability achieved was about 500° C. Surprisingly, an aluminum reflective film on oxidized stainless steel was found stable to at least 600° C in vacuum (table 1, No. 422 and figure 3).

RANEY COMPOUNDS

A novel method for producing a very fine open structure in a metal film should be mentioned. "Raney nickel" type alloys were prepared by co-sputtering nickel, zirconium, or molybdenum with aluminum. After etching the aluminum out of such a $ZrAl_3$ film, the resulting fine structure had a solar absorptance over 0.95 with some degree of spectral selectivity (table 1). Methods of combining the characteristics of controlled morphology of metals with intrinsic selectivity deserve further investigation.

This work was discontinued in September 1976 and will not be resumed because it was determined that it was not within the mission of the Bureau of Mines' metallurgy research program, since the creation of ERDA and DOE.

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1. Blickensderfer, R., R. L. Lincoln, and D. K. Deardorff. Reflectance and Emittance of Spectrally Selective Titanium and Zirconium Nitrides. BuMines Report of Investigations 8167, U.S. Dept. of the Interior, 1976, 24 pages.

2. Blickensderfer, R., D. K. Deardorff, and R. L. Lincoln. Spectral Reflectance of TiN_x and ZrN_x Films as Solar Absorbers. Solar Energy, Vol. 19, No. 4, 1977, pp. 429-432.

3. Masterson, K. D., and B. O. Seraphin. Investigation of High Temperature Performance of Thin Film, Solar-Thermal Energy Converters. Optical Sciences Center, Univ. of Arizona, BuMines Grant No. G0254032, September 1976, 28 pages.

TABLE 1. - Composition and properties of selected $MC_xO_yN_z$ absorbers.

Spec. No.	Outer film	Absorptive film			Reflective film	[1]$\alpha(s)$	[1]$\epsilon 327°$ C	$\frac{\alpha(s)}{\epsilon 327° \text{ C}}$
		Nominal	Gas	Solid				
150	--	ZrO_x	O_2	Zr	Ag	0.72	0.42	2
228	--	TiO_x	O_2	Ti	Ag	.80	.067	12
306	--	CrO_x	O_2	Cr	Ag	.74	.079	9
226	--	ZrN_x	N_2	Zr	Ag	.86	.039	22
264	--	ZrN_x	N_2	Zr	Cu	.82	.059	14
342	--	TiN_x	N_2	Ti	Ag	.88	.065	14
234	--	TiN_x	N_2	Ti	Ag	.80	.034	24
412C	AlO_x	TiN_x	N_2	Ti	Ag	.94	.17	6
489	--	HfN_x	N_2	Hf	Ag	.76	.027	28
325	--	CrN_x	N_2	Cr	Ag	.67	.15	5
329	--	ZrC	--	ZrC	Ag	.81	.075	11
193	--	[2]ZrO_xN_y	air	Zr	Ag	.88	.084	10
187	--	[2]ZrO_xN_y	air	Zr	Ag	.93	.30	3
284	--	ZrO_xN_y	air	Zr	Ag	.77	.086	9
205	--	ZrC_xO_y	CO	Zr	Ag	.71	.034	21
332	--	ZrC_xN_y	N_2	ZrC	Ag	.88	.040	22
422	--	ZrC_xN_y	N_2	ZrC	Al	.85	.074	11
451	--	ZrC_xN_y	N_2	ZrC	[3]Al	.93	.071	13
413c	AlO_x	ZrC_xN_y	N_2	ZrC	Ag	.91	.048	19
331d	ZrO_x	ZrC_xN_y	N_2	ZrC	Ag	.64	.0137	47
208	--	$ZrC_xO_yN_z$	CO + N_2	Zr	Ag	.66	.020	33
395	--	$ZrAl_3$ "Raney"	--	ZrAl	Ag	.97	.29	3

[1] Numerical integration from normal reflectance data, AM2.

[2] Sputtered Zr film "oxidized" in hot air.

[3] Ultra-fine dendritic aluminum.

TABLE 2. - Stability of MC_xN_y-Ag films (on oxidized stainless steel substrates).

In air			
	α(s)	ε327° C	α(s)/ε327° C
AlO_x-ZrC_xN_y-Ag (No. 413c) initially	0.913	0.048	19
Heated 300 hr, 127° C	.903	.039	23
Plus 300 hr, 177° C	.906	.052	18
Plus 300 hr, 227° C	.86	.032	27
Plus 300 hr, 277° C	.83	.146	5.7

In vacuum			
	α(s)	ε600 K	α(s)/ε600 K
ZrC_xN_y-Ag (No. 332) initially	0.83	0.049	17
15 hr each 300°, 350°, --- 600° C	.82	.047	17
After emittance tests to 510° C	.88	.052	16
Plus 500 hr, 500° C	.82	.047	17
Plus 500 hr, 600° C	.88	.071	12
Plus 500 hr, 700° C	.82	.19	4
ZrC-Ag (No. 329) initially	.81	.075	11
After 15 hr each 300°, 350°,--600° C	.78	.048	16
Plus 500 hr, 500° C	.78	.048	16
Plus 500 hr, 600° C	.81	.057	14
Plus 500 hr, 700° C	.80	.15	5
TiN_x-Ag (No. 341) initially	.88	.065	13
After 15 hr each 300°,350°,--600° C	.80	.15	5
Plus 500 hr, 500° C	.80	.15	5

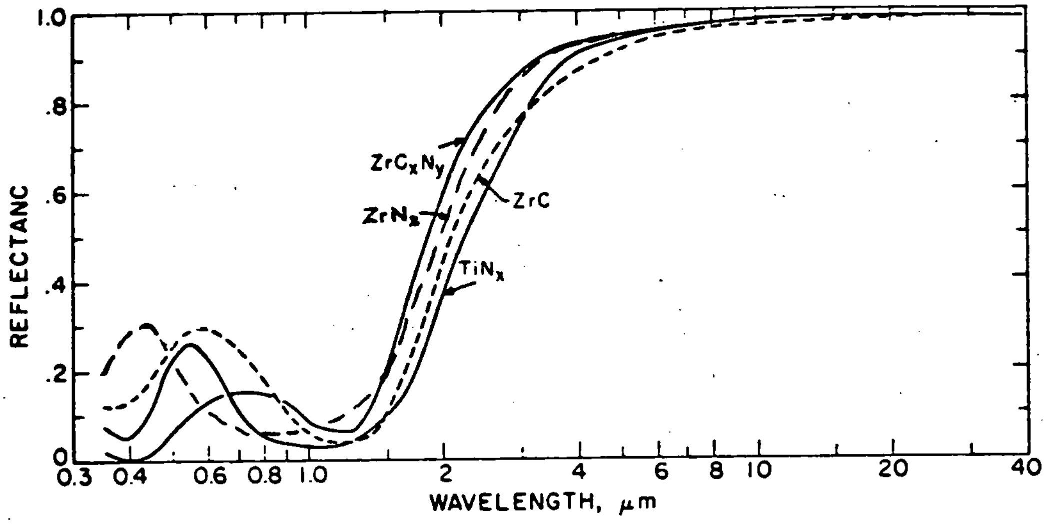

FIGURE 1. - Normal spectral reflectance of selected absorbers.

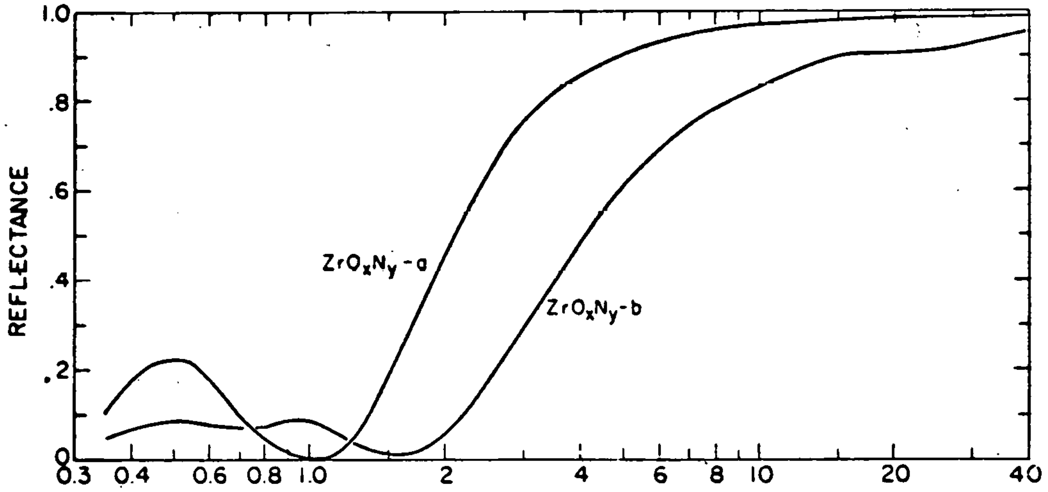

FIGURE 2. - Normal spectral reflectance of stacks prepared by oxidation of Zr.
a. 1,000A Zr film heated in air 24 hrs at 200° C.
b. 2,400A Zr film heated in air 4 hrs at 200° C.

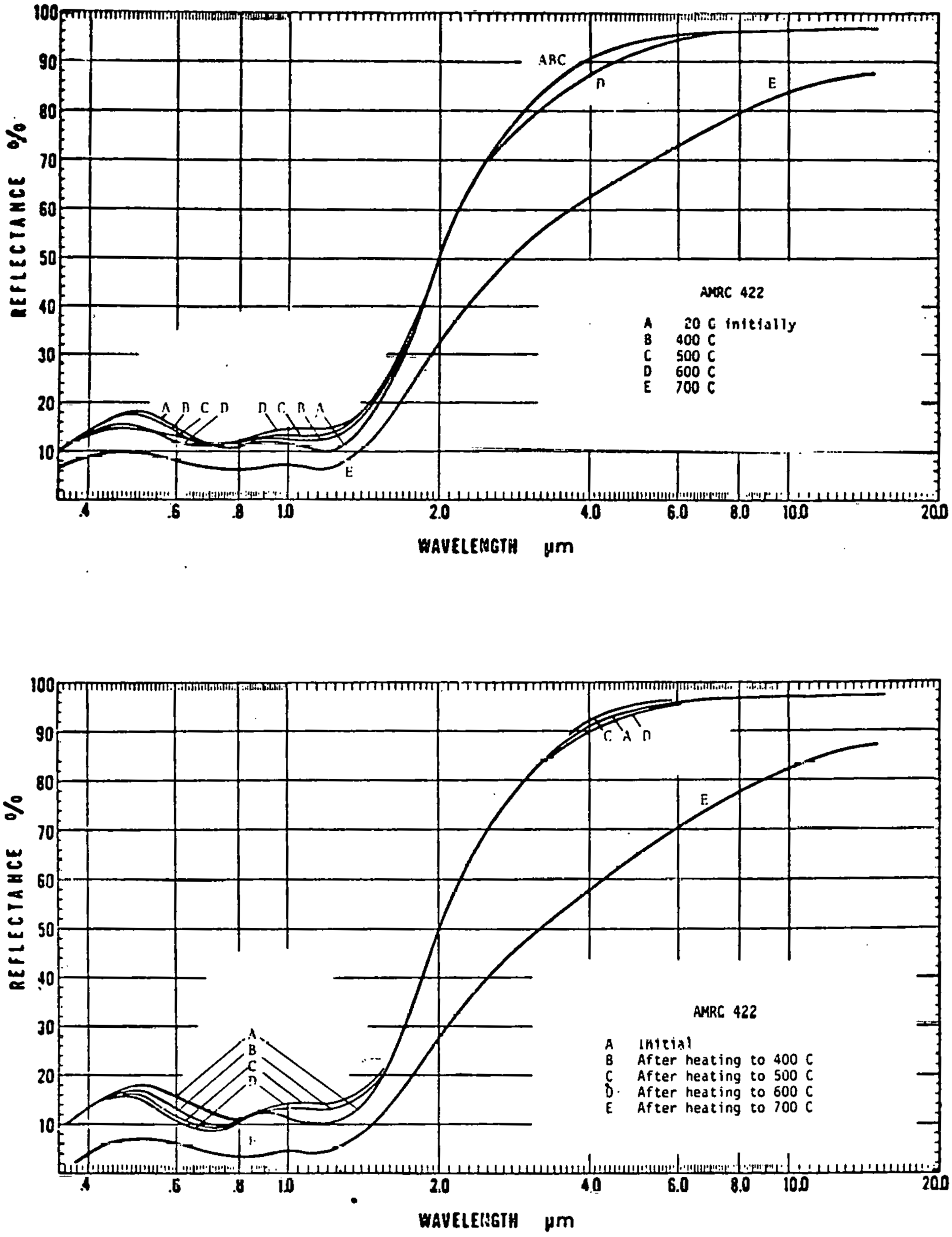

FIGURE 3. - Specular reflectance of ZrC_xN_y-Al, No. 422.
Upper - High temperature. Masterson and Seraphin (3)
Lower - Room temperature. Masterson and Seraphin (3)

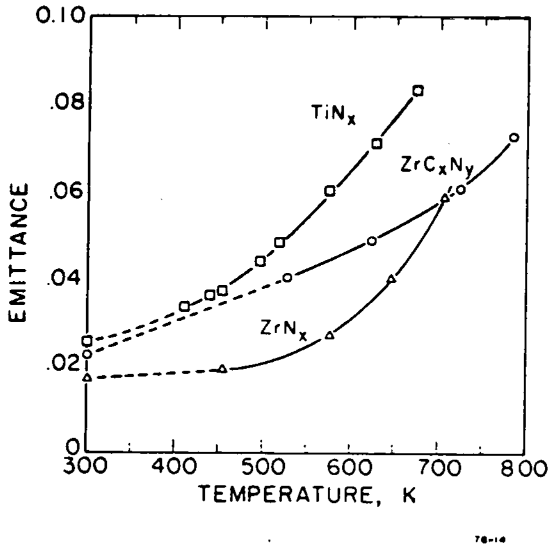

FIGURE 4. - Normal total emittance of three absorbers. Points at 300 K were calculated from room temperature reflectance data.

MR. IGNATIEV: How do you determine stoichiometry of the material?

MR. BLICKENSDERFER: We have determined that on selected specimens by electron microprobe analysis on a nickel substrate.

MR. SERAPHIN: I would just make a general remark with respect to Rob Blickensderfer's work. We have worked for years on this and I was very sorry to see that it was discontinued because it didn't fit the mission of the agency he works for. The materials that he mentioned belong to a group, the transition metal carbides, nitrides, and oxides, and we had for the last two years the contract with NSF in collaboration with the Atomic Energy Commission to study hafnium nitrides, hafnium carbides and titanium nitrides and carbides. What is so interesting about these materials is that they are the materials with the highest melting points in nature. Hafnium carbide with a melting point of about 6000 F is the material with the highest melting point. It is a material from the physicists' point of view that has an extreme degree of flexibility in the design of the optical properties. It is possible in a systematic effort to tailor these materials to whatever kind of applications we have in mind. It is too bad that this work was discontinued because I think it is a very promising avenue.

EFFECTS OF SURFACE OPTICAL CHARACTERISITICS ON POINT FOCUSING SOLAR COLLECTORS

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ABSTRACT

The sensitivity of surface optical characteristics on the performance of representative point focusing solar collectors is assessed from a system point of view. Variations of mirror specular reflectance and selective coating applications inside cavity receivers are the main subject of investigation. The trade-off relationship is presented in terms of rated system efficiency as a function of operating conditions and pertinent design parameters.

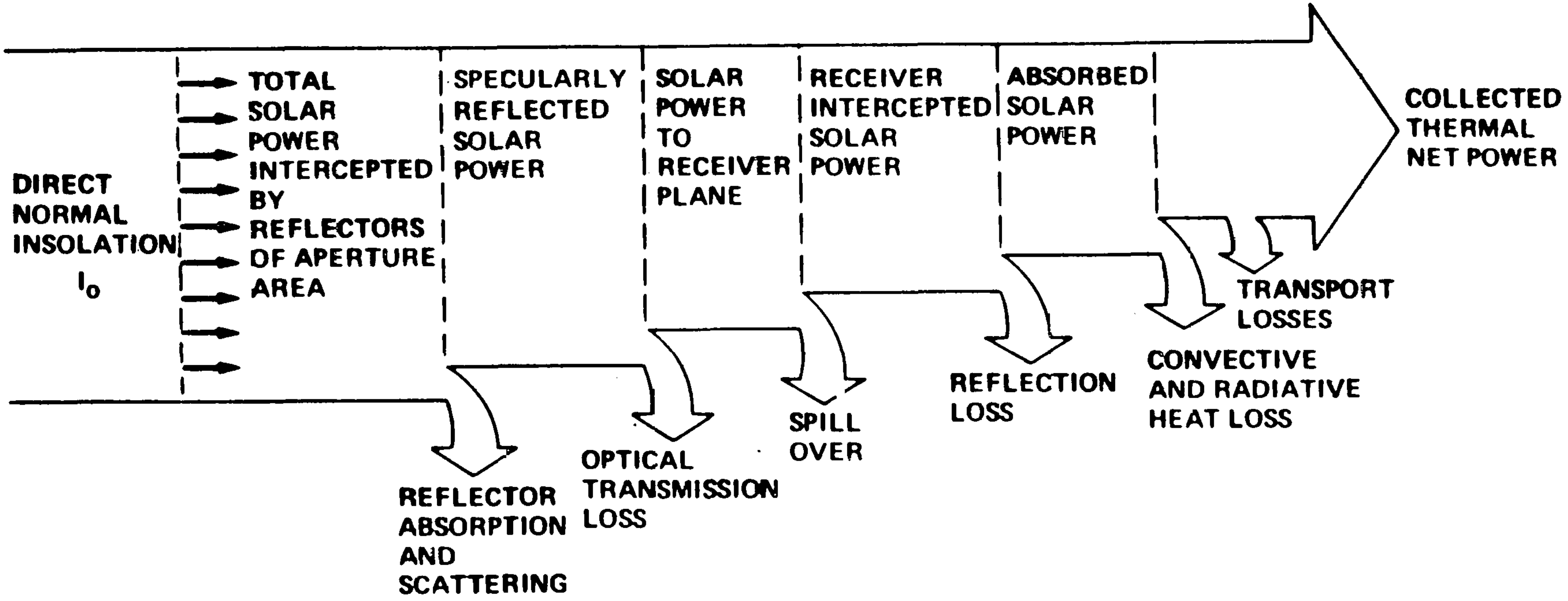
INTRODUCTION

The economic viability of a solar thermal power conversion system depends primarily on the cost effectiveness of the collector design. Design parameters such as material properties and manufacturing tolerance govern not only the system performance but also the capital investment. In order to optimize the solar power plant design for minimum cost per electric power production, it is essential to have a comprehensive understanding of the trade-off relationship among relevent design parameters. In the present paper, emphasis is placed upon the effects of collector optical characterisitcs on the perforamce of a point focusing distributed system. The results are presented in a parametric manner to demonstrate the sensitivity of mirror specular reflectance and selective coating on cavity absorbers for different operating conditions and manufacturing tolerance . The objective is to establish the relative merits of these parameters thus allowing readers to pursue system trade-off optimization as well as for assessing potential pay-offs in related material research programs.

BASIC PARAMETERS

Figure 1 illustrates the conversion process of solar energy into thermal power for a point focusing distributed system. The thermal energy balance relationship can be expressed as the following:

THERMAL ENERGY BALANCE RELATION



[COLLECTED THERMAL POWER AT RECEIVER] = [REFLECTED SOLAR POWER] x [INTERCEPTION FACTOR OF RECEIVER] x [EFFECTIVE RECEIVER SOLAR ABSORPTANCE] − [RADIATIVE + CONVECTIVE HEAT LOSS RATE] x [RECEIVER HEAT LOSS AREA] − [CONDUCTIVE + TRANSPORT HEAT LOSS]

FIGURE 1

$$Q = \rho_s I_o A G \phi \alpha_{eff} - q_r \qquad (1)$$

where

Q = net thermal power collected at the receiver
ρ_s = mirror specular reflectance
I_o = direct normal insolation
A = effective collector area
G = geometrical factor including shading and blocking
ϕ = receiver interception factor
α_{eff} = effective receiver solar absorptance

The heat loss rate from a cavity receiver, q_r , consists of radiative & convective heat transfer from the receiver aperture and conductive heat loss through insulating walls.

$$q_r = \left\{ \epsilon_{eff}\, \sigma\, (T_e^4 - T_a^4) + (h_f + H)(T_e - T_a) \right\} A_o + A_w h_c (T_e - T_a) \qquad (2)$$

where

ϵ_{eff} = effective cavity emittance
σ = Stefan Boltzmann constant
h_f = free convection coefficient; $h_f \simeq 0.6 \times 10^{-3} (T_e - T_a)^{1/3}$ Kw/m^2-°C
H = forced convection coefficient; $H \simeq 0.002\ V$, Kw/m^2-°C
V is the effective wind speed in meters per second
T_e = effective receiver temperature, °C
T_a = effective ambient temperature, °C
A_o = receiver aperture area
A_w = effective cavity wall area
h_c = effective conductive heat loss coefficient, Kw/m^2-°C

In the present study the receiver configuration is assumed to be a cylindrical cavity as shown in Figure 2. The aperture is located at the focal plane of a paraboloidal dish. The size of the solar image at the focal plane is a function of the dish diameter, D, the rim angle , ψ, the mirror slope error, E_s and the reflection spreading angle, $\Delta\omega$. The intensity distribution on the focal plane is highly non-uniform. Majority of the reflected solar energy is concentrated within the focal spot. Away from the image center, the flux density decreases

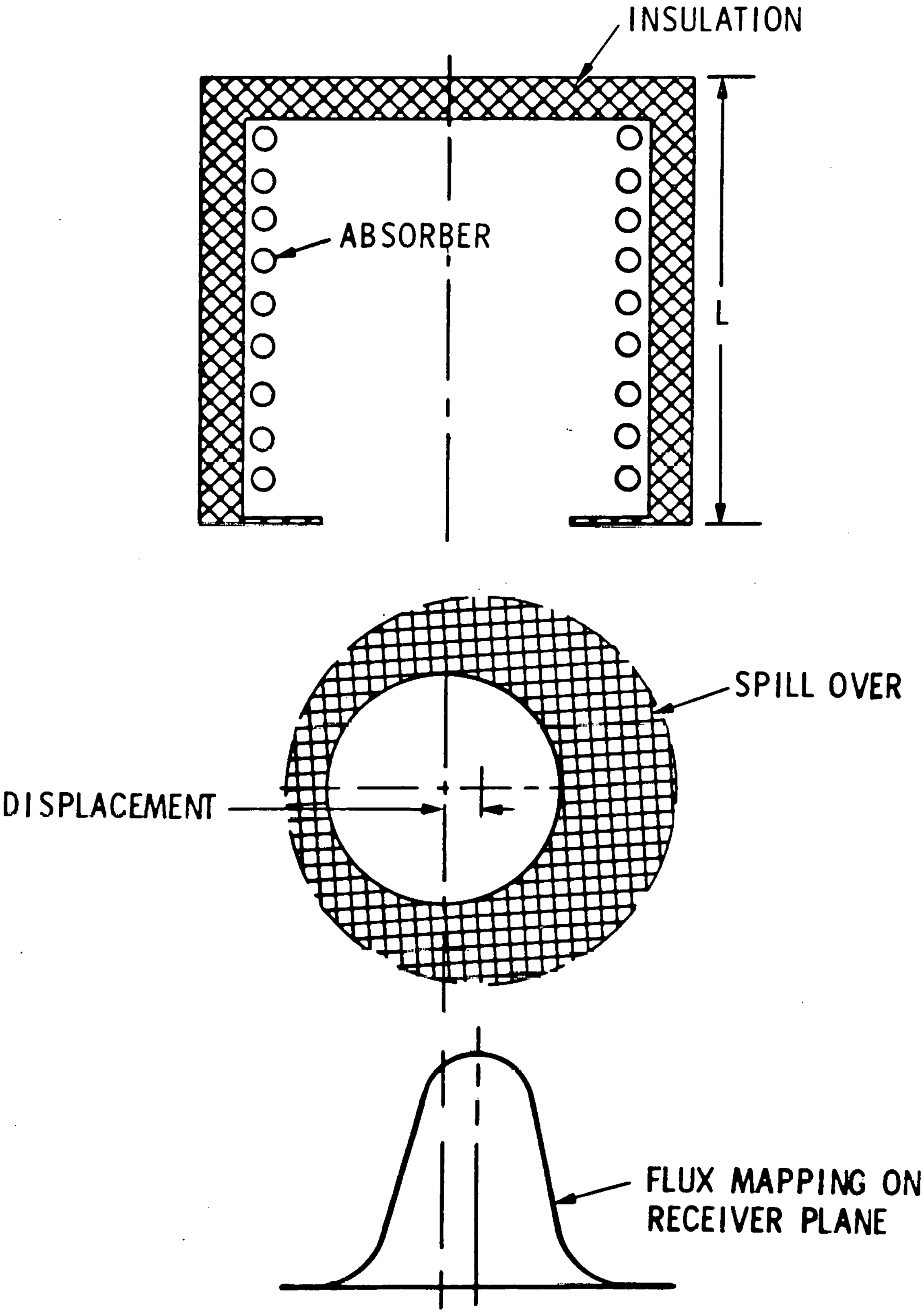


FIGURE 2 REPRESENTATIVE CAVITY RECEIVER

drastically. In general, the geometrical center of the receiver does not coincide with the center of the solar image. This is due to the pointing error, E_p , which includes inaccurate sun tracking, E_t , alignment error and receiver deflection caused by gravity & wind loads, E_d . It should be noted that the receiver aperture size is not an explicit design parameter. The aperture area, A_o , should be sized to allow maximum net thermal energy collection. As shown in Figure 3 the rate of receiver aperture heat loss area change, dA_o/dR, is proportional to the radius while the rate of energy inclusion $d\phi/dR$ decreases sharply when the radius becomes larger than the focal spot. Consequently, the optimal aperture radius would always correspond to an interception factor less than unity. Depending upon the flux distribution and the effective recever temperature, T_e , the optimal receiver aperature area can be less than half the area required for $\phi=1$ with an actual interception factor greater than 90 %.

The electric power production of a solar thermal system is determined by the collector performance and is affected by the transport system, the parasitic features and the power conversion characteristics. The electric power output, P, can be expressed by

$$P = (Q - q_T) \xi \qquad (3)$$

where q_T represents the transport losses and parasitic loads, while ξ is the combined cycle & generator power conversion efficiency.

It can be seen that the performance of a solar thermal conversion system has many design parameters contributing to the cost effectiveness of the overall system. The design variables and the reference values used in the present analysis are listed in Table 1. Conductive heat loss rate is proportional to cavity wall surface area, the thickness and conductivity of thermal insulation and the convective heat transfer between receiver shell and ambient air. The effective conductive heat transfer coefficient, h_c , is assessed to be 0.58×10^{-3} Kw/m^2-°C. The interior cavity surface area is considered to be approximately ten times the aperture area. Transport losses and parasitic loads vary considerably with system designs. In the present analysis the combined losses are assumed to be 10% of the receiver net thermal power. Heat engine performance is another critical variable. Without losing generality, the reference power conversion unit is considered to be a degraded Carnot engine. The working fluid temperature is assumed to be 50°C lower than the effective receiver temperature, T_e .

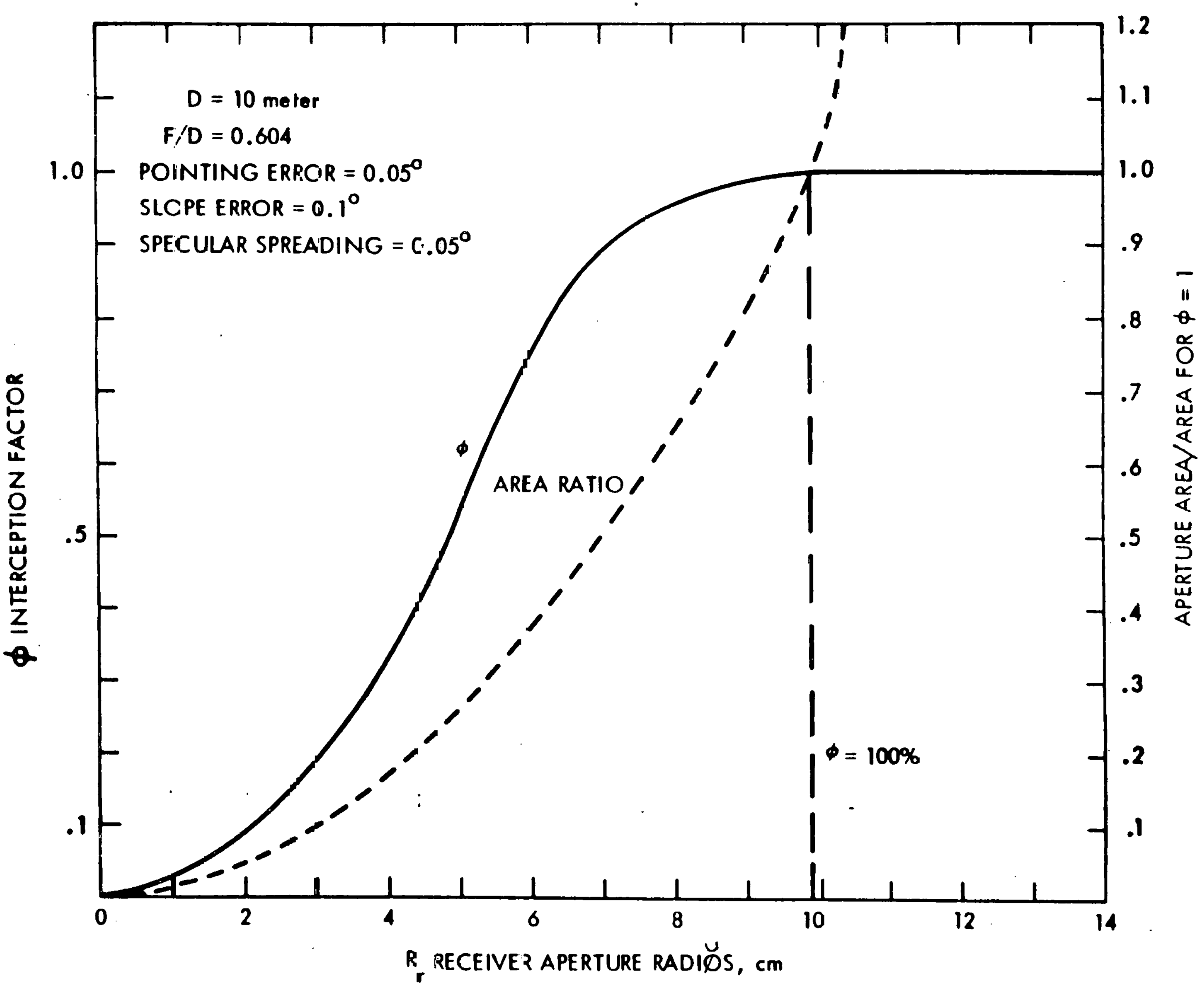


FIGURE 3 INTERCEPTION FACTOR FOR REFERENCE SOLAR COLLECTOR

TABLE 1 SYSTEM PERFORMANCE PARAMETERS AND REFERENCE

• ENVIRONMENTAL AND OPERATING CONDITIONS	
• I_o: DIRECT NORMAL INSOLATION	(0.8 kW/m^2)
• T_e: EFFECTIVE OPERATING TEMPERATURE	$500^oC \sim 1500^oC$
• T_a: AMBIENT TEMPERATURE	20^oC
• V: EFFECTIVE WIND SPEED	2 m/s
• EXPLICIT DESIGN SPECIFICATION	
• D: REFLECTOR DIAMETER	10 m
• ψ: RIM ANGLE	45^o
• ρ_s: SPECULAR MIRROR REFLECTANCE	0.8
• ξ: POWER CONVERSION EFFICIENCY	1/2 OF CARNOT EFFICIENCY
• INDIRECT QUANTITIES AND IMPLICIT DESIGN PARAMETERS	
• G: GEOMETRIC FACTOR - SHADING/BLOCKING	4%
• RECEIVER DESIGN	
• STRUCTURAL SUPPORT	
• R_r: RECEIVER APERTURE RADIUS	
• ϕ: INTERCEPTION FACTORS	
• MIRROR SLOPE ERROR	ε_s 0.1^o
• SPECULARITY	Δ_w 0.05^o
• TRACKING ACCURACY	ε_1
• ALIGNMENT/DEFLECTION ERROR	ε_d $\}$ ε_μ 0.05
• a_{eff}: EFFECTIVE SOLAR ABSORPTANCE	
• ϵ_{eff}: EFFECTIVE CAVITY EMITTANCE	
• RECEIVER DESIGN	$A_w/A_0 = 10$
• a_s: SURFACE ABSORPTANCE	0.95
• ϵ_s: SURFACE EMITTANCE	0.95
• CONDUCTIVE HEAT LOSS THROUGH INSULATION	
• RECEIVER CAVITY AREA	
• EFFECTIVE HEAT TRANSFER COEFF.	0.58 W/m^2 ^oC
• TRANSPORT HEAT LOSS	
• PARASITIC LOAD	10% OF RECEIVER THERMAL POWER

The apparent optical characteristics of a cavity receiver depends strongly on the surface coating as well as the cavity geometrical configuration. Equation (4) is an established simple correlation [Ref. 1] that yields a close approximation for generalized " diffuse ' cavity. The relationship is illustrated in Figure 4. It can be seen that as the area ratio A_w/A_o increases the effective quantity approaches unity asymptotically.

$$\alpha_{eff} = 1 - \frac{1 - \alpha_s}{A_w/A_o - (1 - \alpha_s)(A_w/A_o - 1)}$$

$$\epsilon_{eff} = \frac{\epsilon_s (A_w / A_o)}{A_w/A_o - (1 - \epsilon_s)(A_w/A_o - 1)} \qquad (4)$$

where α_s and ϵ_s are the surface solar absorptance and infrared emittance respectively.

SYSTEM EFFICIENCY

All solar thermal systems are characterized by the fact that they require a high initial capital investment. A solar thermal power plant must be designed to maximize the cost effectiveness . However, system optimization of solar energy application is a complex evolution process. It is governed by many variables such as technology advancement, market penetration (which affects the mass production equipment cost) and the future price as well as the availability of conventional energy sources. All design parameters contribute to the overall system cost effectiveness. Each parameter has its own cost performance trade-off relationship. However, due to the large uncertainties involved in future economic aspects, it is necessary to separate technical performance evaluation from cost assumptions. Technical merits of each design parameter can be evaluated on a relative basis. The information can be used then to pursue system level trade-offs with different cost assumptions and projected economic scenarios.

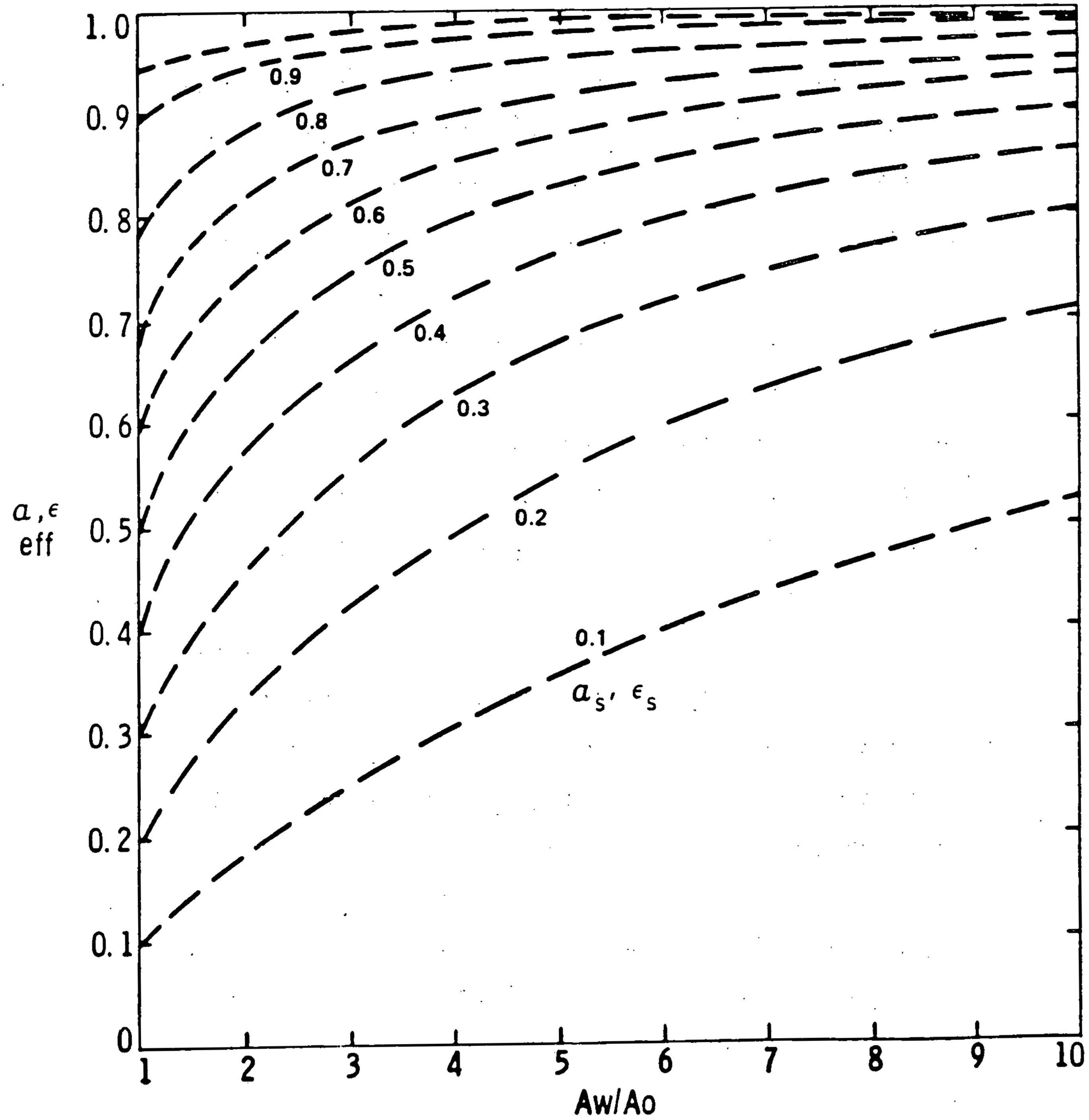


FIGURE 4 EFFECTIVE RADIATIVE CHARACTERISTICS OF A GENERALIZED DIFFUSE CAVITY

Strictly speaking, the term " overall system efficiency " is not very meaningful for a solar thermal conversion system. Not only becasue the energy source is free but also because its availability is uncontrollable. The insolation level depends upon the location, the season, the hour and worst of all, it is subjected to unpredictable interruptions due to weather conditions. Consequently, the solar system efficiency does not bear the same meaning as in the conventional sense. Nevertheless, it is a convenient measure to compare the performance sensitivity of relevent design parameters. As long as the comparison is strictly technical and the efficiency is rated at a specified insolation level, the definition of system efficiency would not be ambiguous.

$$\eta = \frac{P}{I_0 A} \qquad (5)$$

where

η = rated system efficiency
P = electric power output
$I_0 A$ = total incident direct normal solar power

The overall system efficiency of the reference collector (as specified in Table 1) is shown in Figure 5. The relationship between overall system efficiency and power conversion efficiency, ξ, is linear. The influence of insolation level on η is much stronger at high temperature region.

MANUFACTURING TOLERANCE

Manufacturing tolerance is one of the major factor determining the cost of a point focusing collector. The surface random slope error, E_s , can be improved by constructing the macroscopic reflector structure shape more accurately and by decreasing the microscopic surface waviness. The alignment/deflection error, E_d , can be reduced by locating the receiver more precisely and by providing stiffer receiver support structure. Better tracking accuracy can be provided by more precise sensing of the target, frequent calibration and reducing mechanical errors in gears, drives and motors. All improvements of the manufacturing tolerance will increases the direct collector cost. Whether the improved performance can justify the increased cost is one major trade-off consideration. More significantly, the quality of the collector

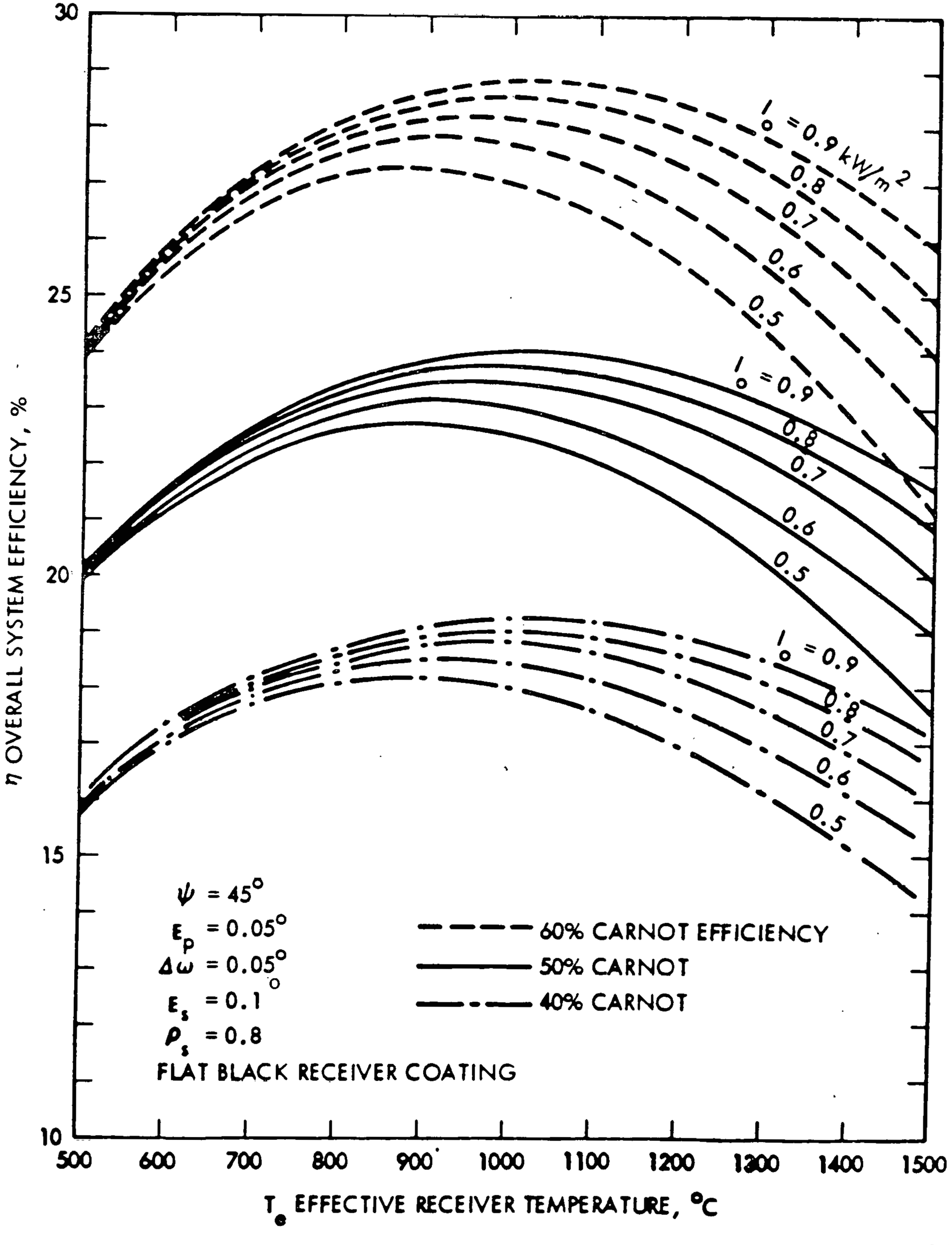


FIGURE 5 SYSTEM EFFICIENCY OF A REFERENCE SOLAR COLLECTOR

has a dominating effect on the entire system design including the receiver, the transport system and the heat engine. It was shown in Figure 5 that the reference collector is best suited for a heat engine operation around 1000°C under a rated insolation level of 0.8 Kw/m^2. This is by no means a conclusion that solar heat engine should be developed for that temperature. Rather, it is only a conditional statement about the system efficiency for the specific collector quality and assumed engine characteristics. A collector with different quality may lead to different conclusions. Figure 6 shows the performance sensitivity of the one of the dominant tolerance factor, the effective surface slope error, E_S . It can be seen that for a specific operating temperature , a reduction in surface slope error always improves the overall system efficiency. The improvement becomes more pronounced as the operating temperature increases. The system trade-off is complex. For example, if all the other design parameters are fixed and a Rankine heat engine operating at 500 °C is chosen , reducing the slope error from 0.55° to 0° increases the system efficiency from 18.3 % to 20.5 % . Then ,the quality improvement would not be cost effective if the associated cost increase is greater than 20.5 : 18.3 . The trade-off is mathematically correct for this specific condition . However, the condition for the trade-off is not rational from a system point of view. Employing such a high quality collector for low temperature application is wasteful. Its full potential will be utilized only when an efficient 1300°C heat engine is developed. By the same token ,associating a poor quality collector of 0.55°slope error with a high efficiency engine operating at 1300°C is irrational even the collector is relatively cheap.

It should be pointed out that degraded Carnot performance is far from the reality of heat engine technology. Depending upon the working fluid and engine development , practical power conversion system for solar energy application may favor certain particular operating temperatures . This could place a different weighting function on the performance sensitivity of collector manufacturing tolerarance.

MIRROR SPECULAR REFLECTION CHARACTERISTICS

As shown in equation (1), mirror specular reflectance is one of the major factor governing the collector performance. The specular characteristics of a mirror can be expressed in terms of two related parameters;namely, the specular reflectance value, ρ_s, and reflection spreading cone angle, $\Delta\omega$.

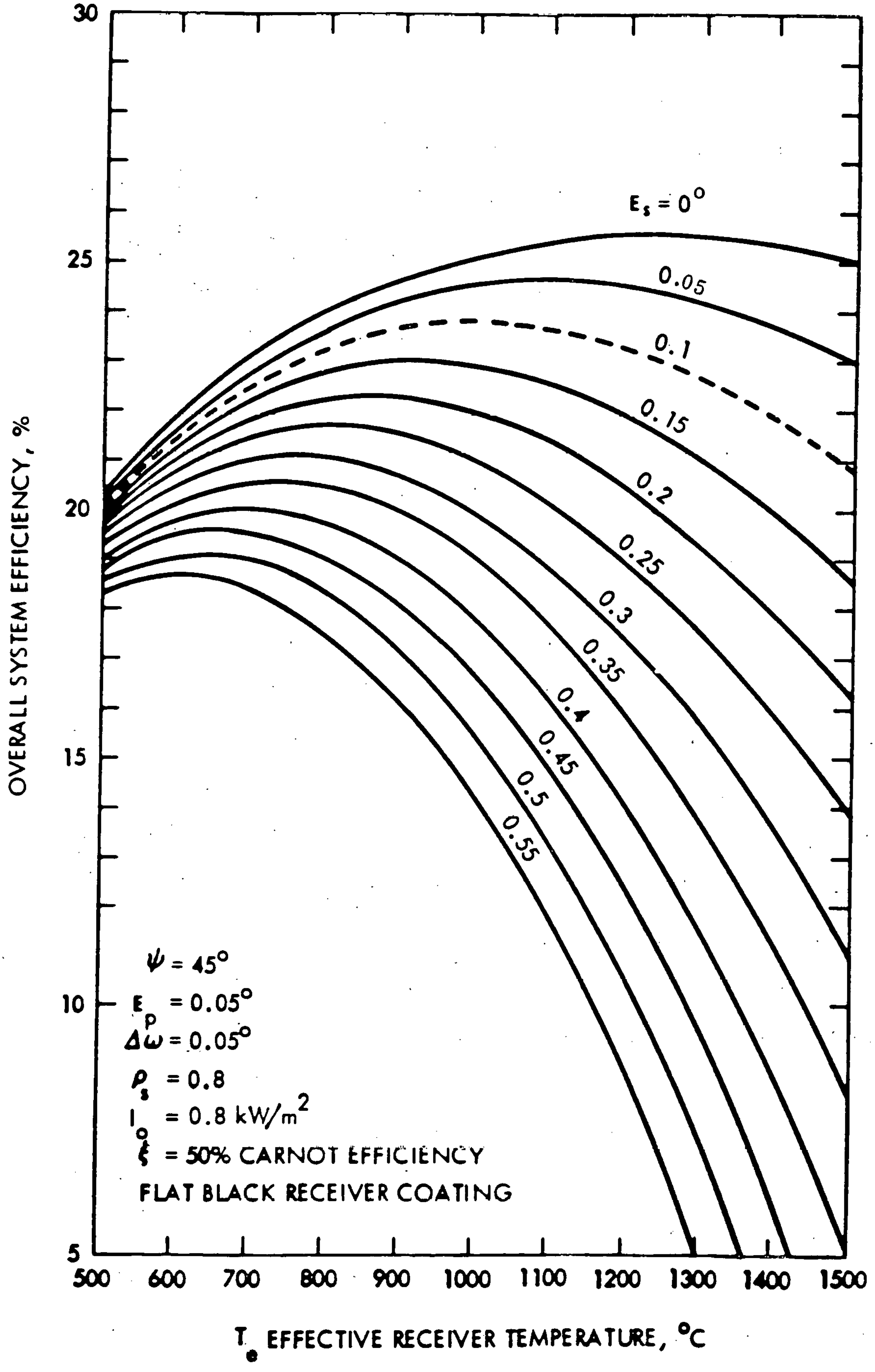


FIGURE 6 PERFORMANCE SENSITIVITY OF COLLECTOR SLOPE ERROR

Figure 7 illustrates representative reflectance characteristics of some mirror surfaces [Ref. 2 & 3] . Significant degradation can be resulted from outdoor weathering and dust build-up. The sensitivity of specular reflectance value, is shown in Figure 8. The relationship between system efficiency and the reflectance value is almost linear . Figure 9 illustrates the sensitivity of spreading cone angle, $\Delta\omega$,. It can be seen that the effect is similar to that of the slope error , but to a lesser extent. Improving mirror reflectance characteristics may involve both direct collector cost (for higher quality mirror) and maintenance cost for periodic cleaning and replacing degraded mirror surfaces.

SELECTIVE COATING

Spectrally selective surfaces have been investigated for over two decades. The application of selective coatings with high solar absorptance and low infrared emittance such as black chrome and black nickle were successfully demonstrated for flat plate solar collectors. Melamed & Kaplan [Ref. 4] surveyed the application of selective coating on external absorbers in the temperature range of 300°C to 500°C, and concluded that a high absorptance is the primary goal of all candidate absorbers. Very little research has been done in the high temperature regime. This is partially because of the material survivability becomes crucial and also due to the significant cross-over region between incident solar spectrum and the high temperature re-emission spectrum. Figure 10 illustrates the overlapping between solar spectrum and blackbody radiation at 1100°C. For the purpose of estimating the potentials of selective coating application for high temperature point focusing solar collectors, an idealized coating characteristics is assumed. The upper and lower limit bounds for both the solar absorptance and the emittance are considered to be 0.95 and 0.05 . The characterisitics of this ideal coating is determined by the specified cut-off wavelength. Figure 11 shows the surface solar absorptance for air mass two solar spectrum and the surface emittance at various temperature levels as functions of the cut-off wavelength, λ_c , [Ref. 5] .

The measure of selective coating effectiveness was suggested to be the so called " absorption of merit", α_m , as defined in the following equation:

$$\alpha_m = \alpha_s - \frac{\epsilon_B \sigma T_e^4}{\rho_s I_o G \phi C} \qquad (6)$$

where

α_m = absorption of merit
C = collector concentration ratio, $C = A/A_o$

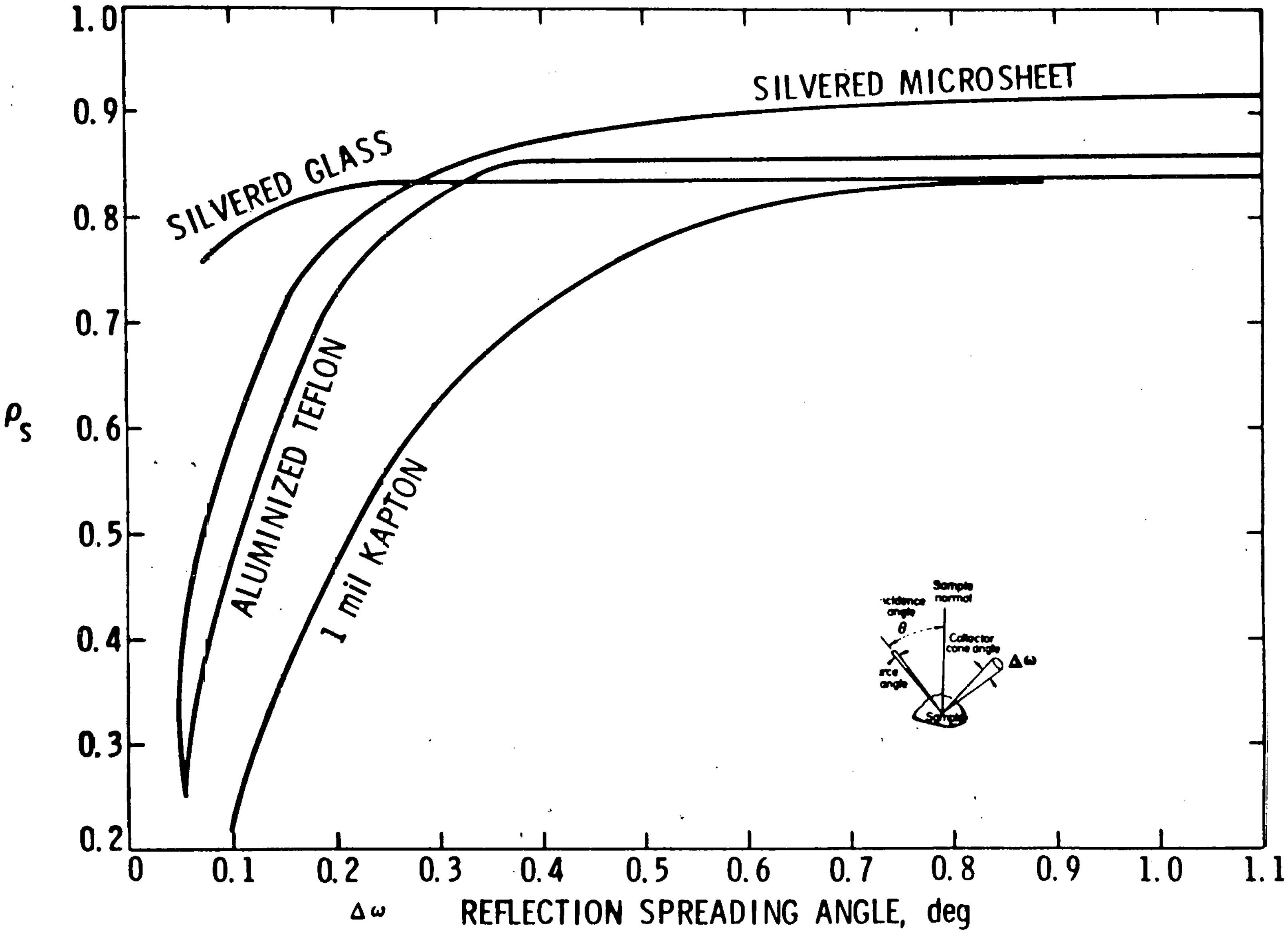
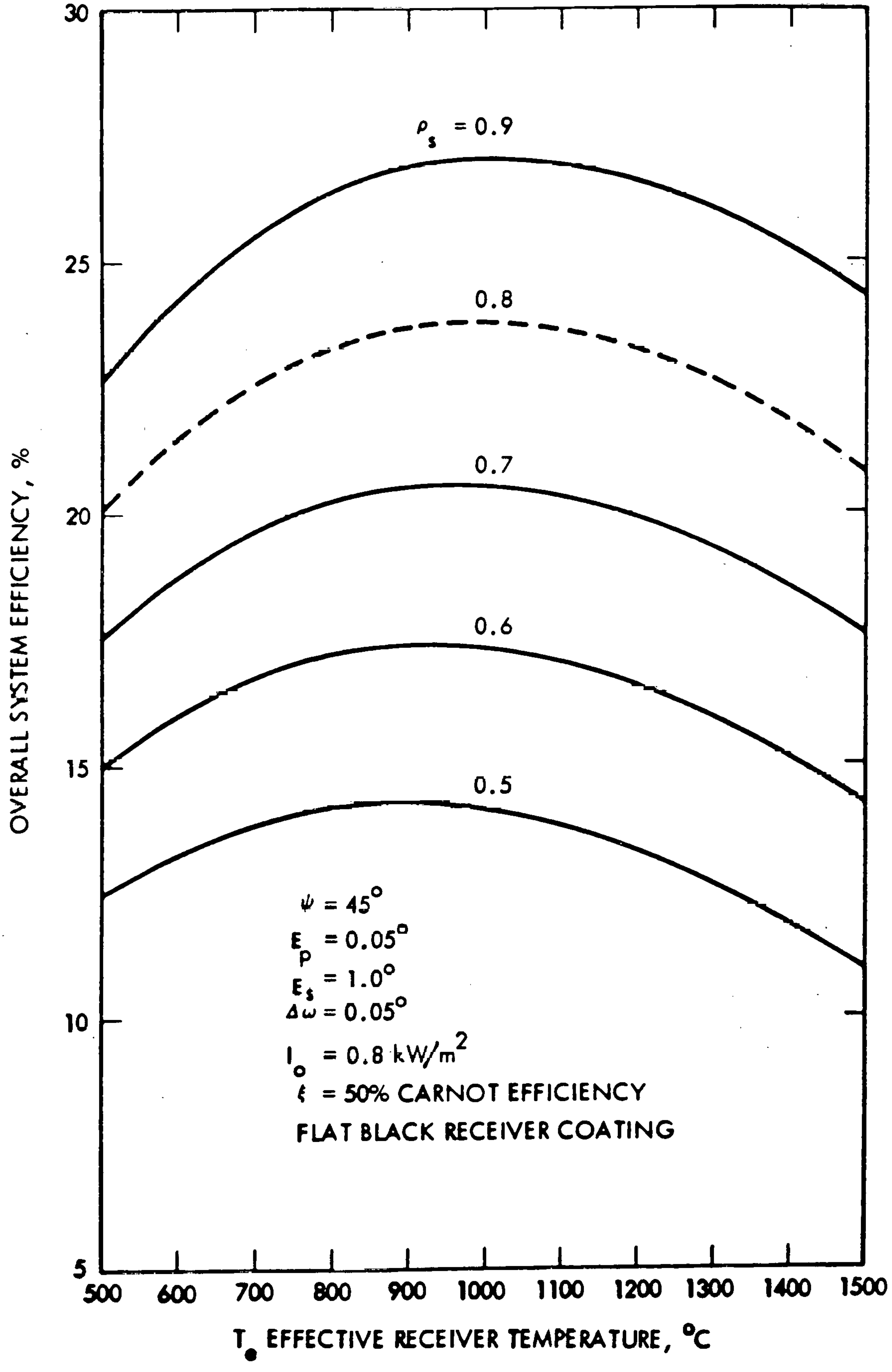


FIGURE 7 REPRESENTATIVE SPECULAR REFLECTANCE CHARACTERISTICS

FIGURE 8 SENSITIVITY OF SPECULAR SURFACE REFLECTANCE



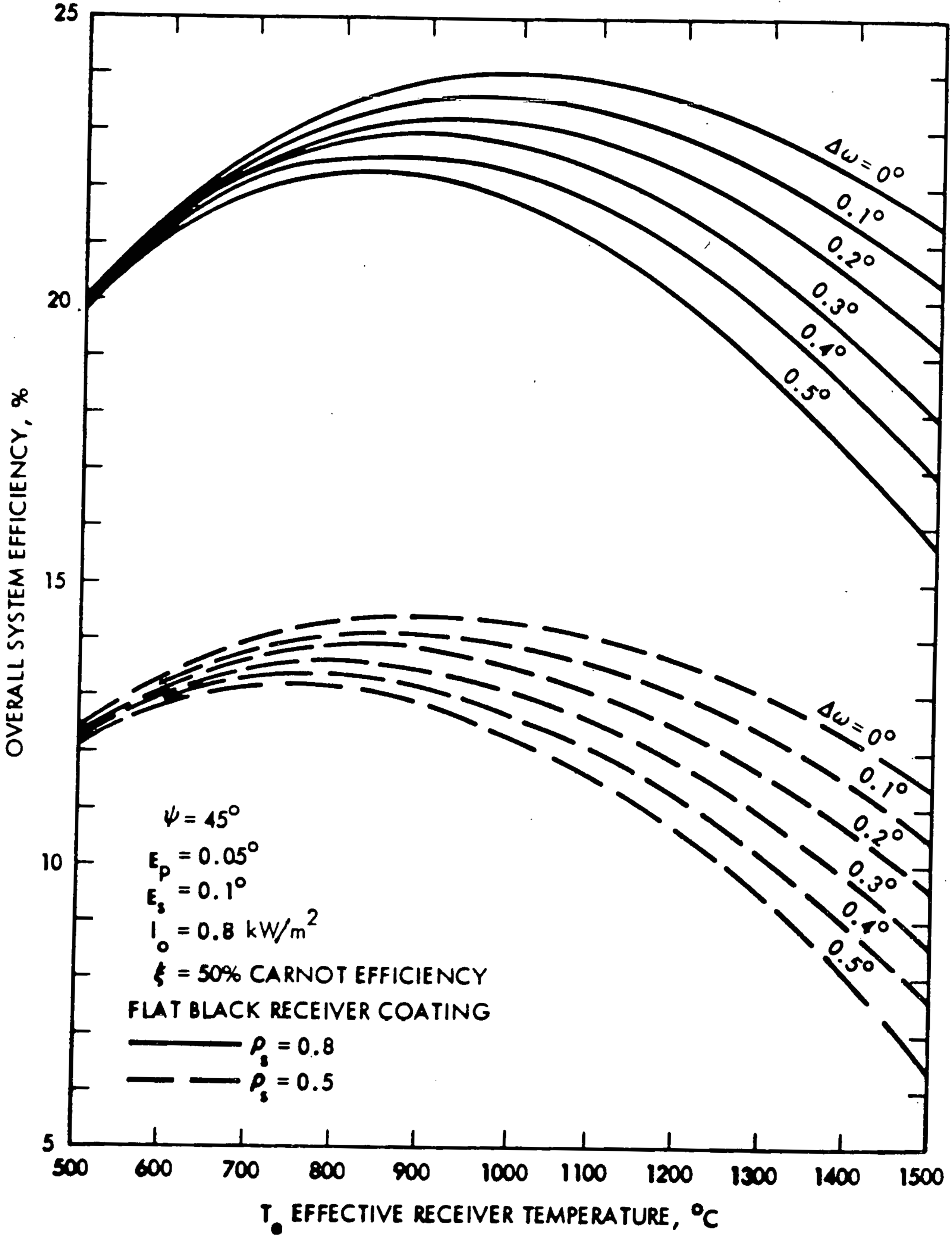


FIGURE 9 PERFORMANCE SENSITIVITY OF MIRROR SPREADING

SELECTIVE COATING

$$\alpha_s \approx \left[0.95\int_{0}^{\lambda_c} e_{b,\lambda}\,(T = 5500\,^{\circ}C)\,d\lambda + 0.05\int_{\lambda_c}^{\infty} e_{b,\lambda}\,(T = 5500\,^{\circ}C)\,d\lambda\right] / E_{b,\,5500\,^{\circ}C}$$

$$\epsilon_s = \left[0.95\int_{0}^{\lambda_c} e_{b,\lambda}\,(1100\,^{\circ}C)\,d\lambda + 0.05\int_{\lambda_c}^{\infty} e_{b,\lambda}\,(1100\,^{\circ}C)\,d\lambda\right] / E_{b,\,1100\,^{\circ}C}$$

AT 1100 °C

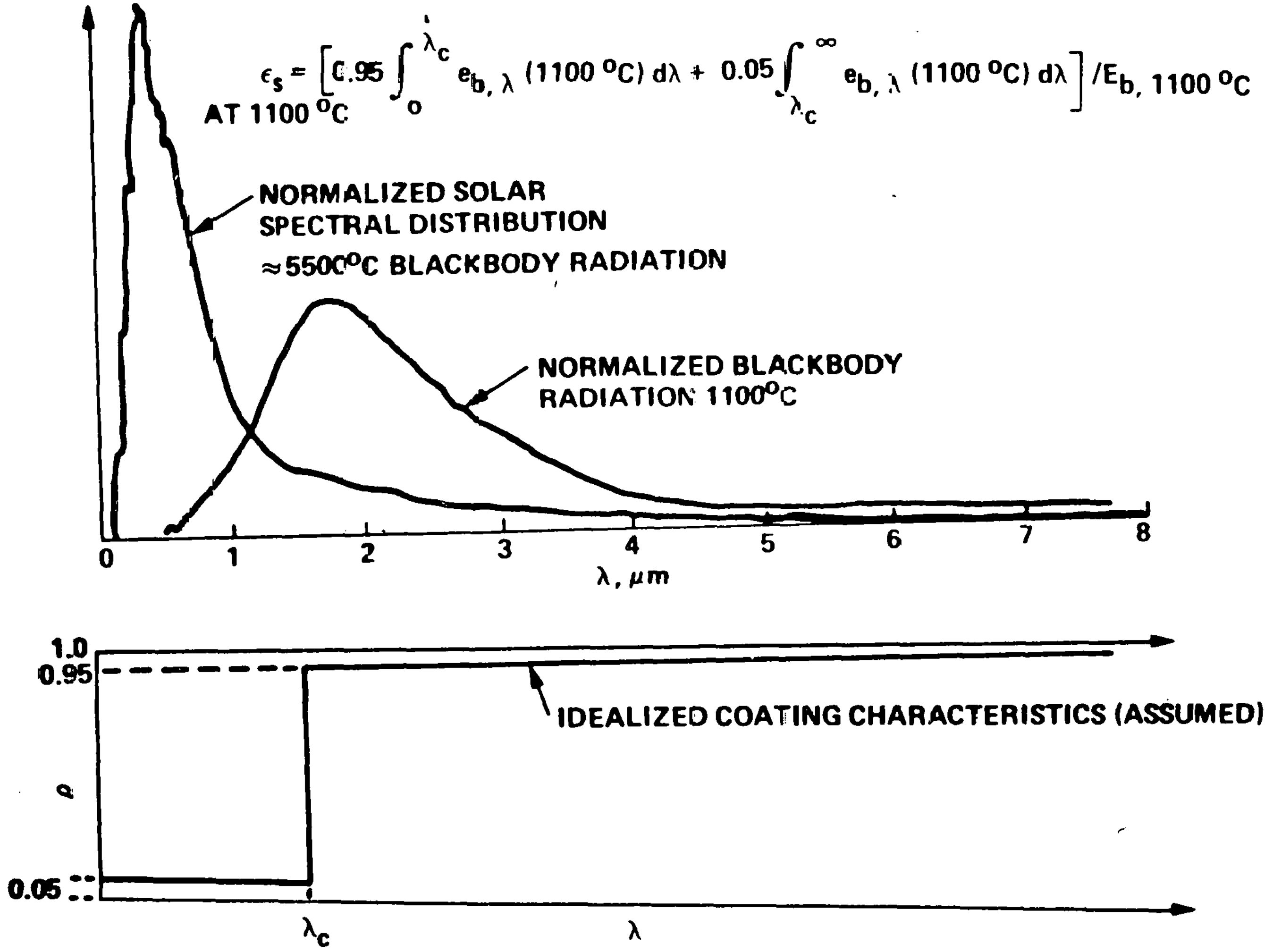


FIGURE 10 SPECTRUM CROSS-OVER AND IDEALIZED SELECTIVE COATING

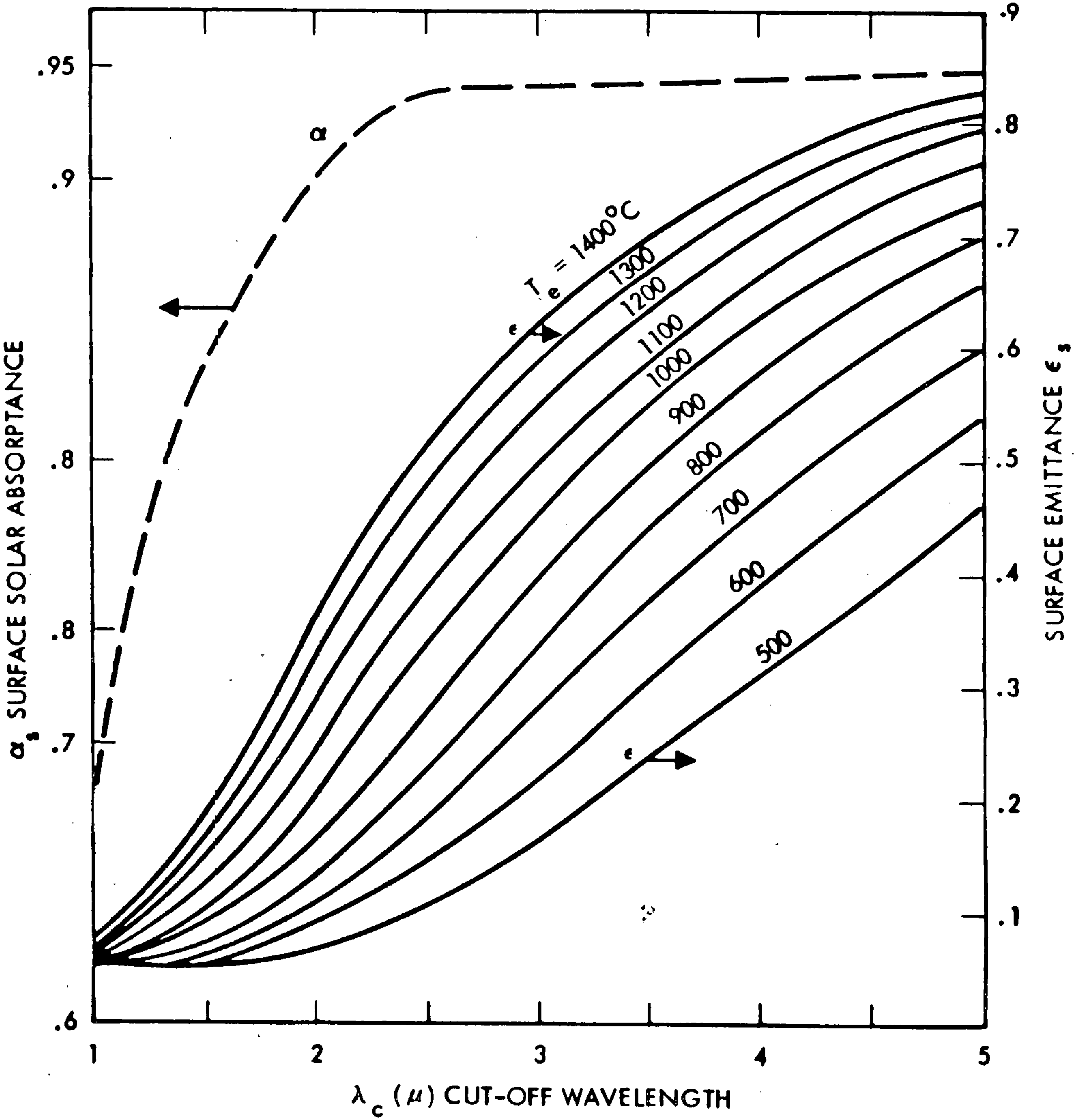


FIGURE 11 SURFACE SOLAR ABSORPTANCE AND EMITTANCE AS FUNCTIONS OF CUT-OFF WAVELENGTH

If one ignores the convective/conductive heat losses and the background radiation from the ambient enviroment, then the energy equations (1) and (2) take the same form as equation (6). The absorption of merit, α_m , is simply the net thermal power across the aperture divided by the total solar power contained in the solar image. This is, of course, assuming a flat external absorber with $\alpha_{eff} = \alpha_s$ and $\epsilon_{eff} = \epsilon_s$. For a cavity receiver configuration one can define an effective absorption of merit in a similar fashion. The effect of a selective coating application is sometime expressed in terms of the ratio of absorption of merit or the difference in α_m with respect to a flat black coating both rated at the same conditions at a specified operating temperature. In either case, it is analogous to compare the corresponding system efficiencies.

The system efficiency of the reference collector is shown in Figure 12. As was discussed previously that the reference collector is best suited to work with a degraded Carnot engine around 1000°C. At this temperature the application of an idealized selective coating would increase the overall system efficiency by 0.5 % or about two percent improvement over a comparable flat black coating of α_s=0.95 and ϵ_s =0.95 . On the other hand, a flat coating of lesser quality would decreases the performance by approximately the same amount. In the same figure it can be seen that when the environmental condition is less favorable, the relative merit of selective coating application is enhanced. With an insolation level of 0.5 Kw/m^2 and a 40 % Carnot efficiency the improvement of performance due to selective coating application is close to four percent.

A similar correlation is shown in Figure 13 for a collector of poorer quality. With a flat black cavity, the collector is best suited for a Carnot engine operating around 700 °C with a system efficiency around 19.3 % . The same collector with a selective absorber can be operated at 900°c to yield a system efficiency of 20.3 %, which represents a five percent improvement due to the selective coating application. Such a comparison will not be reflected in judging the so called " absorption of merit ". The system efficiency of a flat black cavity operating at 900°C is only 18.5 % . The improvement of α_m rated at this temperature would be nine percent , which is unjustifiably optimistic. For the same reason, if the improvement of α_m is rated at 1400°C , one would have a twisted claim of sixty percent improvement for selective coating over flat black cavity.

In the analysis the idealized selective coating is considered to have an adjustible cut-off wavelength. Figure 14 shows a representative system efficiency variation as a function of cut-off wavelength at various operating temperatures. As the temperature increases the optimal cut-off value shifts to shorter wavelength. However, because of the cavity feature the variation is not very sensitive.

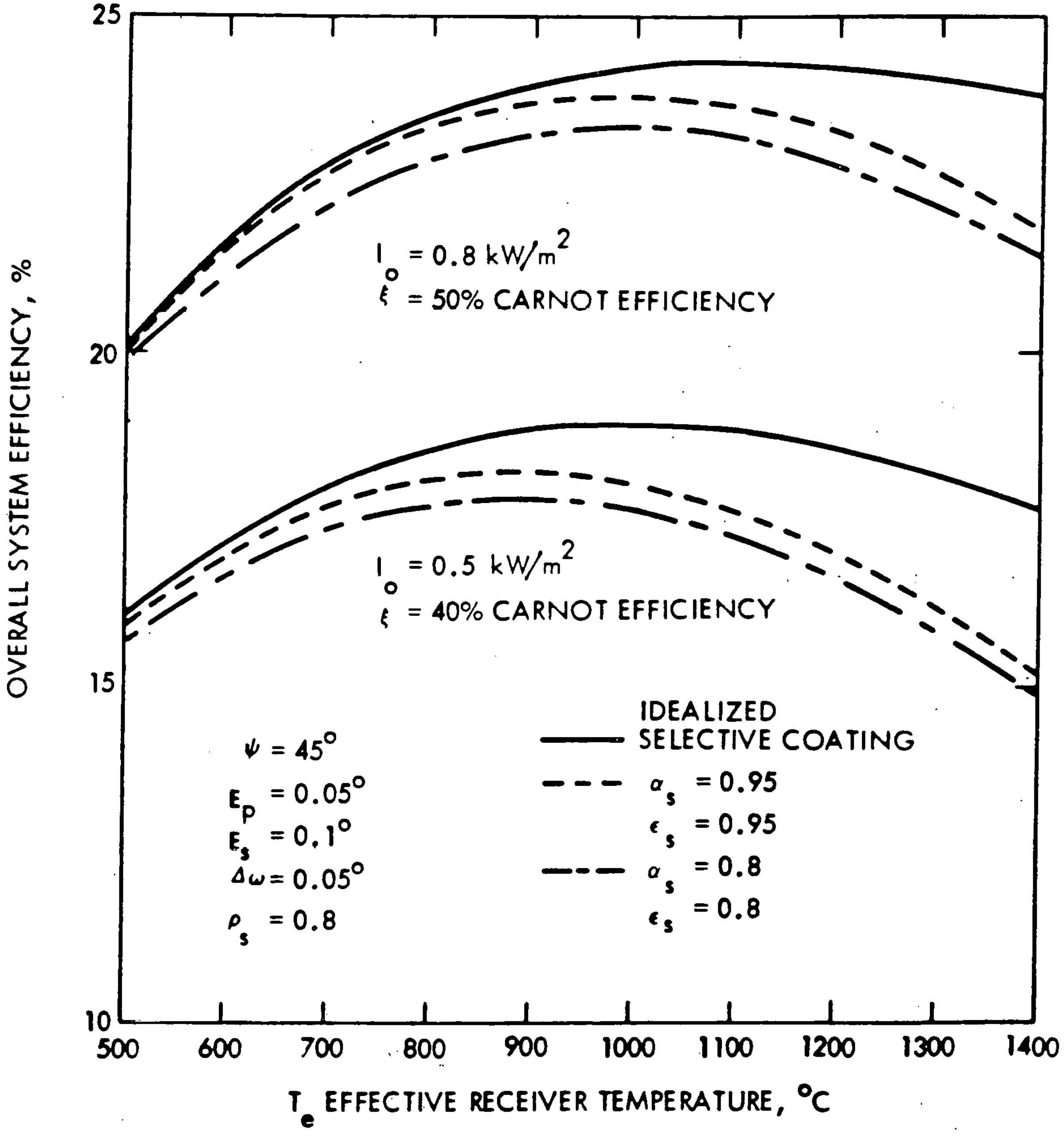


FIGURE 12 EFFECTS OF SELECTIVE COATING ON REFERENCE SOLAR COLLECTOR

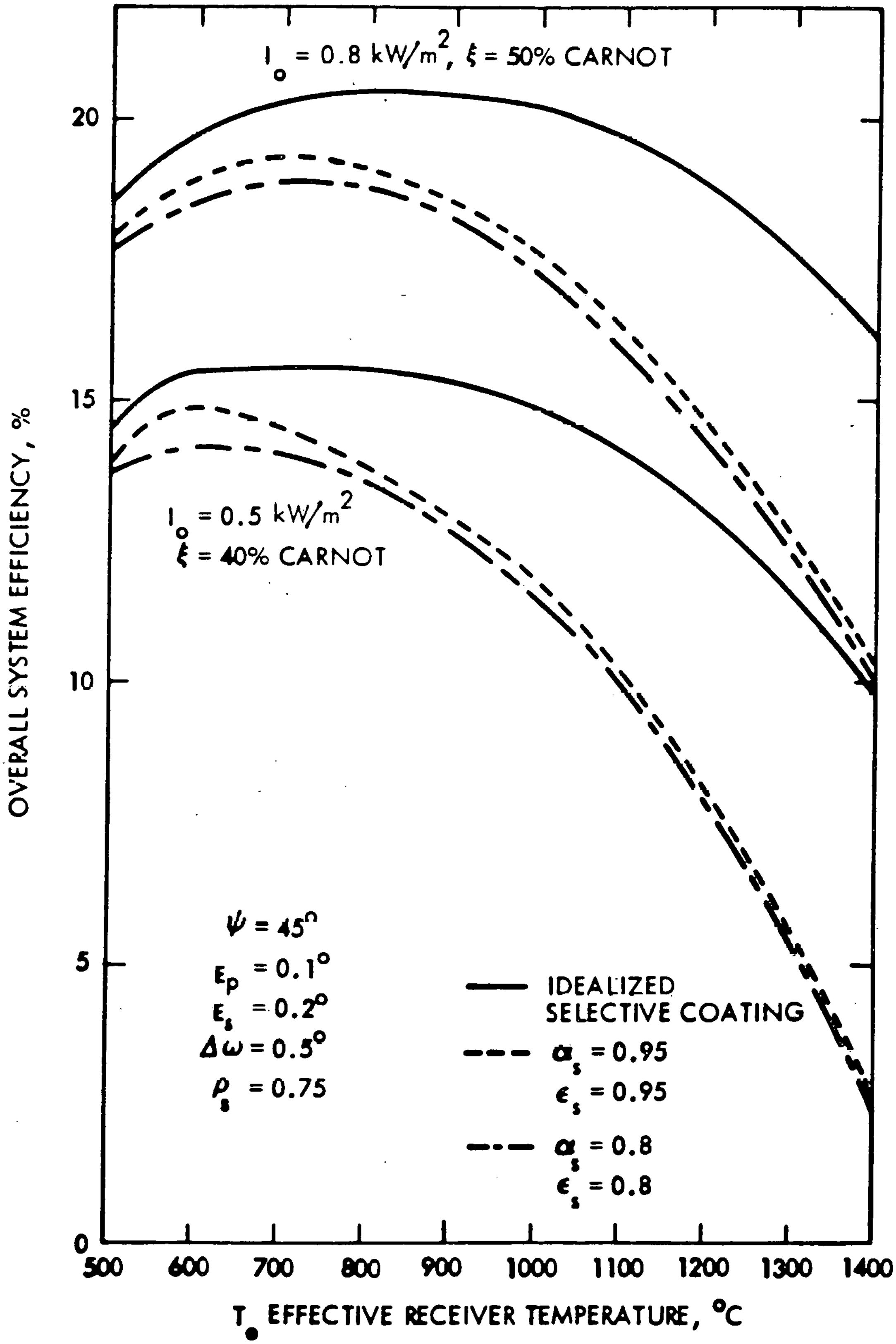


FIGURE 13 PERFORMANCE SENSITIVITY OF SELECTIVE COATINGS

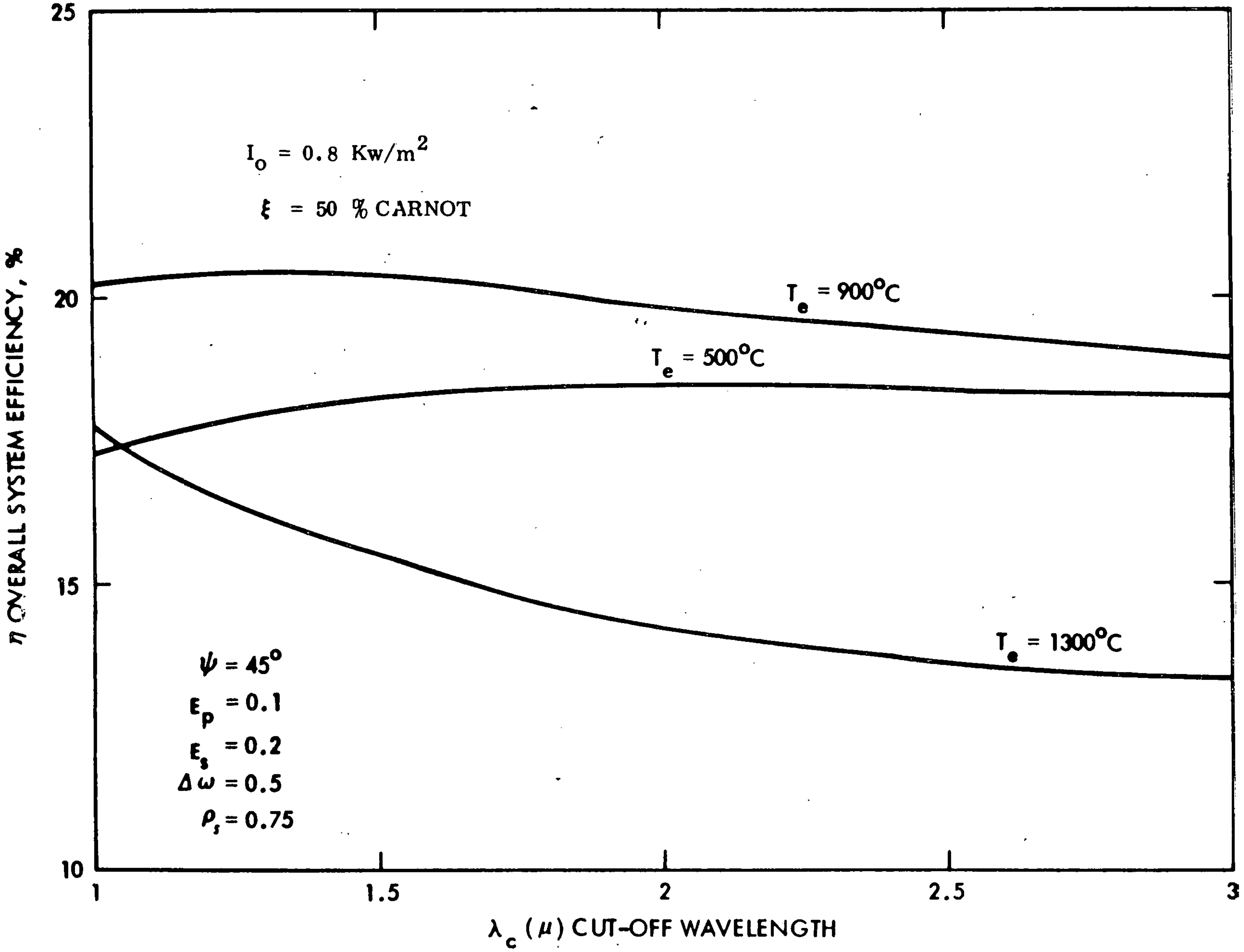


FIGURE 14 REPRESENTATIVE PERFORMANCE VARIATION VS CUT-OFF WAVELENGTH

DISCUSSION AND CONCLUSION

The performance of a point focusing solar thermal power plant is affected by a large array of design parameters. Each parameter has its own cost relationship and performance sensitivity. However, from a system optimization point of view, all design parameters can be grouped into three catagories according to the roles and sequences they play in the system selection and cost performance trade-off processes. The first group is the critical system parameters, which are the pacing items for solar thermal developments. Typically, they are not only very cost sensitive but also are closely related with the state-of -the -art technology advancement. These parameters governs the selection of solar thermal power system concepts preceding detailed system designs. Other design parameters such as collector sizes, structural configurations, etc, that have a major bearing on the construction cost and operational considerations, would play an important role in the system cost-performance trade-off but have little effects on system concept selection. These are the engineering parameters. The third group is best represented by the thermal insulation systems of the receiver and the transport pipeline. The effects on the overall system performance is moderate and the current technology is considered to be adequate. It is desirable to advance the state-of -the-art of insulation characterisitcs and thus to improve the overall system performance, but it would not be critical to the development of solar thermal projects whether better insulation system is available now or in the next ten years.

The quality of the collector (including manufacturing tolerances & mirror spreading angle) and the heat engine characteristics are the two key factors influencing the developments of solar thermal power plants. The two factors are strongly interactive. Developing a high quality collector without a matching high performance heat engine would be wasteful. The existance of a high performance solar heat engine, without an appropriate collector to accomodate it, is virtueless. A manufacturing process, established to produce low cost collectors with certain specified quality, would create a need for research & development of a compatible solar heat engine. On the other hand, the state of engine development would influence heavily on the market demand and cost relationship for collector with certain specifications. The optimization process is complex and iterative. Detailed studies are required to ensure that heat engine research plans and collector manufacturing technology development are compatible. Specular mirror reflectance is probably the most important single parameter affecting the performance of all focusing solar thermal power conversion concepts. Unlike manufacturing tolerance and heat engine characteristics, the variation in mirror reflectance does not have a strong influence on the optimal system operating temperature (as shown in Figure 8). Consequently it is not a governing system parameter, but rather the most important engineering design parameter. The system performance sensitivity of mirror reflectance is almost linear and the cost performance relationship should be relatively straightforward.

Similar to thermal insulation system, cavity receiver coating plays only an accessory function to a point focus distributed solar power conversion system. Because of the cavity feature, the effect of coating application is not significant enough to contribute in the system concept selection process. As shown in Figures 12 & 13 that even an idealized selective coating has limited improvements on a properly design system. A realistic selective coating would even be less impressive. Nevertheless, selective coating application does pocess certain unique characteristics that is different from other major design parameters.

(1) Although selective coating may only have a limited benefit for collector system operated under design conditions, but for off-design situations such as start-up period and low insolation days the application becomes more advantageous. It would serve as a stablizer for system operation during off-design periods.

(2) Selective coating on the cavity receiver can be considered as a remedy for poor or degraded collector quality. The merit of selective coating application appears to be inversely proportional to the quality of the collector.

(3) The current state of solar thermal development is still at its infancy. It is likely that optimal compatibility between collector quality and heat engine development may not be reached for some time. A mis-match situation would be detrimental to the system cost effectiveness. As shown in Figure 15, the application of selective coating will tend to moderate the operating temperature sensitivity on the system performance. A cavity receiver with selective coating would be an effective modifier for a mis-matched collector/ heat engine system.

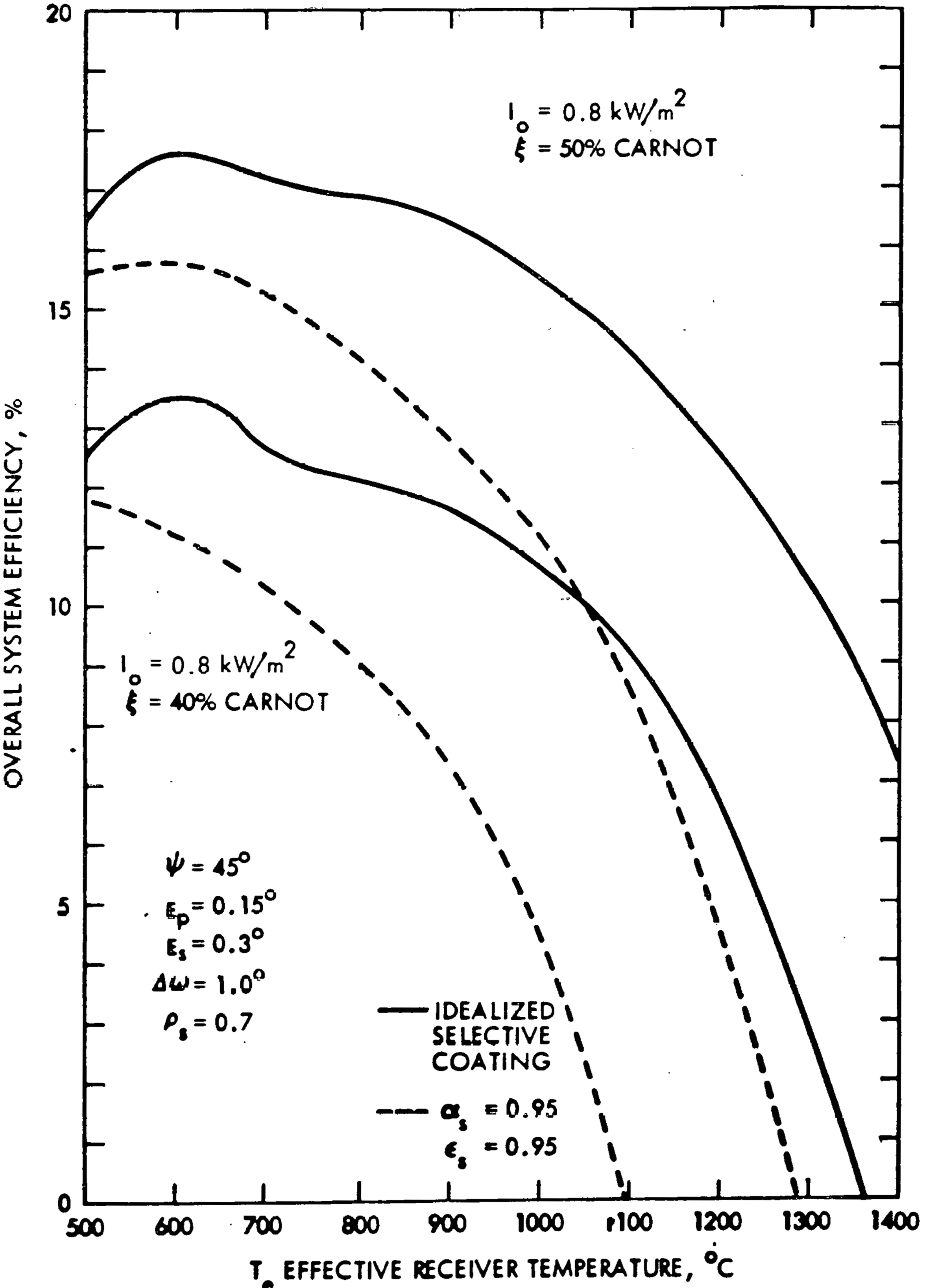


FIGURE 15 EFFECTS OF SELECTIVE COATING ON COLLECTOR QUALITY

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[3] Zentner, R.C., " Performance of Low Cost Solar Reflectors for Transfer Sunlight to a Distance Collector " Solar Energy, Vol.19, pp. 15-21, 1977

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[5] Adams, M.A., W.F. Carroll, R.T.Reeve, and B. Zeldin, " A Methodology for Assessing the Benefits of Absorber Coatings for Solar/Thermal Receivers ", presented at Selective Absorber Coating Workshop-Sponsered by SERI, Golden, Colorado, Dec. 6-7, 1977

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A METHODOLOGY FOR ASSESSING THE BENEFITS OF ABSORBER COATINGS FOR SOLAR/THERMAL RECEIVERS

M. A. Adams, W. F. Carroll, R. T. Reeve, B. Zeldin
Jet Propulsion Laboratory

INTRODUCTION

The development of economically feasible solar thermal power systems requires the improvement of existing technology and breakthroughs in new technical areas. A cost effective program which will lead to viable solar power systems must emphasize those technologies critical to the successful implementation of the system design concepts. Different concepts require different technologies which, in turn, require different kinds of development effort. The question as to whether absorber coatings research and development should be focused to support only current design concepts or whether some portion of such R&D should be of a more general character leading to increased options for future designers (e.g., selective absorber coatings for an external receiver versus only cavity receiver options) is a question of government policy and will not be addressed here.

The first step in the development of a tool for evaluating the relevance and potential benefit of absorber coatings R&D is presented. Using greatly simplified assumptions, this analysis technique has been exercised to identify the potential benefits of improved coatings. By plotting isobenefit curves for the improved coatings on coordinates of incident flux vs absorber surface temperature, the potential improvement in performance may be assessed for any candidate system. A more specific definition of the benefits of particular coatings coupled with the projected costs and risk analyses of candidate systems which might employ such coatings can then be used as the basis of a cost/benefit analysis of proposed coating development work. This cost/risk/benefit analysis can be used in conjunction with similar analyses of other system elements or technologies to determine an appropriate level of R&D for coatings development. Also, the technical analysis of absorber coating effectiveness in the various operating ranges of candidate systems will identify the areas of highest return for coatings development programs and identify where these programs might, at present, be deficient or irrelevant.

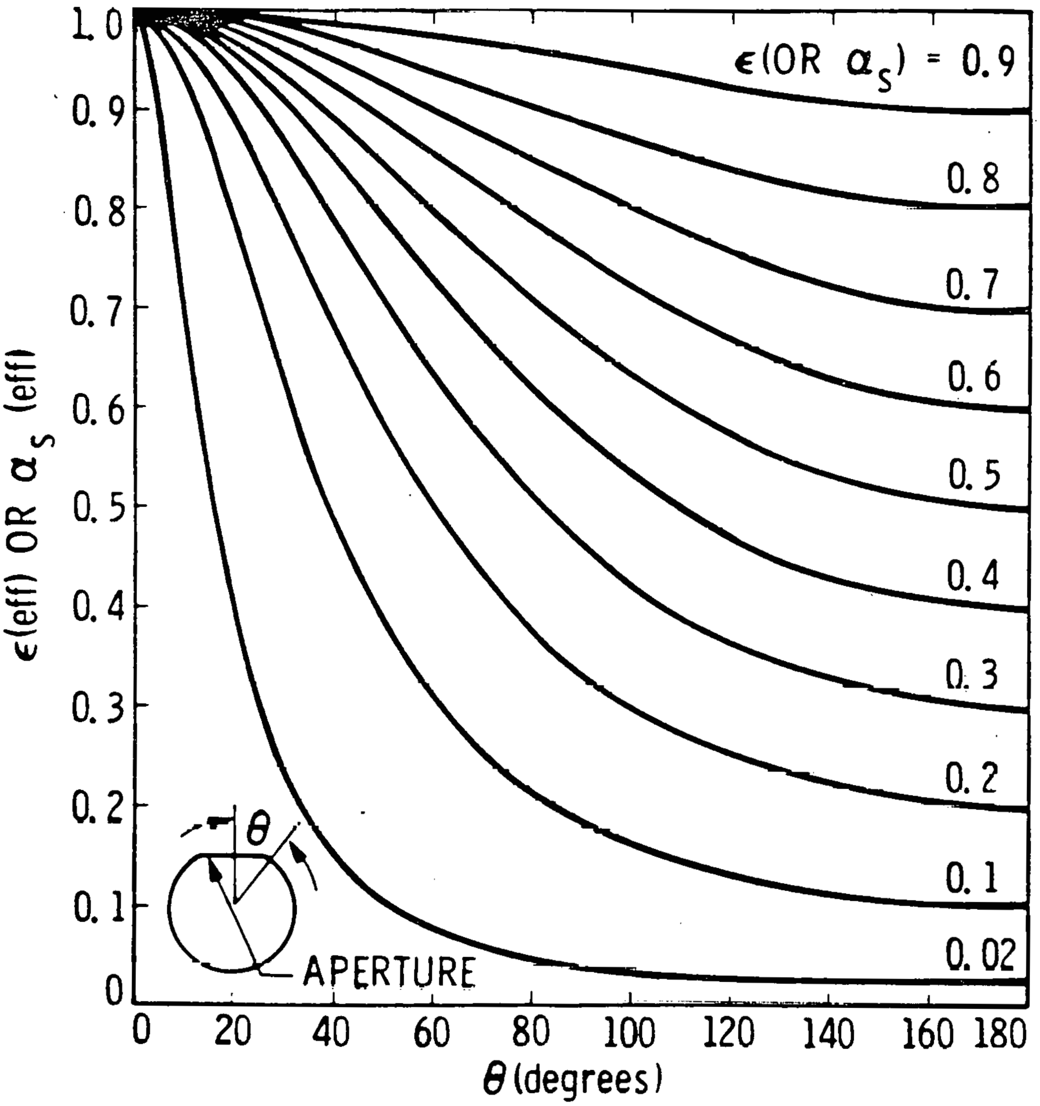
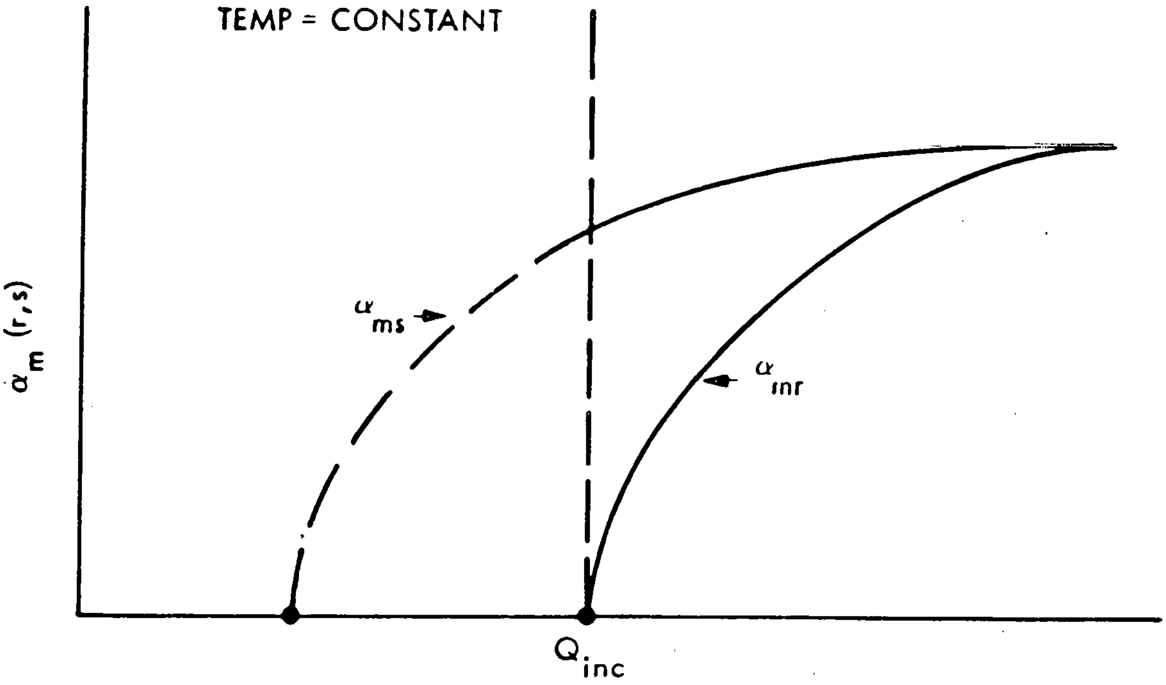
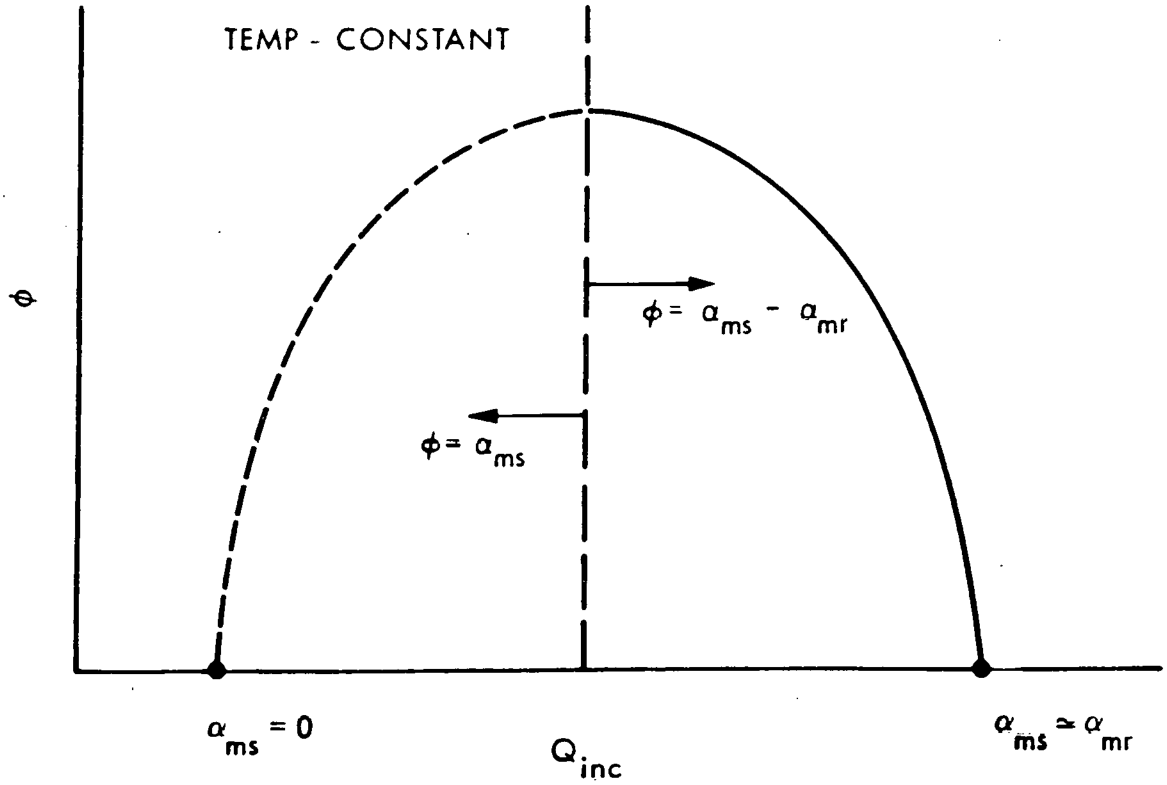


Figure 1. Apparent Emittance (or Absorptance) of an Isothermal, Diffuse, Gray, Spherical Cavity vs Aperture Half-Angle

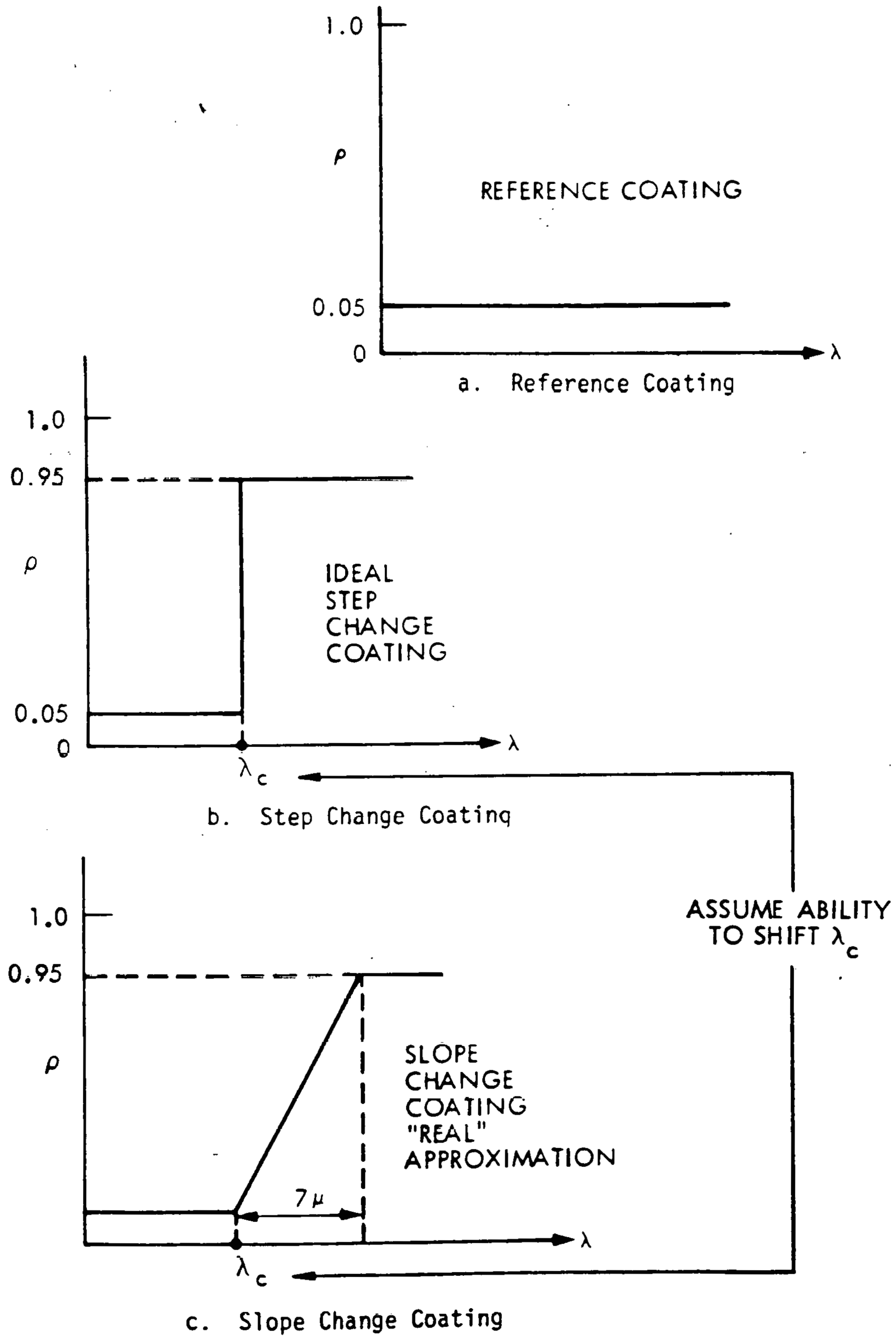


(a) α_{mr} and α_{ms} vs Q_{inc}



(b) ϕ vs Q_{inc}

Figure 2. Absorptance of Merit for Reference and Selected Coatings



a. Reference Coating

b. Step Change Coating

c. Slope Change Coating

Figure 3. Reflectance vs Cutoff Wavelength for Reference and Selected Coatings

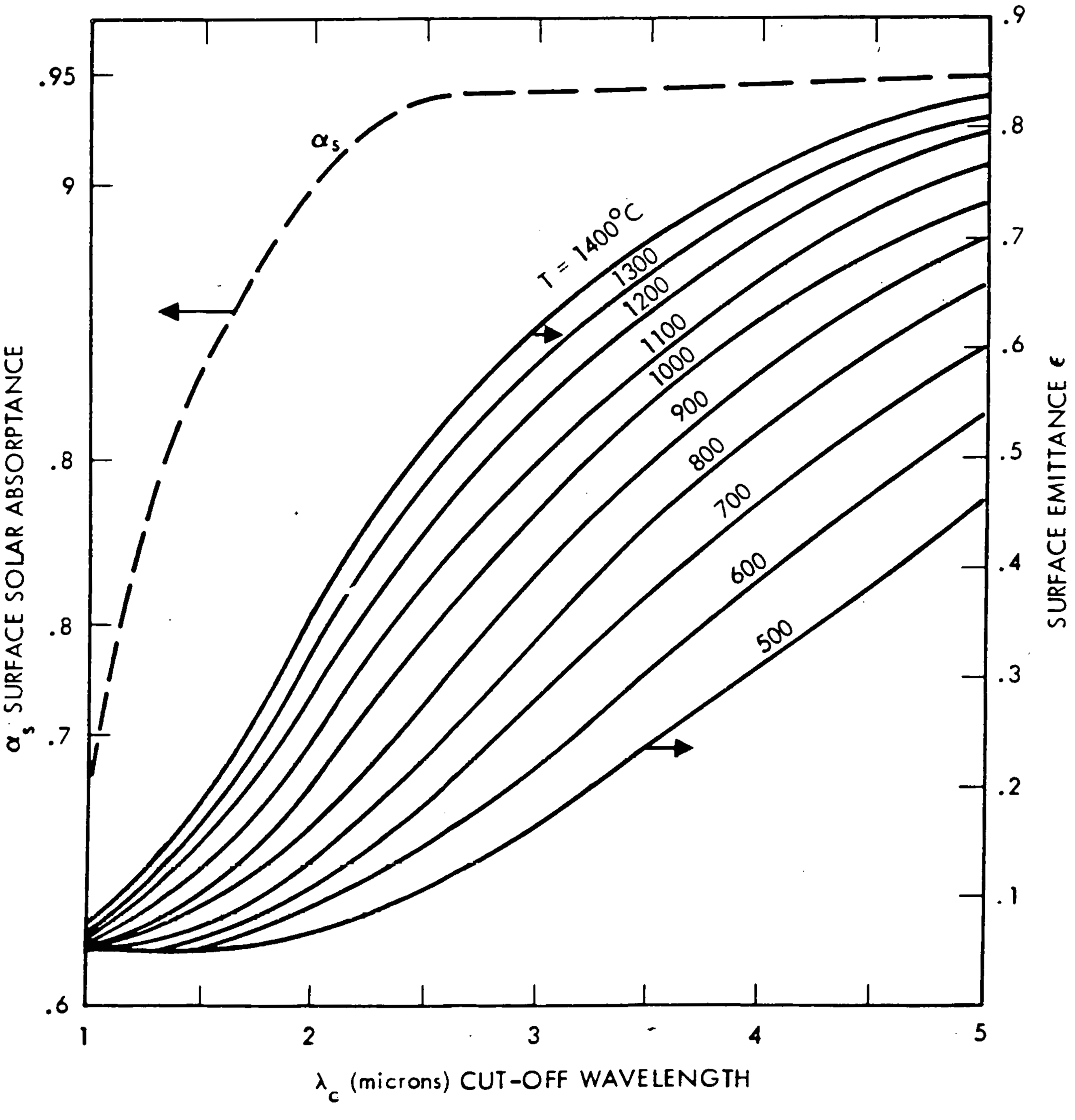


Figure 4. Absorptance and Emittance vs λ_c

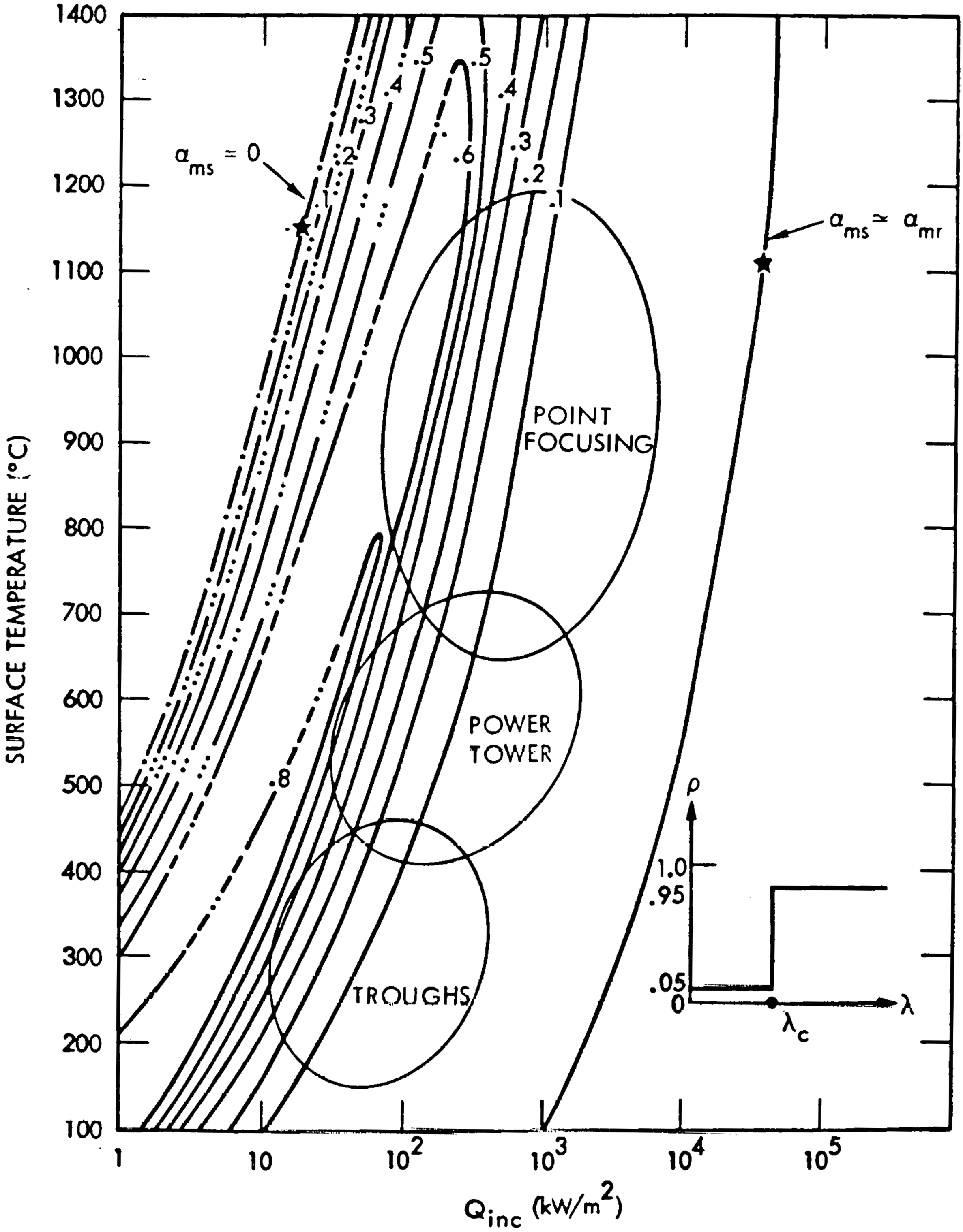


Figure 5. Isobenefit Contours for Ideal Step Change Reflectance Coating

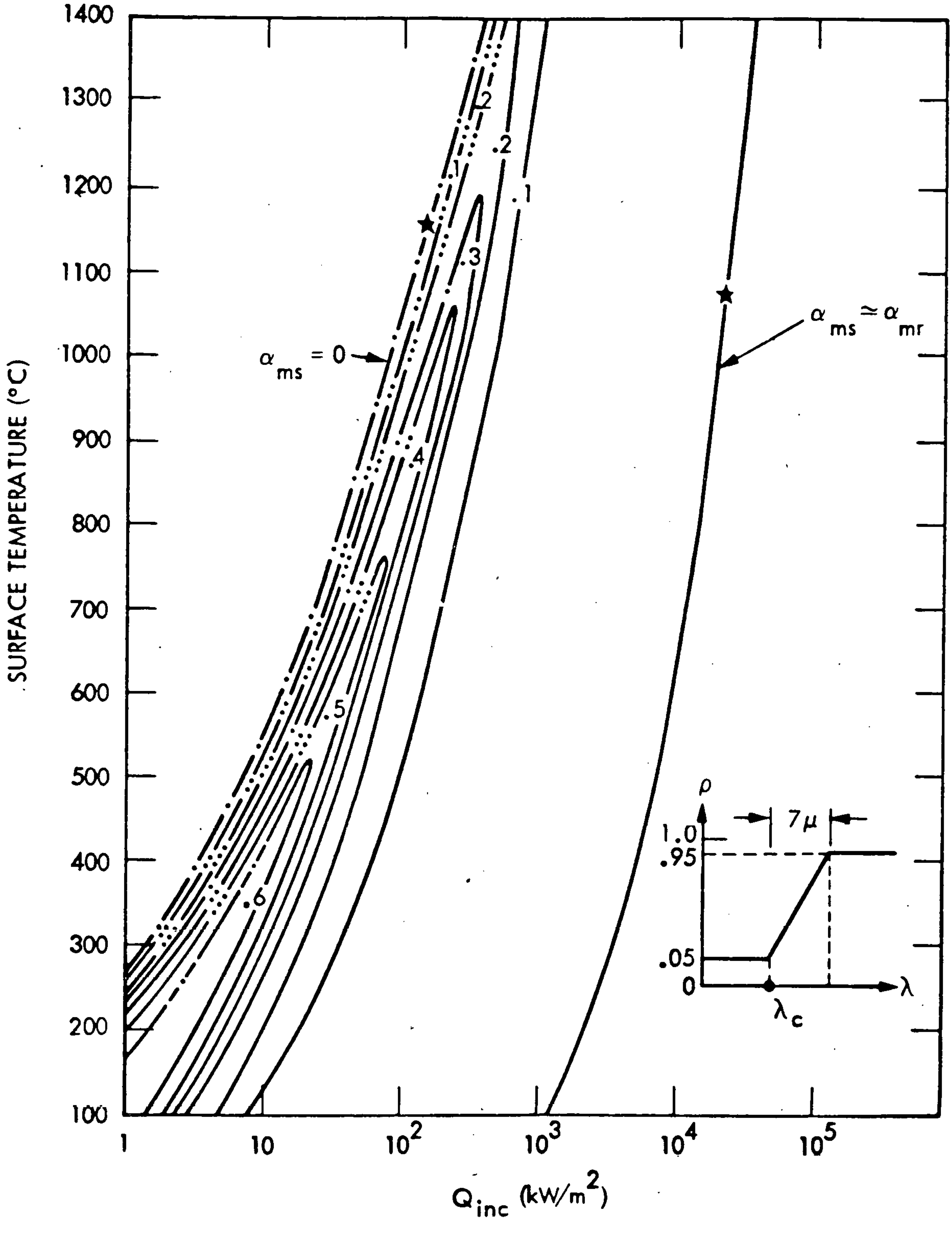


Figure 6. Isobenefit Contours for 7μ Slope Change Reflectance Coating

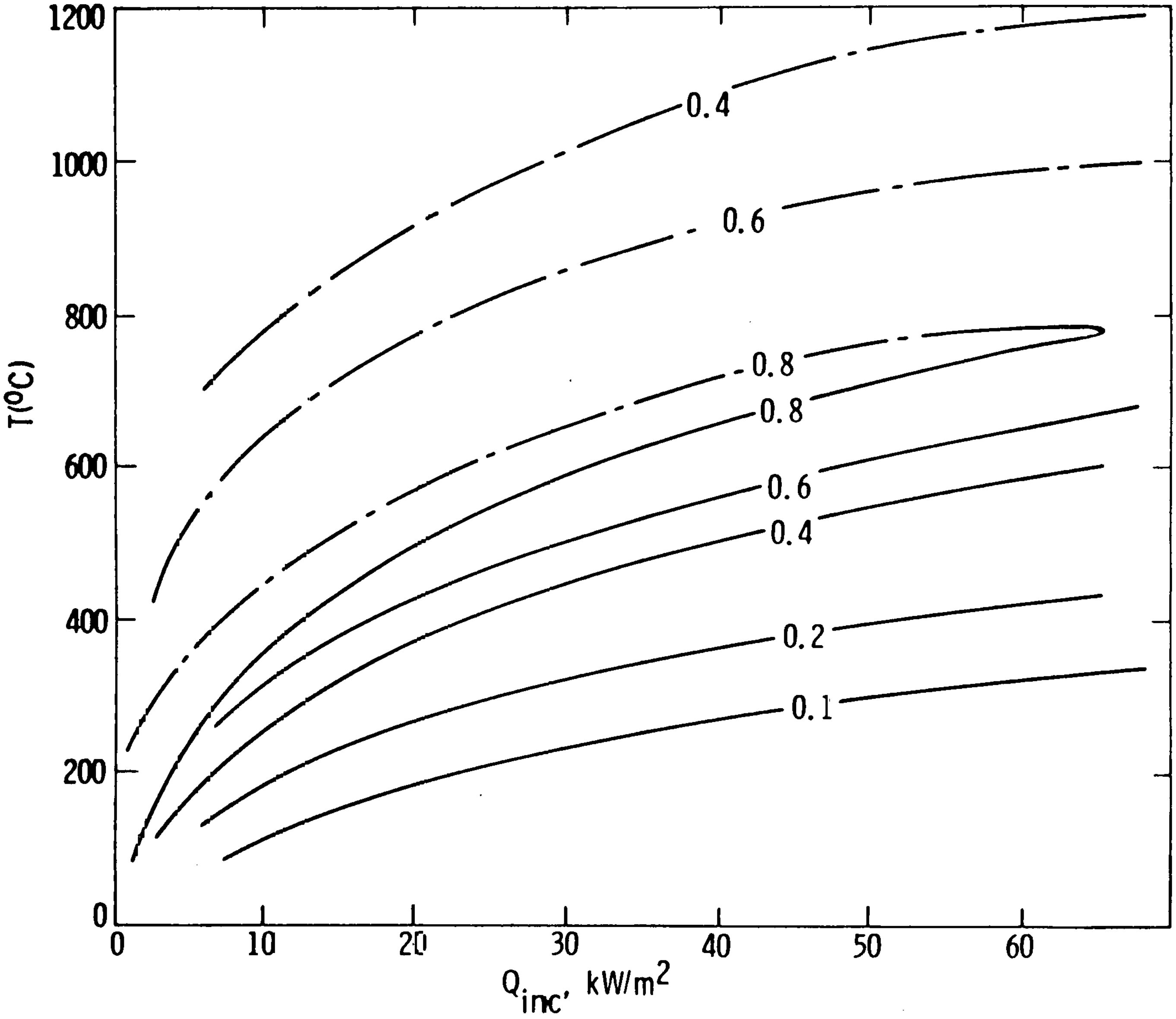


Figure 7. Isobenefit Curves for Step Change Coating

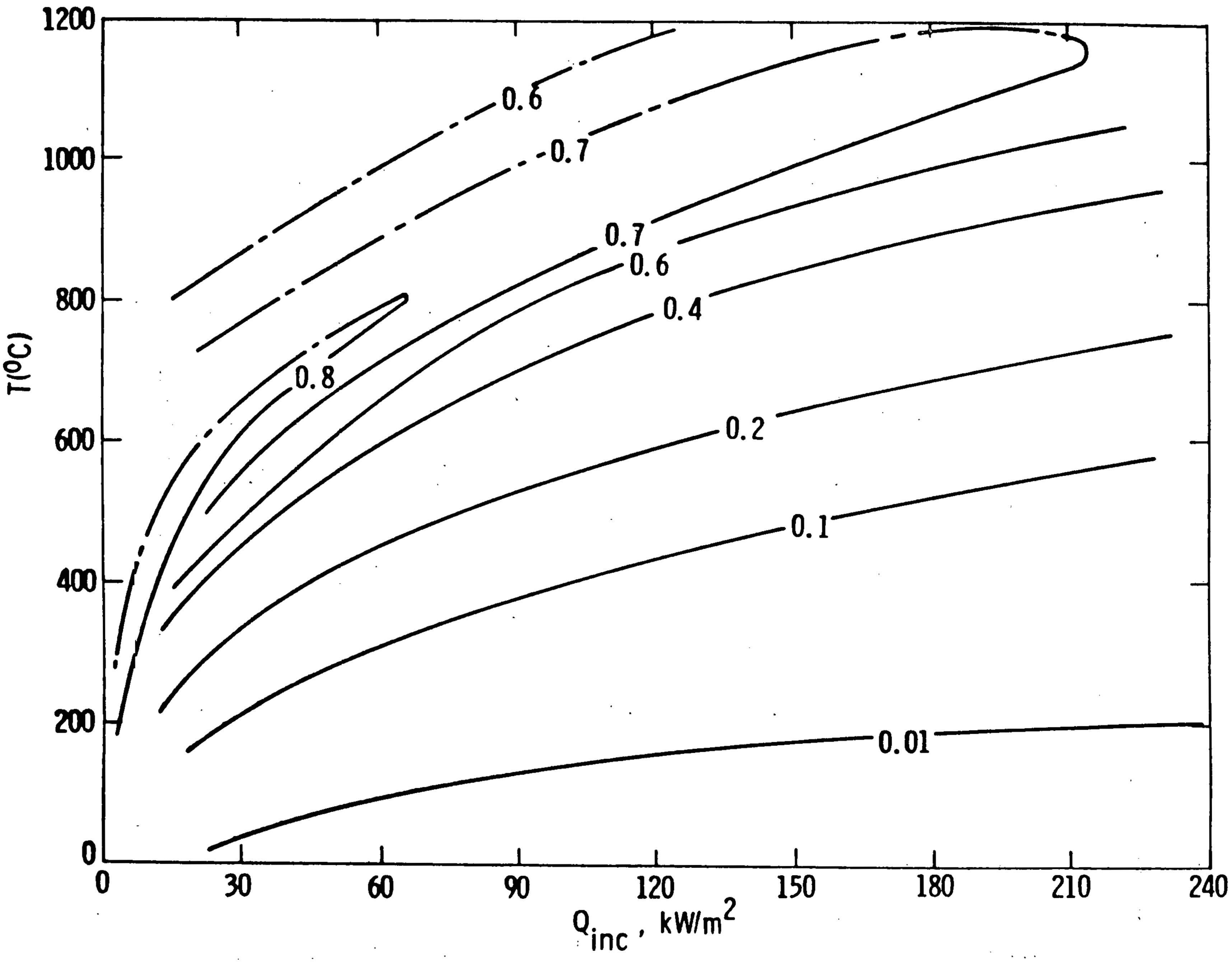


Figure 8. Isobenefit Curves Step Change Coating

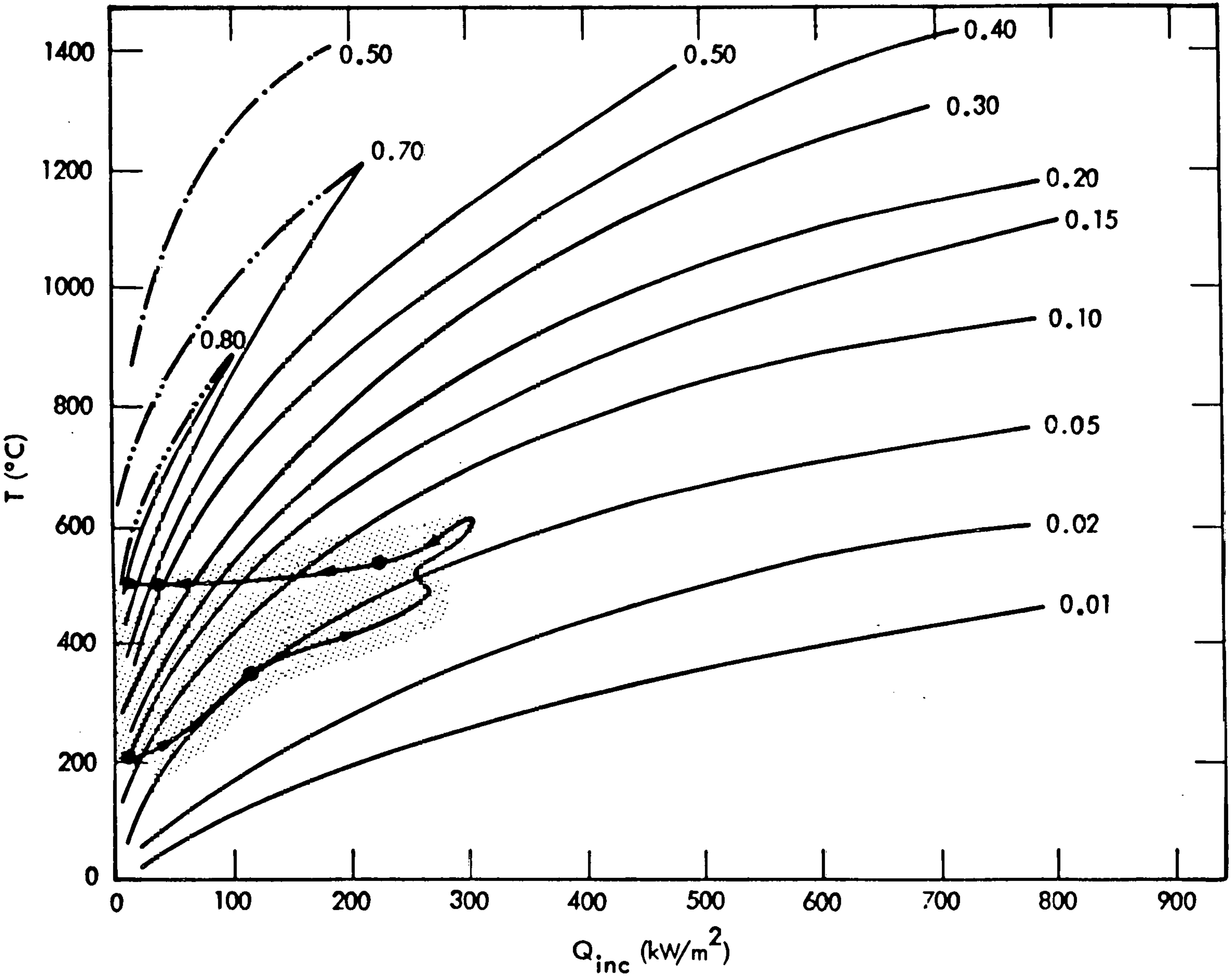


Figure 9. Isobenefit Curves for Step Change Coating

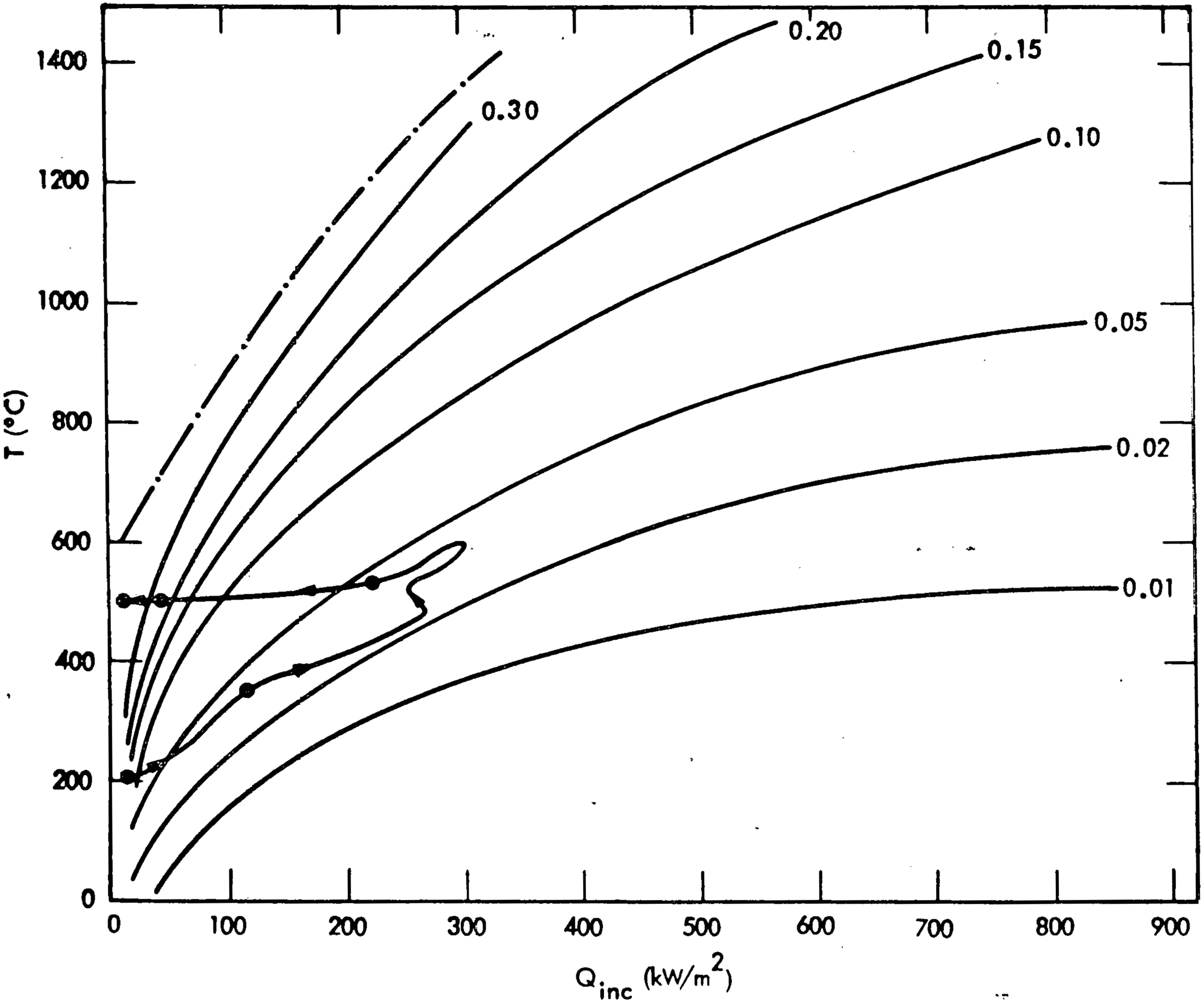


Figure 10. Isobenefit Curves for Slope Change Coating

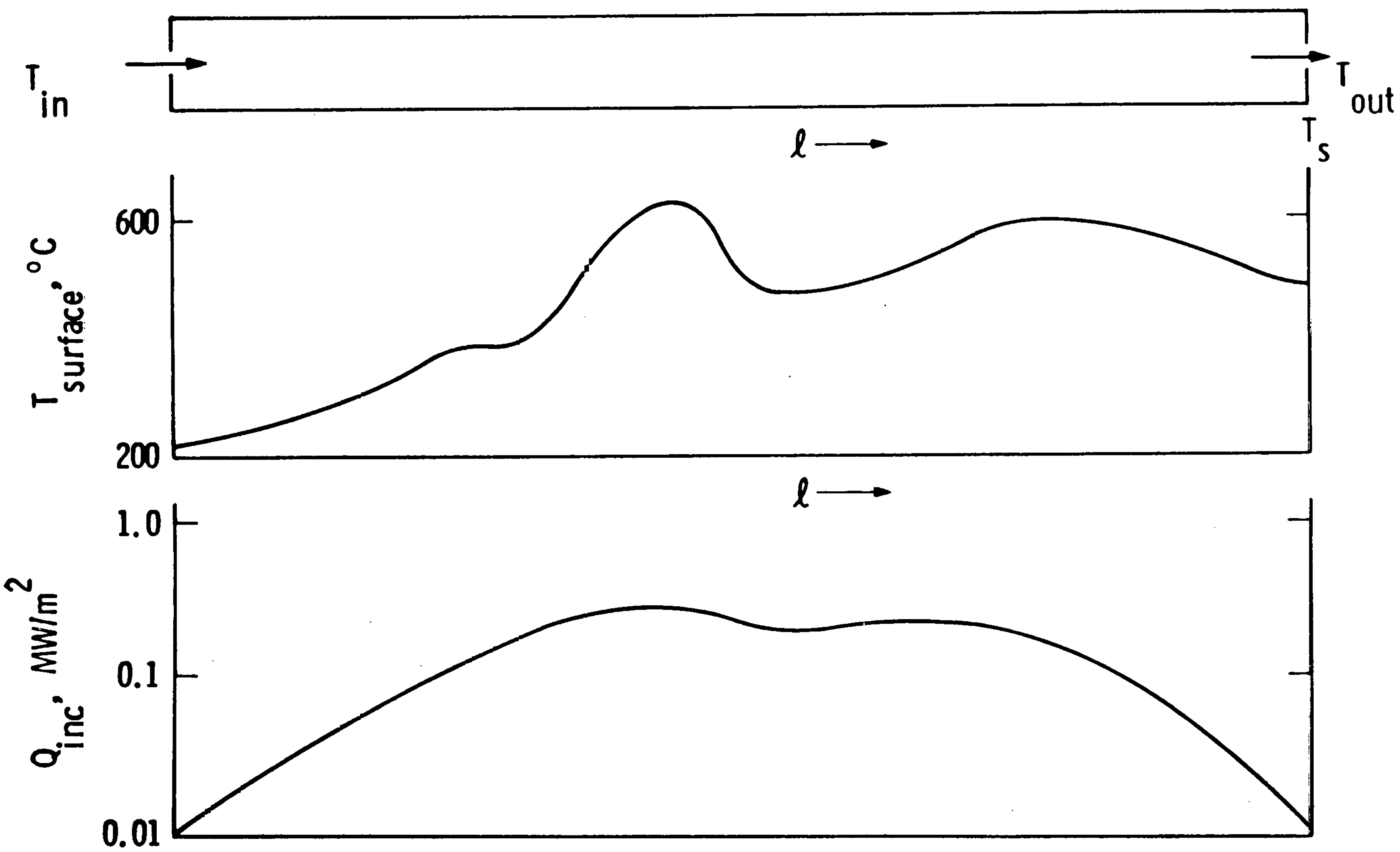


Figure 11. Possible Conditions of Temperature and Flux on an External Central Receiver Tube

THE ASSESSMENT OF TECHNICAL BENEFIT

The benefit or increase in efficiency obtained by using a "black" or spectrally selective absorber coating on the absorbing surface of a receiver may be determined by calculating the useful energy absorbed by the wall of the receiver per unit area and comparing this with that absorbed by a different surface. The expression for the useful energy absorbed per unit area, Q_{use}, is developed below:

$$Q_{use} = Q_{abs} - Q_{loss}$$

$$Q_{use} = \alpha_s \tau S \chi - [\varepsilon\sigma(T^4 - Te^4) + Q_{conv} + Q_{cond}] \qquad (1)$$

where:

α_s ≡ solar spectral absorptance

ε ≡ thermal emittance

σ ≡ Stefan Boltzmann constant

τ ≡ transmittance through the optics

S ≡ solar insolation (direct for most concentrating systems)

U.S. Standard Atmosphere was assumed

- air mass 2
- 20 mm precipitable water vapor
- 3.4 mm ozone
- atmospheric turbidity of $\alpha = 0.66$, $\beta = 0.085$

Q_{conv} ≡ convective heat loss per unit area

Q_{cond} ≡ conductive heat loss per unit area

T ≡ surface temperature of the absorber coating

Te ≡ temperature of surrounding environment

χ ≡ concentration factor

$$\chi \equiv \left(\frac{A_c}{A_R}\right) E\rho$$

where:

A_c ≡ effective aperture area of concentrator mirror

A_R ≡ illuminated area of external receiver or cavity aperture

E ≡ (1-e) where e is the fraction of energy lost due to mirror surface errors and sun tracking errors

ρ ≡ specular reflectance of mirror surface within the maximum useful cone angle

To simplify the comparison of various absorber coatings, the Q_{conv}, Q_{cond} and Te terms are ignored; however, in analyzing total receiver efficiency these terms must be included. Dividing both sides of expression (1) by the flux incident on the absorber surface, $Q_{inc} \equiv S\tau\chi$, we obtain:

$$\frac{Q_{use}}{Q_{inc}} = \alpha_s - \varepsilon \frac{\sigma T^4}{S\tau\chi} \equiv \alpha_m \qquad (2)$$

The quantity α_m in expression (2) is the "absorptance of merit" or a measure of the efficiency of the coating for converting incident concentrated flux into collectable thermal energy in the wall of the receiver. The value of α_m may be calculated for any values of α_s, ε, T, S, τ and χ. The values of the aforementioned variables are not constant for a given receiver design; position on the receiver, time of day, season, meteorology, operating condition of the engine, and a host of other variables affect these quantities. Simplifying assumptions are possible and necessary to calculate α_m but the greater their number the less credible or useful is the prediction. The χ and T terms are particularly troublesome since a uniform illumination is generally not obtained at the receiver in high temperature systems; thus, temperatures are not uniform.

The analysis presented here considers only flat absorbers. The effects of cavities or pseudo-cavities may be estimated by replacing α_s by the effective solar absortance obtained with the cavity configuration, α_s(eff), and replacing ε by ε(eff). The values of α_s(eff) and ε(eff) are illustrated for a simple geometry in Figure 1.

The evaluation technique developed for assessment of coatings compares the α_m of the selected coating to that of a reference coating by expressing ϕ, the benefit, as the difference between them.

Absorptance of merit for reference coating:

$$\alpha_{mr} = \alpha_{sr} - \frac{\varepsilon_r \sigma T^4}{S\tau\chi} \tag{3}$$

Absorptance of merit for selected coating:

$$\alpha_{ms} = \alpha_{ss} - \frac{\varepsilon_s \sigma T^4}{S\tau\chi} \tag{4}$$

$$\left.\begin{aligned} \phi &= \alpha_{ms} - \alpha_{mr} \text{ for } \alpha_{mr} > 0 \\ \phi &= \alpha_{ms} \text{ for } \alpha_{mr} \leq 0 \end{aligned}\right\} \tag{5}$$

The difference rather than the ratio was used for mathematical convenience. Expressions (3), (4) and (5) are plotted schematically in Figures 2a and 2b for a constant temperature. For flux levels above that at which α_{mr} is zero (the stagnation flux level for the reference coating at the specified temperature), the benefit term, ϕ, is the difference between α_{ms} and α_{mr} indicating the relative percent improvement. Since α_{mr} is always less than unity, the absolute percent improvement is greater than this ϕ and can be appreciably greater. Below the stagnation flux level of the reference coating, ϕ equals the absorptance of merit of the selected coating.

One reference coating and two hypothetical selective coatings were chosen to illustrate the methodology (see Fig. 3). The reference coating was a "flat-black" coating with $\rho(\lambda) = 0.05$ for all wavelengths. The ideal "step change" coating possessed a solar reflectance of 0.05 and an infrared reflectance of 0.95. It was assumed that the cutoff wavelength, λ_c, of the step change could be optimized for a given incident solar spectrum and for the thermal emittance at the temperature at which it was operating. This optimization procedure was done for every Q_{inc} and temperature at which the coating was evaluated.

The optimization procedure consisted of finding the cutoff wavelength for which the difference between the absorbed and re-emitted energy was maximized under the given condition of flux and operating temperature. Figure 4 indicates the nature of the absorptance and emittance curves as a function of λ_c and temperature for a step change coating. The optimum λ_c depends not only on these parameters but on the flux level, $S\tau\chi$, which "weights" the importance of the α_s and ε terms in expression (2).

The second hypothetical coating selected was a "slope change" coating in which the solar reflectance was 0.05 and the infrared reflectance was 0.95 (see Figure 3c). The reflectance increased at wavelengths greater than λ_c in a linear fashion over a seven micron range to the infrared value of 0.95. As in the case of the step change coating λ_c was optimized for each condition of surface temperature and incident flux level.

The reference coating used in the analysis is representative of a reasonably good black coating. The step change coating is the theoretical limit which can only be approached by real coatings. The slope change coating is representative of what is probably possible in near term development programs. Any coating may be evaluated by the software developed in this study so long as the reflectance vs wavelength curve is known for the temperatures of interest. As will become apparent in the discussion of the results, accurate assessment of the benefit of a coating in a system is highly dependent on the entire range of the operating conditions for that system.

RESULTS OF THE ANALYSIS

The results of the analysis are presented in Figures 5-10. Isobenefit contours (lines of constant ϕ) are plotted on coordinates of surface temperature T versus Q_{inc}. Figures 5 and 6 are semi-log plots which indicate the general nature of the dependencies. (Figure 2b is a constant temperature section through these plots.) The numbers on the contour lines give the value of ϕ for that line. Plotted on Figure 5 are the typical ranges of operating conditions for trough, central receiver and point focusing systems (e.g., paraboloid dishes). It is seen that the benefits for selective absorber coatings vary considerably under different conditions of temperature and flux. Figures 7-10 present linear plots of the information in Figures 5 and 6.

To interpret the information contained in these figures, one must carefully define the entire operating range of the specific system for which the coating is being considered. A single analysis of the "design point" condition is not sufficient. A weighted average of all operating conditions may indicate a benefit quite different than that obtained by the single design point calculation. Factors such as operation at lower isolation levels or the requirement to maintain high receiver temperatures at night to prevent freezing of a molten salt solution will increase the benefits of absorber coatings.

As an illustration of this, Figure 11 shows the approximate surface temperature and flux distribution along the length of one tube of an external central receiver for one time of day, at a particular season and with a particular meteorology. Figures 9 and 10 plot the "operating condition" for various portions of the tube along the extreme most diameter facing the heliostats. The benefit of the step change selective coating varies from 4% to 80%. If constant temperatures are maintained and one simply adds consideration of geometries and the variation in flux level due to the myriad of factors, the "operating condition" could fall almost anywhere within a region such as the shaded one shown for some area on the receiver under some set of realizable conditions. Clearly a more detailed analysis than that presented here is required to establish the benefits of absorber coatings in specific systems.

COST/BENEFIT/RISK ANALYSIS

A simplified form of benefit/cost analysis which could be used as an aid to decision making in the area of absorber coating R&D is presented in the following expression.

$$\frac{\text{Benefit}}{\text{Cost}} = \frac{\begin{bmatrix}\text{Performance}\\ \text{Improvement}\end{bmatrix}\begin{bmatrix}\text{Projected No.}\\ \text{of Systems}\\ \text{Installed (\$)}\end{bmatrix}\begin{bmatrix}\text{Probability}\\ \text{of Success}\end{bmatrix}\begin{bmatrix}\text{Probability}\\ \text{of System}\\ \text{Installation}\end{bmatrix}}{\begin{bmatrix}\text{Development}\\ \text{Cost of}\\ \text{Coating}\end{bmatrix} + \begin{bmatrix}\text{Hardware}\\ \text{Costs}\\ \text{of Coating}\end{bmatrix}\begin{bmatrix}\text{Total}\\ \text{Quantity}\end{bmatrix} + \begin{bmatrix}\text{Change in}\\ \text{Operating}\\ \text{Costs}\end{bmatrix}}$$

This benefit/cost ratio must be compared to similar benefit/cost analyses done for other components and technology developments and the dollars spent for absorber coatings weighted appropriately. A large uncertainty exists in the quantities in which any proposed system will be built. As the quantities increase, it is easier to recover the R&D investment. Development of better coatings will undoubtedly have effects on other technologies and component costs making them perhaps more feasible and cheaper. Additional considerations include potential changes in technology, new design concepts, potential policy changes including emphasis on other methods of power production and a time table as to when improved coatings will be needed. Although improved coatings may improve performance by only a few percent, the cost of such development is much less than many other components or technologies.

SUMMARY

- A methodology has been developed along with the required computer software for determining the relative benefit (ϕ) or absolute efficiency (α_m) of any absorber coating for which $\rho(\lambda)$ is known. Isobenefit curves are plotted on coordinates of surface operating temperature and incident flux level.
- To define the benefits obtained by using a coating in a specific system, the range of operating conditions for the system must be used to "weight" the various benefits obtained under the different conditions. From this method, some "average" value of coating efficiency can be calculated.
- The benefits are highly dependent on the chosen design point, which is, in turn, dependent on many other factors.
- Systems which operate at the highest flux level possible for a given surface temperature will, in general, obtain diminishing returns for selective absorber coatings. It is not known at present whether such systems will be the most economical.
- If extensions of the present analysis are used in conjunction with a cost/benefit analysis, a rational basis for a coatings development program can be established. Such a cost/benefit analysis must be compared with similar analyses of other technologies and components.

MR. SIEVERS: One of the important things in the solar thermal program is that you've got to make sure you have covered all possibilities when you use this kind of analysis to come to some very specific conclusion, and I would like to give an example of how all possible systems haven't been considered yet and I will do this with just two viewgraphs. Now, this solar thermal business can not only be used in the ways that we've heard so far, but you can also use it in a solar energy transformer mode where you capture the sun's spectrum, the broad solar spectrum with one surface and then you convert it to a narrow band using a second surface which is thermally connected to the first surface, that's solar thermal. I talked to the photovoltaic people and they told me that was solar thermal, don't come to photovoltaics. Now, if you can do that, if you can come up with a narrow spectrum like that, of course you can then match it to a photovoltaic material and you can get much higher efficiencies. So, let's just take a look at a system which relies very heavily on sharp absorptivity, sharp emissivity and knowing everything that is going on both in the visible and in the infrared.

Here's the two surfaces in contact with copper, surface one which is our broad absorber, surface two which is our narrow emitter, and it turns out that if you use lead sulfide, something that people don't even consider for photovoltaics because it is out of the solar spectrum, you can do a very good conversion at room temperature and end up with, forty percent or something like that.

You can't do this with black paint. You've got to come up with a system which has a sharp step function for the outer surface but then has this crazy narrow resonance for the inner surface. These are systems that haven't been developed, but you can imagine for example zirconium dioxide layer on the inner surface doped with OH which has a band right at the lead sulfide energy gap, so you could get this high conversion and of course the outer surface we are still working on. Everybody is scrambling around that one, and I'm not pushing this as practical--I'm trying to put this out as philosophy.

MR. SCHWARTZ: There is merit though to a steam system in comparison to photovoltaics and it has to do with one word, efficiency.

MR. IGNATIEV: By and large what I gathered from the JPL presentations is that there are possibilities for selective coatings. We will have to worry about cost effectiveness and I guess maybe that's what it all boils down to. However, something which has not been really attacked or significantly considered is the fact that if we take and run something up at 600 or 700 C it's not going to stay there. Keith Masterson showed us yesterday that in fact if you put things in the solar furnace and heat it up whatever you have on the surface even if it's a metallic oxide it spalls off, it oxidizes off, it nitrodizes off. The tube burns through in the end and that in itself is also a coating problem. It may not be a black coating problem or a selective coating problem, but it is a coating problem, and the point is that no matter what you decide on selective versus non-selective, you're going to have to attack that problem. It has been said that we make boilers that last for years, but boilers work in a reducing atmosphere, and that is totally different than an oxidizing atmosphere. Do we have anything like that? No.

UNIDENTIFIED SPEAKER: I take issue with that.

MR. IGNATIEV: Good. Then let's take some issue on that. I don't know, maybe I'm --

UNIDENTIFIED SPEAKER: Some old matrix material, they function in vacuum.

MR. IGNATIEV: Fine, but we're not in vacuum, at least by and large the number of the considerations are not in vacuum.

MR. DICKSON: Will you explain to me how gold is going to move the oxygen through? Gold will not move oxygen through, so it's not going to oxidize. Gold is inherently resistent to oxide movement.

MR. IGNATIEV: There may be a system which will work, but the point is that it has not been looked at in detail in terms of high temperatures, oxidation, and corrosion.

MR. DICKSON: What assumptions did you make in the temperature of the inlet and outlet to the effect that it is going to be radiating even though it doesn't have any flux, it is going to be radiating back into the environment?

CHAIRMAN ADAMS: None at all. That is a loss that wasn't included. To answer your question, I don't think we can attack all the problems. I think what JPL is discussing here is a way to determine which problems to tackle. What we gave was an engineering presentation. We are talking about engineering parameters that just barely get out of the systems consideration and into the coatings as far as alpha and epsilon. I think the decision as to which coatings to develop and what directions to go in because of the nature of the Department of Energy and the directions set by ERDA and the emphasis on hardware demonstrations, the direction has to be set beginning with the JPL kind of analysis. I agree with what you say that we don't understand these things and there is a lot of work to be done. We can't set out and start attacking ten things all at once. We have limited resources and we have to pick two or three of the best ones.

MR. RICHMOND: I was kind of disturbed when we were talking about the coatings that were used in the vacuum environment, that we considered only the properties of the coating and not the properties of the enclosure or the window. The window can have a very significant effect. With regard to the durability of the coatings another problem that should be looked into is whether or not there is volatization of any of the constituents of the coating that may deposit on the cold window and degrade the efficiency.

MR. MELAMED: There is one point that confused me a little bit in your presentation, Marc. You made the statement at one point that you considered an improvement in collector reflectivity a major goal in improving system performance and at the same time an improvement in the absorbing surface property would be a minor or a "tweeking" improvement, yet isn't it true that if you have a non-selective but merely highly absorbing coating for your reference coating, that if you could achieve one percent improvement in reflector redirection of energy to the receiver, wouldn't that be identical in performance to a one percent improvement in absorber, absorptance at the receiver?

MR. WEN: For a flat plate you are right. One percent improvement of alpha is equivalent to one percent in reflectance.

MR. SCHWARTZ: I have a comment about alpha/epsilon that I have held off on. As far as the cavities are concerned, everyone claims alpha is very important. I would have to say that you may find that epsilon is more important at the high temperature. If you are at $\alpha = 0.9$ for a material and you're at $\varepsilon = 0.3$, you may want to give ground on the alpha to get a better epsilon, a lower epsilon because you may not be losing very much in the effective absorptivity of the cavity. Basically I'm talking about cavity effects.

UNIDENTIFIED SPEAKER: Yes, but the same property of the cavity that makes improvement in alpha non-consequential also makes it difficult to do much with epsilon.

MR. RICHMOND: There is another point when you are dealing with cavities that I don't think has been discussed before which really is not important when you are dealing with flat receivers. It is important to know how much of the incident flux that is reflected is reflected back out the opening of the cavity on the first bounce. This very largely determines the efficiency of the cavity as a collector, and the very high absorptance coatings have a very pronounced tendency to be retroreflectors so that there may be situations where a very high absorptance coating is not the best coating for a cavity. In fact we made some measurements on several cavities for the Jet Propulsion Lab quite some time ago. We were comparing two different very black coatings. They were both Parsons Optical Black. One was made in England and the other was made by Epley Laboratory in this country. When we measured the reflectance of these two coatings on the flat plate, the coating made in England had about half of the reflectance of the coating made by the Epley Laboratories, and yet when these two coatings were applied to a cavity and we measured the reflectance of the cavity, the two coatings were almost identical. We looked into it in further detail and found that the Parsons Optical Black made in England was a very pronounced retroreflector and while it had only about half of the reflectance of the Epley Parsons Optical Black, most of the energy that was being reflected on the first bounce was reflected right back out the opening.

MR. SCHWARTZ: Can you explain the reasoning for this.

MR. RICHMOND: Many of the very high absorptance coatings obtain their high absorptance by their surface morphology. Now, they tend to be sort of fairy castle structures and when you get these structures they tend to be rather pronounced retroreflectors, although they also have very high absorptance and the Parsons Optical Black made in England had a much more pronounced rough surface than that made by the Epley Laboratory. If you are interested, I can send you a copy of that report.

MR. MELAMED: If what you say is true, then by simply tilting the plane of the receiver aperture to get non retroreflection, you might go in the other direction. It might make the previously poorer surface a better surface. Has this been tried?

MR. RICHMOND: These coatings are retroreflectors regardless of the angle of incidence. They tend to reflect right back in the direction of the incident energy.

MR. MELAMED: Then this isn't a random distribution of stalactites and stalagmites, I take it, it must be something else, because with a "random" distribution this would not be true, would it?

UNIDENTIFIED SPEAKER: No, what you are saying applies primarily to things like 3M and Parsons Black and when you hit them, they do retroreflect, but there are very strong wavelength/temperature effects.

MR. RICHMOND: Yes, but you've got to watch out for these effects.

UNIDENTIFIED SPEAKER: Well, most of the coatings we are dealing with here do not have them. The black chrome wouldn't have them. The black chrome would have a great deal of specularity, but is not a retroreflector.

MR. RICHMOND: Most of the very good diffuse reflectors do have significant retroreflectance. This applies to magnesium oxide, sulfur, all of the integrating sphere coatings do have measurable retroreflectance.

MR. SCHWARTZ: If you have specularity, you may find that you can achieve $\alpha = 0.99$ in a cavity by only having a material that has an $\alpha = 0.7$ because if you get enough bounces in there you have it made. In line with that I think we need bi-directional reflectance measurements. The engineers can then start using Monte Carlo coatings for the cavities, and I understand that there are some heat transfer codes. I believe Boeing has one that is a Monte Carlo code and to just assume that reflectance specular or diffuse I think is very naive, particularly since you can get the increase in performance by assuming the right characteristics which is toward a specular surface.

MR. WEN: Concerning the cavity coating, I think the Russian papers did a lot of experiments to recommend a coating. In fact, it is almost white. They want to even out the distribution so that they would not have hot spots and burn out. They chose to make it a high temperature ceramic and make it highly reflective. In that way they improved not only the efficiency, but also made it a lot easier to design. You don't have to worry about the unevenness of the flux mapping and the burn out and a lot of other problems.

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Summary of Discussion

CHAIRMAN ELLIOTT: We have to know some of the systems safety and survival questions that may arise. In the central receiver, we are very much aware and very concerned. If you blow a tube in this boiler, even a modular boiler in which you can replace a panel, the plant is going to have to shut down until you do this, and this is a very big expensive operation.

We want to know what protection we have against that type of disabling incident, and whether the resources exist in the coatings field to deal with these.

We need to know what is going to happen to that thing out in the real world exposed to everything from dust and rain to birds that perch on it. We have to not always think in terms of hemispherical or normal optical properties.

The incident angle range that you are talking about and what parts of the angular range really contributes to the accrual of energy are very important factors and they will dictate whether you might want to go to a graded filter versus a stack filter.

In normal incidence, stacks work fine, you know where they are going. In off angle, they don't work very well as Bernie illustrated to us.

We need to know about the concentration factor for a couple of reasons. We certainly need to know just how much flux is going on to this thing. It appears that there may be some sort of photon-assisted chemical process that we might wish to think about. They may not be real, they may go away when we look at them. But, they are there potentially, and we need some expertise in photochemistry aspects so to speak.

Al Sievers raised that question, and that's a very pertinent one. You can simulate things by stacking a calrod heater inside a tube, but you are not doing a very good job of simulating how the heat actually flows through a coated tube. You can put it under graphite ilumination and do a little better. But, the ultimate test is the real sun, and the real sun may well differ from anything you can do at the lab bench or in the shop.

We saw from the analysis yesterday afternoon that it is one thing to look at the system design operating point--you know, noon on June 21st, the sun on the meridian shining brightly, no clouds in the sky. You can, of course, and it is a fatal assumption this time the systems people often make that you design for the peak period and the Lord will take care of everything else, and the system is going to work beautifully.

We saw from Marc's analysis and from Al Wen's analysis that your real problem may be in picking up the scraps at three in the afternoon in the winter. And if there are things in the coating field that don't make too great a performance improvement at noon at June 21st, but that really pay off on October 22nd, that may be the difference that puts us in the economic ballpark, and economics is the ultimate name of the game. We are not worried for the pilot money right now that it be cost effective, but it has got to look like it is going to be cost effective someday.

The irrigation systems are going to have to start looking cost effective very soon, and the fine tuning is very important there.

The geometrical configuration, I think we have oversimplified here. I haven't seen anything in the systems that look like a cavity in the sense of the black body integrating sphere. The bench gadgets you look into to calibrate your pyrometers. We are dealing with cavity ratios that are like four, five, maybe eight, maybe ten is the best we are likely to see, and frankly, those are lousy cavities. They are not going to do your emission control for you as cavities.

It is easy to say because it is a cavity, why don't you just smoke it with magnesium oxide or something on the inside. Maybe, maybe not.

We saw that there are situations, Al Wen pointed out situations where you are going to have to think real carefully about what you do with the coatings that you put inside a cavity, the quasi cavities that we are really dealing with.

Sunlight has to pass through the atmosphere. I don't think there is anybody in the game now who is dealing with AMO spectra. If there is, I hope he will realign himself.

AM1 is pretty unrealistic. There is only a narrow strip around the world and a few times in the year in which you are going to be dealing with an AM1 atmosphere. AM2 may be pretty representative of most of the direct insolation.

But when you have heliostats 1,500 meters out that are shining light at something sitting 200 meters up in the sky, you are going through a part of the atmosphere that the optics people and astronomers don't very often think of. You are dealing with very near surface phenomena, you are dealing with horizontal structure in the atmosphere as far as the water and dust burdens may be concerned. We find we get a tremendous attenuation loss, it is three, four, five percent from some of those remote heliostats, and it is to the point where it really pushes that last couple of heliostats out there in the corner of the field into cost ineffectiveness, and we have got to recoup that somewhere else, and here we have possibly an opportunity.

A big gap we saw in the measurements, and again, I am not sophisticated enough to know whether this is a real information gap or a verification gap. But, we have very, very little information on direct measurements of what the absorption and emission of these surfaces at temperature, under working conditions at the angles that we want to look at over time and wavelengths.

We certainly need to verify the calculations so that room temperature values taken with a particular geometric configuration can be extrapolated to the particular configuration used.

We also need integrated values for quick checks and quick summaries of performance, but to do that, we may have to get down into the spectral dependence in very, very deep and rigorous fashion at least once through each time to make sure we know where we are.

We have to know the way the coatings behave over time both through the diurnal cycle and the annual cycle. The possibility of reversible and irreversible changes, step changes, continuous changes, all these things go into this scenario that we use for discussion between the user and the supplier.

MR. RICHMOND: One of the things that we discussed last night that is not indicated on that diagram yet is the need for more dialogue and more interaction between the systems design people and the coating development people, and we ought to sort of close that loop.

MR. SCHWARTZ: I think there ought to be a high risk type of activity called basic research that is divorced from this in which you are not always that clairvoyant that you know which way research ought to go. Research opens up new avenues, new break throughs, and you should not constrain research to development.

CHAIRMAN ELLIOTT: We have heard quite a bit generally disfavorably about what you can do in the laboratory that will tell you in a short time what your material is going to do out in the real world over a long time without the kind of loving attention that you can afford to provide it in the lab or shop.

We certainly need to know how to correlate real time with the kind of time that nature provides us, and there are all kinds of problems with cycling and temperature time rates and so on that make this not an easy question. You don't simply throw eight suns on a piece of material for one-eighth of the time and assume that you would know the same thing that you would know at the end of eight years on the one year. So, those are nonlinear relations.

We have got some special concerns about the particular environment these things might be in. I naively said that if you worry about the kind of environment of a central receiver in the middle of Denver--I think the newspaper said yesterday we had some sort of a pollution alert going here--all you do is phone up the local environment office and ask what their levels are SO_2 and NO_x, and so on, are. No way. Those pollutions are defined on an institutional and convenience basis, and they may well not be the ones that are either burning your eyes or turning your nice black coating pale gray. So, I guess there are some more inputs for the chemically-oriented among you.

The effects of the humidity, rain, and dust, they are part of the natural environment, and the humidity or absence thereof or the sudden pulsations thereof are characteristic of the desert environment where a lot of these things are going out early. The dust in the desert tends to be quite alkaline. There may be some chemical interactions there.

Aluminum put out in parts of the desert gets pitted and eventually disappears. Redwood fence posts which last forever last six or eight months stuffed in the alkaline soil.

The combination of real photons cascading in all of these things. Where do you get photons other than out in the real world at Odeillo or White Sands or Albuquerque? John Vossen suggested that you could make an oxygen glow discharge. Is there something there than we can use to simulate the effect of real photons falling on what may be a rather delicate material with some potential for oxidation?

We also, of course, have the possibility of what happens if you get a crack or leak in a system. With the advanced central receiver system, you are spraying sodium out in the sky through a small pinhole, I think what happens to your coating in the immediate vicinity of this pinhole is going to be maybe secondary or tertiary consideration. But, there may be systems where you have the long strings of linear absorbers strung through 400 hundred feet of trough with all kinds of flexure and U-shaped joints. You want to know whether you could tolerate leaks of your working fluid.

We talk about vacuums as if they were vacuums and air as if it were air. Well, air isn't air, it has got all kinds of things in it and falling through it. Similarly, vacuums are not vacuums. You really can't afford much better than a roughing pump for a major installation, and you are going to have residuals floating around in there. Obviously, things like pump oil and oxygen from the air that leaks in. You might have some volatile from sealants, and bonding materials and coating solvents. How tolerant is your system of the kind of levels it will meet in the internal environment both in normal operation and in various situations ranging up to the loss of coolant. The resistence heating is good for a first cut. I think you want to think very carefully about where those therms are flowing, which way they are flowing, what gradients exist within the tube wall, within the coating itself if the coating is fairly thick. You want to use actual photons, playing with a real atmosphere, looking at things like adhesion and cohesion of films.

We have to look at the reversible as well as the irreverible effects of optical properties. The irreversible effects are to some degree evident when you take your sample or your gadget up to temperature and bring it back down again. It looks different, it has things peeling off of it, it has blisters, whatever.

Some of the reversible effects may not be so evident. You measure the reflectance, absorptance and the emittance at room temperature, and you think you know where you are, and you make some simple textbook extrapolations. You get up there at 500 C, things may not be behaving the way you anticipated. This argues back making at least spot checks at real temperatures and something simulating the real configuration.

We know what we mean when we talk about a solar spectrum, right? We know what we mean when we talk about absorptance and emittance. It is very evident that each of us in his own discipline uses these words with a slightly different flavor, slightly different understanding.

What do you want? You want a dictionary. Do we want to sit here as a workshop and compile a lexicon of all radiant transfer terminology that might apply to this field? Why should we bother? Joe brought us a stack of books that give us a very good place to work from.

MR. RICHMOND: The point that I wanted to bring up is that in all of this testing, particularly testing at temperatures and also when considering the effect of leaks on coatings that are to be used in a vacuum environment, you want to be very much aware of the possibility of contamination of the enclosure which will reduce its transmittance and reduce the optical efficiency of the system, and I think that ought to be included in the summary.

CHAIRMAN ELLIOTT: That's a very, very good point. We ran into this on a macro scale in the central receiver project. As you know, all of our heliostats are iron and glass gadgets except for one, and that consisted of very delicate mylar foil protected from the environment inside a tent, a nice spherical dome which is now a very expensive, but reasonably high transmission plastic, and the film looks great. The mirror looks great. The gravity even sags the thing into something resembling the right focal distance that improves your image a little bit.

First of all, there is that dome sitting out there. It has in and out transmittance of .75 when it is clean, it isn't always clean.

Sometimes I wander out to see the sample that was set up in a live outdoor museum at Livermore from the 5MW test. It was one of these funny days that you get there with the sunlight and cold with frost all over the inside of the enclosure.

In a sense, one of the things we did when they specified heliostats is that the heliostat is the whole package including whatever you put over it to protect it from the real world. You have the same thing with an envelope. The envelope is in a sense a part of your coating. It is there because it retains a vacuum that you need to make the coating work. It also is there to protect the coating from the weather, so it doesn't get covered with dust or humidity.

Anybody who has driven a European-made car in the last 10 years has probably noticed that if it is five years old, you still get that residual film from the vinyl solvents in the dashboard. It is a nuisance, and it is hard to get off.

One thing I would like to throw out to the floor, but I think we might defer discussion on it to give you a chance to think about it, how do we best insure that the communication, the handshake that was started here over these past two-and-a-half days continues and we continue talking to each other, and we continue talking the same language? We could start a standard UC-173 distribution list. However two years from now, that is going to be totally inoperative.

One thing that was suggested is the answer that emerges everytime, but I think it is a good one, take the attendance list at this workshop and add any colleagues that ought to be on it.

MR. RICHMOND: Since we don't have another workshop scheduled, there is a meeting coming up in about six months that I suspect many of us will be present at, and that is the meeting of the Bureau of Standards in May on testing of solar energy materials and systems.

CHAIRMAN ELLIOTT: We need testing and measurement. We need to find out what the testing and measurement resources are.

But basically, I think we have a canvas going out to find out what measurement resources exist. It started with the discussion of --

MR. SCHWARTZ: Just one thing, hot alpha.

CHAIRMAN ELLIOTT: Okay; I didn't understand you completely on that.

MR. SCHWARTZ: It is very preliminary.

CHAIRMAN ELLIOTT: If anybody wants to add a couple of sheets listing other resources to that--no?

MR. SCHWARTZ: No. Joe is going to handle that. That's what DOE has commissioned him to do.

CHAIRMAN ELLIOTT: Is that a correct understanding, Joe?

MR. RICHMOND: I think so.

CHAIRMAN ELLIOTT: One very good example, the one that is very dear to my heart is that we had a workshop on large scale solar test facilities in Las Cruces I think it was in early 1975, and being in Las Cruces probably the reason it was there, we wandered out in a caravan of cars through the White Sands Range and found ourselves down at the south end of the range at this pretty impressive structure. For many of us, it was the first solar facility of any credible magnitude that we'd seen.

That thing was set up in Natick, Massachusetts, would you believe, to collect sunlight and see how protective clothing, protective gear, various materials would respond to the very sharp rise time, high intensity photon flux that you might get from some military event.

And when it apparently had answered all of the questions of the people who were asking those questions, and they went away or got involved in other things, it sat there gathering cobwebs and somebody said, hey, should we tear it down? It is pretty, it has a lot of glass in it, it cost a lot of money, maybe it has got some life in it. You know, the Army has got a spot down in New Mexico, I bet they have got lots of sunlight down there, and this is really a solar gadget, why don't we ship it to New Mexico.

Well, we went down to see thing thing and it was sitting there with about 15 percent of the mirrors missing or broken, and the others in a severely degraded state. A large paraboloid faceted up from many slightly curved mirrors. It is fed by a large heliostat, the first really big heliostat any of us had seen in spite of all of the talk about heliostats. You see they are 20 to 40 feet square and that's a darn impressive piece of glass to move around, and keep pointed. So, we learned a lot there.

The heliostat picks up the sunlight, bounces it off the paraboloid, which brings it to a focus up on a building siding up on top of a ladder.

We all clamored up and down in a 25 knot wind, and we began to see what it might be like atop a central receiver tower.

You know, in about three months, that thing was polished up, the mirrors had been replaced, it was running. It has been turning out concentrated solar fluxes, I think well beyond the 35 kilowatts that people had designed it for, and we saw the output of half a dozen test programs that have been conducted with that thing in the last couple of days.

There is a facility which had fallen into disuse which still had its potential. I don't know what it cost to rehabilitate it, but I don't think it was very much.

One of the rather exciting things, I think, was the last hour spent here yesterday afternoon before the discussion session. I have been involved peripherally in an awful lot of system analysis, and I have seen some stuff that didn't really excite me too much and I have seen some very good things.

I was very impressed when Marc presented sort of a general philosophy from JPL, and then Al Wen applied it to one specific configuration. As it happens, a configuration that I am not too familiar with and hadn't thought too much about at least not for a long time.

The illumination that I got from this was that it is the off-design performance that is going to make or break you in any kind of a economic system. There may be cost effective things you can feed in that will beef up your off-design performance to the point that this research will not only pay for itself, but actually pay for all the implications of it over and over again.

What I want to do is go back and take the numbers that we have for the selected design for the central receiver and get Al Skinrood and Marc and some other people together and run some of the numbers we have through a system, see if they come out looking like the numbers that we think we are getting out, maybe we will come back and we will be making a real heavy and real near term request for some support on what we put on the outside of that big pipe organ.

MR. SCHWARTZ: I think that the weakness of the coatings program is basically that people don't know the requirements.

If somebody were to ask me today what kind of coating you need, I couldn't tell you.

CHAIRMAN ELLIOTT: We have a whole spectrum of requirements out there, and they are an enormous spectrum, and they are a moving target. And I don't think even a real time continuing workshop could keep up with specifying requirements because those requirements change.

By that time, you have a project going, you are focused down with a much more narrowly-directed bunch of people who are dealing in great depth with the parameters, but only for that particular system with some sensitivity ranges around them.

If you wanted that level of detail what you need to do is a proper analysis, I don't see any broad analyses that are going to give you credible output. I think you need to get really into design details.

You saw what Marc needed on one element of one collector at one point in time. We could overwhelm you with detail.

The coatings community unfortunately doesn't frequently interact with the systems designers.

MR. CARROLL: Please do not take the results of Al Wen's paper and Marc Adams' paper and consider those a direction. These are a first step indicating the types of things we need to do to determine where the coating program ought to go.

CHAIRMAN ELLIOTT: Sure.

MR. CARROLL: Don't over interpret them. Don't take those as a final answer, they are not, either one of them.

CHAIRMAN ELLIOTT: But, they are an example of innovative systems analysis. Hopefully, there will be more examples and some of these will come to fruition as working analytical tools.

MR. NELSON: Rick Nelson, Acurex. I really don't understand why there seems to be this prevailing attitude here that black chrome has kind of laid to rest the problems below 350 C for distributor collector heads.

MR. MELAMED: As a matter of fact, not only has it not been laid to rest, but I think the people at Albuquerque who have been looking at numerous instances of black chrome receivers have developed some concern in the last several months as to how durable black chrome may, in fact, be.

They have observed, for example, gray spots on receivers which have been cycled under real live conditions with parabolic troughs and ratios of about 40 to 1. Right now, this is an area of concern.

As a matter of fact, although this first regime was dedicated to the capability of black chrome, it seems to me, that one of the things we ought to do and I have been pushing for it is to have a material which is at least as good as if not better than black chrome in the same temperature regime.

These may not be anomalies that Albuquerque people have observed. It could be a real thing which hasn't emerged before only because there hasn't been enough real world observation of the long-term effects. Their effects are long term because they haven't looked at the performance of reservoirs coated with black chrome over that long period of time, nor have the concentrations been that high. I think the maximum concentration they have looked at has been about 30 or 40 to 1. And yet even at these levels, at these temperatures, there have been problems.

Now, regarding photon flux and high energy photochemistry, in the case of the low concentration ratio receivers, we have what may be a natural barrier to this because the glass is probably opaque to UV below 350 nm

CHAIRMAN ELLIOTT: So is the atmosphere pretty much.

MR. MELAMED: No, the atmosphere really isn't. The atmosphere is opaque only below 290 nm. But between 290 and 350nm you have a fairly good absorption by the glass. So really, concerning photochemical effects in the case of isolated receivers surrounded by an evacuate glass tube you only have to worry about photons lower energy than 350 nm

There are 30 or 40 people, working independently, who have designed systems and opted for black chrome. At the very least, it seems to me that we should provide the technical community sufficient knowledge about black chrome properties that they can have some justification in their choice, and if it turns out that research or examination of the properties of black chrome in an area which is not related necessarily to systems development the way we have been talking about can uncover certain weaknesses of black chrome, certainly we are in a position to do and we should do it. There is no question in my mind about that.

If there is anything that we can uncover about the weakness of black chrome, we should uncover it rapidly and make it known so that people can switch tracks. Right now, there is no other track and that's a weakness of our program. We should have an alternate track.

MR. GUTSTEIN: You are aware that there is a solar thermal test facility users association, and they can coordinate experiments in which we want to get exposure to sunlight, concentrated sunlight. They will coordinate not only the STTF, the five megawatt STTF, but there is also the White Sands and the Georgia Institute of Technology has another facility which will accept experiments, and you ought to be aware of that capability, and there are more than one facility to put experiments in.

CHAIRMAN ELLIOTT: That's great, Marty, and I am particularly delighted to hear that the users association is going to undertake coordination of all the major facility usage.

MR. GUTSTEIN: In fact, they will coordinate with the Odeillo facility if they need to go to the French.

CHAIRMAN ELLIOTT: The users group is going to be awfully glad to receive well thought out, well planned test programs at any level. They have a good bunch of people. Who is chairman or a contact on that Marty?

MR. GUTSTEIN: Well, actually SERI is a good possibility. The users association itself is located at Albuquerque. They have an executive director, Frank Smith. Al Hildebrandt at the University of Houston is the director.

MR. SERAPHIN: The day before I left they sent out a manual on how to go about getting into the act, how to apply for using the facility, and so on. It is a very detailed procedure that you have to go through. (See attached Users Association intention.)

MR. DICKSON: I want to respond to Doug's comments in particular about gold, and I think some of the comments that Bernie made about the status of where our films are.

First of all, gold is a metal, and its value is how it is used, and I think that the films that are devloped with the gold matrix are probably very essential for the short-term application of solar thermal energy, in particular, when we are talking about working in the range 450 C, 500 C, and above.

I think from the indications we have and I have to admit that Engelhard has not gone into a deep analysis of the cost, but I think when you look at the material values of the gold that would be in this type of film and the proces costs of applying these films, I think you are going to see that these gold films are probably going to be quite cost effective. And I think probably for the next few years, we are going to see this type of situation, probably the next decade at least.

Of course, at Engelhard, we always live with the fact that you come up with a precious metal use and then live until the day that someone comes along with a base metal that can replace it. But right now from what I have heard, I don't see something that is going to replace a gold matrix material in a selective absorber. You want a metal matrix material to keep the emissivity low. It is the development of getting the absorptivity up to the levels that you want to discuss.

In the first 12 months of our program, we moved from a 0.5 to a 0.8 absorptance. The last six months, we stopped development in the golds because we came up with a silver matrix material.

I hope that when the users start looking at these films, they will see the cost effectiveness and since gold is a material, it is available, we are not going to use the world's supply of gold in solar energy. In response to Bernie we are quite confident that this silver matrix material with the 0.9 alpha that I reported can be brought up to 0.94. We actually have materials with alpha = 0.92 and with an alumina and a reflective material put down from metallic organic solutions also.

We feel that this film is approaching commercial development. Engelhard feels that the development of these films is far along and in particular that they have extremely good adhesion. We feel in the very nature of the uses that these films have been put in in the past have particularly good environmental resistance and we hope that the metal matrix will not be as sensitive to photon interactions.

I think that's about the issue. So please don't be afraid of gold. We keep hearing it, but it is just a metal.

MR. SERAPHIN: I think that it is very essential that you mentioned your laboratory development of = 0.94. This is a room temperature absorptance, have you taken it up to around --

MR. DICKSON: No, we do not have that capacity.

MR. SERAPHIN: Could we maybe collaborate on this. If this could be pinned down at high temperature, it would really be an essential result.

MR. DICKSON: We will do that Bernie.

CHAIRMAN ELLIOTT: Let me pick that up, Bernie, because I think that was what I was going to give Jim as an action item.

In the first place, I appreciate your comments on gold, they are very true. I have in other arenas encountered the statement that gold, electroplated gold for certain applications can be the cheapest coating, when you consider its resistent to oxidation. Unfortunately, gold carries an emotional connotation, and I am sure you live with this day in and day out.

My remark about explaining to the Jack Andersons and Senator Proxmires was not intended to be facetious. If we plate that receiver with gold, no matter how cost effective it is or how cheap it is, it is going to be a PR problem in a sense, technological, political, and everything else. You are right, we all believe you.

I can lay an action item on you, tell us about it on paper, more than just words, and tell us about the costs, that's one of the things.

I think you mentioned something about cost ideas, but I am afraid it didn't register if you did.

MR. DICKSON: The actual gold value in a square foot appears to be eighty-eight cents.

CHAIRMAN ELLIOTT: We were guessing about a buck.

MR. DICKSON: Silver is about three to four cents.

CHAIRMAN ELLIOTT: What is the process cost?

MR. DICKSON: That we have not determined because you are talking about unknown volumes.

CHAIRMAN ELLIOTT: I suspect even with gold, your process cost is at least commensurate with the material cost, and probably above it?

MR. DICKSON: No, that's not true.

CHAIRMAN ELLIOTT: We need those figures and we need the performance figures on the solar-based material for comparison. If the gold is really better, we want to see why it is worth the extra cents or dollars per square foot.

MR. PETTIT: How can the coating developer really interact with the system designer because I know there has been a lot of systems analysis done on these specific collectors in total energy and central receiver?

There is a lot of that work available on coating tradeoffs and coating performance studies. It is in the proceedings and final reports of a lot of projects. A lot of it is very buried and hard to obtain. I don't know the answer.

CHAIRMAN ELLIOTT: One answer we have by example here, I think we could try and make sure that more Ron Tobins turn up at these meetings and that more Marc Adams turn up at these meetings.

There are people at Aerospace and people in the Sandia orbit who are also involved in systems analysis. Sure, there are many others who could benefit and contribute. I am sure the people who are down there on the line trying to make the gadgets work have an awful lot to contribute.

I think that if there is one thing I would change in the workshop, I think I would emphasize the user and the analyst.

MR. PETTIT: I think the people in selective coatings should be aware of the workshops that are carried out from the systems point of view in actual collector designs, and if they are interested, if that collector covers a temperature or a receiver configuration that appears to be attractive or the coating that that person is working on, they should be aware of it and able to attend those meetings.

CHAIRMAN ELLIOTT: It looks like there is a little bit of a coordination and communication job here then too, bearing in mind, that some of these things may get to a level of detail that may be sort of oppressive.

It seems to me some of the burden falls on the labs to make sure that the systems work and the design work as it applies to coatings ought to be made available to this community. You know, it is one thing to come here and tell us that we need more of this interaction, but really the information I think generally resides best in those labs particularly in total energy, and it is the responsibility of the labs to get that out.

MR. PETTIT: I think you can make that comment, besides coatings, you can make it in almost every facet of a collector, the mirror, the heliostat, the structures, every area has that problem.

MR. GUTSTEIN: We are going to have to probably do a similar thing on reflecting surfaces too. I think the labs ought to make available that information. The burden really is on the labs that are the focal point for that kind of information.

MR. VOSSEN: I will put it very bluntly: if the program is going the way it has been described up until now, I wouldn't touch a thin film project on this with a ten-foot pole. The reason is simply that there is apparently not in anyway enough feedback from the designers of systems to the designers of film processes and structures. That's got to be improved.

The two groups have to talk to each other, and if they don't, you are going to find ultimately an infinite catalog of thin films that nobody wants.

There is a finite number of possible systems that people are envisioning, from what I gather, and an infinite number of possibilities for film techniques.

So, the beginning of this process is, in fact, incumbent, I think, on the systems designers to tell the coatings people just what it is you want.

Another point that is more in a technical vein is, there is a lot of emphasis here on high temperature, but I would caution you not to forget low temperatures as well. These things get cold, they don't only get hot. They cool down at night. In the winter, they get cold and the stresses that are induced in film structures at low temperatures can often times be much, much worse than they are at high temperatures depending on the intrinsic stress in the film itself. So, I would not neglect environmental testing at low temperatures.

The third point I would like to make is beware of cost projections for scale ups of thin film techniques. Be very wary. That is not a trivial exercise to go from a small lab process to coating square miles of stuff. Most processes can only be sensibly scaled by factors of three at a time. You try to jump more than that, you are asking for trouble. Especially, if it is a very critical process. Some you can get away with. The machine or whatever that you make to generate this coating is probably going to turn out to be the tail that wags the dog.

MR. WEHNER: I would suggest that it probably would help the program if we have some good survey papers. For instance, if there is a good survey paper on what is cooking at the moment in photoelectric things, I think many of us are not completely up to date.

MR. SCHWARTZ: It would be very worthwhile at possibly the next workshop to have people who do get around such as

Dr. Seraphin give a report to the group of what is going on internationally so that people that don't follow what is in this area could get up to date. You just can't sit in the United States and say that we are the knower of everything, it is ridiculous.

MR. CZANDERNA: It might even be useful to have some of the experts from those countries come and participate.

As I sat through this meeting, it was a tremendous opportunity for me to get an exposure and an overview to an area in which I have done very little, if anything.

But what I could see coming out is that there are a lot of solid-gas reactions at elevated temperatures such as oxidation in real environments that are generally not addressed by the surface science community. Also, that the reactivity of a number of thin film phenomena are going to be different compared with that from the bulk.

There have been a number of statements on surface preparation which certainly need greater attention, and it means better characterization of those surfaces should be made. I mentioned a couple of things such as oxide thickness in my comments. Certainly, there are interface problems, there are adhesion problems, the stresses that take place because of temperature cycling. There is a general area of activity which frankly I know nothing about, but it is worth looking at. What are the radiation-induced reactions on surfaces in real environments? We are talking about towers at 300 - 400 C under a high intensity of radiation. What induced surface reactivities will result? And most importantly the lifetime of these films is a most important parameter that has to go into the equation for cost effectiveness. This means that the degradation of the films has to be studied, and such things as the morphology of the surfaces in SEM to evaluate what those surfaces look like, what is the surface composition before you subject a surface to some sort of a cycling temperature because it is well known that the degradation of a surface can be greatly affected by small quantities of impurities on them, and that that can produce the morphological changes which may be changing the optical properties.

Certainly, there is a great need for a standard way of comparing time-temperature relationships. If you have heated something in the air at 300 degrees, how long? I saw a number of slides where either the time was given or the temperature was given, but not too frequently where both were given.

I also picked up some comments that there are interdiffusion processes taking place in thin films, and these are interface problems. There are very interesting interface problems, the reverse of a gas-solid interaction, the solid-gas desorption process in some of the curing processes that are taking place. How much curing agent remains after a paint has been cured, and what effect will that have on the long-term stability, five, ten, 20 years?

And finally, there is a very blank area that I could mention, substrate reactions. What substrate preparations, what lack of substrate preparations can produce various reactions? I could just mention very briefly that we believe that we have just uncovered in some of the recent work at Clarkson, that there is a reaction in which oxygen is diffusing from a substrate into a metal, from a glass substrate into a metal that has been deposited on it, and we are trying to track that particular mechanism.

MR. GILLIGAN: I would like to make a comment here. We have a publication coming out that contains a lot of information that people here would like to have. We have 88 materials that have been out in the field, and we have had one year's exposure on them. We are going to continue out to a period of about six years both in real and accelerated testing time.

A lot of materials that were talked about in the last two-and-a-half days are in here. A lot of you will be surprised to see some of the effects that occurred, some of the things that have happened to the real materials.

Eventually, you are going to find out that dust is far more important than you might have believed, weathering is more important than you might have believed.

There is an on-going program in the heating and cooling branch that shouldn't be restricted to heating and cooling. I think the photovoltaics, solar thermal and any other branch of solar energy is going to require detailed materials characterization.

I wanted people to know that there is an on-going program.

MR. HAHN: A lot of standard tests that people have used for thin film coatings over the years have been accepted standards for specifying coatings. Trying them with some of the solar coatings, in some cases, you find out that the test is just fine. I am talking about temperature cycling, humidity test, salt corrosion, etc. Put them out in the field, sometimes in a cold temperature on the coast, sometimes in a warm environment, one fails and the other doesn't. The correlation between accelerated testing and the testing that you want for your live time international collector could be very different.

Alzak and Coilzak, coat those with a coating, sometimes they hold up better, sometimes they are much worse. And why? Alzak and Coilzak are generally regarded by most people to have pretty good weathering characteristics.

So, I think these problems are something we have to address, and I think we are really in our infancy in this area.

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APPENDIX I

Measurement Facilities

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A Laser-Source Integrating Sphere Reflectometer[1]

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Measurement Capability

A reflectometer was developed for measuring the absolute spectral reflectance of materials at temperatures up to 2500°K. The equipment included (1) a helium-neon laser as the source, capable of operation at 0.6328, 1.15 or 3.39 um, (2) a 35 cm diameter integrating sphere coated with sodium chloride, (3) a lead sulfide detector, and (4) a radio frequency generator for heating the specimen by induction. A spike filter transmitting at the laser wavelength in front of the detector abosrbed most of the background radiation from the hot specimen, and a chopped incident beam together with synchronous amplification of the signal from the detector was used to eliminate the effect of the remaining background radiation. The integrating sphere could be evacuated, or operated under a slight positive pressure of purified helium. An error analysis showed that the measured absolute reflectances are in error by less than one percent. Preliminary data are presented for thoria, tungsten and graphite. Graphite was found to be stable in reflectance on heating to 2150°K in vacuum. Both thoria and tungsten were somewhat unstable on heating in vacuum.

Current Status

The radiofrequency generator for heating samples, and the complete integrating sphere, including the induction coil, for the laser-source reflectometer are still available. The sphere will have to be recoated. The vacuum system will have to be replaced, and will include a roughing pump, a diffusion pump, vacuum gauges, a refrigerated baffle to prevent backstreaming of the pump oil, and numerious vacuum valves, etc. The laser, chopper, detectors, spike filters, phase locked amplifiers (2), digital voltmeter and acoustic coupler will have to be replaced. It will probably be desirable to use several lasers, to get high temperature reflectance at a number of points in the transition region. Probably an argon and a helium-neon laser would be enough.

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[1] adapted from NBS Technical Note 439, "A Laser-Source Integrating Sphere Reflectometer," 1968.

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OPTICAL MEASUREMENT FACILITIES

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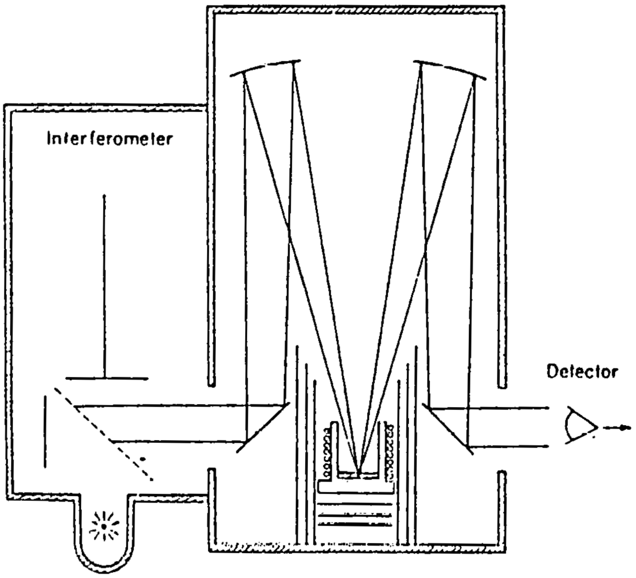
Our current optical instrumentation is as follows:

a) Hemispherical emittance calorimeter for coated or clean metal surfaces. This instrument can be used from 1000°C to room temperature. An induction heater is used for metal samples so in this case we could actually go as high as 2000°C.

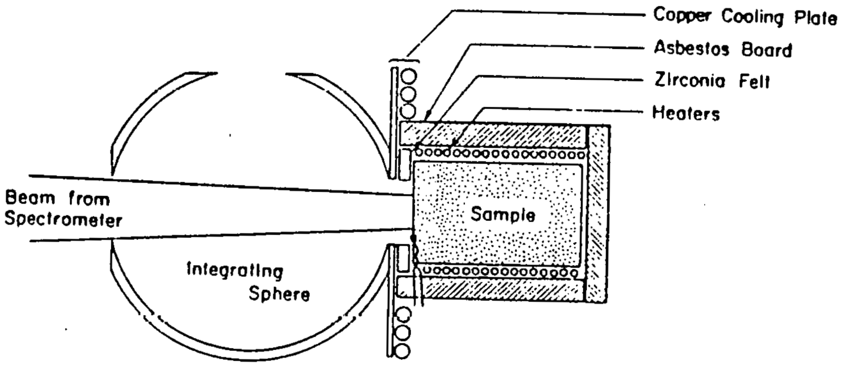
b) Fourier transform spectrometers from 1000 micron to 1 micron wavelength. We currently have a specular reflectance attachment which works from 400°C down to room temperature. This optical arrangement is shown in Figure 2 of the enclosed summary. We are currently building an angular emissivity measuring attachment which will work to 1000°C. The attachment looks essentially the same as that shown in Figure 2 except the furnace plus sample is now the source and the detector is on the other side. By measuring this emissivity as a function of angle we can then calculate the integrated hemispherical emissivity. This instrument together with the emittance calorimeter described above should take care of emittance measurements in this temperature region.

c) Our Cary spectrophotometer plus integrating sphere is being used for hemispherical reflectance measurements from 2.5 micron wavelength to 2000 Å. Sample temperatures can be maintained between 300°C and room temperature. We are currently building a specular reflection attachment for the Cary which will work up to 1000°C.

IR interferometer plus high temperature specular reflection attachment. Spectral range 1 → 8 microns temperature range room T → 400°C.



Integrating sphere plus high temperature sample attachment.



THERMOPHYSICAL PROPERTY MEASUREMENTS

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adapted by Pat Call, SERI, from
"Facilities and Service Available for Aerospace Applications"
(TRW 99900-7490-TO-00)
and
"Capabilities for High Temperature Solar Absorptance
Measurements at TRW DSSG."

TRW Systems has developed and acquired extensive facilities to support the thermal control subsystem designs of the major TRW spacecraft programs. These programs started in 1958 with the Pioneer I spacecraft and have continued with Explorer IV, Pioneer 5 through 9, Vela, OGO, INTERSAT 3, and a number of military spacecraft. During the last 12 years, TRW has also provided thermal control subsystem design services to space experimenters, testing laboratories, government sponsored laboratories, and other aerospace firms. A service frequently requested is the measurement of thermophysical properties. The following description of facilities and available services has been prepared in order to facilitate future requests for the measurement of thermophysical properties.

TRW Thermophysics Laboratory Facilities

Thermal radiation property measurements are performed at TRW with both spectral and total energy devices. Spectral reflectance measurements of materials at approximately room temperature are made with the improved Gier Dunkle heated cavity reflectometer over the wavelength range of from 2 to 25 microns. This newer design (Reference 1) eliminates a number of errors noted in the earlier version of the instrument (References 2 and 3) and provides angular measurements from 15 to 75 degrees from the normal. A TRW developed instrument for performing measurements similar to those performed by the heated cavity reflectometer is the paraboloid reflectometer. With this design, sample temperatures up to 1370°K in air have been obtained. Measurements made at these temperatures are independent of sample emission over the 2 to 25 micron wavelength range. The paraboloid can also be operated in an inert atmosphere where oxidation is an important parameter. This instrument provides relative measurements, whereas the heated cavity is "absolute".

An Edwards-type integrating sphere reflectometer of Gier Dunkle manufacture is used for measurements of spectral reflectance for the wavelength range 0.25 to 2.8 microns; i.e., wavelengths corresponding to solar emission. Supplementing this instrument is a Beckman DK-2A spectrophotometer with a TRW-constructed integrating sphere attachment. This modification, based upon the Edwards design, eliminates the errors commonly found in the commercial instruments and, in addition, provide angular measurements (up to 75 degrees from the normal).

Supplementing the previously-described instruments is the TRW goniometric bidirectional reflectometer for the measurement of specular reflectance (e.g., optical surfaces) and the distribution of reflected energy; i.e., reflection distribution function.

Calorimetric measurements of the total hemispherical emittance of surfaces are performed with two vacuum systems. In the first apparatus, the sample temperature is limited to the approximate range of 167 to 400°K by the errors inherent in the calorimetric technique and the liquid nitrogen-cooled baffle. Above 400°K, these measurements can be performed using another baffle coolant; e.g., water, or with the second high temperature apparatus. In each case, the analysis errors of the calorimetric method (Reference 5) governs the design and operation of the apparatus.

Capabilities for High Temperature Solar Absorptance Measurements

The solar absorptance of materials can presently be determined by the TRW Thermophysics Laboratory at temperatures up to 545°F (285°C). These temperatures have been attained for aluminized polyimide film specimens measured in a vacuum during measurements on the Jet Propulsion Laboratory Solar Sail Materials Development Program (7).

The test technique used the "test tube" specimen chambers described in Reference 8, and allows evacuation of the specimen during measurement or purging with any gas or gas mixture including air. This method consists of a fused silica tube enclosure which allows accurate spectral reflectance measurements to be performed. The specimen, normally 3/4-inch to 1-inch square, is mounted on a specimen holder which is in turn mounted on a vacuum flange. The flange is attached to a vacuum "tee" which has a small ion pump on one port, a feed through flange on another port and the silica tube on the third port. The specimen can be heated or cooled during measurement or exposure using either 1) the fluid lines which feed through one flange and supply hot or cold fluid to the specimen holder or 2) a thin heater mounted behind the specimen. The specimen may be translated approximately 1.5 inches while inside the tube via a bellows translation feedthrough. This allows proper calibration of the reflectometer during the reflectance measurement.

The spectral directional reflectance of the specimen can be measured at wavelengths from 0.28 to 2.5 microns and at any desired angle of energy incidence up to 70 degrees from the specimen normal. The silica tube functions to contain the desired specimen environment (vacuum, gaseous, etc.) and reduce the thermal coupling of the specimen to the integrating sphere reflectometer and detector. This advantage of the tube is due to its extremely high transmittance to solar energy wavelengths - 0.28 to 5.0 microns - and virtual opaqueness to the infrared energy emitted by the hot specimen. During the reflectance measurement, the alternating incident energy is transmitted through the silica tube and is then incident upon the specimen. The reflected portion is re-transmitted through the tube and is collected and detected by the integrating sphere and detectors. The majority of the continuously emitted energy from the hot specimen is absorbed by the silica tube and convected or radiated away. That is, the tube acts as a radiation shield to the emitted infrared energy.

Because the tube acts as a thermal barrier between the hot specimen and the thermally sensitive detectors used in the reflectometer, much higher specimen temperatures are possible than in a system with no such barrier.

The silica tube has very little effect on the reflectance measurement since it has essentially zero absorptance. The little effect it does have on the measurement can be reduced out of the data by performing spectral reflectance runs on the specimen both out of the tube and in the tube. The difference is the silica tube effect and can be factored out of the data taken at elevated temperatures.

This technique shows very accurately any changes in reflectance/absorptance of the specimen due to temperature increases.

Near-Future Measurement Capabilities

TRW is currently increasing the temperature limits of the reflectance/absorptance measurements to as high as 1200°F (649°C) by constructing and installing a thin ceramic sample heater in place of the polyimide heater.

It is felt that still higher specimen temperatures may be attained by additional minor modifications to the reflectometer.

Typical Measurement Description

The following list of measurements includes those most often required in thermal control design. Consultation with our laboratory personnel is recommended prior to requesting the test performance.

a. Integrating Sphere Solar Absorptance Measurement (α): For any specified pair of polar and azimuthal angles of incidence up to 75 degrees from the normal; calculated from spectral reflectance using the Thekaekera (Reference 6) solar curve; sample material temperature approximately 300°K; results reported as calculated solar absorptance and a plot of spectral reflectance as a function of wavelength, $0.28\mu \leq \lambda \leq 2.5\mu$.

b. Heated Cavity Directional Emittance Measurement (ε): For any specified pair of polar and azimuthal angles of emission up to 75 degrees from the normal; calculated from spectral reflectance using a material temperature of 300°K (approximately that of measurement); results reported as a calculated emittance and a plot of spectral reflectance as a function of wavelength, $2.0\mu \leq \lambda \leq 25\mu$.

c. Directional Emittance at Temperatures up to 1370°K in Air (ε): For any azimuthal angle but a fixed viewing angle of 9 degrees; temperature limited by oxidation resistance of sample in air; measured as a spectral reflectance and converted to emittance or absorptance by the appropriate black body energy distribution; results presented as a calculated value of emittance and as a plot of spectral reflectance as a function of wavelength (wavelength range determined by temperature but restricted to $2.0\mu \leq \lambda \leq 25\mu$).

d. Solar Transmittance Measurement (τ): Either directional or direct beam; solar transmittance calculated from Thekaekara curve; results presented as a calculated solar transmittance and as a plot of spectral transmittance as a function of wave length, $0.28\mu \leq \lambda \leq 2.5\mu$.

e. Total Hemispherical Emittance Measurement in Vacuum $(\bar{\varepsilon})$, $167°K \le T \le 400°K$: Calorimetric measurement of hemispherical emittance; three different temperatures within limits of test; sample 4 inches square, two pieces required; data presented as hemispherical emittance for the measured temperatures.

f. Total Hemispherical Emittance Measurement in Vacuum $(\bar{\varepsilon})$, $700°K \le T \le 2480°K$: Calorimetric measurement of hemispherical emittance; six different temperatures within limits of test; sample on conductive substrate; dimensions subject to discussion; data presented as hemispherical emittance for the measured temperatures.

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FACILITIES FOR THE MEASUREMENT OF RADIATION PROPERTIES OF SELECTIVE ABSORBER COATINGS

Optical Sciences Center

University of Arizona
Tucson, Arizona

As a part of the solar energy effort in thin films and materials technology, and as a service to the remainder of the University of Arizona's Optical Sciences Center, the measurement laboratory at the Center maintains the following instrumentation.

1. Perkin-Elmer 450 recording dual beam spectrophotometer, wavelength range 0.2 to 2.7 um and equipped with a variety of transmission and reflectance attachments.

2. Perkin-Elmer 137 recording dual beam spectrophotometer, wavelength range 2.5 to 15 um and equipped for transmission and reflectance measurements.

3. Integrating sphere spectrophotometer for diffuse reflectance and transmission measurements. Based on modified Perkin-Elmer 21 spectrophotometer, wavelength range 0.35 to 2.5 um.

4. High temperature reflectometer with Leiss double monochromator, wavelength range 0.4 to 15 um and temperatures up to 800°C.

5. High temperature diffuse reflectometer under development for use in 0.4 to 15 um wavelength range together with Perkin-Elmer 99 monochromator.

6. Leitz orthoplan metallurgical microscope.

7. Calorimetric emissometer for determining high temperature thermal emittance of solar-thermal selective surfaces (under development).

8. A variety of tube and annealing furnaces for sample preparation and lifetime testing.

9. Microprocessor computer system for data retrieval and processing.

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HONEYWELL FACILITIES FOR THE MEASUREMENT OF RADIATION PROPERTIES OF SELECTIVE ABSORBER COATINGS

Ray J.H. Lin and Jaan Jurisson
Honeywell Inc.
Systems and Research Center
Minneapolis, Minnesota 55413

A complete radiation properties measurements facility is available in the Systems and Research Center, Honeywell, Inc. The following are of special interest to the measurement of optical properties of selective absorber coatings.

High-Temperature Emittance Measuring Apparatus

Generally, it is considered the best to make radiation property measurements directly at the temperature of interest so as to include any temperature-dependent material properties. At Honeywell an apparatus is available* for measuring emittance up to 1800°F. The emittance measurements are made using the transient calorimetric technique.

Figure 1 shows the apparatus which consists of four calorimetric chambers mounted on a single vacuum manifold. Each chamber has its own main vacuum valve and roughing valve so that they can be operated individually. The calorimetric chamber is shown in Figures 2 and 3. The sample, supported by thermocouple leads, is suspended in the water-cooled and blackened chamber. The sample is heated to the desired temperature by illuminating it through a quartz window with a GE DXW 1000-watt tungsten-halogen lamp. The lamp is then turned off and a water-cooled black shield inside the chamber is rotated to protect the sample from emitted and reflected thermal radiation off the hot quartz window and surrounding area. The sample is then allowed to equilibrate with the cool chamber while its temperature is monitored. The thermocouple output is monitored with a nano-voltmeter and plotted with a chart recorder. A typical chart recorder output is shown in Figure 4.

Under the presently designed conditions the sample can be assumed to be small with respect to the chamber size. That is, an insignificant amount of radiation from the sample is reflected by the chamber or shield back onto the sample. This was verified experimentally by moving the sample position relative to the shield on several runs with no effect on the measured emittances.

Compared to the radiation coming off the sample, even at a temperature as low as 500°F, the amount of background chamber radiation being absorbed

---

*The apparatus has been partially torn apart. It needs some minor work to be operational.

by the sample is small. Thus, for a sample coated on both sides, to a first approximation the emittance as a function of temperature can be computed from

$$\varepsilon = \frac{MC(\Delta T_S/\Delta t)}{\sigma T_S{}^4 A_T}$$

where

T_S = sample temperature

ε = sample total hemispherical emittance

M = sample mass

C = sample specific heat

σ = Stefan Boltzmann constant

$\Delta T_S/\Delta t$ = sample change in temperature with respect to time

A_T = total surface area of sample

To include the small effect of absorbed background radiation, the above expression is used to estimate the sample absorptance α_b (= ε_b) to background room temperature T_b radiation, and then the more exact value of ε is calculated from the expression

$$MC(\Delta T_S/\Delta t) = \sigma A_T(\varepsilon_b T_b{}^4 - \varepsilon T_S{}^4)$$

There also is a small amount of heat flow from the sample to the attached thermocouple leads. A numerical calculation of the heat flow and radiation balance along the thermocouple leads showed that this heat loss would cause less than a 1 percent correction to the emittance values and hence can be ignored.

If the sample has an uncoated edge area, as usually the case for vacuum evaporated discs, one final computation has to be made to get the emittance of the coating ε_c:

$$\varepsilon_c = \frac{A_T\varepsilon - A_E\varepsilon_E}{A_T - A_E}$$

where ε is the measured emittance for the partially coated sample, ε_E is the emittance for an uncoated surface, and A_E is the area of the edge.

The accuracy of the final emittance values should be better than ±5 percent, which is about the extent of the scatter in the values of $\Delta T/\Delta t$.

Spherical Reflectometer

This instrument is used to measure the hemispherical-angular spectral reflectance. In the past, integrating spheres were limited to the shorter wavelengths by the diffusely reflecting coating (usually magnesium oxide) on the interior surface. Honeywell has built an integrating sphere reflectometer which covers the spectral range from ultraviolet to far infrared by employing a novel diffusing scheme. A six-inch hollow glass sphere is dimpled extensively with small, spherical depressions approximately one-eighth inch in diameter. This results in the formation of small, convex, spherical bumps over the inside surface of the sphere. This surface is then coated with evaporated aluminum. The result is a highly reflective, diffuse source over a broad spectral range.

Figure 5 is a schematic of the sphere, sample holder, and energy source. The sample can be rotated, as shown, so that reflectance measurements can be made from normal to grazing angles. The capabilities of this instrument include:

- spectral range from 0.25 μm to 15 μm
- sample temperature from room temperature to $\sim 600^{\circ}$F
- ambient pressure $\sim 10^{-6}$ torr.

Other Equipments

- Low Temperature Emissometer--Measures total hemispherical emittance from -100 to 200°F in vacuum.
- Gier Dunkle Solar Reflectometer Model MS-251--Gives the room temperature solar absorptance in a single measurement.
- Gier Dunkle IR Reflectometer Model DB-100--Gives the room temperature emittance in a single measurement.

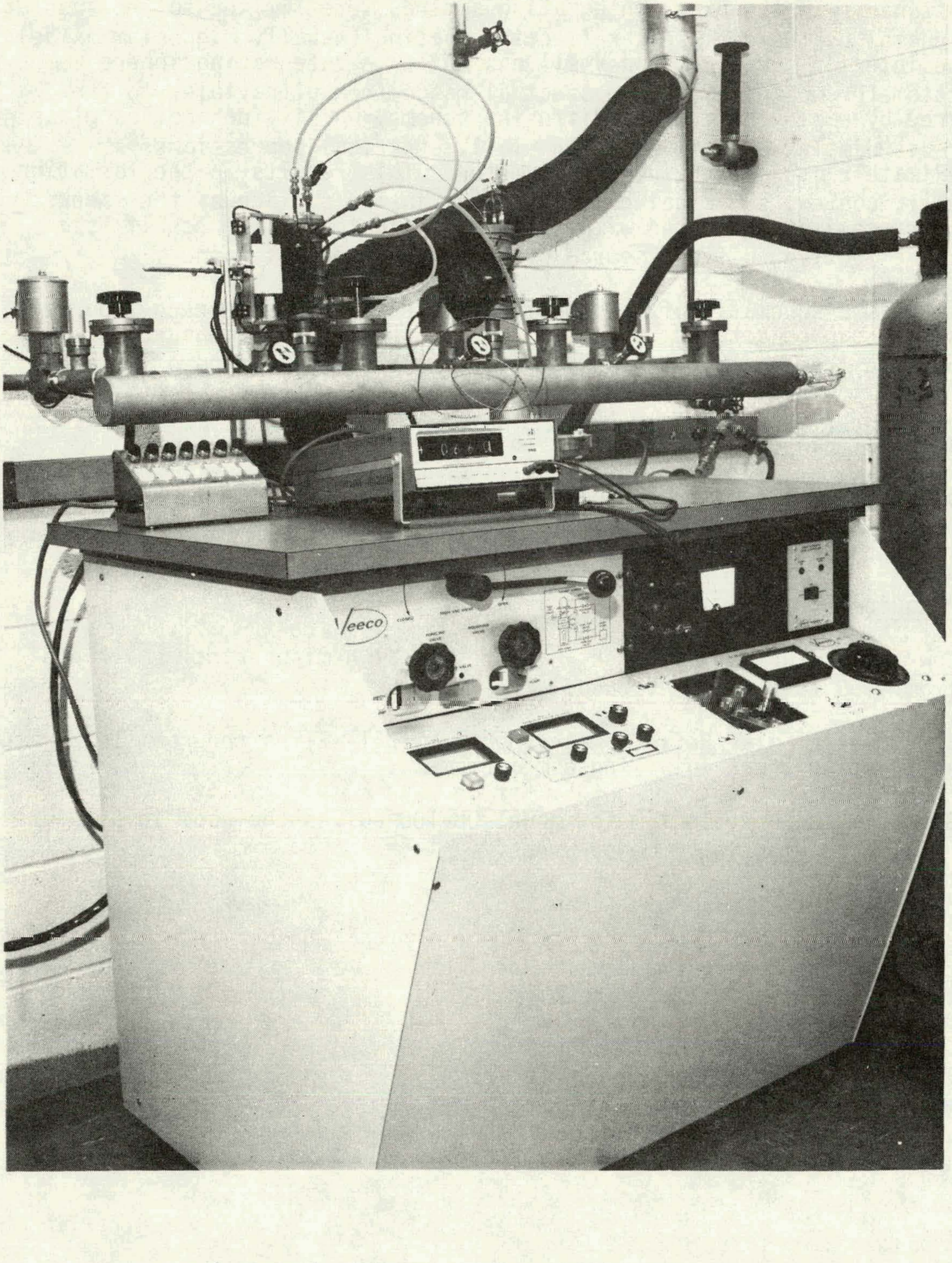


Figure 1. System for Emittance Testing

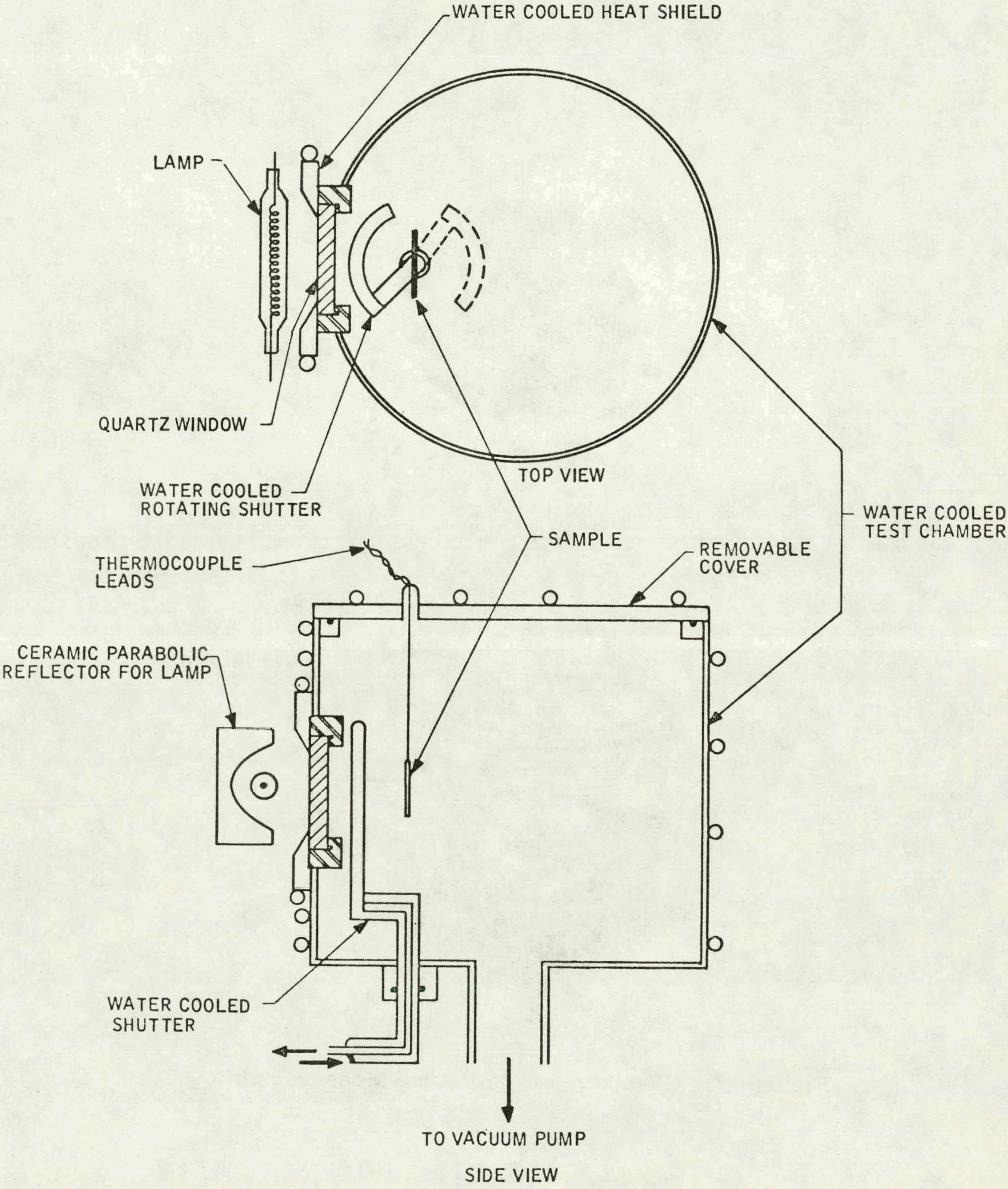


Figure 2. Test Chamber for Emittance Measurements

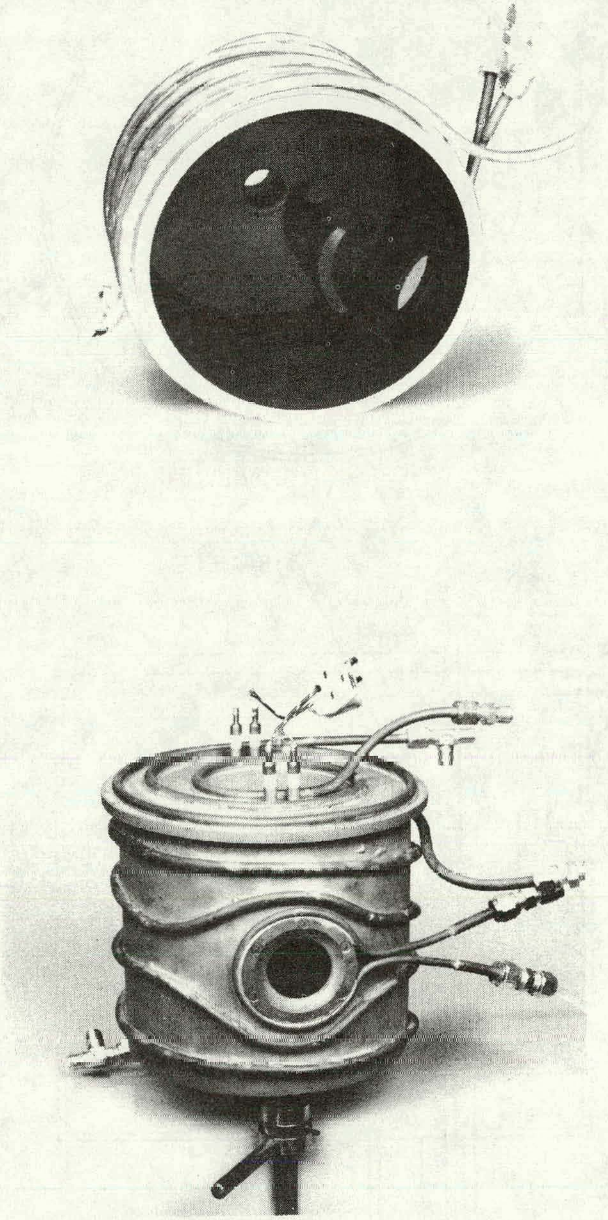


Figure 3. Chamber for Emittance Measurements

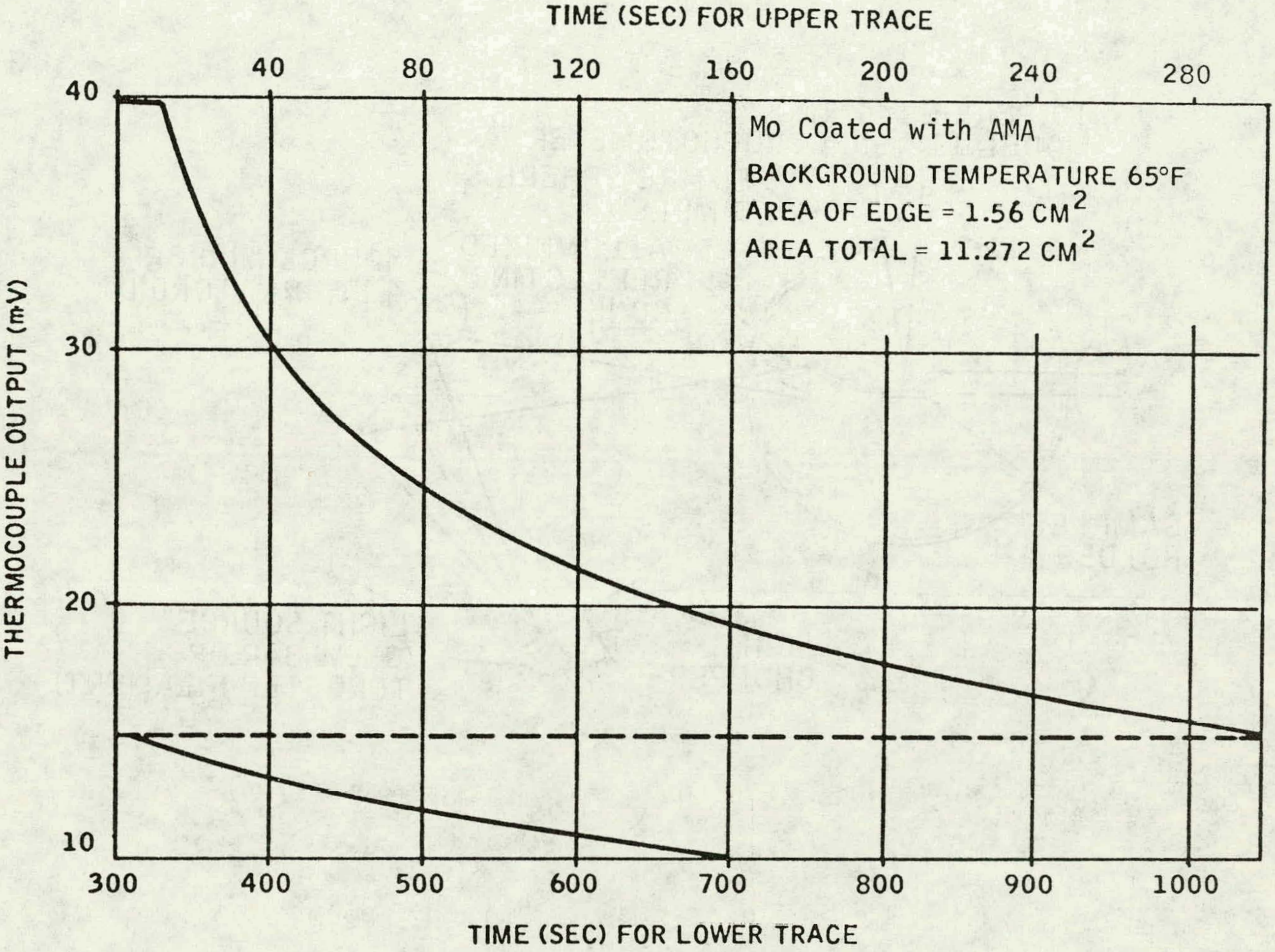


Figure 4. Typical Chart Recorder Output for Emittance Test

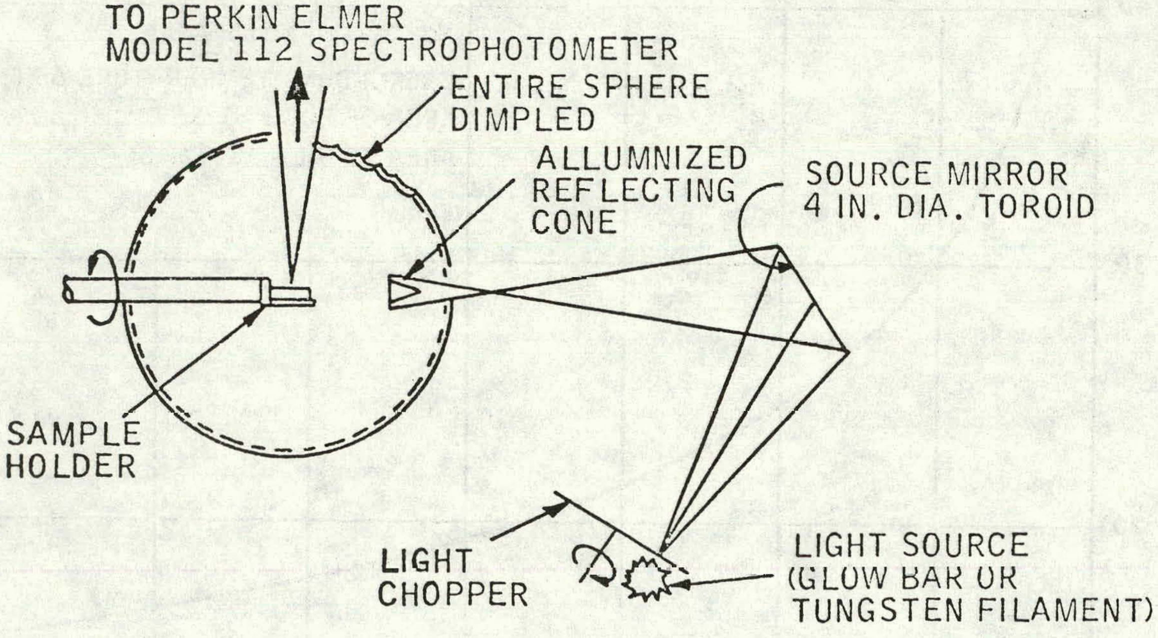


FIGURE 5. INTEGRATING SPHERE, ENERGY SOURCE, AND SAMPLE HOLDER

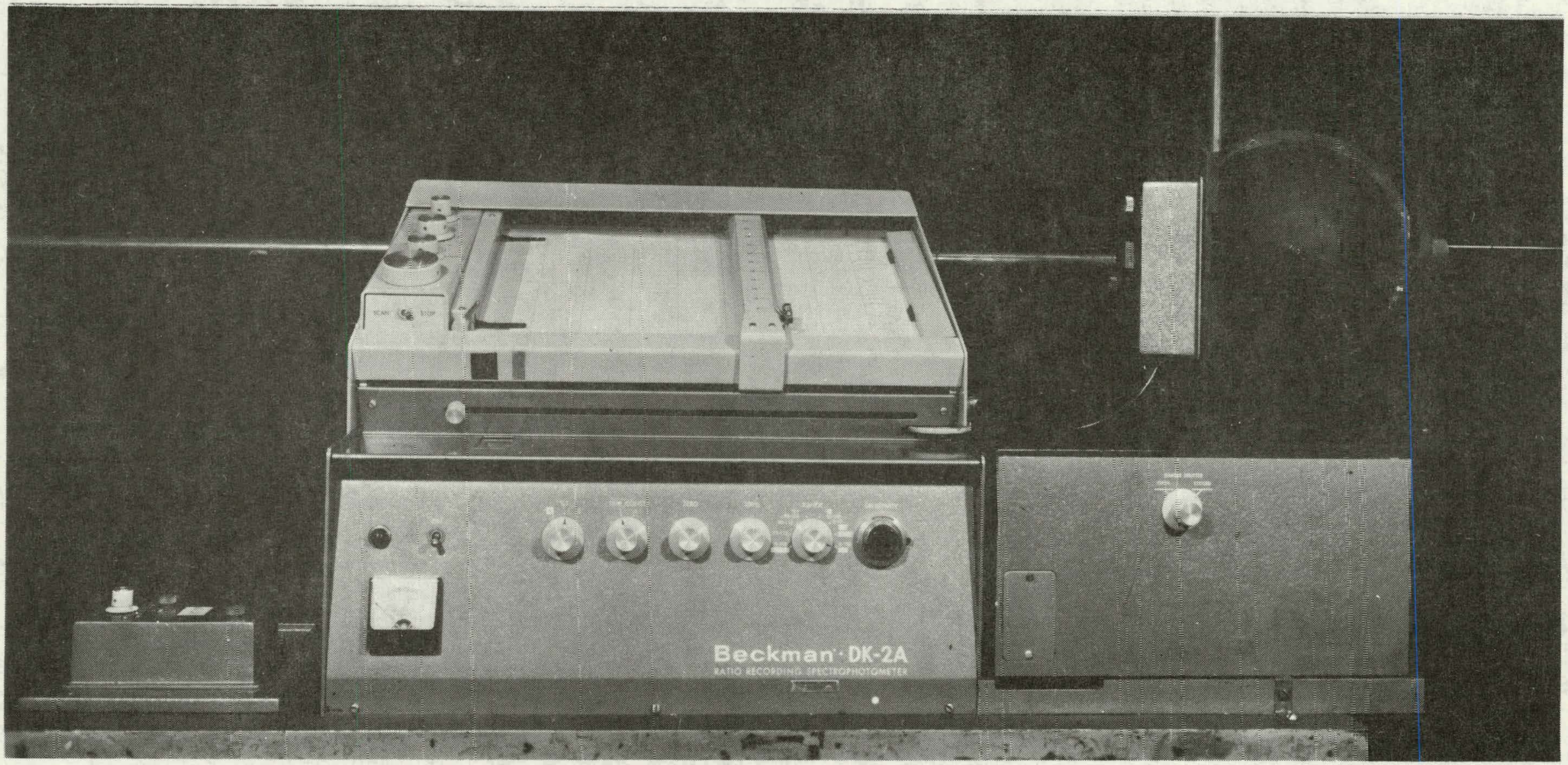
IITRI's Optical Measurement Capabilities in Solar Energy Utilization

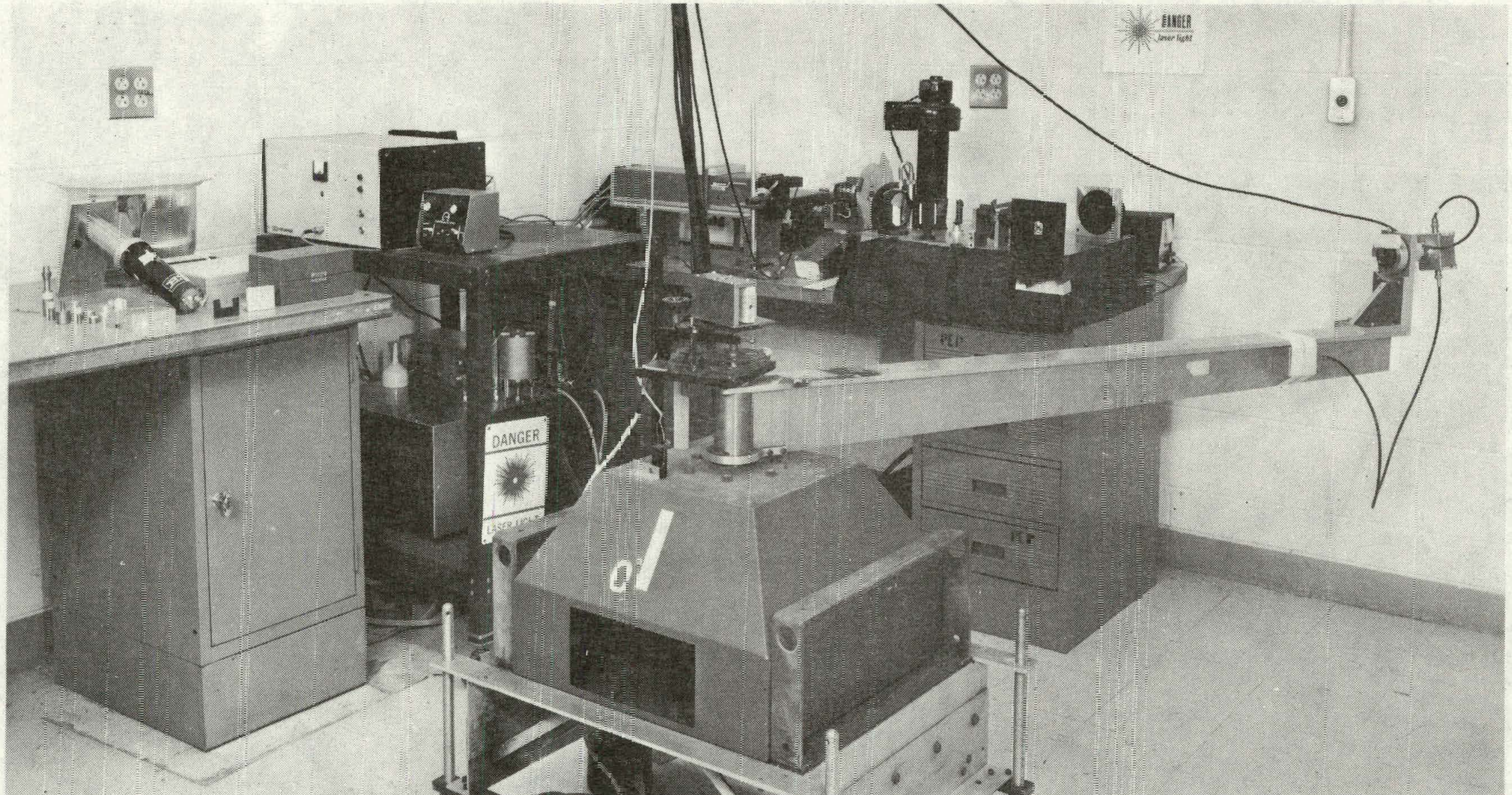
IITRI has extensive facilities for the optical characterization of Solar Utilization (SU) materials. Four UV-Vis-NIR spectrophotometers are available, three of which are equipped with integrating spheres for measurements of normal and hemispherical optical properties. The Beckman DK-2A with its integrating sphere is shown in Figure 1. All operate in the spectral region from 325 to 2600 nm (0.325 - 2.6 μ). Measurements are routinely carried out with the samples either in air or in vacuo at room temperature; an high temperature stage in one of the integrating spheres can maintain samples at temperatures up to approximately 1000°F.

In addition to the spectral measurement capabilities, a spectrogoniometer facility (SGF) is available. SGF, shown in Figure 2, allows very high resolution measurements of the angular and spatial distribution of reflected (and/or transmitted) radiation. Figure 3 illustrates the various modes in which SGF can operate and the spectra typical of each. Several lasers are available for monochromatic measurements, along with tungsten, quartz-iodide and globar sources which may be used in conjunction with plane and circular monochromators, filters, beam-splitters and other optical elements. Sources and detectors are available to cover the spectral range from

350 nm to 10,600 nm (0.35 - 10.6μ). The SGF is also equipped with an high temperature stage capable of maintaining samples at and upto 1100°F.

For spectral hemispherical reflectance measurements in the wavelength region from 2000 to 20,000 nm (2-20μ) the spectroemissometer, shown in Figure 4, is used. The light source is a globar; but two small integrating spheres (one coated with MgO for NIR, the other with sulfur for wavelengths beyond 3μ) can be used in conjunction with lasers to obtain precision values of hemispherical reflectance at the laser wavelengths. In this device also the samples may be heated to and maintained at temperatures as high as 1000°F.

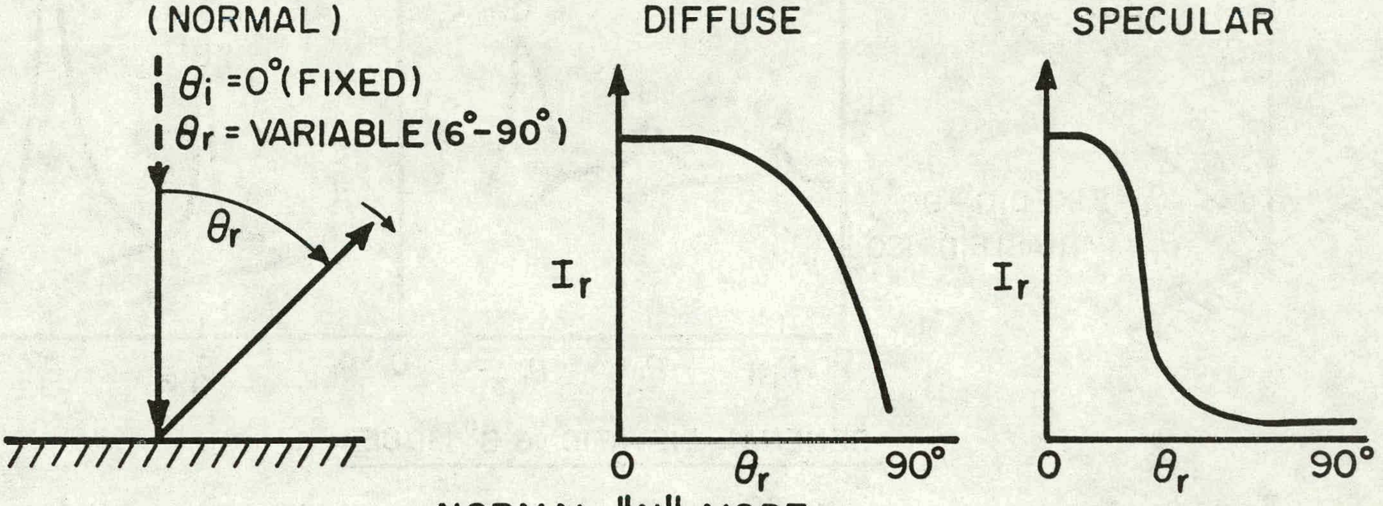

SCAN
STOP
Beckman DK-2A
RATIO RECORDING SPECTROPHOTOMETER


DANGER
laser light
DANGER
LASER LIGHT

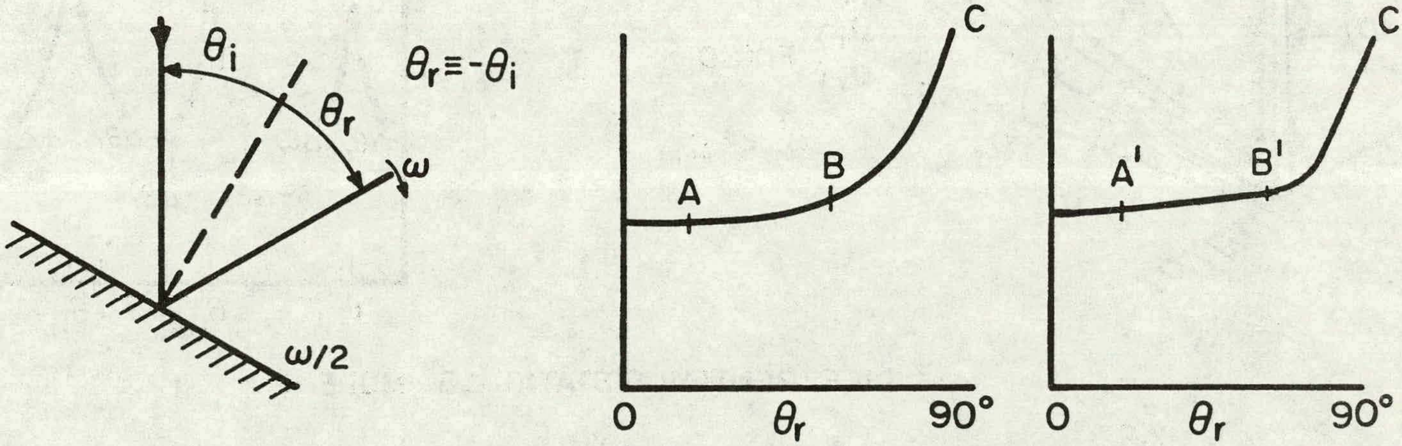
BIDIRECTIONAL REFLECTANCE MEASUREMENTS

GEOMETRY

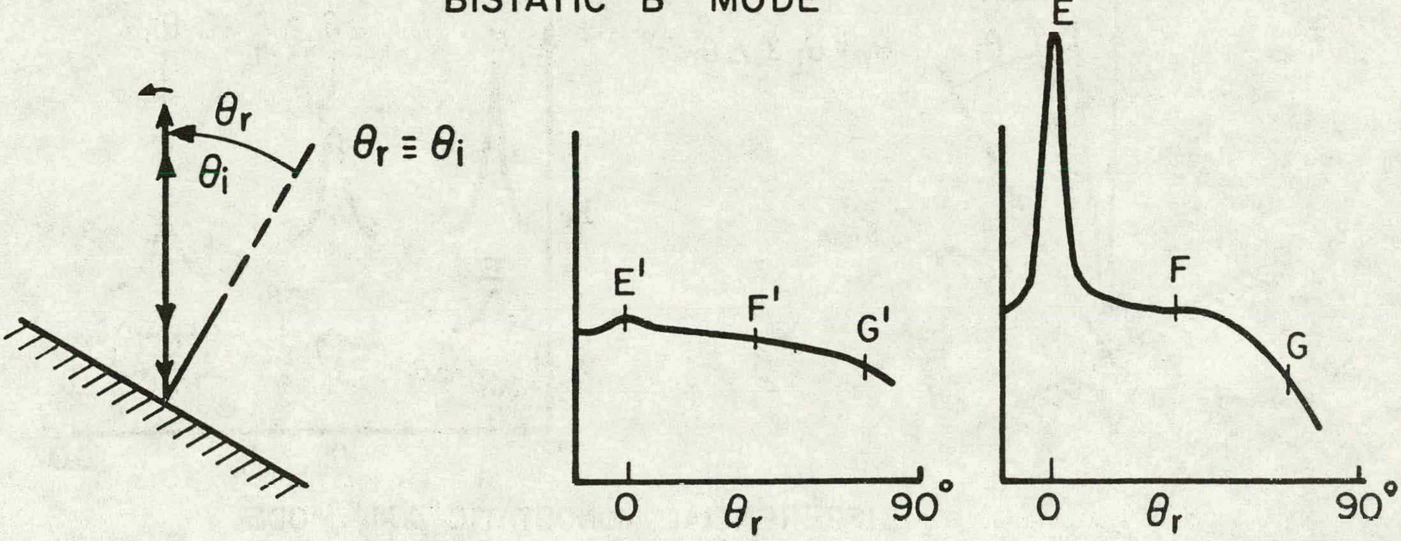
TYPICAL SPECTRA



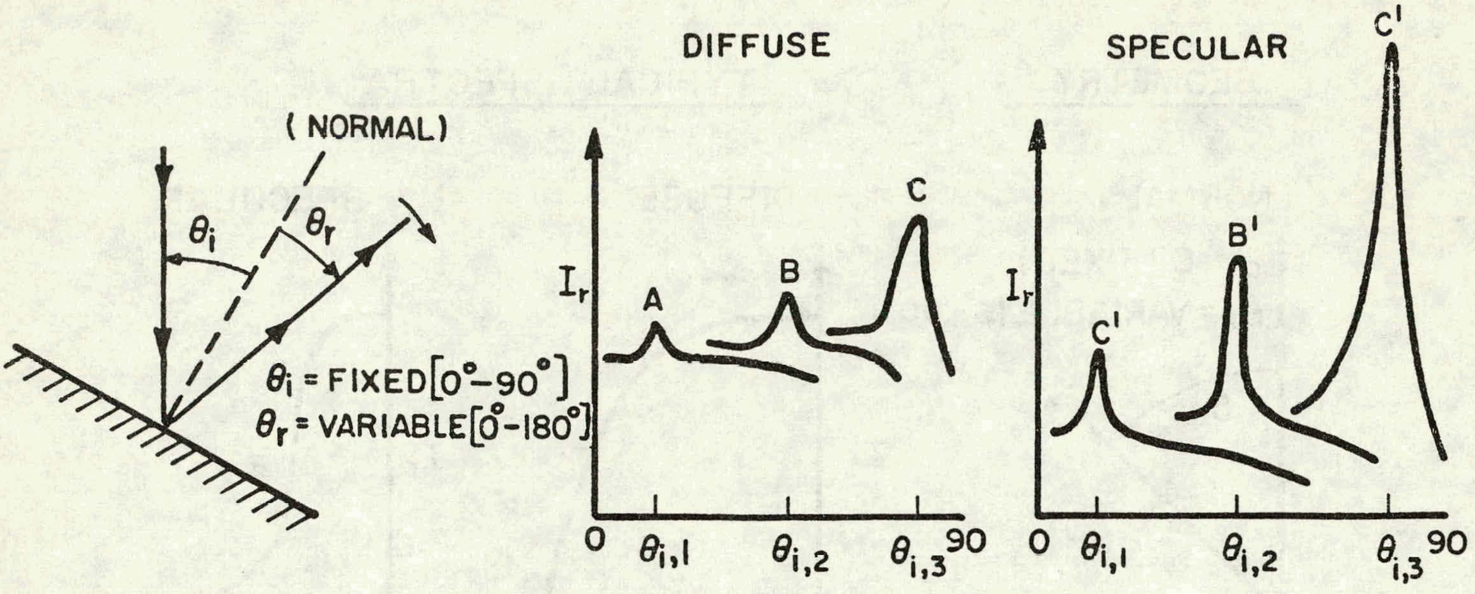
NORMAL "N" MODE



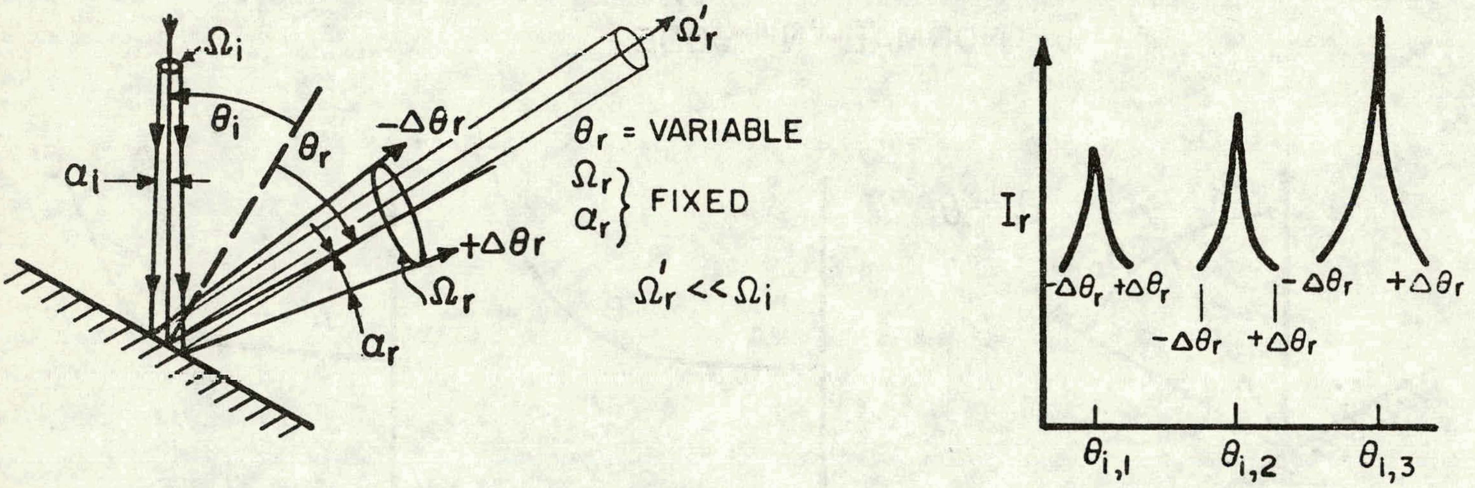
BISTATIC "B" MODE



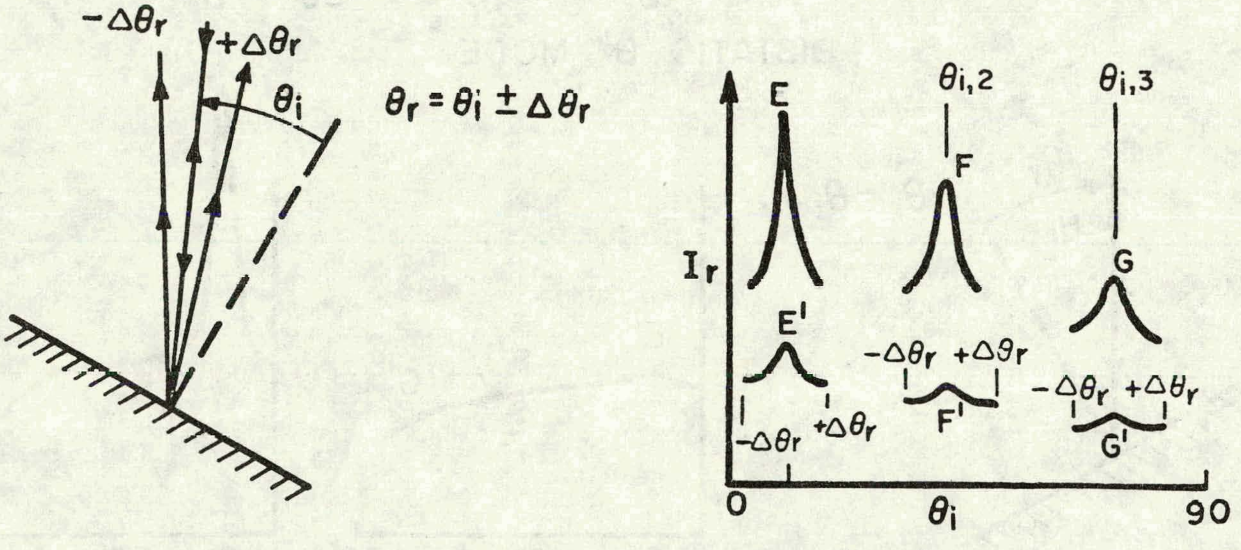
MONOSTATIC "M" MODE



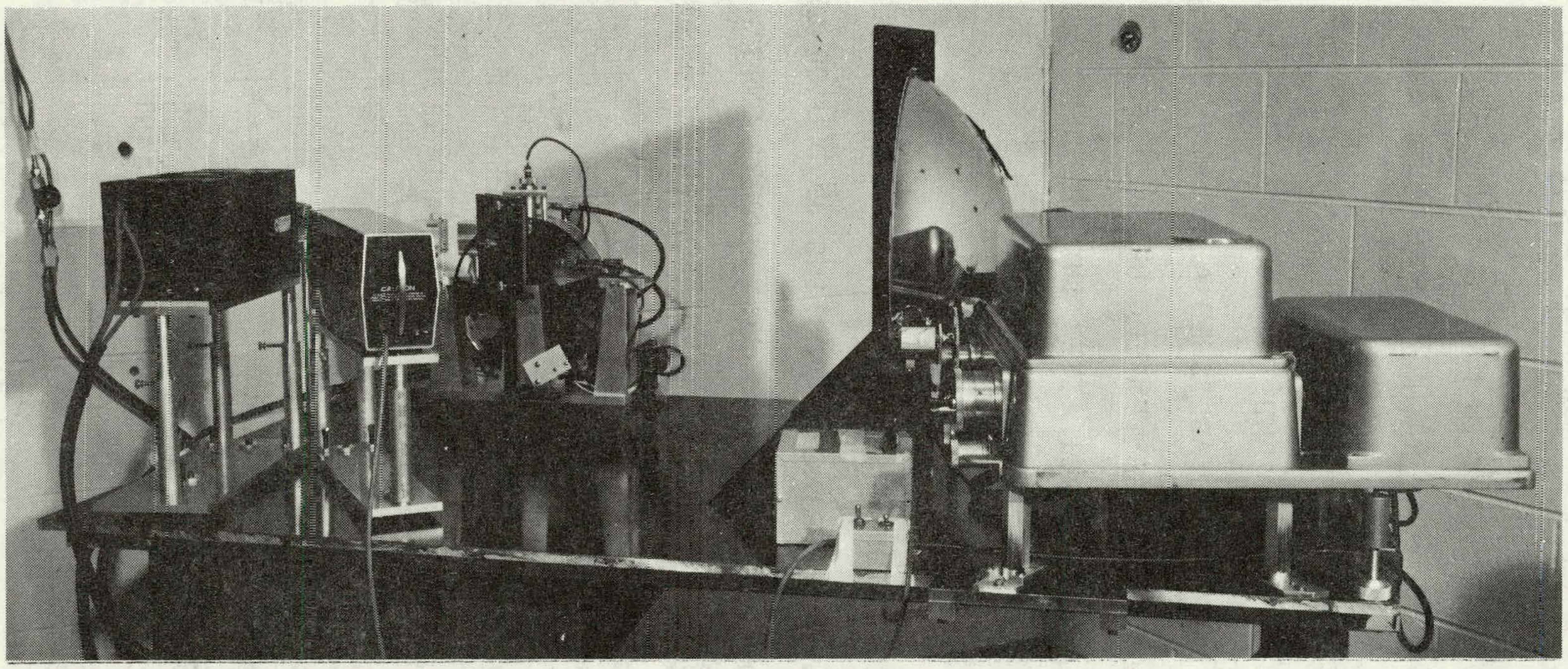
GENERAL BISTATIC "G B" MODE



DIFFERENTIAL BISTATIC "ΔB" MODE



DIFFERENTIAL MONOSTATIC "ΔM" MODE



Solar Thermal Test Facilities
USERS ASSOCIATION

USERS ASSOCIATION TO HANDLE PROPOSALS FOR HIGH-TEMPERATURE SOLAR R&D

The Department of Energy and the Solar Energy Research Institute (SERI) have established a Users Association to review proposals for high-temperature (2000-3800°C) R&D on Solar Thermal Test Facilities in Albuquerque, Atlanta, White Sands, and southern France.

The Users Association has funds available for direct funding of small experiments costing $5,000 or less. Approved proposals for more costly experiments will be funded directly by SERI based upon Users Association recommendations.

More information on the solar facilities, the Users Association, and proposal submission and review procedures follows.

STTF Users Association
Suite 1507
First National Bank Building East
Albuquerque, NM 87108
Phone: (505) 268-3994

Frank Smith
Executive Director

SOLAR THERMAL TEST FACILITIES USERS ASSOCIATION
AND
PROCEDURES FOR SUBMITTING PROPOSALS

The Solar Thermal Test Facilities Users Association is an organization of persons and institutions interested in solar thermal facilities and solar electric power generation. It is funded by the Department of Energy (DOE) through the Solar Energy Research Institute (SERI) and is authorized to solicit and review proposals from outside (non-DOE) experimenters who are interested in using the following Solar Thermal Test Facilities:

1. Sandia 5 MW STTF, Albuquerque, New Mexico
2. Georgia Tech 400 KW STTF, Atlanta, Georgia
3. White Sands 30 KW STTF, White Sands, New Mexico
4. French 1000 KW STTF, Odeillo, France

These facilities are described in the following pages.

The Users Association, in cooperation with DOE, SERI and the facility operators, will expedite use of these facilities for R&D or testing which helps advance solar energy applications or increases knowledge of high-temperature materials or processes. In addition to use of the facilities, it is also anticipated that about $250,000 will be available for STTF users in FY 78 to cover costs such as hardware fabrication and installation, shipping, travel, data processing, etc.

Approved projects costing $5,000 or less can be funded directly by the Users Association; more costly experiments, if recommended by the Association and approved by SERI, can be funded through SERI contracts.

If you are interested in using these facilities, a proposal (3 copies), or preproposal, describing the work you have in mind and estimating testing times, schedules, costs, etc., should be sent to the Users Association at the address shown on the reverse side of this sheet. Your proposal should also state the potential value of your proposed experiment to high-temperature solar energy development.

If you or your institution wish to join the Association, please complete the attached form and forward your dues payment to the Association office in Albuquerque. Annual dues are $15 for individuals and $150 for institutions. Individual Associates will be allowed one vote on matters coming before the Association during its annual meetings; institutions do not have voting privileges, but their staff members may participate in all technical meetings of the Association. Those submitting dues before December 31, 1977, will be Charter Associates.

Solar Thermal Test Facilities
USERS ASSOCIATION

THE SOLAR THERMAL TEST FACILITIES AND SOLAR FURNACES

The Users Association will review proposals for work on the Sandia 5 MW STTF in Albuquerque, New Mexico, the Georgia Tech 400-KW facility in Atlanta, Georgia, the Army 30 KW Solar Furnace at White Sands, New Mexico, and the French 1000 KW Solar Furnace in Odeillo, France.

The Sandia 5-MW and the Georgia Tech 400-kW facilities both use large fields of sun-tracking mirrors to concentrate the sun's energy on test areas located at the focal points of the mirror fields. The White Sands 30-kW and French 1000-kW furnaces use double reflector systems consisting of flat mirrors which track the sun and reflect its energy to parabolic reflectors which in turn focus the energy onto the test area. A summary of the specifications of the four facilities is given in the table below and a brief description of each facility follows.

APPROXIMATE SPECIFICATIONS FOR STTFs AND SOLAR FURNACES

Facilities	Sandia	Georgia Tech	White Sands	Odeillo
Total Thermal Energy, kWth	5000	400	30	1000
No. of Heliostats	222	550	356	63
Heliostat Size, m	6 x 6	1.1D	0.6 x 0.6	6.0 x 7.5
Total Heliostat Area, m^2	8257	532	137	2835
Test Area Diameter*, m	2-3	0.3-1.0	0.08-0.15	0.25-1.0
Peak Flux✶, W/cm^2	250	375	400	1600
Max. Calculated Equilibrium Temperature✶, °C	2300	2500	2600	3800

*First number is area receiving approximately one-half of total energy; second number is area capturing 95% of total energy.

✶Small area at center of beam.

Sandia Solar Thermal Test Facility

The Sandia STTF in Albuquerque, New Mexico consists of a 200-foot central tower initially surrounded by 222 heliostats capable of directing 5 MW of thermal energy to various locations on the tower. Each of the 400-sq. ft. heliostats consists of 25 4' x 4' mirrors which are focused to produce a concentrated beam of solar radiation on a target test area. Peak thermal flux levels up to 250 W/cm will be available at the center portion of the beam. Approximately 1 MWth will be available within a 1-meter diameter circle, 2.5 MWth within a 2-meter circle, and 5 MWth within a 3-meter circle.

The facility is designed to provide flexibility for a variety of solar receivers and various combinations of heliostats. The experiment tower is 200 feet high with test bays located at the 120, 140, 160, and 200-foot levels. Other test locations will also be available in the future for small experiments.

The Georgia Tech Solar Thermal Test Facility

The Georgia Tech 400-KWth Solar Thermal Test Facility (GT/STTF) in Atlanta, Georgia utilizes 550 round mirrors each, 111 centimeters in diameter, which may be operated flat or focused to provide radiant heat fluxes from 25 to 200 W/cm^2 to a test area centrally located 20 meters above the mirror field. The mirrors are mechanically linked through a common clock-controlled drive mechanism so that they move together to track the sun.

Typically, with an incident direct solar flux of 800-950 W/m^2 the nominal radiant heat flux will range from 25 to 50 W/cm^2 with the mirrors flat and 50 to 200 W/cm^2 focused. The nominal black body equilibrium temperatures associated with these fluxes are 1100^o-1400^{o}C for 25 to 50 W/cm^2 and 1400^o-2100^{o}C for 50 to 200 W/cm^2.

The White Sands 30-KWth Solar Furnace

The U. S. Army 30-KWth solar furnace, operated by the U. S. Army at White Sands, New Mexico uses a double reflecting system. The primary reflector consists of 356 flat reflectors, each 62 x 62 centimeters, for a total area of 137 square meters. These mirrors track the sun and relfect its energy to a concentrator consisting of 180 62 x 62-cm parabolic mirrors which in turn reflect the energy to the target area delivering about 30 KWth with a maximum heat flux of about 400 W/cm^2 in a 5-cm diameter area at the center of the beam. The facility also incorporates a shutter system to provide thermal pulses of variable intensity and duration.

The French CNRS 1000-KW Thermal Solar Furnace

The CNRS 1000-KWth Solar Furnace, located in the Pyrenees at Odeillo-Font Romeu (altitude, 5900 feet), about 40 miles east of Andorra consists of 63 heliostats (each 24½ x 19½ feet) which follow the sun and reflect the sun's rays onto a parabolic reflector. The parabolic concentrator (20,000 square feet) concentrates one megawatt of thermal energy into an area of about two feet in diameter at the focal point of the parabola. At the center of the focal point in an area two inches in diameter the heat flux is 1400 Btu/ft^2-sec (1600 W/cm^2) and the temperature reaches 6900^{o}F.

For more information on the solar facilities or the Users Association, contact:

STTF Users Association
Suite 1507, First National Bank Building East
Albuquerque, New Mexico 87108
Phone: (505) 268-3994

STATEMENT OF INTEREST IN STTF TESTING AND/OR ASSOCIATION MEMBERSHIP

NAME: ________________________

POSITION: ________________________

INSTITUTION: ________________________

ADDRESS: ________________________

PHONE: ________________________

TYPE OF INSTITUTION: (Size, kind of business, profit/non-profit, etc.)

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Statement of Interest in STTFs and/or description of kinds of testing you may be interested in. (Attach any supplementary information considered helpful in describing your research or thermal testing needs.)

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I wish to join the Users Association

as individual Associate @ $15.00/year, dues for 1978 enclosed ( )

as Institutional Associate @ $150.00/year, dues for 1978 enclosed ( )

Please send the following additional information:
STTF Users Manuals: Sandia ( ), Georgia Tech ( ), White Sands ( )

Put us on list for further general information on STTFs and Users Association when available ( )

Other: ____

Please pass this onto or give us the name of anyone else who may be interested.

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