

SERI/TP-743-1027
UC CATEGORIES: UC-58,63
CONF-801171--1

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ENVIRONMENTAL REGULATIONS:
APPLICABILITY TO ADVANCED
PHOTOVOLTAIC CONCEPTS

MASTER

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PAPER PRESENTED AT THE
SEVENTH NATIONAL CONFERENCE
ON ENERGY AND THE
ENVIRONMENT, HYATT REGENCY HOTEL,
PHOENIX, ARIZONA, DECEMBER 1980;
SPONSORED BY THE U.S. DEPARTMENT
OF ENERGY AND THE
ENVIRONMENTAL PROTECTION AGENCY

JANUARY 1981

PREPARED UNDER TASK NO. 1091.70

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Prepared for the
U.S. Department of Energy
Contract No. EG-77-C-01-4042

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David A. Schaller

Introduction

Relative to many competing forms of energy conversion technologies, photovoltaic systems are considered among the most environmentally benign. This is especially apparent during the projected 20-30 years of system operation. However, in a life cycle context, which includes manufacture, installation, operation and maintenance, and decommission, photovoltaic system development poses a number of potential environmental, health, and safety issues. Federal environmental regulatory programs will apply to waste streams generated in the development of photovoltaic systems and will ultimately determine the degree of environmental acceptability of the technology.

The Solar Energy Research Institute (SERI) has lead national laboratory responsibility for advanced research and development within the federal photovoltaics program. Advanced materials undergoing research at SERI are being evaluated in light of many criteria, including materials availability and environmental effects. Environmental research efforts in FY80 have focused on two advanced photovoltaic cell materials: copper sulfide/cadmium sulfide and polycrystalline silicon. Information and conclusions presented in this paper are adapted from SERI's 1980 work. A final report is in preparation and will be available in early 1981.

As these materials may be fabricated into photovoltaic cells in numerous ways, four representative processes were selected for analysis: the front wall $\text{Cu}_2\text{S}/\text{CdS}$ approach; a diffused p/n junction in a polycrystalline silicon wafer; spray deposition of a tin oxide junction on a polycrystalline silicon wafer; and the epitaxial deposition of high purity

polycrystalline silicon onto a low cost substrate. In very simplified terms, the front wall $\text{Cu}_2\text{S}/\text{CdS}$ approach involves vacuum deposition of CdS onto an electroformed copper foil substrate. A Cu_2S layer is formed and added through a wet chemical dip.

While four representative cell fabrication approaches were considered in the environmental review, only the $\text{Cu}_2\text{S}/\text{CdS}$ approach will be highlighted in this paper. SERI's forthcoming report on the FY80 research will provide a detailed look at all four processes. In this report, the environmental effects of manufacture are presented for each of the cell production options. In addition, the potential effects of installation, operation and maintenance, and decommissioning are evaluated. The report also discusses the potential for controlling and avoiding any adverse environmental effects identified. Finally, a major section of the analysis is dedicated to an overview of federal environmental, health, and safety programs applicable to each advanced material option. It is this last stage, the regulatory overview as applied to the $\text{Cu}_2\text{S}/\text{CdS}$ option, that is covered in this paper.

The $\text{Cu}_2\text{S}/\text{CdS}$ Process

There are two methods of fabricating copper sulfide/cadmium sulfide thin-film heterojunction cells: the front wall (or front surface) cell and the back wall (or back surface) cell. Development of the front wall $\text{Cu}_2\text{S}/\text{CdS}$ cell is supported by the U.S. Department of Energy (DOE) and the Solar Energy Research Institute through contracts with Westinghouse Corporation and the Institute of Energy Conversion at the University of Delaware. Both have proposed processes for commercial scale production (shown schematically in Figure 12.2.1).

Although this cell is constructed of a layer of Cu_2S and CdS , the Cu_2S layer is extremely thin ($0.2\mu\text{m}$). The CdS film ($5\text{-}30\mu\text{m}$) comprises the bulk of the semiconducting region and dominates the process considerations and operations of the cell. The heterojunction is formed from the CdS and Cu_2S layers. The CdS , primarily because of the stoichiometric deficiency of sulfur, is an n-type semiconductor; the Cu_2S is a p-type semiconductor due to a deficiency of copper.

Environmental Regulations and the $\text{Cu}_2\text{S}/\text{CdS}$ Process

Commercial scale production of the $\text{Cu}_2\text{S}/\text{CdS}$ photovoltaic material option will result in various by-product waste streams and associated health and safety risks at one or more stages of the cell production process. These waste streams may affect air, water and land environments depending on the handling, treatment and disposal methods employed. Federal environmental regulatory programs will apply to these waste streams much as they apply to a variety of wastes from other industrial activities.

SERI's FY80 research identified those regulatory programs which will likely apply at each of six discrete stages of the technology's development: 1) materials extraction; 2) materials processing; 3) cell fabrication; 4) installation; 5) decommissioning; and 6) materials, processing inputs and waste transportation (see Figure 12.2.2).

The analysis has been limited in part due to the strictly qualitative information available on the materials inputs and waste stream by-products of the $\text{Cu}_2\text{S}/\text{CdS}$ process. However, pollutant emission standards, limitations and exposure thresholds have been identified and can be used

to help suggest whether there may be regulatory constraints at the commercialization stage of technology development.

As the cell fabrication stage is unique to the photovoltaic industry, its waste stream characterization and regulatory profile is of great interest to both SERI and the participating industries. Figure 12.2.3 presents a summary of the emissions, effluents, and solid wastes expected from front wall $\text{Cu}_2\text{S}/\text{CdS}$ cell fabrication.

Air Quality

From an air quality standpoint, the fabrication of $\text{Cu}_2\text{S}/\text{CdS}$ cells generates few atmospheric contaminants. Hydrogen sulfide and hydrogen chloride are both emitted during the etching process and in the formation of the Cu_2S barrier. Nitrogen gas is also emitted during the Cu_2S barrier formation process step. Silicon monoxide or tantalum pentoxide particulate matter may be emitted if an antireflective (AR) coating is used. Interconnection of the cells is accomplished by soldering, which emits various acid fluxes, such as zinc chloride, ammonium and stannous chlorides, lead suboxides, and formaldehyde and fluorine fumes. ¹ Hydrocarbons are produced during the degreasing done in the substrate preparation stage; however, these may be controlled with ventilation hoods, and activated carbon or other absorbing means. ²

The particulates which are emitted in AR coating and the hydrocarbons produced by degreasing are both criteria pollutants for which National Ambient Air Quality Standards have been established. $\text{Cu}_2\text{S}/\text{CdS}$ cell manufacturing facilities are not now classified as major stationary sources by the Environmental Protection Agency and therefore do not automatically qualify for Prevention of Significant Deterioration review or Non-attainment rules. It does not appear that such facilities would emit greater than 250 tons per year of a regulated pollutant. Without the creation of a new stationary source category by EPA, cell manufacturing facilities would probably not be subject to either PSD or Non-attainment rules. Additionally, there are no New Source Performance Standards which now apply to such fabrication facilities, nor do any of the National Emission Standards for Hazardous Air Pollutants appear currently applicable to the $\text{Cu}_2\text{S}/\text{CdS}$ process.

Occupational Health

Worker health and safety standards regulating air quality issued by the Occupational Safety and Health Administration are applicable to the $\text{Cu}_2\text{S}/\text{CdS}$ cell manufacturing industry. Standards for workplace exposure have been developed for many of the atmospheric contaminants generated in production of the cells. Selected time weighted average workplace air contaminant levels are listed in Figure 12.2.4.

OSHA also regulates several chemicals as carcinogens. Recently, regulations have been issued to further identify, classify and control potential occupational carcinogens. ³ As part of an initial screening of more than 2,000 substances. OSHA has listed 107 substances as candidates for further review as potential carcinogens. Only a few of these 107 are used as material inputs or created as waste by-products in either of the $\text{Cu}_2\text{S}/\text{CdS}$ or polycrystalline silicon options. However, a number of substances on an earlier OSHA list of potential carcinogens are prominent in the two cell processes. Among these are cadmium, cadmium oxide, cadmium sulfate, cadmium sulfide, sulfuric acid, nickel ammonium, chromium and chromium compounds. ⁴ Nevertheless, listing

does not represent a scientific determination of carcinogenicity.

Water Quality

Water used during several of the process steps as a rinse solution can become contaminated with metal salts and other wastes. Specific liquid effluents may include: phosphorus detergent, zinc fluoroborate bath solution, which typically consists of zinc fluoroborate, ammonium chloride ammonium fluoroborate, and hydrogen chloride, and methanol from the substrate preparation steps; cadmium sulfide and hydrogen chloride from etching; sodium, copper, and cadmium chlorides generated during barrier formation; and gold, nickel and copper bath solutions used in the metallization step.

These liquid effluents may be discharged directly into receiving waters, indirectly via publicly owned treatment works, or they may be stored and treated as solid wastes. If they are directly discharged, the cell manufacturing facility may be considered a point source subject to the National Pollutant Discharge Elimination System permit program under the Clean Water Act. Under this program, manufacturing operations producing the $\text{Cu}_2\text{S}/\text{CdS}$ cells could be considered a primary industry source under the electronic component manufacturing category. Effluents generated will have to undergo pre-permit application testing for toxic, metals, conventional, non-conventional, and hazardous pollutants as defined by EPA.

No industry specific effluent limitation guidelines have been issued for $\text{Cu}_2\text{S}/\text{CdS}$ cell or module manufacturing operations. However, there are effluent guidelines which apply to electroplating and etching operations performed during the cell manufacturing process.⁵ Plating operations may be used for substrate preparation and grid application during metallization. Clean Water Act regulations also control discharges resulting from the electroplating of common metals, such as zinc in the substrate preparation step or copper and nickel in the metallization step. Applicable standards depend upon the size of the regulated facility, the volume of discharge water, and the number of plant employees.

There are no New Source Performance Standards developed to date for the $\text{Cu}_2\text{S}/\text{CdS}$ cell manufacturing industry, nor for any of the specific process steps involved. Additionally, none of the toxic pollutant effluent standards issues to date by EPA appear applicable to the manufacture of these cells.

Some of the liquid effluents generated by the manufacture of the $\text{Cu}_2\text{S}/\text{CdS}$ cells are listed as hazardous substances under the CWA. Ammonium chloride and ammonium fluoroborate, which are generated during substrate preparation, and cadmium chloride resulting from barrier formation, are listed and their discharge is generally limited. Deep well disposal of any liquid effluent produced during the manufacture of $\text{Cu}_2\text{S}/\text{CdS}$ cells must be in compliance with applicable Underground Injection Control (UIC) programs under the Safe Drinking Water Act.

Solid and Hazardous Wastes

The disposal of nonhazardous waste produced in $\text{Cu}_2\text{S}/\text{CdS}$ manufacture is regulated via state programs established under the Resource Conservation and Recovery Act. Some of the wastes generated in the cell production process qualifies for regulation under the Hazardous Waste Management (HWM) program under RCRA if it is to be disposed of on land or if stored for treatment. Wastes containing any of the toxic constituents listed

by EPA are considered hazardous wastes. Wastewater treatment sludges, spent bath solutions, bath sludges, spent stripping and cleaning bath solutions from electroplating operations, and certain spent solvents used in degreasing operations are all listed as hazardous wastes by EPA. Their occurrence in the cell fabrication process would likely trigger application of the stringent handling, reporting and treatment provisions of the HWM program.

Occupational Safety

In addition to the workplace air quality standards established by OSHA, that agency also issues safety and health regulations. These job safety rules address handling, labeling and warning requirements with respect to materials and prescribe protective gear for workers. Manufacturing operations, such as photovoltaic cell fabrication, would be covered by these additional OSHA stipulations.

Regulatory Trends

Changes in the environmental regulatory framework may easily modify this analysis. It is not uncommon for variances and other exceptions to regulations to be instituted. Patterns of enforcement are also not well established for many of the programs, as legal challenges and revisions to the regulations occur frequently. These factors will all be important in the determination of specific regulatory applicability at the commercialization stage of each PV material option. Also, alternative manufacturing processes may be adopted at later stages of technology development. This could easily result in the addition or subtraction of regulatory programs from the sets identified.

Findings and Conclusions

SERI's analysis identified the range of federal environmental, health, and safety regulatory programs which will likely be applicable to one or more stages of $\text{Cu}_2\text{S}/\text{CdS}$ and polycrystalline silicon photovoltaics development. No attempt was made, nor is it indeed possible, to indicate with certainty whether any stage of PV development would experience regulatory compliance difficulties. At best, the analysis indicates the potential applicability of environmental regulatory programs.

Based on the qualitative review of regulations which has been done, and on an understanding of waste stream control options, it is possible to identify the two or three most significant regulatory programs affecting the two advanced PV material options which should receive continuing and more detailed study. The regulatory programs which appear to be of most consequence are the effluent limits and permit procedures of the Clean Water Act, the workplace exposure regulations of the Occupational Safety and Health Act, and the hazardous waste disposal regulations under the Resource Conservation and Recovery Act.

It is important to note that there are no present effluent limitation guidelines which apply specifically to the industrial category of photovoltaics manufacture, whether by cadmium or silicon process. The ultimate size and nature of the emerging PV industry will be the force which triggers industry specific standards. At other stages in the production process for PV cells, the manufacturing, mining, and processing activities are sufficiently common as to already be addressed by regulations on an industry specific basis (i.e., electroplating, glass manufacture, inorganic chemical manufacturing). Figure 12.2.5 lists these industries

and the regulatory programs which apply.

The processing, fabrication and installation of PV cells under each materials option will be subject to the general workplace exposure and safety standards authority of the Occupational Safety and Health Administration. Standards have been and will continue to be established for specific hazardous chemical substances which must be controlled in the work environment irrespective of the industrial category affected. A stringent cadmium exposure standard for the workplace will have implications for a variety of industries besides $\text{Cu}_2\text{S}/\text{CdS}$ cell production.

OSHA will be considering a variety of factors in individual rulemaking procedures on occupational carcinogen determinations. These include: a) the estimated number of exposed workers; b) the estimated levels of workers' exposure; c) the molecular similarity of the substance to a known carcinogen; and d) the availability of safer substitute substances.

Qualification of a substance under OSHA's rules of evidence for carcinogenicity will trigger regulation at "lowest feasible" levels.⁶ This level of control will include the economic costs of compliance. Specific work practices to limit exposure will be determined on an individual chemical basis. If substitutes for the substance exist, the substance could be banned. Suspected carcinogens which do not meet OSHA's rules of evidence may still be regulated in the workplace at less stringent levels.

Under RCRA, there will be a tight regulatory program developed for the "cradle-to-grave" tracking and monitoring of hazardous wastes. To the extent that the PV materials options examined include the use or disposal of hazardous chemicals, there will be regulatory responsibilities to be maintained.

In summary, then, the extent to which $\text{Cu}_2\text{S}/\text{CdS}$ and polycrystalline silicon materials options will be affected by environmental, health, and safety regulations depends on three major determinants:

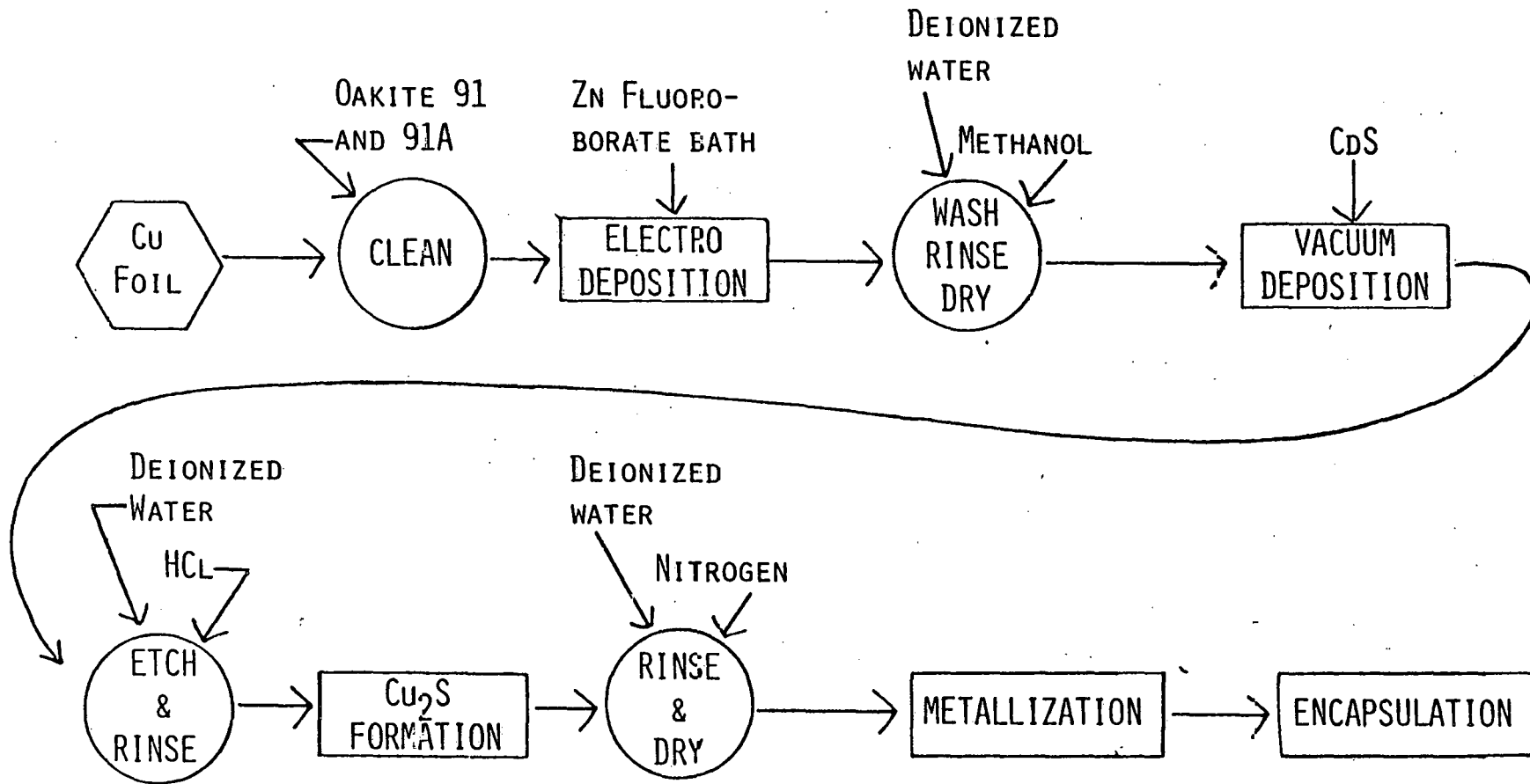
- the specific quantitative dimensions of waste streams, control options, and discharge sites to be employed;
- the modifications which may occur within waste-generating industrial processes at all stages of PV development and use; and
- the changes, either more or less restrictive, in quantitatively enforced environmental, health, and safety standards.

As progress is achieved in materials R&D and as forecasts may be made of the quantitative dimensions of the PV cell production process, more conclusive findings as to regulatory compliance and associated costs may be reached. The qualitative regulatory review comprising part of SERI's FY 80 research can help guide the direction of subsequent research into these important questions.

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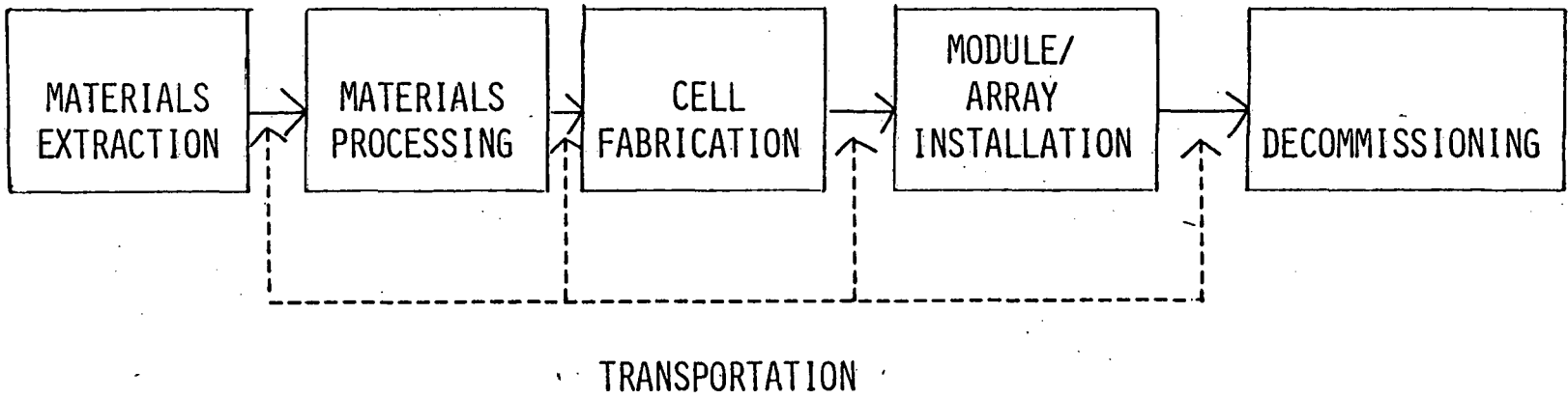
1. T.M. Briggs and T.W. Owens; Industrial Hygiene Characterization of the Photovoltaic Solar Cell Industry; Report No. NIOSH-80-112; PEDCO Environmental, Inc.; March 1980.
2. K. Lawrence, S. Morgan, D. Schaller and T. Wilczak; Life Cycle Environmental, Health and Safety Effects of Selected Advanced Photovoltaic Material Options; TR-743-799; Solar Energy Research Institute; (publication pending).

3. U.S. Department of Labor, Occupational Safety and Health Administration; "OSHA Names 107 Substances as Candidates for Further Scientific Review;" News; USDL: 80-502; August 12, 1980.
4. U.S. Environmental Protection Agency; A Handbook of Key Federal Regulations and Criteria for Multimedia Environmental Control; EPA-600/7-79-175; August 1979; pp. 128-129.
5. 40 CFR Part 413.
6. "OSHA Develops New Cancer Policy;" Science; Vol. 207; p. 742; (1980).



FABRICATION OF FRONT WALL $\text{Cu}_2\text{S}/\text{CdS}$ PHOTOVOLTAIC CELL

FIGURE 12.2.1



LIFE CYCLE STAGES OF PHOTOVOLTAICS DEVELOPMENT
FIGURE 12.2.2

| PROCESS STEP/WASTE | POSSIBLE TREATMENT | PROBABLE EFFLUENTS |
|----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|
| 1. SUBSTRATE PREPARATION CHROMATE COATING | LOWER PH WITH H_2SO_4 , AD AGENT (SO_2) REDUCE Cr^{+3} , ADD LIME (PATTERSON, '75; SITTIG '76) OR ION EXCHANGE W/ RECYCLE (PATTERSON '75) | $Cr(OH)_3$ |
| OAKITE 91 AND 91A (PHOSPHORUS DETERGENT) | BIOLOGICAL, ACTIVATED SLUDGE, MUNI- CIPAL OR LIME TREATMENT AND ANAERO- BIC DIGESTION (CALLELY, '76) | PRECIPITATE (INSOLUBLE) |
| 2. ZINC PLATING | | |
| $ZnBF_4$ | ADD Ca^{++} , RAISE PH (YEHASKEL '79) | CaF_2 , $Al(OH)_3$, H_3BO_3 |
| NH_4Cl | ADD $NaOH$ (POWERS, '76) | $NaCl$; NH_3 |
| NH_4BF_4 | ADD Ca^{++} (YEHASKEL '79) | CaF_2 , H_3BO_3 |
| LICORICE RCOT SOLUTION | ACTIVATED CARBON | |
| HCL (TO PH 3 TO 4) | RAISE PH WITH $Ca(OH)_2$ (POWERS '76) | $CaCl_2$ |
| CH_3OH (METHANOL) | SOLVENT EXTRACTION, FLUIDIZED BED, ACTIVATED CARBON (ROSS '68, POWERS '76) | |
| 3. CDS DEPOSITION AND ETCH | | |
| HCL(G) | LIQUID ABSORPTION AND NEUTRALI- ZATION (AMMONIA) (STERN '77) | $NaCl$ |
| $CdCl_2$ | ADD LIME (SITTIG '76); LIME AND $FeSO_4$ (PATTERSON '75) | $Cd(OH)_2$ (INSOLUBLE); $Fe(OH)_3$ |
| $H_2S(G)$ | LIQUID ABSORPTION (AMMONIA) (STERN '77) | S OR H_2SO_4 |
| 4. Cu_2S BARRIER FORMATION | | |
| $NaCl$ | ION EXCHANGE IF CONCENTRATION EXCESSIVE | $NaCl$ |
| $CuCl$ | ADD LIME (SITTIG '76; PATTERSON '75) | $Cu(OH)_2$ |

| PROCESS STEP/WASTE | POSSIBLE TREATMENT | PROBABLE EFFLUENTS |
|----------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------|
| H ₂ S(G) | LIQUID ABSORPTION (AMMONIA) (STERN '77) | S OR H ₂ SO ₄ |
| CdCl ₂ | ADD LIME (SITTIG '76); OR LIME AND FeSO ₄ (PATTERSON '75) | Cd(OH) ₂ ; Fe(OH) ₂ |
| HCl(G) | LIQUID ABSORPTION (+AMMONIA?) (STERN '77) | NaCl |
| N ₂ (G) | VENT | N ₂ |
| 4A. ALTERNATE Cu ₂ S FORMATION | | |
| CdCl | ADD LIME (SITTIG '76) OR LIME AND FeSO ₄ (PATTERSON '75) | Cd(OH) ₂ ; Fe(OH) ₂ |
| CuCl | ADD LIME (SITTIG '76; PATTERSON '75) | Cu(OH) ₂ |
| 5. GRID | | |
| Au | ION EXCHANGE | |
| Ni | ADD LIME (SITTIG '76; PATTERSON '75) | Ni(OH) ₃ |
| CU PLATING BATH | ADD LIME (SITTIG '76; PATTERSON '75) | Cu(OH) ₂ |

Cu₂S/CDS FRONT WALL PROCESS WASTE STREAM AND TREATMENTS

FIGURE 12.2.3

ACCEPTABLE MAXIMUM PEAK ABOVE
THE ACCEPTABLE CEILING CONCENTRATION
FOR AN 8-HOUR SHIFT

| MATERIAL | 8-HOUR TIME WEIGHTED AVERAGE | ACCEPTABLE CEILING CONCENTRATION | CONCENTRATION | MAXIMUM DURATION |
|---------------------------------|------------------------------------|----------------------------------------|---------------|----------------------------------------------------------------------|
| CADMIUM FUME (Z37,5-1970) | 0.1 MG./M ³ | 0.3 MG./M ³ | | |
| CADMIUM DUST (Z37,5-1970) | 0.2 MG./M ³ | 0.6 MG./M ³ | | |
| CHROMIC ACID AND CHROMATES | | 1 MG./10M ³ | | |
| FORMALDEHYDE (Z37,16-1967) | 3 P.P.M. | 5 P.P.M. | 10 P.P.M. | 30 MINUTES |
| HYDROGEN FLUORIDE (A37,28-1969) | 3 P.P.M. | | | |
| HYDROGEN SULFIDE (Z37,2-1966) | | 20 P.P.M. | 50 P.P.M. | 10 MINUTES ONCE ONLY IF NO OTHER MEASURABLE EXPOSURE OCCURS |
| FLUORIDE AS DUST (Z37,28-1969) | 2.5 MG./M ³ | | | |
| MERCURY (Z37,8-1971) | | 1 MG./10M ³ | | |

SOURCE: OSHA

SELECTED TIME WEIGHTED AVERAGE WORKPLACE
AIR CONTAMINANT LEVELS

FIGURE 12.2.4.

INDUSTRY

REGULATORY PROGRAM

| | CLEAN AIR ACT | | CLEAN WATER ACT | | | RCRA |
|---------------------------------------|---------------|------|--------------------|---------------------------|--------------------|--------------------|
| | NESHAPS | NSPS | EFFLUENT LIMITS | PRETREATMENT STANDARDS | TOXIC STANDARDS | HAZARDOUS WASTE |
| CEMENT MANUFACTURING | | X | X | | | |
| ELECTRONIC COMPONENT PRODUCTION | | | | | X | X |
| ELECTROPLATING | | | X | X | | X |
| FERROALLOY MANUFACTURING | | X | X | | | X |
| GLASS MANUFACTURING | | X | | | | |
| INK FORMULATING | | X | | | | X |
| CHLORINE PRODUCTION | | | | | | X |
| SULFURIC ACID PLANTS | | X | | | | |
| IRON AND STEEL MANUFACTURING | | X | X | | | |
| MINERAL MINING AND PROCESSING | | | X | | | |
| NONFERROUS METALS MANUFACTURING | | X | X | X | | |
| ORE MINING AND DRESSING | X | | X | | | |
| PAINT FORMULATION | | | X | | | X |
| PLASTICS AND SYNTHETICS MANUFACTURING | | | X | | | |

INDUSTRIES RELATED TO PV CELL PRODUCTION
SPECIFICALLY ADDRESSED BY FEDERAL
ENVIRONMENTAL REGULATIONS

FIGURE 12.2.5