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Environmental, Health, Safety, and Regulatory Review of Selected Photovoltaic Options

(Copper Sulfide/Cadmium Sulfide and Polycrystalline Silicon)

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ENVIRONMENTAL, HEALTH, SAFETY, AND REGULATORY REVIEW OF SELECTED PHOTOVOLTAIC OPTIONS

(COPPER SULFIDE/CADMIUM SULFIDE AND POLYCRYSTALLINE SILICON)

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PREFACE

This report contains a review of the environmental, health, safety, and regulatory impacts of selected advanced photovoltaic cells. The reviews cover the front-wall copper sulfide/cadmium sulfide cell and three cell fabrication techniques for polycrystalline silicon. This study was conducted in support of the Solar Energy Research Institute's (SERI) Photovoltaics Advanced Research and Development Program within the U.S. Department of Energy's Federal Photovoltaics Program. SERI's research in advanced photovoltaic materials includes the evaluation of important environmental, health, and safety impacts of PV cell production, installation, and use. The information in this report serves as a foundation for subsequent environmental, health, and safety analyses, as advanced photovoltaics processes evolve from initial research stages to technology development.

The authors thank SERI staff who gave so generously of their time in the preparation of this final report. Invaluable contributions also were made by individuals at the Institute of Energy Conversion, University of Delaware; Westinghouse R&D Center; Exxon Research and Engineering Company; David Sarnoff Research Laboratory, RCA; SES, Inc; Bureau of Mines, Rolla, Missouri; Applied Solar Energy Corp.; Jet Propulsion Laboratory; The Analytic Sciences Corporation; ASARCO; and Arizona State University. This report was prepared under SERI Task Nos. 3825.40 (FY80) and 1091.70 (FY81) for the U.S. Department of Energy.

Approved for

SOLAR ENERGY RESEARCH INSTITUTE

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SUMMARY

OBJECTIVE

To review the environmental, health, safety, and regulatory impacts of selected copper sulfide/cadmium sulfide and polycrystalline silicon photovoltaic (PV) cells.

DISCUSSION

Polycrystalline silicon (poly-Si) and copper sulfide/cadmium sulfide (Cu_2S/CdS) photovoltaic systems are two of several developing technologies that could emerge as commercial products with wide application. Normal operation of the systems will not produce air or water pollutants, thermal pollution, or bothersome noise. These benefits are substantial because they will occur throughout the 20 to 30 years of system operation. However, some potential environmental, health, and safety (EH&S) effects from manufacturing, installing, operating, and decommissioning poly-Si and Cu_2S/CdS systems do exist.

This report presents an overview of the life-cycle environmental, health, and safety effects that can result from a photovoltaics industry based on poly-Si or Cu_2S/CdS cells and examines the regulatory programs applicable to their manufacture, use, and disposal. Many effects result from using specific materials necessary for fabrication of the solar cells. Effects generally are controllable, however, given currently available pollution abatement and waste disposal techniques and industrial experience, since all of the required material inputs are used in other industries. For example, the semiconductor industry has a successful environmental, health, and safety record relative to its use of silicon compounds and dopants. In addition, smaller quantities of materials will be used to produce poly-Si and Cu_2S/CdS photovoltaic cells in the future. Advanced option photovoltaic cell concepts must meet U.S. Department of Energy cost goals to achieve large-scale deployment. One of the many ways to reduce cell costs is to improve the efficiency of materials used (both those within the cells—silicon, cadmium, etc.—and those used for manufacture—acids, etchants, etc.). As materials efficiency improves, there will be environmental benefits: fewer wastes and effluents that must meet regulatory standards for pollution control and waste disposal.

Environmental, health, and safety risks, discussed in Part I of this report, are highly dependent upon system life-cycle phases; i.e., materials acquisition and cell fabrication, installation, operation and maintenance (O&M), and decommission. Materials acquisition and cell fabrication pose relatively high occupational health and environmental risks because of the toxicity of the materials used. Mining and processing the primary materials required for manufacture of poly-Si and Cu_2S/CdS solar cells (silicon and cadmium) entail environmental degradation and occupational hazards (for example, inhalation of Si, SiO_x and cadmium particulates). However, net increases in adverse effects from the photovoltaic industry initially will be small to imperceptible, especially in the raw materials sector; e.g., production of metallurgical-grade (MG) silicon and cadmium recovery at zinc smelters. For example, only about 1% of the projected year 2000 production of MG silicon would be required to fabricate 1 GW of polycrystalline silicon photovoltaic cells (Watts 1980). Some of the industries producing secondary materials, especially polycrystalline silicon, may have to increase capacity to meet the demands of the photovoltaic industry. In this case, there may be a net increase in environmental, health, and safety risks associated with expanding the industries. However, the significance of such an increase will have to be evaluated in terms of the life-cycle effects of photovoltaic-generated electricity compared with the electricity or other energy source that is displaced.

Some potential environmental, health, and safety effects are common to all photovoltaic systems, regardless of cell type. However, some are unique to the selected poly-Si and Cu_2S/CdS cell options which are the focus of this report. Key effects, both common and unique, for each life-cycle phase are presented in this report.

Overall, the environmental, health, and safety risks of a photovoltaic industry based on poly-Si or Cu_2S/CdS cells appear to be acceptable and controllable, given current knowledge. However, regulatory pressures for cadmium release control are expected to continue and possibly increase in the future. Cadmium production waste products must be disposed of in an environmentally sound manner (e.g., in approved landfills) to minimize dispersion by wind-blown particles, runoff, or leaching. The principal health risks of cadmium processing are occupational and result from inhalation of cadmium-containing particles; but these risks should be controllable by using respirators or other worker protection devices.

Environmental and health hazards from disposing of solid wastes from metallurgical-grade (MG) silicon production appear to be minimal because of the stability and low toxicity of silicon. Atmospheric emissions of submicron-sized silicon-containing particulates from electric arc furnaces (used to produce MG silicon) need to be analyzed to determine emission levels and size ranges before occupational and public health risks can be assessed, however.

Residential, commercial/industrial, and intermediate load photovoltaic applications will probably be located at highly disturbed sites. Ecological effects of their installation are expected to be small to nonexistent. Major ecological effects of central-station photovoltaic applications include: (1) soil compaction, (2) fugitive dust, (3) erosion due to wind and water runoff, and (4) destruction of some to all of the wildlife in the immediate area. These effects are common to all large-scale construction activities. Their severity, however, will be highly influenced by the site—its ecological fragility, amount of grading and clearing, accessibility, and so forth.

Acquiring large tracts of land for deployment of central-station photovoltaic systems (independent of cell type) could be difficult in some areas, especially if the area is relatively pristine. The Endangered Species Act may be a key consideration in some site acquisitions.

Public health risks may result from atypical events, such as outgassing or fire. The risk is greater for residential and commercial/industrial applications because they generally are located in more densely populated areas. In addition, these systems are often mounted directly onto combustible materials, like those used in roofing. Outgassing should not occur if systems are properly designed and tested before sale. Poly-Si panels should pose relatively few hazards in case of fire because of the low toxicity of most panel materials. Hazardous levels of cadmium compounds could be released if Cu_2S/CdS panels are burned. However, dilution by outdoor air of any toxic fumes will help to mitigate health hazards.

Entry of toxic materials into the environment from cracked or broken panels is not expected to be a problem for poly-Si options. It is possible that rain could leach cadmium from damaged Cu_2S/CdS panels, but this is not likely because damaged panels probably will be rapidly replaced. However, the feasibility of entry by this route has not been determined, nor its significance, if any, analyzed.

It is possible that an industry to reclaim and recycle the materials in poly-Si and Cu_2S/CdS panels may develop if incentives are provided (e.g., the cost of new materials versus recycled ones, materials availability, or environmental regulations). If poly-Si panels are not recycled, they can be crushed and disposed of in ordinary landfills. Disposal of unrecycled Cu_2S/CdS panels may require care. Cu_2S/CdS cells may require encapsulation or sealing before disposal to ensure that cadmium is not leached by drainage.

Part II of this report examines major environmental, health, and safety regulatory programs that may apply to the manufacture, use, and disposal of photovoltaic cells developed with Cu_2S/CdS and poly-Si materials. Summaries of programs that appear to apply to one or more PV production stages are presented. The analysis is based on qualitative information about the characteristics of waste streams expected from each of the two PV materials options. Without quantitative data on waste stream components, discharge rates, selected waste stream control options, and discharge sites, regulatory compliance reviews specific to array sites cannot be performed.

Based on the qualitative review of regulations and on the explanation of waste-stream control options presented in Part I, we can identify the three most significant regulatory programs affecting photovoltaics that should receive more detailed study. These regulatory programs are the effluent limits and permit procedures of the Clean Water Act (CWA), the workplace exposure regulations of the Occupational Safety and Health Act (OSHA), and the hazardous waste disposal regulations under the Resource Conservation and Recovery Act (RCRA).

Note that there are no current effluent limitation guidelines under CWA regulations that specifically apply to the industrial category of photovoltaics manufacture, whether by the cadmium or silicon process. The ultimate size and nature of the emerging PV industry will be the forces that prompt standards specific to the industry. At other stages in the production process for PV cells, manufacturing, mining, and processing activities are common enough to be addressed by existing regulations affecting specific industries (i.e., electroplating, glass manufacture, and inorganic chemicals manufacturing).

The processing, fabrication, and installation of photovoltaic 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 that must be controlled in the work environment, regardless of the industrial category affected. A stringent cadmium exposure standard for the workplace will have implications for a variety of industries besides PV cell production.

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 here include the use or disposal of hazardous chemicals, regulatory responsibilities will have to be maintained. In the absence of air or water quality standards or workplace exposure limits specific to the industry, no federal regulatory programs addressing environment, health, or safety exist that are unique to the PV industry under either materials option.

Some of the more established PV materials options have already been the focus of environmental research by industry. The data bases being developed in such efforts should facilitate the analysis of quantitative environmental effects and regulatory forecasts of PV materials options now in early research and development phases.

One of the conceptual issues that merits further discussion concerns the extent to which regulatory analyses of PV materials options should repeatedly address the "front-end" waste streams from materials extraction. If the PV industry were to develop more extensively than expected, basic input materials could represent a significant percentage of industry output. However, it is unlikely that the PV cell fabrication industry would experience the direct regulatory responsibility for such pollutant burdens. Should tighter environmental regulatory controls be applied outside the cell fabrication stage of PV development, alternative material input sources, if not alternate materials themselves, may limit the effects of controls on advances in the technology.

In summary, then, the extent to which Cu_2S/CdS and poly-Si materials options will be affected by environmental, health, and safety regulations depends on three major determinants:

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

As more progress is achieved in PV materials R&D and as forecasts are made of the quantitative dimensions of the PV cell production process, more conclusive findings as to regulatory compliance potential and associated costs may be reached. The qualitative regulatory review presented in this report can help determine the direction of subsequent research into these important issues.

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LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
ANSI	American National Standards Institute
AQCR	Air Quality Control Regions
BAT	Best Available Technology
BCT	Best Conventional Technology
BACT	Best Available Control Technology
BMP	Best Management Practice
BOD	Biological Oxygen Demand
BOD$_5$	5-Day Biological Oxygen Demand
CAA	Clean Air Act
CFR	Code of Federal Regulations
COD	Chemical Oxygen Demand
CWA	Clean Water Act
EPA	Environmental Protection Agency
FR	Federal Register
FWPCA	Federal Water Pollution Control Act
GC/MS	Gas Chromatography/Mass Spectrophotometry
LAER	Lowest Achievable Emission Rate
NA	Nonattainment
NAAQS	National Ambient Air Quality Standard
NEPA	National Environmental Policy Act
NESHAP	National Emission Standards for Hazardous Air Pollutants
NIOSH	National Institute for Occupational Safety and Health
NPDES	National Pollutant Discharge Elimination System
NSPS	New Source Performance Standard
OSHA	Occupational Safety and Health Administration
PSD	Prevention of Significant Deterioration
PV	Photovoltaics
RCRA	Resource Conservation and Recovery Act
SDWA	Safe Drinking Water Act
SIP	State Implementation Plan
TDS	Total Dissolved Solid
TLV^R	Threshold Limit Value
TSCA	Toxic Substances Control Act
TSS	Total Suspended Solids
TWA	Time Weighted Averages
USC	United States Code

PART I

LIFE-CYCLE ENVIRONMENTAL, HEALTH, AND SAFETY EFFECTS OF SELECTED COPPER SULFIDE/CADMIUM SULFIDE AND POLYCRYSTALLINE SILICON PHOTOVOLTAIC MATERIALS

SECTION 1.0

INTRODUCTION

Relative to many competing forms of energy conversion technologies, photovoltaic systems are deemed to be some of the most environmentally benign (Demeo and Bos 1978). This is certainly true over their projected 20 to 30 years of operation. However, the entire life-cycle—manufacture, installation, operation and maintenance, and decommission—is not without potential environmental, health, and safety effects. Part I of this report presents a life-cycle effects review for two advanced photovoltaic cell materials: copper sulfide/cadmium sulfide (Cu_2S/CdS) and polycrystalline silicon (poly-Si). The purpose of the review is to identify environmental, health, and safety (EH&S) problem areas or areas for which data are inadequate for an EH&S analysis. Problem areas and critical data gaps provide the basis for recommendations presented in the summary.

In addition, the EH&S review of selected copper sulfide/cadmium sulfide and polycrystalline silicon cell options provides support to the Photovoltaics Division of the Solar Energy Research Institute (SERI). SERI is chartered with lead center responsibilities for Advanced Research and Development (AR&D) within the Federal Photovoltaics Program. The AR&D program comprises three elements: (1) advanced materials and cell research (copper sulfide/cadmium sulfide and polycrystalline silicon are included within this program element); (2) high-risk materials research; and (3) research support and fundamental studies (an element including such topics as materials availability, cost analysis, environmental effects, etc.) (DOE 1979). Materials undergoing research at SERI are periodically evaluated to determine whether (1) they are promising but still in need of further research and development; (2) the probability of success is too low to justify additional research funding; or (3) they are sufficiently developed for administrative transfer to the Jet Propulsion Laboratory's (JPL) Technology Development and Applications portion of the Federal Photovoltaics Program. Many parameters must be considered before materials research is deemed ready to transfer to JPL, including technical feasibility; potential for lower cost than current photovoltaics options; and environmental, health, and safety acceptability. Thus, the information provided in this report will assist the SERI Photovoltaics AR&D personnel in their decision-making processes.

The results of the EH&S review for copper sulfide/cadmium sulfide and polycrystalline silicon also provide support to Brookhaven National Laboratory (BNL), designated by the U.S. Department of Energy (DOE) as the lead center for photovoltaics environmental, health, and safety research. BNL is currently performing EH&S studies for single-crystal and ribbon silicon, gallium arsenide, and copper sulfide/cadmium sulfide back-wall* photovoltaic cells. Critical information gaps or problem areas (or both) for copper sulfide/cadmium sulfide and polycrystalline silicon solar cells will be related to BNL for research attention.

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*The analysis of the front-wall copper sulfide/cadmium sulfide option presented in this report has been coordinated with BNL to assure complementarity and to avoid unnecessary duplication of effort.

The two materials options examined in this report can be fabricated into photovoltaic cells by a number of research approaches. There are two basic techniques for producing copper sulfide/cadmium sulfide (Cu_2S/CdS) photovoltaic cells: back wall and front wall. In simple terms, the back-wall approach involves the chemical spray deposition of cadmium sulfide (CdS) onto a heated glass superstrate followed by a layer of chemically spray-deposited copper sulfide (Cu_2S). The environmental implications of this approach are being examined at Brookhaven National Laboratory. In the front-wall approach, the CdS is applied via vacuum deposition onto an electroformed copper foil substrate. The Cu_2S layer is presently formed through a wet chemical dip. (A more complete discussion of the back-wall approach and a detailed description of the front-wall approach can be found in Sec. 2.0.) SERI is primarily funding research for only the front-wall approach to producing Cu_2S/CdS photovoltaic cells. To support SERI's AR&D program, an EH&S analysis was performed only for the front-wall Cu_2S/CdS approach.

There are numerous cell fabrication techniques for polycrystalline silicon receiving research attention. It would be premature to examine all potential options at their current stages of development and it would probably not provide the more detailed information necessary for insightful and worthwhile EH&S analyses. Therefore, three representative approaches were selected for study: a diffused p/n junction in a polycrystalline silicon wafer, spray deposition of tin oxide on a polycrystalline silicon wafer, and epitaxial deposition of high-purity polycrystalline silicon onto a low-cost substrate.

The environmental effects of manufacture for each of the selected cell production options are presented in Sec. 2.0. The discussions are organized by material option and include raw materials processing (e.g., production of silicon, cadmium, and cadmium sulfide) where appropriate. Environmental effects in this and all future discussions include both the physical and human environment; therefore, discussions include potential risks to ecosystems, human health (both occupational and public), and safety.

Section 3.0 presents an evaluation of integrated life-cycle environmental effects including a summary discussion of the time distribution of emissions and physical effects (i.e., are effects "one-time" insults or annual, occurring throughout system operation); the toxicity, persistence, and mobility of emissions; and the potential for controlling and avoiding or reversing adverse environmental effects. Based on the integrated evaluation, critical information gaps and research needs are identified.

The potential environmental effects of installation, operation and maintenance, and decommission are presented in Sec. 4.0. For each of the material options, three generic end-use applications are assumed: residential; commercial and industrial; and large-scale utility deployment. In all instances, energy "storage" is assumed to be supplied by tying in with the utility grid.

SECTION 2.0

ENVIRONMENTAL, HEALTH, AND SAFETY EFFECTS OF FABRICATING SELECTED ADVANCED PHOTOVOLTAIC CELLS

2.1 FABRICATION PROCESS FOR FRONT-WALL COPPER SULFIDE/CADMIUM SULFIDE PHOTOVOLTAIC CELLS

2.1.1 Cadmium and Its Production

Cadmium is a relatively rare metal found throughout the earth's crust. In nature, it is always associated with zinc (National Environmental Research Center [NERC] 1975) and is also associated with lead. Cadmium content varies from traces to 0.4% in lead and zinc ores (Dennis 1961). Although the zinc-to-cadmium ratio may vary by deposit, the ratio tends to be uniform throughout the deposit. Both metals occur in ore deposits principally as sulfides. Only ore deposits rich in cadmium and areas contaminated by man have concentrations exceeding fractions of a part per million (ppm) (NERC 1975). A summary of average natural levels of cadmium is shown in Tables 2-1a and 2-1b.

2.1.1.1 Sources and Uses of Cadmium

Cadmium is recovered as a by-product of metal refining, particularly zinc. It is also recovered from the flue dust of lead and copper smelting. Although the U.S. is the largest consumer of cadmium, Japan is the largest producer of refined cadmium. The zinc smelter residues from which cadmium is extracted are often stockpiled in times of low prices or low demand. Consequently, zinc production is not an accurate indicator of cadmium production (Lucas 1979).

Coating and plating consume 35%-40% of commercially available cadmium. It is highly resistant to alkali environments, very solderable, very ductile, and in plating operations is deposited at uniform thickness at high rates. Cadmium is used in battery production (particularly nickel-cadmium batteries). Pigments for paint consume the largest amounts of cadmium compounds. Colors in the orange-to-red range are produced by cadmium sulfides and selenides. Cadmium is also used in producing plastic stabilizers, television picture tube and flourescent light phosphors, catalysts for production of primary alcohols and esters, nuclear controls, low-melting-point alloys used in fire detection, molding applications, and solders (Lucas 1979, National Research Council Canada [NRCC] 1979).

2.1.1.2 Cadmium Refining

Cadmium follows the zinc with which it is closely associated in its recovery from polymetallic sulfide ores—lead-zinc and copper-zinc. Only electrolytic recovery, the major cadmium refining process, is described here. Air pollution problems have led to increased electrolytic production and to the closing of the older pyrometallurgical plants (Kirk-Othmer 1978). Electrolytic recovery is also more labor and energy efficient. Shutdown of the last U.S. pyrometallurgical plant is scheduled for mid-November 1980 (Metals Week 1980).

Table 2-1a. REPRESENTATIVE NATURAL CONCENTRATIONS OF CADMIUM IN VARIOUS COMPONENTS OF THE BIOGEOCHEMICAL CYCLE

Component	Concentration (μg/g)
Lithosphere	0.5
Atmosphere	0.0004-0.028 (μg/m^3)
Hydrosphere	
Seawater	0.00011
Freshwater	$<$0.08
Pedosphere	600
Biosphere	
Marine plants	0.4
Marine animals	1.5-13.0
Terrestrial plants	0.6
Terrestrial animals	$\leq$0.5

Table 2-1b. CONCENTRATION RATIOS FOR CADMIUM IN AQUATIC AND TERRESTRIAL ECOSYSTEMS

Biota	Habitat Medium	Concentration Ratio[a]
Invertebrates	Freshwater	2,000.0
Fish	Freshwater	200.0
Invertebrates	Marine	250,000.0
Fish	Marine	3,000.0
Scallops	Marine	2,300,000.0
Plants	Terrestrial	11.0
Plants	Terrestrial	5.5

[a] $[\mathrm{Cd}]_{\mathrm{biota}}/[\mathrm{Cd}]$ habitat medium.

Source: Adapted from ANL-ES90 1980.

The following are simplified descriptions of very complex and differing operations. The descriptions and figures were developed from interviews and references (Engineering and Mining Journal July 1980, AIME World Symposium on Mining and Metallury of Lead and Zinc 1970, Kirk-Othmer 1978.) By-products of these processes are generally refined, reprocessed, recycled, or stockpiled until other uses for them are identified.

Mining and Milling. The polymetallic ore is ground in stages to particles 20μ to 75μ in size. The resulting fine rock and sulfides are agitated with small amounts of organic xanthate collector and a froth promoter, usually pine oil. The mixture is treated in banks of flotation machines—shallow tanks in which a rotating impeller induces finely dispersed bubbles of air. If the pH and reagents are correctly adjusted, the air bubbles carry the sulfide minerals to the surface of the mixture for removal. The proper combination of reagents allows for selective flotation of lead sulfides, copper sulfides, and zinc sulfides and for the rejection of the iron sulfides and rock to tailings. The metal concentrates are dewatered, dried, and shipped to metallurgical plants. The water is recycled to the mill and the tailings go to a tailings pond. Since these tailings contain cyanides (from the reagents) and heavy metals, they are classified as both hazardous and toxic wastes. Each of the sulfides is sent to an appropriate smelter.

The Zinc Smelter. The electrolytic zinc process consists of four main operations:

(1) An oxidizing roast at high temperature to eliminate sulfur and to convert the zinc, iron, and cadmium to oxides. The sulfur dioxide is recovered as sulfuric acid.

(2) A sulfuric acid solution leach that dissolves the maximum amount of zinc and yields a neutral solution of zinc sulfate and other acid-soluble metals.

(3) Purification of the solution by first precipitating iron, then (with zinc dust) precipitating copper, cadmium, cobalt, arsenic, antimony, and nickel—resulting in a highly purified solution of zinc sulfate and impure solid residues containing copper and cadmium.

(4) Electrodeposition to recover metallic zinc from the zinc sulfate solution and regeneration of the equivalent amount of sulfuric acid (NRCC 1979).

Additional processes—further leaching, smelting, and electrolysis—increase the recovery of zinc and cadmium (NRCC 1979). Zinc electrolytes may contain as many as 64 elements.

Major cadmium recovery plants use these raw materials for cadmium recovery: cadmium sponge from electrolytic zinc production and cadmium-enriched lead dusts from lead smelting furnaces. Zinc sulfide concentrates, dusts from the electrostatic precipitators of multiple-hearth roaster furnaces (Athanassiadis 1969), and recycled zinc metal that contains cadmium are also used (Briggs and Owens 1979).

Cadmium Production from Zinc Electrolyte Purification Residue. The cadmium sponge, a product of purifying the zinc sulfate solution with zinc dust at the zinc smelter, is 99.5% pure cadmium. This cadmium sponge is shipped from the smelter to a cadmium recovery facility.

The cadmium sponge is oxidized, usually in steam, for approximately two days. The resulting cadmium oxide is leached with spent cadmium electrolyte and sulfuric acid to produce a new electrolyte. The electrolyte is filtered and impurities are precipitated with a strong oxidizing agent, manganese dioxide or potassium permanganate. The resulting purification by-products include arsenic, thallium, and lead.

Cadmium is recovered from the purified electrolyte by electrowinning. Animal glue is usually added to enhance the smoothness of the resulting cadmium cathode. Noncorrosive, silver-lead anodes are used. The cathodes are removed approximately every 24 hours, rinsed, and stripped. The two major by-products of electrowinning are sulfuric acid and water, both of which are recycled. The stripped cadmium is melted under caustic or resin and cast into shapes.

Cadmium Production from Lead Smelter Fumes and Dusts. Lead smelters enrich their dusts, depending on industrial source, anywhere from 8%-60% before shipping to the cadmium recovery plant. Numerous processing variations exist. The first step converts the cadmium in the dusts into a water- or acid-soluble form. The resulting calcine is leached—in this example, with water. The solution is filtered to remove lead. The filtered lead sulfate from this process is recycled to the lead smelter. The cadmium, at this process stage, can be cemented from the solution with zinc dust, briquetted, melted under caustic, and cast.

In a different process, the cadmium sulfate solution is further purified to remove arsenic, iron, copper, and thallium. The resulting electrolyte is 99.995% pure. Glue may be added during the next step—electrowinning. The cadmium cathode is stripped, melted under flux, and cast into shapes. The spent electrolyte is recycled at the cadmium recovery plant. When impurities in the spent electrolyte become excessive, the solution is recycled to another use, e.g., selective flotation at the mine, or is discarded after neutralization.

Preparation of Cadmium Sulfide. Cadmium sulfide can be prepared by several methods (Kirk-Othmer 1979). The most common processes for producing cadmium sulfide are (1) to dissolve cadmium oxide in dilute sulfuric acid, or (2) to dissolve cadmium sulfate in water. The product of either of these methods is cadmium sulfate in solution.

The solution undergoes purification to remove heavy metals and organic contaminants (Briggs and Owens 1979). Cadmium sulfide is precipitated from solution with hydrogen sulfide gas. The precipitate is washed, filtered, and dried. A high-temperature firing of the precipitate in an H_2S atmosphere removes excess sulfate and other volatile contaminants (Briggs and Owens 1979). Cadmium sulfide for semiconductor or solar cell end uses requires this degree of purity. The by-products of these processes are H_2SO_4 in solution, heavy metals (solids), H_2S, H_2S dissolved in the mother liquor, and volatile contaminants.

Cadmium Production Health and Safety Considerations. The dissolution of cadmium precipitates and the galvanic precipitation of cadmium with zinc require special precautions to remove possible mist and toxic gases such as arsine. The melting of the cathode may produce a dangerous fume. Suitable exhaust hoods and scrubbers must be provided. Since most cases of cadmium poisoning result from inhalation of dust or fumes, affecting the respiratory tract, properly designed exhaust ventilation systems or individual filtered or air-supplied respirators will provide workers with protection (Kirk-Othmer 1979). This report discusses occupational health and safety hazards associated with cadmium and its compounds in Subsec. 3.1.3.

2.1.1.3 Environmental Considerations

A cutback in zinc production has reduced U.S. production of cadmium. Both reduced cadmium levels in new sources and changes in environmental regulations have influenced this situation (Kirk-Othmer 1978). For example, a major environmental concern at zinc smelters is the emission of sulfur dioxide and particulates (Bureau of Mines 1977). However, regulators' concerns over the disposal of toxic materials have had the effect of increasing cadmium recovery at primary smelters (Lucas 1979).

Smelting operations are a major source of cadmium pollution in localized areas. For example, during the 20 years of a Kansas smelter operation, cadmium levels in the topsoil within a 2-km radius increased sevenfold (NRCC 1979). Mine tailings are another source of cadmium pollution. Dispersal from solid wastes is attributed mainly to wind erosion, percolating waters, and surface drainage waters (Roberts and Johnson 1978). If baghouse dusts or scrubber slurries contact acid effluents from acid plants which frequently produce H_2SO_4 as a smelter by-product, cadmium mobility increases significantly (Gale and Wixon 1979). Although cadmium concentrations decrease with distance from point-source emissions, cadmium's mobility—compared with lead, zinc, and copper—results in appreciable amounts of dissolved cadmium in the watershed runoff (Gale and Wixon 1979).

One estimate of emissions puts cadmium releases at 300 pounds for each ton of cadmium throughput (Neff 1979). The largest cadmium releases, as previously stated, appear to occur during primary zinc refining. The loss rate in the United States is presently 15%-16% (by weight) of the cadmium present in the input zinc ore (Neff 1979). Neff, using this estimate, judges about 50 metric tons of cadmium would be released for each 200 MW_e of photovoltaic capacity produced. The estimate is open to question, however, since it is based on national mass balances (Neff 1979).

New smelters replacing the old pyrometallurgical smelters and using available current technology will also change these mass balances. For example, monitoring of air emissions at the Jersey Miniere Zinc Co. (J.M.Z.) in Clarksville, Tenn., a new zinc and cadmium complex which began full production in 1979, demonstrates that ambient SO_2 and particulate concentrations have remained essentially unchanged from levels that prevailed before plant start-up (Engineering & Mining Journal 1980). Effluent from the J.M.Z. wastewater treatment system must meet discharge limits established in the company's National Pollution Discharge Elimination System (NPDES) permit (Engineering & Mining Journal 1980).

During cadmium refining and cadmium sulfide production, an additional 5.6% of the cadmium is released to the atmosphere. At this rate, the loss would be equivalent to 14 metric tons per 200 MW_e peak capacity (Neff 1979). These estimated cadmium releases are also open to question in view of currently available pollution control technology and environmental regulations.

An ongoing Purdue University study states that, with few local exceptions, there is little evidence to suggest that on a national scale man's activities have resulted in either significant cadmium intake by humans or notable ecological effects in the United States. Among the local exceptions are those found in the vicinity of lead and zinc smelters. These exceptions appear to be the result of totally uncontrolled releases from cadmium sources. Currently available control measures are able to remove approximately 95% of heavy metals from aqueous water streams and 98% (other sources claim 99%-100%) of metal-bearing particulates in gaseous emissions (Yost 1979).

Air Emissions of Cadmium. Sinter units emit chloride salts and roasters emit sulfide salts. Both are soluble. Process details suggest, however, that only 15% of total cadmium emissions are salts (Fleischer et al. 1974). Particulate sizes range from submicron to possibly 100 microns or greater in diameter. Wind, particle size, and other physical and meteorological factors determine retention time in the air. Large particles settle out immediately, while small particles may remain suspended indefinitely (NERC 1975). Rainfall is considered a major factor in clearing cadmium from the air and depositing it on the soil (NRCC 1979).

Soil lead, zinc, and cadmium concentrations decrease exponentially downwind of metalliferous soil heaps (Roberts and Johnson 1978). Results of a study conducted in Helena Valley, Montana, showed that soil samples collected nearest a lead smelter and zinc recovery plant smelter stack had consistently higher cadmium levels than those farther away (NERC 1975). The high cadmium levels, as determined in the National Air Surveillance Network Studies, in the air of El Paso, Texas, may be attributed to the emissions of a large lead smelter located in the area (NERC 1975).

Water Transport of Cadmium. Water pollution by cadmium results from industrial and domestic sources and tends to be localized. Airborne particulates settle and accumulate in forest litter and concentrate as the litter decomposes. Litter decomposition slows as heavy metal concentration increases (NRCC 1975). Cadmium's solubility and its lower levels of complexation with organic ligands in the litter allow it to move along with water runoff (Gale and Wixson 1979).

Cadmium is soluble in either mineral or organic dilute acids (Environment Directorate 1975). Dissolved cadmium does not tend to appear in ocean water because of high pH (NRCC 1979). Rather, unsoluble cadmium precipitates occur in sediments.

One of the major ways cadmium enters surface waters is from the leaching of mine tailings (Fleischer et al. 1974). Acid mine waters and neutral waters flowing through highly organic terrain may cause cadmium pollution from zinc mine tailings. If transporting water becomes neutral or alkaline, cadmium may precipitate, be absorbed in the soil, or be transported in suspension (Bureau of Mines 1979). Heavy rains may mobilize the cadmium from the sediment (NRCC 1979, Fleischer et al. 1974). The drainage from strip mines yields 30,000 tons of sediment/mi^2 annually, which is 10-60 times the yield from agricultural lands. Subsurface mines, like most zinc mines, are not expected to enhance sediment drainage, but significant drainage from abandoned mines may occur if they are flooded (Fleischer et al. 1974).

Contamination of surface waters can be abated by tailings ponds. Limestone is a common constituent of zinc mine tailings and tends to reduce cadmium mobility (Bureau of Mines 1979). Cadmium is likely to be fixed in dumps of alkaline soils. Granitic soils, soils high in humic content, or soils in areas with sulfide minerals would have the opposite effect.

Cadmium compounds will dissolve in the presence of chloride ions; but if carbonate is present, cadmium will precipitate as $CdCO_3$, which is relatively insoluble in water. The presence of ions more noble than cadmium (Hg, Cu, Pb, Ag, etc.) will cause cadmium to dissolve; e.g., $Cu^{++} + Cd^{o} \longrightarrow Cd^{++} + Cu^{o}$ (Environment Directorate 1975).

2.1.2 Production of Copper Sulfide/Cadmium Sulfide Photovoltaic Cells

There are two methods of fabricating copper sulfide/cadmium sulfide (Cu_2S/CdS) thin-film heterojunction cells: the front-wall cell and the back-wall cell. This study focuses on the front-wall cell production approach. Brookhaven National Laboratory is examining the environmental impacts of the back-wall cell.

Development of the front-wall Cu_2S/CdS cell is supported by DOE and managed by SERI through contracts with several organizations, such as Westinghouse Corporation and the Institute of Energy Conversion at the University of Delaware. SES, Inc., Newark, Delaware, maintains an independent R&D effort in Cu_2S/CdS, uses a batch process approach, and is a semicommercial producer of front-wall copper sulfide/cadmium sulfide cells for large-scale applications. Photon Power, El Paso, Texas, is developing a commercial back-wall cell.

Although these cells are constructed of a layer of Cu_2S and CdS, the Cu_2S layer is extremely thin (0.2 μm). The thickness of the CdS film is usually in the range of 4-30 μm, depending on the cell type and process being used. The cell is frequently referred to simply as a cadmium sulfide cell. The combination of the CdS layer and the Cu_2S layer constitutes the heterojunction of the cadmium sulfide cell. 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.

2.1.2.1 Back-Wall Cell Production Approaches

The back-wall cell is illuminated so that the light passes through the junction before entering the absorbing Cu_2S layer. Photon Power, Inc., uses the technique of chemical spray deposition of cadmium chloride and thiourea to obtain a thin film of cadmium sulfide in producing their back-wall cells. The cells are made by depositing (by spray pyrolysis) approximately half-a-micron-thick layer of conductive, transparent tin oxide on a sheet of glass. The cadmium sulfide layer is sprayed to a thickness of nearly 4 microns. Part of this CdS layer is converted into copper sulfide by ion-exchange reaction in a saturated solution of cuprous chloride (Singh 1978). Metal electrodes (reported to be Iconel R* or Iconel-aluminum, copper, and lead) are then vacuum-deposited to make ohmic contact with the copper sulfide (Briggs and Owens 1979). These cells have yielded efficiencies up to 5.3%, but their typical values lie in the 4%-5% range (Singh 1978). It is possible that the CdS layer may be replaced by a $Cd_{1-x}Zn_xS$ alloy.

2.1.2.2 Front-Wall Cell Production Approach

General Description. Production of front-wall cells begins with a substrate of metal—molybdenum, steel, silver, or, usually, copper (see Fig. 2-1). Silver or zinc-coated copper are often used as electrodes. The zinc coating eliminates the tendency of the CdS layer to form a rectifying contact with the metal substrate. The CdS layer is formed by thermally evaporating CdS in a vacuum chamber. The range of CdS thickness is estimated to be from 5 μm-30 μm. The more defect-free the CdS film is, the thinner it can be (Briggs and Owens 1979).

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*Iconel is a trademark of the Huntington Alloy Products Div., International Nickel Co., Inc.

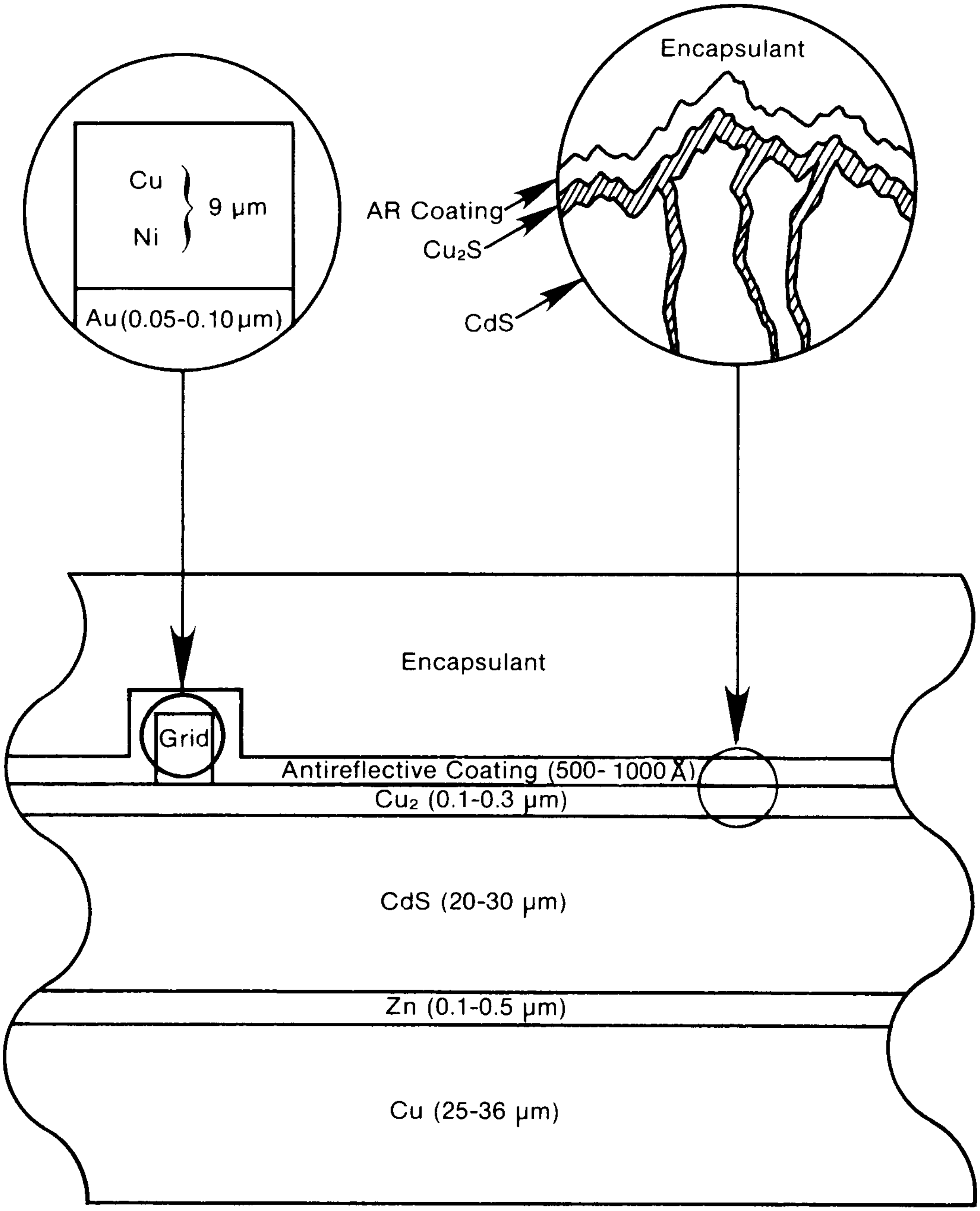

Figure 2-1. Copper Sulfide/Cadmium Sulfide Cell Structure

The CdS layer is etched in an acid bath, generally hydrochloric acid. The purpose of the etch is to texture the cell surface. The resultant pyramidal top of each CdS grain enables the textured surface to act as a light trap.

The Cu_2S layer is formed next. This layer is very thin; 0.1 μm-0.2 μm thick. The layer is presently formed using a wet chemical process. The wet chemical process involves dipping the cell into an aqueous cuprous chloride solution for a few seconds. The Cu^+ ions displace the Cd^{2+} ions at the surface of the CdS. The Cu_2S barrier layer is formed at the original CdS film surface. Several solutions are used to form the Cu_2S layer. One solution contains deaerated distilled water, hydroxylamine hydrochloride (NH_2OH-HCl), potassium chloride (KCl), hydrochloric acid (HCl), and cuprous chloride (CuCl). Another solution consists of deaerated distilled water, NaCl, HCl, and $CuCl_2$ (Briggs and Owens 1979, Shirland and Rai-Choudhury 1978).

Several "dry" methods are proposed for deposition of the Cu_2S layer. One method involves evaporating a dry film of Cu_2Cl_2 onto the CdS layer and carrying out an ion exchange reaction by heat treatment at 180°C. Another method uses an RF sputter to deposit the Cu_2S layer onto the cell (Briggs and Owens 1979).

The application of a front-contact metal grid is the next process step. The current conducting paths must be kept very short in order to minimize electrical resistance losses. Consequently, the grid must be close-spaced. Since light must pass between the grid lines, the lines must be very thin. Gold, copper, silver, nickel, and graphite have been used for grid application (Shirland 1978). The grid may be applied by evaporating the metal grid onto the cell using a shadow mask or photoresist technique. Electroplating may be used instead of vacuum evaporation (Briggs and Owens 1979). When gold (the only metal demonstrated to produce acceptable ohmic contact with the Cu_2S) is evaporated onto the cell, copper may be electroplated over it (Szedon et al. 1979). Screen printing a metal ink is a proposed commercial process. A preformed grid attached with a plastic encapsulant or a conductive adhesive is another potential grid-formation method (Briggs and Owens 1979).

To date, various antireflective (AR) coatings, including SiO, Ta_2O_5, TiO_2, and SiO_2 have been physically vapor deposited onto cells in the laboratory. Effective coatings are 500-1000 Å thick (Institute of Energy Conversion 1979). An AR coating may not be included in commercial processes for economic reasons (Briggs and Owens 1979, Szedon et al. 1979).

Encapsulation is the final step in the process. Encapsulation may use either glass or plastic or a combination of the two. Hermetic sealing of a transparent, impermeable material is necessary for terrestrial use since air and moisture cause the cell to degrade.

2.1.3 Proposed Commercial Processes

Westinghouse and a group at the Institute of Energy Conversion, University of Delaware, have both proposed processes for commercial-scale production. These particular processes are examined here in detail and are shown schematically in Fig. 2-2.

2.1.3.1 Substrate Preparation

Electroformed copper foil, 25 μm-36 μm thick, is cathodically degreased in Oakite 91 and 91A, commercial phosphate detergent electrocleaning solution. The copper sheet is cut to size, 1.49 m^2 (2 ft x 8 ft), in the Westinghouse process.

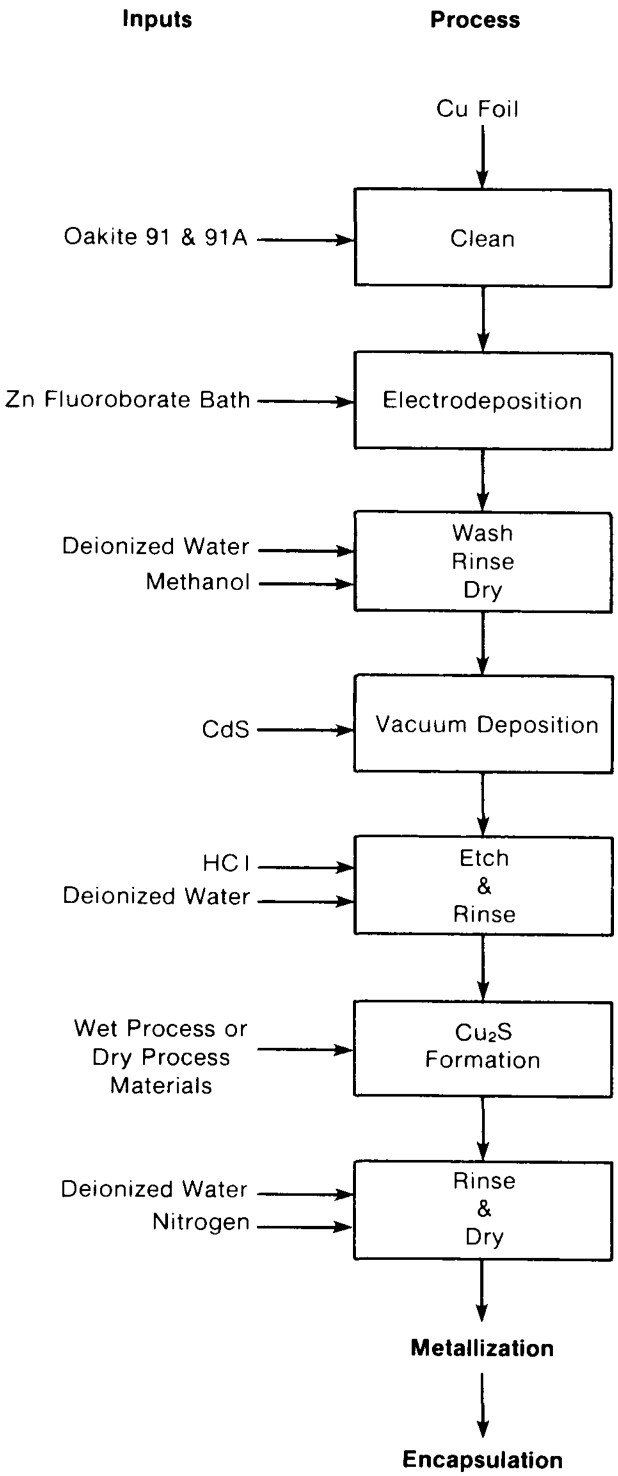

Figure 2-2. Fabrication of Front-Wall Cu_2 S/CdS PV Cell

Wastes:

Proprietary coating, possibly a chromate coating dissolved in
Oakite 91 and 91A (a strong phosphorus detergent)

Process Alternatives:

Commercial cell manufacturers may buy copper foil which is already zinc plated.
Continuous processing may use a reel-to-reel operation and either sputter clean or vapor degrease (see Fig. 2-3).

2.1.3.2 Zinc Plating

Both sides of the copper sheet are electroplated with a layer of zinc 0.1-0.5 μm thick. The standard zinc fluoroborate bath composition is 325 g/L (30.5 oz/gal) zinc fluoroborate, 4.07 g/L (4.8 oz/gal) ammonium chloride, 57.6 g/L (6.7 oz/gal) ammonium fluoroborate, and 2 ml of 10% licorice-root solution/liter (0.12 oz licorice/gal). The pH of the bath is adjusted to between 3 and 4 with dilute HCl before plating. The bath is replenished for continuous use. Plating is conducted at 50°C at a current density of 0.1 A/cm^2. The plated foil is rinsed in deionized water, rinsed in methanol, and dried.

Wastes:

Potential dumping of ruined plating bath which contains:
- zinc fluoroborate,
- ammonium chloride,
- ammonium fluoroborate,
- licorice-root solution, and
- hydrochloric acid

Deionized water containing traces of electroplating solution
Methanol

Process Alternative:

Alternative zinc plating solutions are available.

2.1.3.3 CdS Deposition

The foil sections are clamped, supported in special holders, and introduced into a vacuum deposition unit through continuously pumped gates. The plated sheets are heated. Luminescent grade CdS powder is vaporized at a temperature of 1000°C-1100°C and deposited onto the substrate. Growth rates range from 1.5-2 μm/min to 2 μm/min. The CdS layer is 10-30 μm thick. The vacuum chamber operates at 3×10^{-5} Pascals. Since the CdS powder and the substrate are cold when placed into the chamber and since the CdS is vaporized after the chamber is evacuated, there are no CdS emissions.

Wastes:

CdS— The CdS that collects in the vacuum chamber will probably be recycled. It is presently scraped off the walls of the chamber. It may also be removed by a wash of hydrochloric acid.

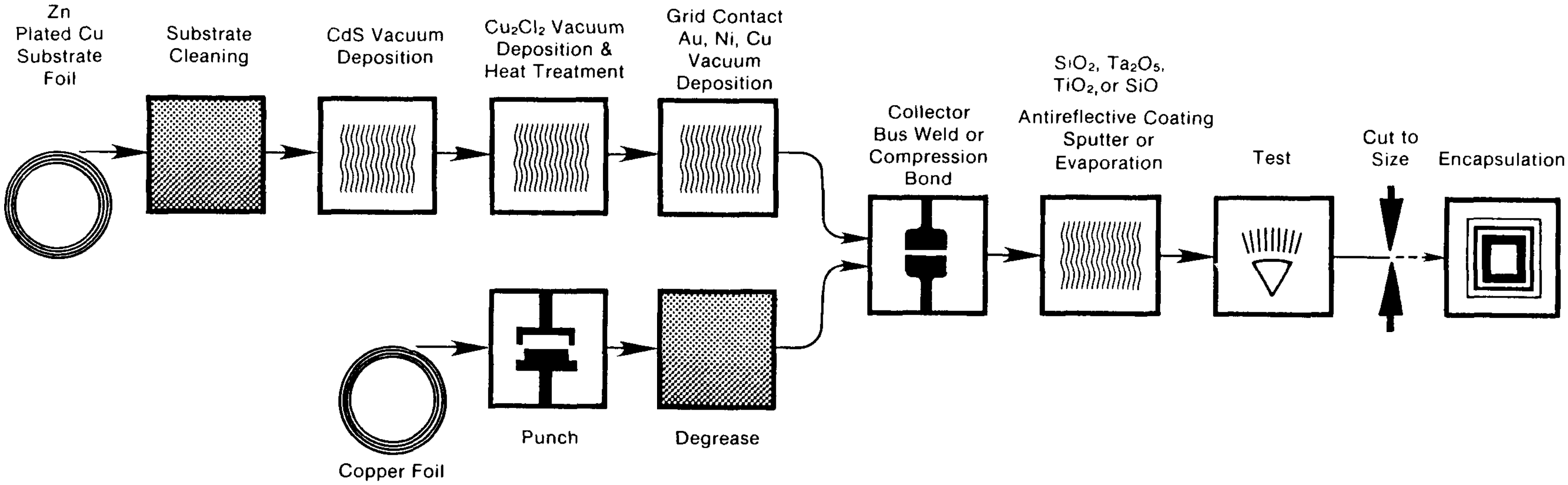

Figure 2-3. **Cadmium Sulfide Front-Wall Reel-to-Reel Commercialized Production Schematic**

CdS solar cell production--front-surface cell using a vacuum process.

2.1.3.4 Etching

The CdS surface is etched in a HCl solution at 60°C. About 2% of the CdS layer is removed during the process. The module is rinsed with deionized water.

Wastes:

- H_2O—liquid
- HCl—gaseous
- $CdCl_2$—salt in solution and particles
- H_2S—gaseous

2.1.3.5 Cu_2S Barrier Formation

The Cu_2S barrier is formed by dipping in a 90°-100°C aqueous cuprous chloride solution. The solution's makeup is deionized water, 6g Cu_2Cl_2 and 2g NaCl/L. The pH of the solution is adjusted to 2-2.5 with 10% HCl. The reaction time to form the barrier, 0.1-0.3 μm thick, is 4-12 seconds. The cell is rinsed in deionized water and transferred through an oven for about 2 min in an air or nitrogen environment at 250°C.

Wastes:

- NaCl—salt in solution
- CuCl—salt in solution
- H_2S—gaseous, small amounts
- H_2O—liquid
- $CdCl_2$—salt in solution and particles
- HCl—gaseous, small amounts
- N_2—gaseous, small amounts

Process Alternatives:

The formation of the Cu_2S layer by a wet chemical dip may be replaced by the processes previously discussed; i.e., vacuum deposition, sputtering, or sulfurization. The dry processes would produce fewer wastes. In vacuum evaporation, for example, cuprous chloride is evaporated onto the CdS film. Reaction takes place in a 3-5 min heat treatment in a nonoxidizing atmosphere. The cell is then rinsed in a solvent or water rinse and dried.

Wastes:

- Solvent or water—liquid
- $CdCl_2$—particles
- Cu_2Cl_2 (on evaporator walls)

2.1.3.6 Grid Application

A Westinghouse report describes a method in which a 5 μm-thick photoresist layer is applied. Gold, 0.1 μm thick, is evaporated onto the cell. The gold adhering to the resist portion is reclaimed. The patterned gold grid on the cell is then plated to a thickness of 1 μm. Copper, 9 μm thick, is plated over the gold and completes the front contact metallization. This process is postulated from existing technological applications and has not been applied to cell fabrication. Cell fabrication would probably require a gold-nickel-copper plating sequence to prevent the copper from diffusing through the gold into the Cu_2S layer.

Wastes:
Photoresist
Standard gold, nickel, and copper plating baths

Since the final processes have not been developed, wastes have not been identified.

Process Alternatives:
An alternate method of grid application may involve a conducting ink which is screen printed onto the cell. Since the process has not been developed, the wastes have not been identified.

Graphite-coated copper wire is also presently used.

2.1.3.7 Antireflective Coating

An antireflective coating appears to be an optional processing step at the present stage of development. This step is not included in the commercial process suggested by Westinghouse. Russell et al. (1980) assume the initial encapsulation coating will be an evaporated or sputtered glass 0.1-1 μm thick. The AR coating may be silicon monoxide, tantalum pentoxide, or some other material.

Wastes:
Depend on the specific coating technique and material.

2.1.3.8 Encapsulation

The cell is then laminated to a sheet of double-strength glass 1.49 m^2 (16 ft^2) using a room-temperature curing adhesive in the Westinghouse process. Russell et al. (1980) suggest a protective layer of 1/16-in. tempered glass which is bonded to the cell with polyvinyl butyrol. Questions relative to electrical terminals and edge protection have not been addressed.

Wastes:
Since the processes have not been developed, wastes are not yet identified.

2.1.4 Summary of Manufacture Emissions, Effluents, and Solid Wastes.

The Cu_2S/CdS photovoltaic material option is undergoing research to identify optimal cell processing techniques and materials. As a result, the Cu_2S/CdS cell fabrication technique that might become commercially viable in 10-20 years could differ considerably from the process flow shown in Fig. 2-2. Expert predictions on potential changes in the fabrication process (often listed in the previous subsection as process alternatives) have been incorporated into identification of process wastes from a commercially viable Cu_2S/CdS front-wall cell fabrication process. The results of this analysis are shown in Table 2-2. Emissions, effluents, and wastes are grouped by (1) those that (based on current knowledge) probably will be associated with cell fabrication; and (2) those that are questionable, because they result from process steps which may be replaced or deleted. Environmental, health, and safety hazards are discussed in Sec. 3.0.

Table 2-2. EMISSIONS, EFFLUENTS, AND SOLID WASTES SUMMARY FOR FRONT-WALL Cu_2S/CdS CELL FABRICATION

	Probably Will Result From Cell Fabrication	Questionable: From Process Steps That May Be Replaced or Deleted
Particulate and Gaseous Air Emissions	H_2S and HCl from cleaning CdS deposition chambers with HCl, and from CdS etch $CdCl_2$ and Cu_2Cl_2 particulate from vacuum deposition of Cu_2S	N_2, HCl, H_2S from Cu_2S wet dip process SiO, Ta_2O_5, etc., particulates from AR coating application
Liquid	CdS removed from deposition chamber via HCl clean; solution will contain H_2O, $CdCl_2$ salt, and HCl HCl etch solution containing $CdCl_2$	Oakite 91 and 91A containing chromate coating from Cu-foil, if foil is not purchased preplated with zinc Zinc plating bath if preplated foil is not purchased Cu_2S dip solution containing Cu_2Cl_2, NaCl, H_2O, $CdCl_2$, from wet chemical process
Solid Wastes	Miscellaneous wastes such as polyvinyl butyrol and glass from encapsulation	

2.2 SELECTED FABRICATION PROCESSES FOR POLYCRYSTALLINE SILICON PHOTOVOLTAIC CELLS

2.2.1 Production of Metallurgical-Grade (MG) Silicon

Silicon is one of the more abundant minerals and makes up 25% of the earth's crust. Elemental silicon, or silicon metal, does not occur in nature; it is found mostly as silica and silicates. Silicon metal is formed by the carbothermic reduction of silica, generally in the form of quartz or quartzite, to produce 99% pure silicon. The principal use of silicon metal is as an alloying compound in the iron and steel industries. In fact, silicon is present in most commercial grades of cast iron and steel. The silicon alloys are often referred to as silicides (Kirk-Othmer 1969).

The starting material for production of high-purity (i.e., semiconductor-grade) silicon suitable for use in photovoltaic cells is metallurgical-grade (MG) silicon. MG-Si is prepared by the direct reduction of quartz according to the following reaction:

$$SiO_2 + 2C \rightarrow Si + 2CO \ .$$

The following secondary reaction may also occur:

$$2SiC + SiO_2 \rightarrow 3Si + 2CO \ .$$

The carbothermic reduction reactions occur at 2500°-3000°C in electric arc furnaces. The reaction energy is supplied through Soderberg electrodes to arcs that are submerged in the silicon charge. The carbon is generally supplied to the reaction in the form of coke, although charcoal or wood chips can be used (Kirk-Othmer 1969, Kolderup 1977a).

The United States produces and consumes substantial quantities of MG-silicon annually for nonsolar applications.* Total U.S. consumption of MG-Si in 1976 was 548,000 MT; this is projected to climb to 1,090,000 MT in the year 2000 (Watts 1980.) MG-silicon is used primarily as an alloying agent for various nonferrous metals such as aluminum, copper, nickel, etc. About 40% of annual MG-silicon production is used in the manufacture of silicones. Relatively small amounts are used in the electronics industry in the production of integrated circuits and power devices (Shekarchi 1975, Schottman 1980.) Projected supplies of MG-silicon should be more than adequate to meet the projected future demands of the photovoltaics industry. Production of 1-GWp polycrystalline-silicon cells utilizing a 500-μm MG-silicon substrate would require only about 1% of the MG-silicon consumption for nonsolar uses in the year 2000 (Watts 1980).

As implied in the reduction reactions, a principal emission is carbon monoxide (CO). In addition, 10%-15% of the original silicon charge is believed to be lost as SiO_2 smoke. Based on analyses of a ferrosilicon (75% Si) production plant, the SiO_2 constituted 85%-95% of all the particulates released from the electric arc furnace. The silicon was lost from the charge as Si and SiO vapors which reacted with the air above forming amorphous SiO_2 fumes (Kolderup 1977a). The hourly emissions from a furnace producing 99% pure silicon can vary ±40%-50% depending on whether reactive gases are being blown through the melt and on the effect of poking and charging. Most of the SiO_2

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*Large quanities of ferrosilicon are also produced annually, and are used for alloying iron and steel (Shekarchi 1975).

particulates (about 70% by weight) have a diameter of 0.2-2.0μm; approximately 20% by weight fall within the 10-50-μm-diameter range. The particulates are carried in the carbon monoxide gas stream (Kirk-Othmer 1969, Kolderup 1977a, Kolderup 1977b). Fabric filters with collection efficiencies of 99% are generally used to control the SiO_2 particulates. Worker safety is generally addressed by proper plant ventilation, and possibly by the availability or use of respirators.

After the MG-Si melt cools to about 1700°C, reactive gases may be blown through the melt to remove impurities (Mintzer 1980). Gases such as chlorine or hydrogen chloride (HCl) are effective in removing impurities more reactive than Si (for example, aluminum present at more than 1000 ppm, and titanium present at 30-300 ppm), but the less reactive impurities such as copper (present at 10-100 ppm) and iron (a major impurity, with levels above 1000 ppm) are not removed (Chu 1979). A recent publication indicates that blowing chlorine through the crucible to reduce aluminum levels has been discontinued in the United States (J. McCormick in BNL 1980a). The molten MG-Si is poured into trays to cool.

Quartz and quartzite, the starting materials for production of MG-Si, are generally mined from open pits. Mining requires use of pneumatic drilling and cutting plus blasting and materials transfer. These activities, along with the movement of mining equipment and trucks along unpaved and paved roads covered with dirt, release large amounts of dust particulates. Data on particulate releases from stone mining and processing, which approximate open-pit quartz and quartzite mining, have been quantified. If fabric filters are used for control, dry stone crushing operations and miscellaneous operations such as screening, conveying, and handling would release 0.08-0.10 kg/MT (0.15-0.21 particulates/ton) of stone product. Uncontrolled suspended emissions (i.e., emissions that do not settle out within the plant) are estimated to be 3.9 kg/MT (7.7 lb/ton) (EPA 1977). Wetting the compounds before handling would reduce particulate releases considerably. Further, processing quartz and quartzite will probably create fewer dust problems than stone because of their hardness. Therefore, particulate emissions from stone mining and processing should be considered an extreme upper bound if applied to quartz or quartzite mining and processing. If sand is used as the starting material for MG-Si production, particulate emissions from mining and processing would be about 0.05 kg/MT (0.10 lb/ton) (EPA 1977).

2.2.2 Refinement of MG Silicon to Polycrystalline Silicon

Once the MG-Si has been prepared via reduction of quartz, it is allowed to solidify and crystallize. The MG-Si is then partially purified to produce a substrate-quality polycrystalline silicon or highly purified to produce semiconductor-grade (SG) silicon suitable for device fabrication.

2.2.2.1 Preparation of Substrate Quality Polycrystalline Silicon

A variety of approaches are being examined for preparation of substrate quality poly-Si. The substrates serve as a support for deposition of high purity silicon, as in epitaxial deposition of poly-Si (discussed later in this section). Preparation of the substrate involves some form of purification of MG-silicon followed by a crystal growth technique to obtain polycrystalline silicon sheets/wafers suitable for epitaxial deposition. Low-cost MG-silicon is a very attractive starting material for the preparation of silicon substrates. However, the metallic impurities in the MG-silicon degrade solar cell performance and, hence, they must be reduced to an acceptable level. Several purification techniques are currently being investigated by various research programs funded by SERI. The processes being examined include: (1) acid leaching, (2) phase separation, (3) reactive gas treatment, (4) slagging, (5) vacuum treatment, and (6) directional solidification. With the exception of acid leaching, these purification processes are carried out with the silicon in the molten state just before or during (in-situ) solidification. Research is being conducted for SERI by Crystal Systems, Motorola, Poly Solar, and Westinghouse. In this report, only the acid leaching purification approach pursued by Poly Solar, Motorola, and Westinghouse is examined in more detail.

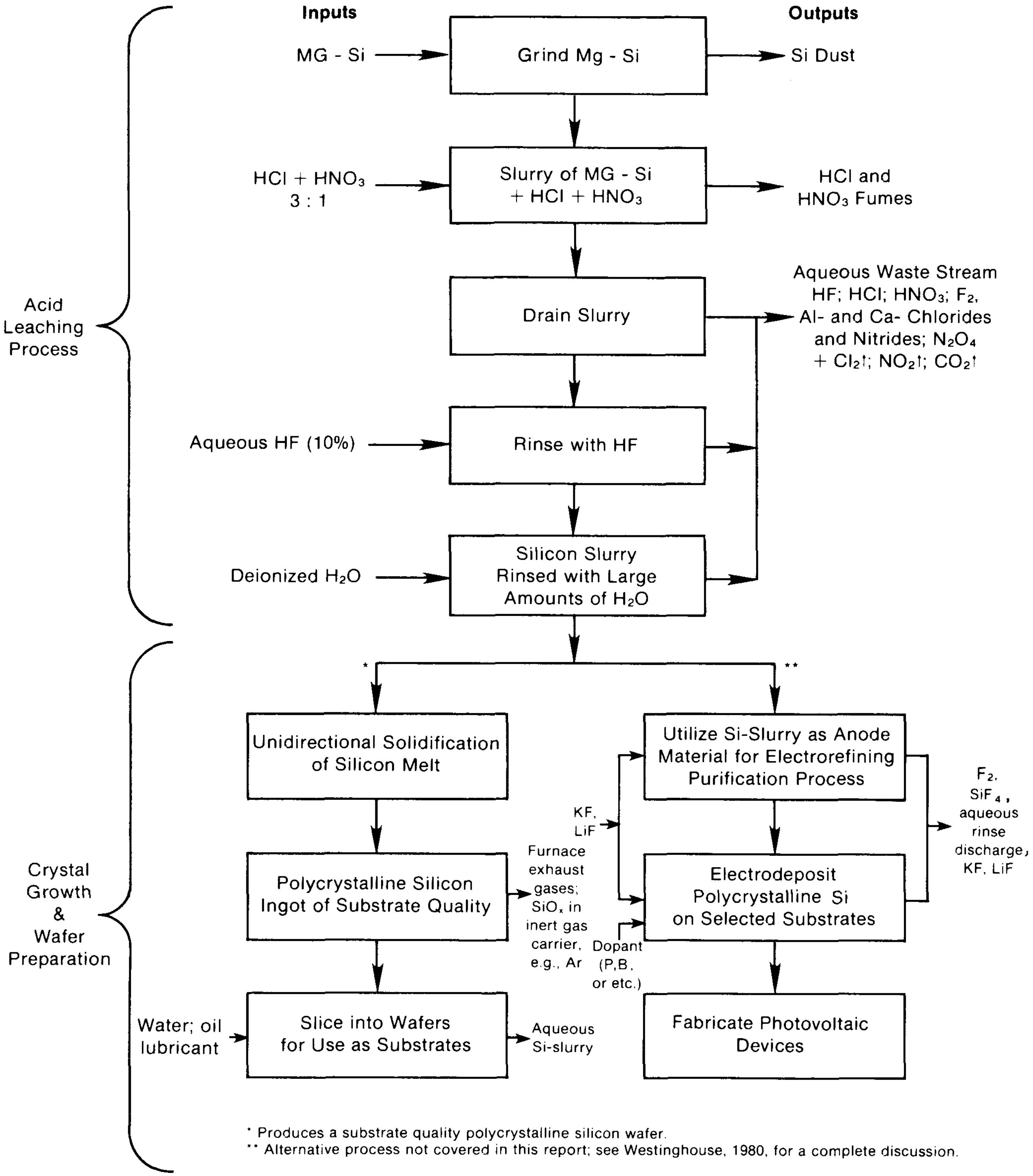
Various methods of crystal growth, using purified MG-silicon as the feedstock, are being investigated to produce low-cost polycrystalline silicon substrates. Research programs funded by SERI are investigating the following crystal growth techniques: (1) silicon ingot casting by the heat exchanger method—HEM (Crystal Systems); (2) silicon ingot pulling by the Czochralski (CZ) technique (Motorola); (3) crystallization of silicon sheet in a graphite substrate by the moving hot-zone technique (Poly Solar); (4) silicon sheet on ceramic by silicon coating by the Inverted Meniscus technique—SCIM (Honeywell); and (5) silicon sheet on foreign substrate by electrodeposition (Westinghouse). In this report, the ingot growth techniques are examined in detail, and the electrodeposition process is considered briefly.

The acid leaching process was developed at Southern Methodist University. This technique is used to purify MG-silicon to an acceptable level suitable for the growth of silicon sheets/ingots. Acid leach purification is based on the theory that a major portion of the low solubility impurities in the MG-silicon melt (i.e., impurities not removed by the reactive gases) will precipitate at the grain boundaries or at interstitial positions during solidification and crystallization. When the MG-Si is pulverized, breakage tends to occur along the grain boundaries. The impurities are therefore concentrated at the surfaces of the MG-Si crystals or crystal-aggregates formed by crushing. The impurities are then removed by chemical reactions with acids. The effectiveness of a variety of acids has been examined; these include HCl, aqua regia (mixture of HCl and HNO_3), and an equal volume mixture of H_2SO_4 and HNO_3. HCl was the least effective in removing iron, a major impurity. Aqua regia has been effective in significantly reducing levels of iron, aluminum, and calcium. The acid leach process using aqua regia followed by the ingot growth process will therefore be discussed in detail. A diagrammatic summary of the process is shown in Fig. 2-4. The acid leached MG-Si can also be used as feedstock for electrodeposition of Si on selected substrates. This option is shown in the lower right portion of Fig. 2-4. For a discussion of this process, not included in detail here, see Gass (1980).

Crushing the MG-Si. The MG-Si may be purchased primarily as ingots or in crushed form. If it is supplied as ingots, it must then be crushed. As previously mentioned, breakage tends to occur along the grain boundaries.

Wastes:
    Silicon dust controllable with fabric filters

Slurry with Aqua Regia. The pulverized MG-Si is mixed with a 3:1 mixture of hydrochloric acid (HCl) and nitric acid (HNO_3), allowed to react, then drained.



* Produces a substrate quality polycrystalline silicon wafer.

** Alternative process not covered in this report; see Westinghouse, 1980, for a complete discussion.

Figure 2-4. Metallurgical Silicon Purification Via Acid Leach

Wastes:
HCl and HNO_3 with various Al-, Fe-, and Ca-chlorides and nitrides; chlorides and nitrates of other impurities such as Cr, Mg, Mn, Ni, Ti, etc., at ppm levels

Rinse with Hydrofluoric Acid and Water. The silicon slurry is rinsed with 10% HF to remove the various oxides formed during the acid leach process. The slurry is then rinsed with large amounts of deionized water.

Wastes:
Large aqueous waste stream containing HF, SiF_4, and small amounts of chlorides and nitrides formed from reaction of the aqua regia with impurities.

Polycrystalline Silicon Ingot Growth. After it is dried, the leached MG-silicon is melted in a quartz crucible inside a furnace. Directional solidification of the melt is then carried out to produce silicon ingots either by the HEM casting technique or by the conventional CZ growth technique. In the CZ growth process, the crucible and the seed are rotated in the opposite direction, a seed is dipped into the melt, and, after thermal equilibrium is reached, the seed is withdrawn from the melt to grow the ingot. In contrast, the HEM technique does not involve moving parts; the seed is contained in the bottom of the melt and then the seed is cooled by blowing helium gas (in a closed-loop system) to allow solidification of melt. With these techniques, the last part of the solidified silicon contains more impurities than that near the seed.

Wastes:
Furnace exhaust gas (usually an inert carrier such as argon) containing SiO_x

Process Alternative:
The purified MG-silicon can be used as a feedstock for electrodeposition of silicon in another advanced cell production option. (See Fig. 2-4.)

Slice Into Substrates. After the ingot has cooled, it is cropped (i.e., trimmed) to remove surface and shape irregularities; the last regions to freeze, which contain most of the impurities, are also removed. The ingot is then sliced into substrate wafers with inside diameter saws using oil and water lubricants. Alternative saws include diamond wire and multiblade.

Wastes:
Ingot croppings (if ingot is cropped), generally sold to the iron- or steel-alloying industry
Silicon water/oil slurry from substrate wafer slicing; may lose 50%-70% of silicon in the original ingot as croppings and saw kerf

Process Alternative:
The major alternative to formation of an ingot is to grow a silicon ribbon or sheet from the melt. These will require far less cutting and, therefore, will have much smaller saw-kerf losses.

The silicon substrates resulting from polycrystalline silicon ingot growth and slicing the ingot into substrates or from the electrodeposition alternative are not suitable for direct fabrication into solar cells. Solar cell quality material is produced by epitaxial deposition of silicon on the substrate, as discussed in Subsec. 2.2.3.

2.2.2.2 Preparation of High-Purity Polycrystalline Silicon

Commercially produced high-purity poly-Si is currently prepared by the Siemens Process, shown in Fig. 2-5. In this process, pulverized MG-Si is reacted with HCl in the presence of a copper catalyst to form a mixture of chlorinated silicon compounds ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2, and SiH_3Cl). Emissions resulting from the grinding of MG-Si and mixing with HCl are Si-dust and H_2. The chlorinated silicon gas stream is separated and the lighter silanes (SiH_2Cl_2 and SiH_3Cl) are recycled for further reaction with HCl. The remaining $SiCl_4$ and $SiHCl_3$ gas stream is fractionated to form $SiHCl_3$; the by-product SiH_2Cl_2 is recycled and the $SiCl_4$ is stored for subsequent sale. Silicon is deposited on a silicon crystal seed rod at 1100°-1160°C through chemical vapor deposition (CVD) using the $SiHCl_3$. The ingot is then melted and allowed to solidify slowly to form properly oriented large crystals. H_2 saturated with undeposited $SiHCl_3$ is recycled. The deposition chamber exhaust contains HCl, various chlorinated silicon compounds, silane (SiH_4), and H_2. The gas stream is separated and recycled. The ingot is cropped and sliced into wafers as previously described. The resultant wafers are then processed into poly-Si photovoltaic cells.

The semiconductor industry presently purchases poly-Si produced by the Siemens Process primarily for use in integrated circuits and power devices. At present, poly-Si production capacity is not expected to increase in the next few years—for several reasons. First, the cost of poly-Si from new Siemens-based plants (the current technology) would be significantly greater than poly-Si from existing plants, installed between 1967 and 1974 and now mostly depreciated. Second, there is reluctance to invest in constructing plants based on the Siemens Process as the research options being investigated by DOE may result in a lower-cost poly-Si production approach. (One approach being investigated by Union Carbide is discussed later and is shown in Fig. 2-6). As a result, recent industry surveys indicate that a shortage of poly-Si may occur as early as FY 1982. The estimated nonsolar poly-Si market in 1980 is 2357 MT, of which 2110 MT is for integrated circuits. Production capacity in 1980 is estimated to be 2695 MT. Demand in the photovoltaic industry is estimated to be between 20 and 122 MT, depending on the market demand scenario. This high market demand results from the deployment scenario of the Solar Photovoltaic Energy Research, Development, and Demonstration Act of 1978, P. L. 95-590. By 1982, nonsolar industries' demand for poly-Si are projected to be 3056 MT, matched against a production capacity of 3050 MT. Demands by the solar industry are estimated to range from 146 to 420 MT (Costogue et al. 1979). Thus, the emerging photovoltaics industry may be subject to poly-Si supply limitations resulting from production capacity constraints.

One alternative to the Siemens Process is being investigated by the Union Carbide Corporation. Poly-Si produced by this technique, shown in Fig. 2-6, is estimated to cost about $14/kg. Process steps follow.

Hydrogenation of Silicon. The initial process step involves the hydrogenation at 500°C and 500 psig of silicon tetrachloride and MG-Si according to the following reaction:

$$3SiCl_4 + 2H_2 + \text{MG-Si} \underset{}{\overset{\text{Cu-catalyst}}{\rightleftharpoons}} 4SiHCl_3 \ .$$

The resultant trichlorosilane undergoes redistribution in the presence of an ion amine catalyst to form dichlorosilane, SiH_2Cl_2.

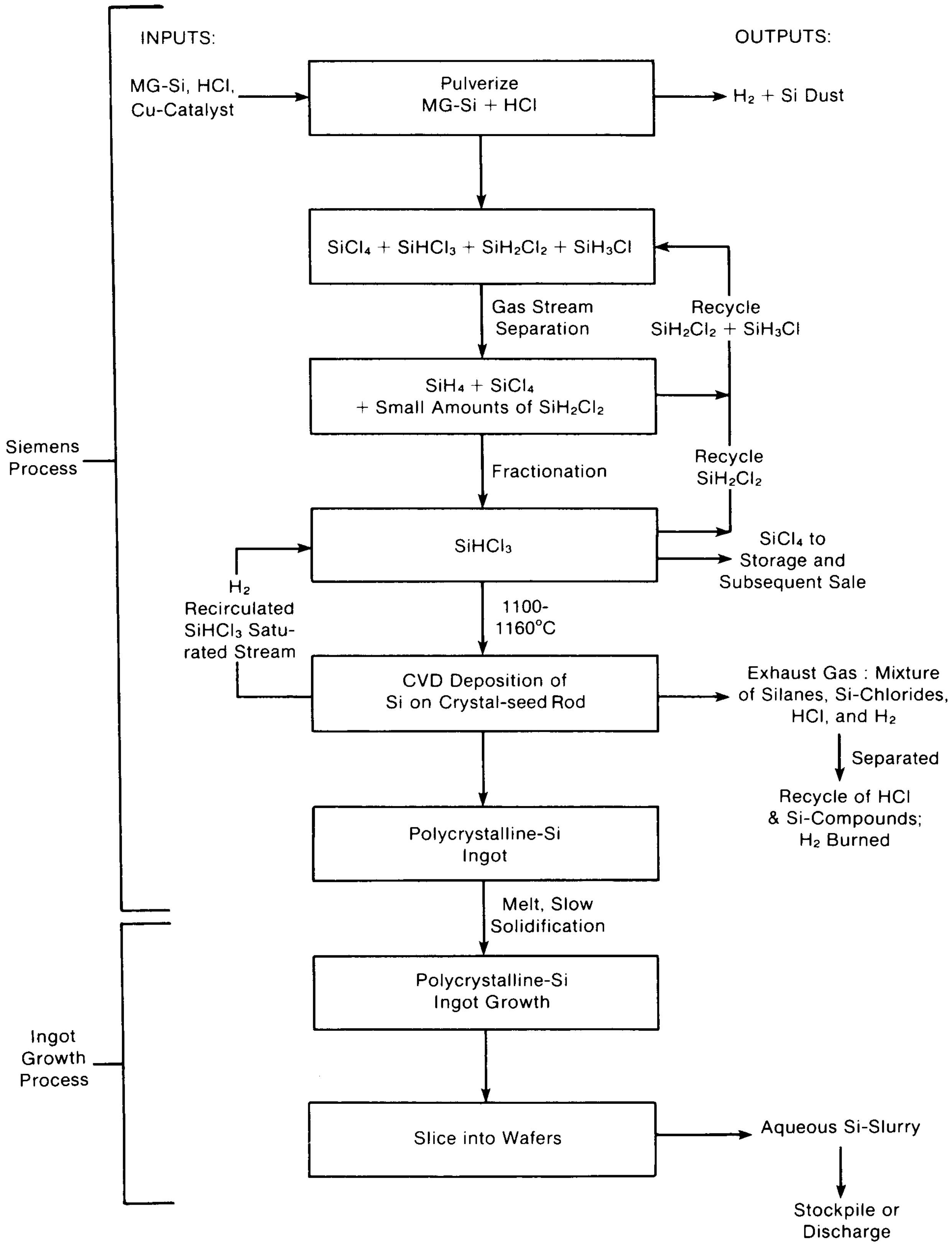


Figure 2-5. Polycrystalline Silicon Production Via The Siemens Process

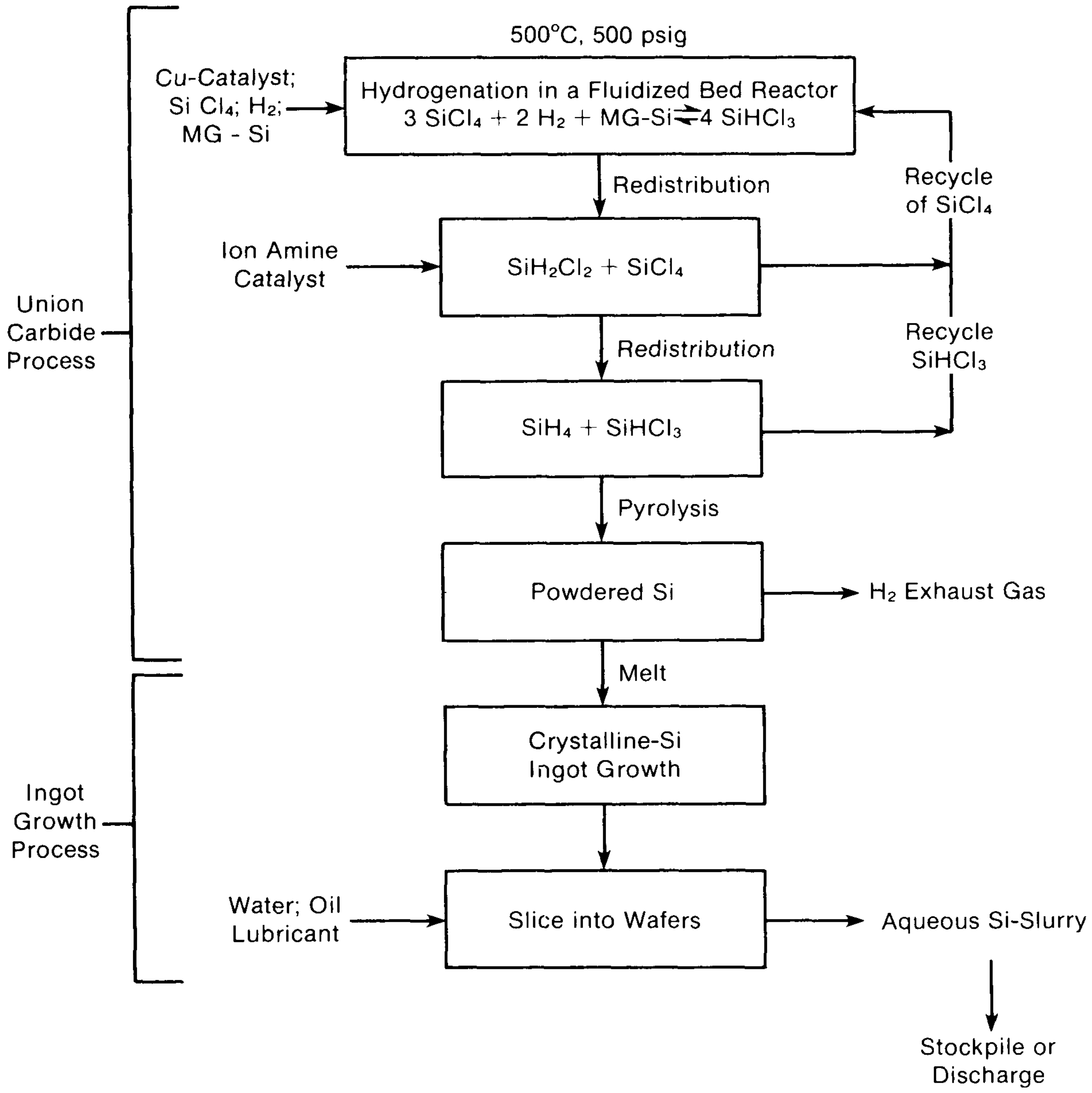


Figure 2-6. Polycrystalline Silicon Production Via The Union Carbide Process

Wastes:

$SiCl_4$, recycled to the hydrogenation step

Formation of Silane. The SiH_2Cl_2 gas stream undergoes another redistribution reaction to form silane (SiH_4).

Wastes:

$SiHCl_3$, recycled to the hydrogenation step

Formation of Powdered Silicon and Ingot Growth. The silane formed in the previous step is pyrolyzed to produce powdered, high-purity silicon. The silicon powder is melted and silicon ingot is grown either by a casting or pulling technique.

Wastes:

H_2 exhaust gas; may be recycled

Slice into Wafers. The ingot is cropped to remove impurities formed through interaction of the silicon melt with the quartz furnace crucible. The cropped ingot is mounted on a graphite tray and sliced into wafers using an inside diameter saw with an oil/water lubricant system.

Wastes:

Ingot croppings which are generally sold to the iron and steel alloying industry; trimming from the top of the ingot may be recycled to the melt

Silicon slurry from wafer slicing; 50%-70% of the original ingot is lost as croppings and saw kerf

Process Alternatives:

Rather than formation of a poly-Si ingot, a ribbon or sheet may be grown from the silicon melt. Subsequent kerf losses will be far fewer than with ingot slicing, and there will be little or no cropping loss.

2.2.3 Production of Polycrystalline Silicon Photovoltaic Cells

There are numerous approaches to the fabrication of polycrystalline silicon (poly-Si) photovoltaic cells. Some approaches are very similar to current methods used to produce state-of-the-art single-crystal silicon cells; a principal exception is the crystalline form of the silicon material. Other approaches being investigated are novel methods of forming homojunctions or heterojunctions within the cell. Still other techniques include new methods of forming the poly-Si material. Regardless of the approach, the goal is the same: fabrication of a 10%-12%-efficient photovoltaic cell at a total cost per watt below costs of methods using single-crystal silicon.

It is doubtful that all poly-Si solar cell fabrication approaches being examined will prove to be viable options within the next 5-10 years. In addition, some approaches are more developed than others and, based on current knowledge, are viewed as having a higher probability of success than less-developed options. Viability of a specific poly-Si cell fabrication option is a function of a variety of factors: cost; potential for mass production; reproducibility of results; and environmental, health, and safety acceptability. Environmental assessment of all poly-Si cell fabrication techniques would probably be premature. Further, there are often many similarities between approaches in process steps and chemicals used. As a result, three of the more promising and representative approaches were selected for environmental analysis through consultation with personnel in the Photovoltaics Advanced Materials Research and Development Center at SERI. The three approaches selected are (1) a diffused p/n junction (i.e., homojunction) in a high-purity poly-Si wafer; (2) spray deposition of a tin-oxide junction (i.e., heterojunction) on a high-purity poly-Si wafer; and (3) epitaxially deposited high-purity poly-Si with a diffused or epitaxially formed p/n homojunction on a lower-purity silicon substrate. The following subsections provide a general description of each fabrication option and a detailed discussion of process steps, their waste streams, and potential alternatives, if known. All process flows and discussions are based on literature sources, where available, and interviews with selected research teams (Exxon 1980, RCA 1980, Gass 1980).

2.2.3.1 Poly-Si Photovoltaic Cell Fabrication: General Description

Two of the selected fabrication options—a diffused p/n homojunction and a spray-deposited tin-oxide heterojunction—require a high-purity poly-Si wafer as the starting material. The poly-Si wafer is currently produced primarily by the Siemens Process, where pulverized MG-Si is reacted with hydrochloric acid (see Fig. 2-5.) As noted, the Siemens Process is energy-intensive and expensive. Wafers from poly-Si ingots produced by the reaction of silicon tetrachloride, hydrogen, and MG-Si (see Fig. 2-6) can also serve as suitable starting materials. Regardless of the silicon purification technique, the diffused p/n and spray-deposited, tin-oxide approaches require a high-purity poly-Si wafer. A poly-Si substrate produced by acid leach purification of MG-Si is not of sufficient purity for use in the p/n diffusion and tin-oxide spray-deposition processes.

Diffused p/n Homojunction in a Poly-Si Wafer. The ingot from which the poly-Si wafer is sliced is generally doped (with one dopant type) prior to its crystallization. The dopant can be either an n-type (e.g., phosphorus or arsenic) or p-type (e.g., boron or gallium). For purposes of discussion, the wafers are assumed to be n-type. The wafers are vapor-degreased with an organic solvent (such as an alcohol) to remove surface organic contaminants. Degreasing and other elaborate cleaning processes may not be required if a production facility is integrated and automated such that the time between process steps and wafer handling is minimized. After the wafers are degreased, they are etched by a one-minute dip in aqueous 10% hydrofluoric acid. Wafers are next cleaned in a peroxide-ammonia-water solution followed by a peroxide-hydrochloric acid-water solution, then dried. The wafers then proceed to a diffusion furnace where they are placed in trays within a quartz reaction tube. The furnace is maintained at approximately 1000°C. The reaction tube is purged with nitrogen gas. The flow of the dopant gas (in this case, a p-type dopant such as boron trichloride) at a parts per million (ppm) level in nitrogen is begun. The wafers continue at a high temperature following dopant gas flow to "drive-in" (i.e., diffuse) the p-dopant compounds. The predeposition and diffusion processes take a total of approximately 30 min. The wafers are removed from the furnace, allowed to cool, and undergo removal of the diffused layer on the back surface (i.e., a diffused p-type layer remains only on the front of the wafer). Wafers are then etched in a nitric acid-water solution, rinsed in water, etched in aqueous 40% hydrofluoric acid, rinsed in water again, and dried.

Wafers are now ready to be metallized, coated with an antireflection (AR) compound (to reduce losses of useful sunlight due to reflection from the cell surface), encapsulated, and placed into module frames. Metallization involves application of electrical contacts to the front and back of the cells in order to collect and channel the electricity produced from the photovoltaic effect.* In one currently used technique, the back contact is applied by thermally evaporating on 1000 Å titanium followed by 5000 Å silver. The entire back surface is coated. The front grid pattern is formed by thermally evaporating on 1000 Å titanium followed by 10,000 Å silver through a shadow mask. The grid pattern can also be made by other techniques (such as photoresist).

The AR coating is applied to the front of the cell. A number of materials are suitable as AR coating: titanium dioxide (TiO_2), silicon nitride (Si_3N_4), tantalum pentoxide (Ta_2O_5), and, most commonly, silicon oxides such as SiO and SiO_2. The AR coating is most commonly applied via evaporation and is usually about 620-Å to 700-Å thick.

Copper wire (which may be solder dipped) and, typically, lead/tin solder are used to interconnect the cells. Encapsulation is accomplished by heat and back pressure on the following front-to-back sequence of materials: glass superstrate, Craneglass, clear ethylene vinyl acetate (EVA), the busbar and solar cell, white EVA, aluminum foil, and mylar. A schematic cross section of the finished panel is shown in Fig. 2-7. A variety of approaches to encapsulation are currently used by the photovoltaics industry. The encapsulation approach selected for study and shown in Fig. 2-7 was developed at the Jet Propulsion Laboratory and is viewed as a commercializable, low-cost option. Following encapsulation, the panel is placed in aluminum framing to form a module. The extruded aluminum framing is typically purchased by the photovoltaics manufacturer. Modules are interconnected to form an array, and arrays may be connected to form a field, as shown in Fig. 2-8. A more detailed discussion of cell processing is presented later in this part.

Spray-Deposited Tin-Oxide Heterojunction on a Poly-Si Wafer. As with the diffused p/n junction approach, the starting material for the tin-oxide (SnO_2) spray process is a poly-Si wafer, again assumed to be n-type. The wafers are degreased (as previously noted, this need not be necessary in an integrated production facility) and chemically polished by a hydrofluoric acid-nitric acid etch. They are then washed with deionized water and dried. Wafers are placed in a spray deposition furnace and heated to 400°C. Tin chloride ($SnCl_4$) in a solvent (ethyl acetate is currently used) is sprayed onto the wafer surfaces; a layer of tin oxide (SnO_2) forms through oxidation with air. Cells are then metallized, interconnected, encapsulated, and placed into module frames by the methods described under the diffused p/n junction approach. However, no AR coating is required; the SnO_2 layer forms both the junction and the AR coating.

Epitaxial Deposition of Poly-Si on a Silicon Substrate. A variety of materials are suitable substrates for the epitaxial deposition process. To date, substrate materials which have been considered or used include MG-Si, poly-Si wafers of high purity (i.e., produced by the Siemens Process or the $SiCl_4$ process shown in Fig. 2-6), upgraded MG-Si (slightly purified MG-Si), silicon-on-ceramics, and wafers produced by acid leach purification methods, similar to that presented in Fig. 2-4. A high-purity poly-Si substrate is not a stringent requirement. The starting silicon material serves as a support (substrate) for

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*For a complete discussion of the photovoltaic effect, see Kazmerski (1980) and Fann (1978).

* EVA = Ethylene Vinyl Acetate

Figure 2-7. Module Cross Section

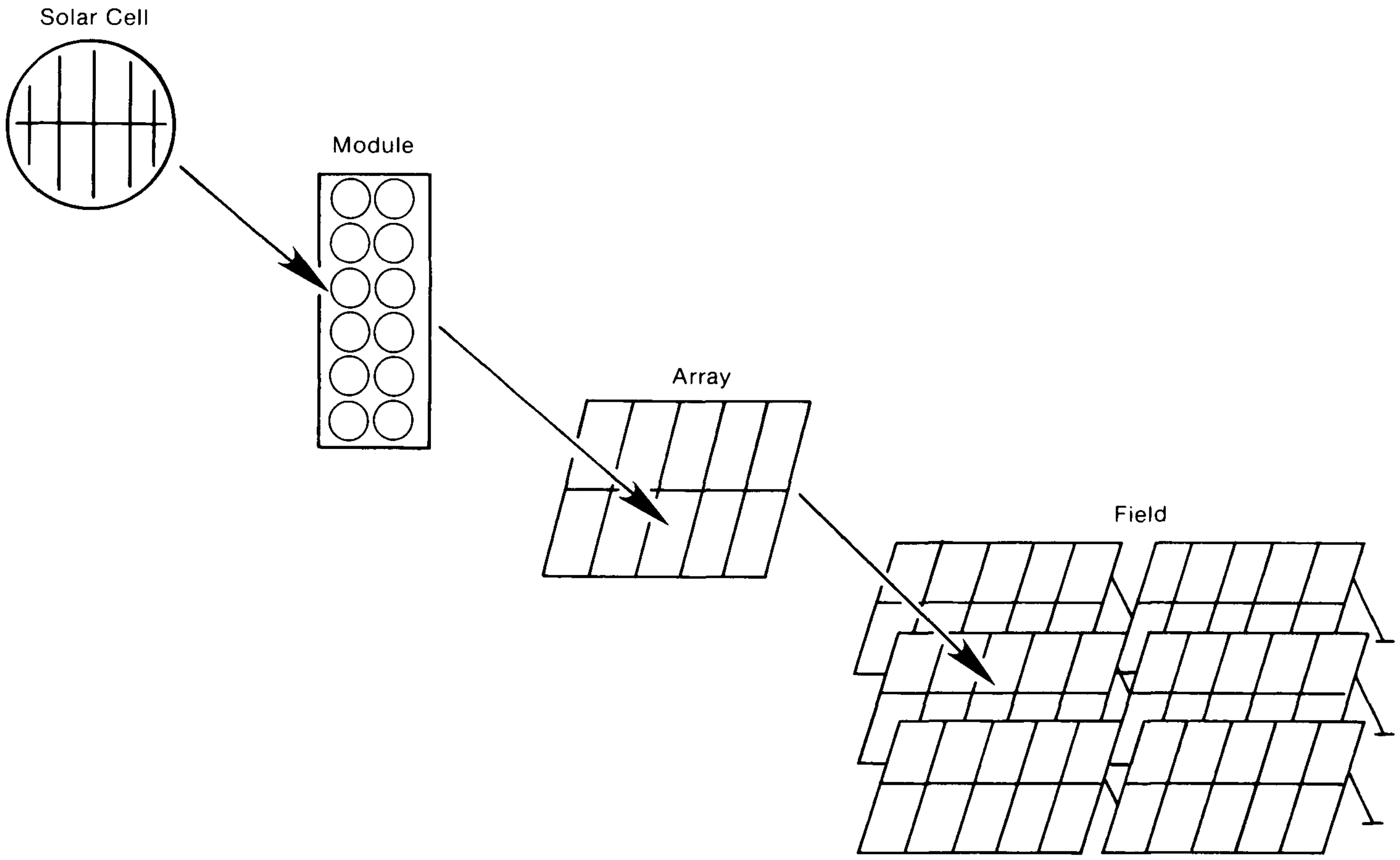


Figure 2-8. Relationship of Cell, Module, Array, and Field

the cell and orients crystal growth during epitaxial deposition of the poly-Si photovoltaic material.

The substrate material is etched in a basic solution (such as 30% NaOH) and rinsed in deionized water. The substrates are introduced into an epitaxial reactor which is heated to 900°-1200°C, depending upon the silicon gas source. A silicon gas (containing a dopant) such as silane (SiH_4), tetrachlorosilane ($SiCl_4$), or most probably trichlorosilane ($SiHCl_3$) is introduced, and a layer of pure silicon is grown on the substrates. The layer of epitaxially grown silicon is polycrystalline. The wafers then require formation of a p/n junction, which can occur through several methods. Researchers are now examining two techniques: (1) diffusion and (2) epitaxial growth of another appropriately doped silicon layer. In the diffusion approach, the junction would be formed in a diffusion furnace as previously described. If epitaxial growth is selected, the epitaxial reactor is purged with an inert gas (such as nitrogen) to avoid cross-contamination of the epitaxial layers. Flow of the appropriately doped silicon gas source is begun, and another high purity poly-Si layer is grown epitaxially. Cells are then etched, cleaned, and dried. Metallization, AR coating application, interconnection, encapsulation, and module framing proceed as previously described.

2.2.3.2 Proposed Commercial Processes

Diffused p/n Junction in a Poly-Si Wafer. The diffused p/n poly-Si cell is very similar in form and fabrication to traditional single-crystal, diffused p/n solar cells. The primary advantage is lower cost of the poly-Si wafer compared with that of a single-crystal wafer. However, because of losses at the grain boundaries, the efficiency of a diffused p/n poly-Si cell is about 10% compared with 12% for a diffused p/n single-crystal silicon cell. It is doubtful that major processing changes will occur.

Substrate Preparation. As noted, the initial process input (the poly-Si wafer) can be either n- or p-type. If it is p-type, the wafer has been doped during crystallization with a p-dopant such as boron. The p-type poly-Si wafer must be polished, typically by a dip in a hydrofluoric-nitric acid mixture ($HF-HNO_3$), followed by a rinse in deionized water. The dip is presently a batch process.

Wastes:
- Liquid $HF-HNO_3$, contaminated with various reaction products (such as SiF_x)
- Acid fumes
- Small amounts of H_2
- Deionized water containing small amounts of $HF-HNO_3$ and reaction products (unidentified)

Process Alternatives:
- Replenishment of the $HF-HNO_3$ dip bath to allow continuous processing
- Use of an n-type poly-Si starting material

For purposes of discussion, the wafer processed in the diffused p/n junction approach will be assumed to be n-type. The n-type wafer (doped during crystallization with an n-dopant such as phosphorus or arsenic) does not require a polish step. However, the n-poly-Si wafer may require degreasing by means of vapors of alcohol (e.g., isopropanol) or possibly trichloroethylene. Wafers are then etched to remove the silicon-oxide (SiO_x)

layer which forms from oxidation in air. The etch consists of an approximately 1-min dip in 10% aqueous HF. Wafers are then cleaned for 10 min in a 75°C hydrogen peroxide-ammonia-water ($H_2O_2 : NH_4 : H_2O$) bath and receive a second 10-min clean in a 75°C $H_2O_2 : HCl : H_2O$ bath and are dried.

Wastes:

Isopropyl alcohol (or other organic degreaser) with various organic contaminants

Dilute aqueous HF containing small amounts of SiF_4

Aqueous mixture of cleaning compounds ($H_2O_2 : NH_4 : H_2O$ and $H_2O_2 : HCl : H_2O$) containing unidentified reaction products

Process Alternative:

It is very possible that wafer degreasing and cleaning in $H_2O_2 : NH_4 : H_2O$ and $H_2O_2 : HCl : H_2O$ may not be required in a commercial production facility. If production of the poly-Si wafers (i.e., ingot or ribbon growth and slicing) is done at the same site as cell fabrication and is automated to minimize handling, wafers may be sufficiently clean as to require only the 10% HF oxide removal etch.

Junction Diffusion. After the wafers are cleaned and dried, they are placed in trays and loaded into the diffusion furnace. The trays are placed in a quartz tube which is heated to approximately 1000°C by resistance-heated coils. The quartz reaction tube is purged with an inert gas, nitrogen, and flow of the dopant is begun. In the process flow shown in Fig. 2-9, the p-dopant is boron trichloride (BCl_3) (or an alternative boron compound such as boron nitride) in parts per million (ppm) concentration in nitrogen. The total diffusion process requires about 30 min; the dopant gas flows only about half this time—predeposition. The wafers are baked the remainder of the time to "drive-in" the dopant. The boron-doped layer is about 0.5-1 μm thick.

Wastes:

Nitrogen gas

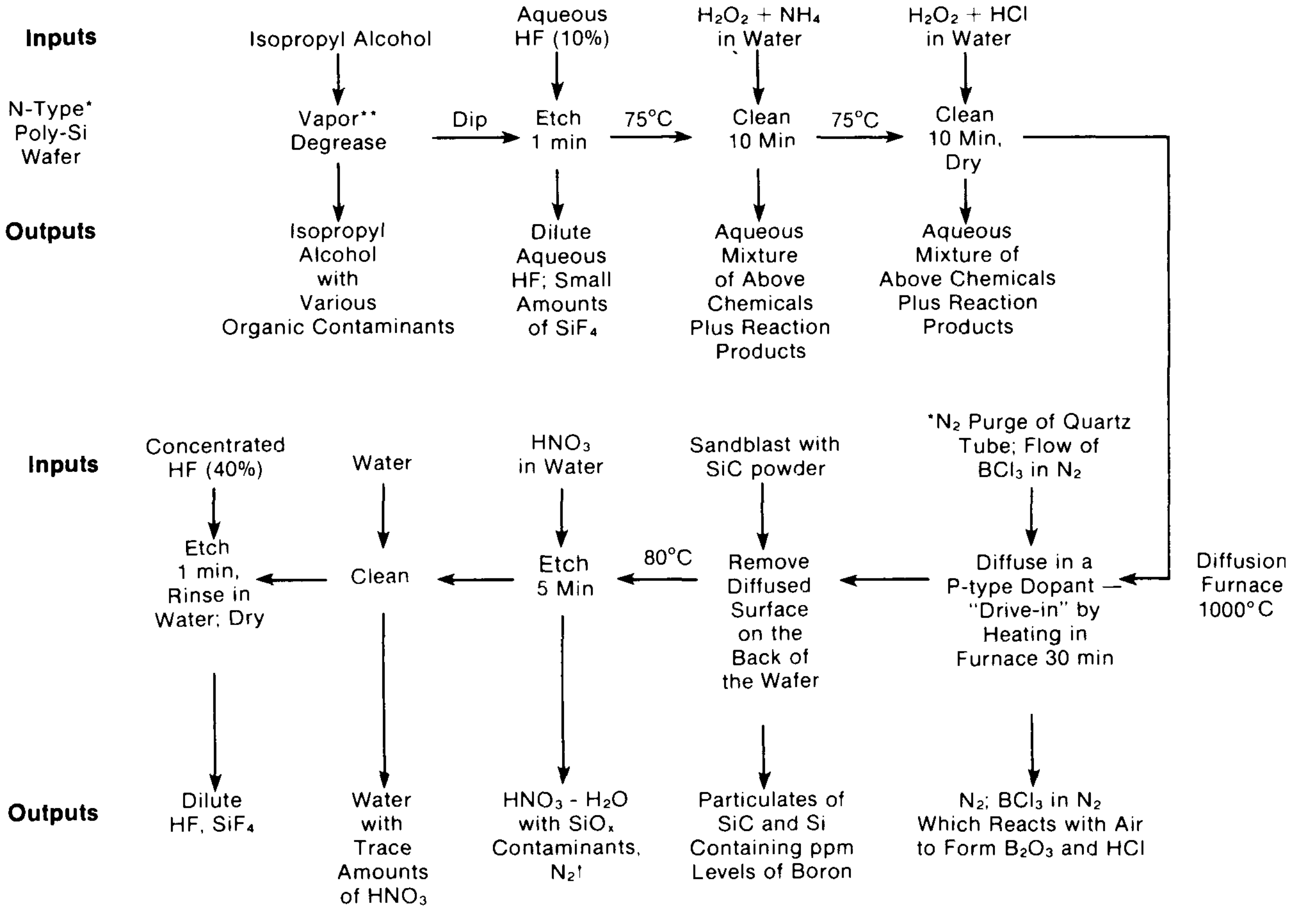
BCl_3 in nitrogen gas

BCl_3 reaction products, B_2O_3 and HCl, formed upon contact with moist air

Process Alternatives:

Thermodiffusion furnaces are commercially available and have been used by the semiconductor industry for years. Diffusion is a high-temperature batch process which ties up equipment 30 min or more. A lot of process monitoring and "hands-on" steps (e.g., manual loading of wafers into trays) are involved in the predeposition gas flow, and there is no obvious way to automate. As a result, traditional diffusion may be replaced in automated photovoltaic cell fabrication facilities. One of the alternatives being examined is a spin-on/bake process. A dopant solution (e.g., phosphorus pentoxide for the n-type or boric acid for the p-type) plus an organic silicon compound (e.g., tetraorthosilicate) and a binder (e.g., glycerine) is dripped onto the wafers. The wafers are spun to evenly distribute the dopant solution, then baked at about 200°C to drive off the organics, leaving a SiO_2-layer containing the dopant. Next, the wafers are heated to about 1000°C in a nitrogen atmosphere to drive the dopant out of the SiO_2 layer into the wafer. The SiO_2 layer is removed by the standard quick-dip etch in HF.

Other alternatives to predeposition include e-beam deposition, ion implantation, and ion-beam sputtering of the dopant layer onto the wafer. However, these have fairly stringent operational requirements and are less developed than other available junction-formation techniques. Of course, e-beam deposition and ion-beam



*Commercial processes may use a p-type wafer as the initial process input. The diffusion dopant would then be an n-type, such as phosphorus. N_2 would be bubbled through $POCl_3$ (a liquid) and flow into the diffusion furnace with oxygen. See text for a further discussion.

**Vapor degreasing plus other wafer cleaning processes not shown above may not be necessary in an integrated plant where Metallurgical Grade Silicon [(mg)-Si] is purified, formed into ingots, and sliced into wafers on-site, if time between process steps and handling is minimized.

Figure 2-9. Fabrication of Diffused p/n Junction Poly-Si Solar Cells

sputtering still require "drive-in." Ion implantation also requires a furnace cycle to repair the damage caused by the ions and to supply thermal energy to move the ions to useful locations in the crystal.

Remove Diffused Layer on the Back of the Wafer. In a thermodiffusion furnace, dopants are driven into all surfaces of the wafer. The final cell requires a diffused p-layer only on the front of the n-type wafer; therefore the back diffused layer must be removed. A variety of techniques can be used. In the process sequence examined in this report, a sandblast is used to remove the back surface diffused layer.

Wastes:
Doped silicon particulates

Process Alternatives:
A thin layer of SiO_2 is deposited on the back surface of the wafers before diffusion. After diffusion is complete, the SiO_2 layer is removed in an HF-water etch.

Etch and Clean. Following removal of the back diffused surface, the wafers are etched 5 min in an 80° C HNO_3-water solution. Wafers are then rinsed in water.

Wastes:
HNO_3-H_2O contaminated with SiO_x particulates
Small amounts of nitrogen gas
Wastewater containing very small amounts of HNO_3

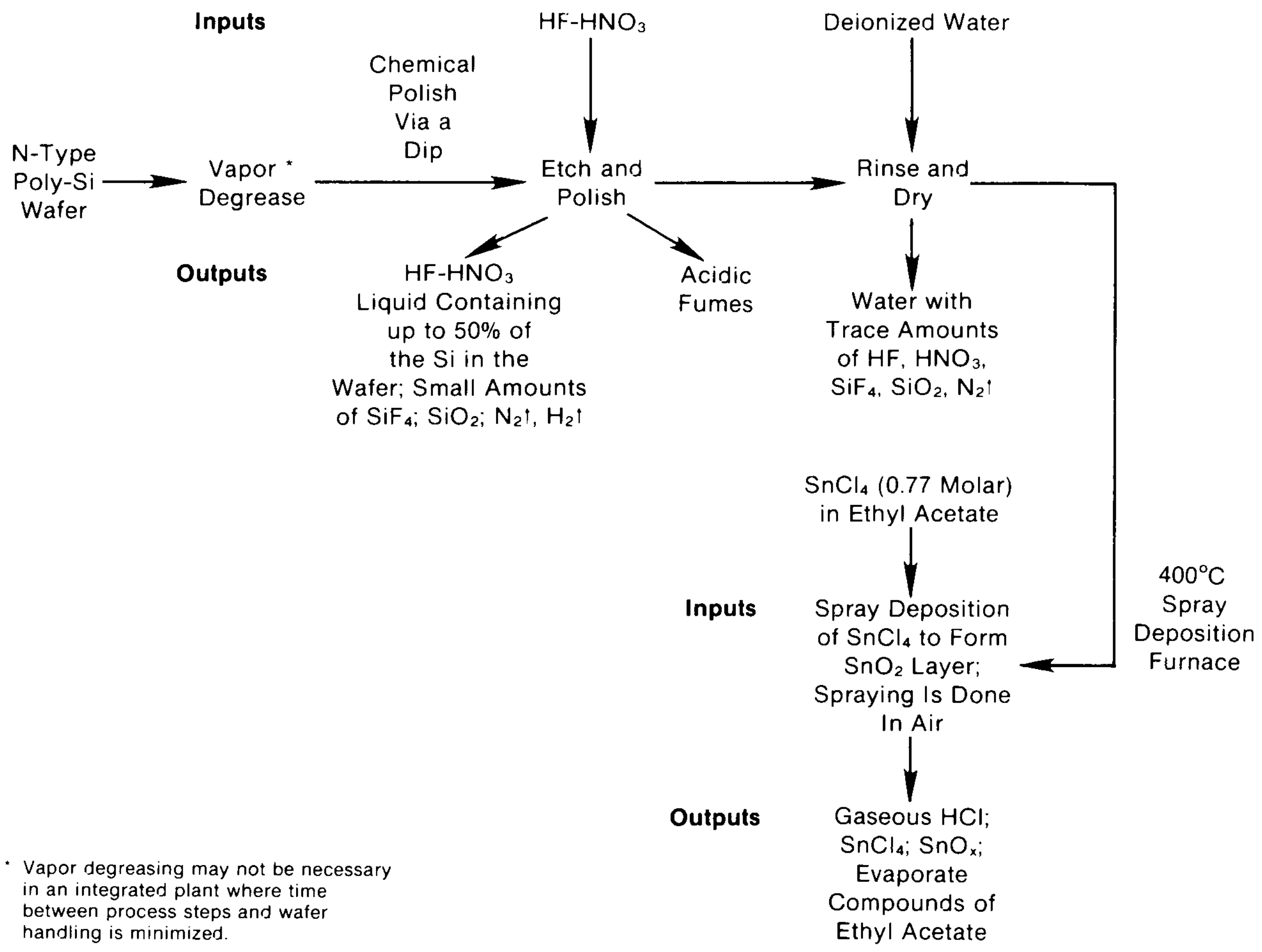
Etch. The final step (prior to cell processing) is an oxide etch. Cells are dipped for 1 min in 40%-concentrated HF, rinsed with water, and dried.

Wastes:
Dilute HF containing SiF_4
Wastewater contaminated with trace amounts of HF

At this point, cells are ready for processing. Processing involves metallization, application of an antireflection coating, interconnection, encapsulation, and framing. Cell processing is discussed separately, since it is approximately the same for all the selected poly-Si cell fabrication options.

Spray-Deposited Tin-Oxide Heterojunction on a Poly-Si Wafer. As in the diffused p/n process, the starting material for tin oxide/poly-Si cell is an n-type poly-Si wafer. The tin oxide serves both as the heterojunction and the AR coating and is about 1000 Å thick. Cell efficiencies to date have been about 10%. Figure 2-10 presents a summary of the cell fabrication steps.

Substrate Preparation. The poly-Si wafer must be polished, and wafers are presently purchased polished and precleaned. No further cleaning is required unless oils and dirt have been deposited on the wafers from handling. A commercial cell production facility will probably produce wafers on-site. To perform a chemical polish, the wafers are vapor degreased (if necessary) with isopropyl alcohol or trichloroethylene (or some other



* Vapor degreasing may not be necessary in an integrated plant where time between process steps and wafer handling is minimized.

Figure 2-10. Fabrication of Poly-Si/Tin Oxide Solar Cells

organic solvent) and then etched and polished in a mixture of HF-HNO_3. Wafers are then rinsed in deionized water and dried in nitrogen.

Wastes:

Vapor degreasing: isopropyl alcohol with various organic contaminants such as oils
Etch and polish: HF-HNO_3 liquid containing up to 50% of the silicon originally in the wafer; small amounts of SiF_4, SiO_x, and nitrogen gas

Process Alternatives:

If the production of wafers and cell fabrications are integrated such that handling and time between process steps are minimized, vapor degreasing will probably not be required. A chemical polish will be required in the cell-fabrication process.

Spray Deposition of Tin Oxide. After the wafers are cleaned and dried, they are placed in a spray deposition furnace and heated to approximately 400°C. Tin chloride ($SnCl_4$) is sprayed onto the wafer surfaces for 30-50 s. A layer of tin oxide (SnO_2) forms as the $SnCl_4$ is oxidized by air. Spraying occurs under atmospheric conditions.

Wastes:

Gaseous HCl formed from hydrolysis of $SnCl_4$
SnO_x
Chlorine gas
Evaporative compounds of the ethyl acetate solvent

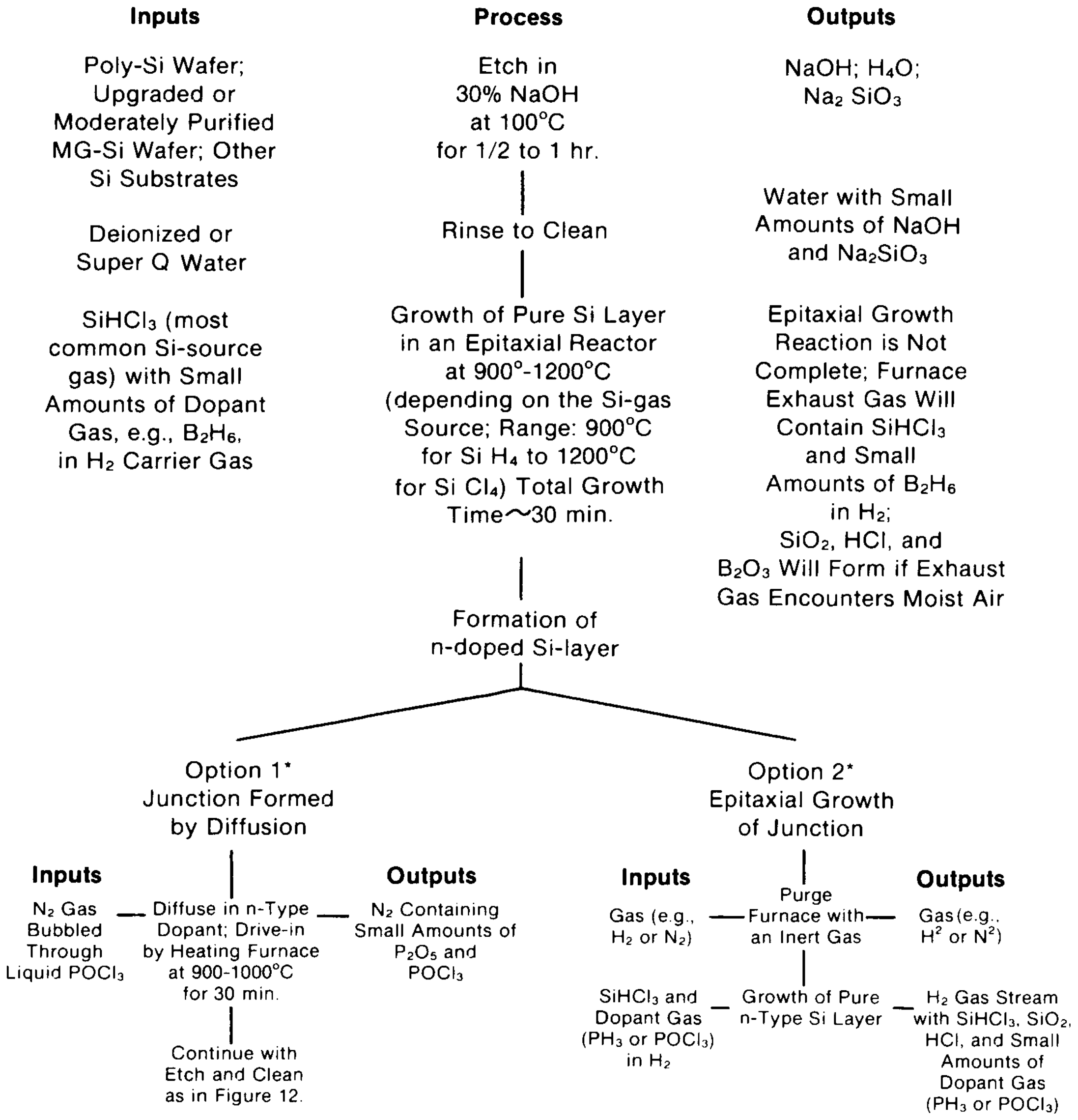
Process Alternatives:

Commercial poly-Si/SnO_2 cell fabrication plants will probably use a modified version of commercially available tin oxide conveyor furnaces. These furnaces are presently used to deposit thin SnO_2 coatings on such products as tinted glass, sunglasses, windshields, etc. Typical operation temperature is 500°-550°C with a deposited SnO_2 layer of 600 Å. The furnace throughput speed and operating temperature may have to be modified to get 1000 Å SnO_2 applied at 400°-450°C. The furnace is equipped with a wet scrubber system to treat the toxic, corrosive fumes of HCl, $SnCl_4$, solvents, etc., that exit from the furnace.

Alternative heterojunction coatings have also been investigated. A 10-to-1 mixture of indium chloride and tin chloride ($InCl_3$:$SnCl_4$) dissolved in ethanol, methanol, and water has been spray deposited on n-type poly-Si wafers. The resultant indium tin oxide (ITO) layer is more conductive than tin oxide, and therefore fewer metallized grid contacts are required to collect the current. However, the ITO results are less reproducible and more expensive than the tin oxide option. In addition, the ITO cells are no more efficient than SnO_2/poly-Si cells, and present the problem of handling toxic indium vapors in addition to those released from spraying tin chloride. Therefore, the SnO_2/poly-Si process currently seems to merit support for commercialization somewhat more than the ITO process.

Cells are ready for processing after spray deposition of the tin oxide; no cell cleaning or etching is required.

Epitaxial Deposition of Poly-Si on a Silicon Substrate. A silicon substrate is the required starting material for the epitaxial deposition cell fabrication process as shown in Fig. 2-11. High purity is not a stringent requirement of the substrate. A number of



* Currently, Option 1 is the preferred approach due to reproducible results. Option 2 may be exercised in future cell production facilities.

Figure 2-11. Fabrication of Solar Cells by Epitaxial Deposition of Poly-Si on a Silicon Substrate

silicon materials have been considered substrates: doped and undoped poly-Si wafers, MG-Si wafers, silicon wafers treated by acid leaching (as shown in Fig. 2-3), and silicon-on-ceramic. For purposes of discussion, the substrate was considered to be a low-cost option such as an MG-Si or an acid-leach-prepared silicon wafer.

Epitaxial reactors have been used by industry for over 20 years to make transistors. However, epitaxial growth of silicon layers poses two main occupational health risks: growth requires use of poisonous, possibly pyrophoric materials, and there is the potential for explosions resulting from use of hydrogen gas. Precautions against poisonous gas exposure include hoods; furnace exhaust air pollution control equipment; and, in larger fabrication facilities, workroom air monitoring units that detect trace releases of toxic gases. Explosion hazard control is handled through regulation of hydrogen flow. In the laboratory-scale process, the hydrogen flow rate is 30 L/min and the hydrogen is stored as a gas. In a commercial-scale operation, the flow rate may be as high as 200-300 L/min, and the hydrogen will probably be stored in liquid form. At very high flow rates, a flame source would probably cause the hydrogen to catch fire rather than explode. An automatic switch would turn off the hydrogen and begin flow of nitrogen.

Substrate Preparation. The silicon wafers are etched in a 30% sodium hydroxide (NaOH) solution for one-half to one hour. They are then rinsed in deionized or Super Q (high-purity) water.

Wastes:

30% NaOH/water etch solution containing Na_2SiO_3 deionized water, that has trace amounts of NaOH and Na_2SiO_3

Process Alternatives:

At present, wafer etch is a batch process. Commercial facilities may utilize a continuous process where NaOH is replenished, and the etch solution is used many times before disposal. The Na_2SiO_3 is currently discarded; future operations may reclaim and recycle Na_2SiO_3 (if economically attractive) for use or sale as an antireflective coating.

Epitaxial Growth of Silicon Layers. After etch and clean, the low-cost silicon substrates are placed in trays, called graphite susceptors, which are inserted into the epitaxial reactors. The deposition of the silicon takes place in a quartz reaction tube which is presently 1-2 ft (0.3-0.6m) long. Maximum tube size is unknown. Heating is by rf induction to 900°C for SiH_4 to 1200°C for $SiCl_4$. The silicon gas, typically $SiHCl_3$, and a dopant at a ppm concentration level are introduced into the reactor using hydrogen as the carrier gas. The concentration of the silicon gas determines the silicon deposition rate. The desired thickness is 15-20 μm deposited at a rate of 5 μm/min. The tube is heated for 5 min to the appropriate temperature and the temperature is allowed to stabilize for about 5 min. Introduction of the $SiHCl_3$, H_2, and dopant gas is begun, and 15-20 μm of silicon are deposited. For purposes of discussion, the dopant is assumed to be p-type; e.g., diborane, B_2H_6. The quartz reactor tube must be cooled by air or water to prevent deposition of silicon on reactor walls. Silicon is deposited on the graphite receptor trays, and they are cleaned in a high-temperature HCl etch every 5-10 runs. Following silicon growth, the reactor is cooled to about 400°C with the hydrogen flowing. After 400°C is reached, hydrogen is turned off and nitrogen flow is begun. The silicon crystals form as the silicon gas is deposited. The epitaxial reaction does not go to completion.

Wastes:

Exhaust gases from the reactor: H_2, $SiHCl_3$, which forms SiO_2 and HCl upon contact with air; B_2H_6 and B_2O_3 in small amounts

Graphite susceptor trays: HCl containing silicon and carbon etched from the trays

HCl fumes

Process Alternatives:

Substrate etch and silicon layer growth may be combined into an integrated step. Etching can be done within the epitaxial reaction tube through a flow of HCl gas at a high temperature. The reactor would then be purged with an inert gas, and epitaxial growth of the silicon layer would proceed as discussed. Although this alternative would integrate step 1 and step 2, it ties up the reactor for a long time.

Graphite susceptors will probably be cleaned once a day in commercial production facilities, rather than every 5-10 runs as is done in the laboratory. The cleaning solution, at least in the future, is assumed to be HCl.

Junction Formation. The p/n junction can be formed by several techniques discussed under previous alternatives. The prime alternatives are diffusion (also discussed under alternatives) and epitaxial deposition of, in this case, an n-type layer of silicon. No etch is required. The epitaxial growth process is repeated but requires less time since the n-type layer needs to be only 0.5-1.0 μm thick. The principal operational hazard with this approach is cross-contamination of the p- and n-layers. Gas inflow comprises H_2 + $SiHCl_3$ + n-dopant such as phosphorus formed by bubbling nitrogen through liquid $POCl_3$. Cells emerge from the epitaxial reactor clean and ready for processing; no etch or clean is required.

Wastes:

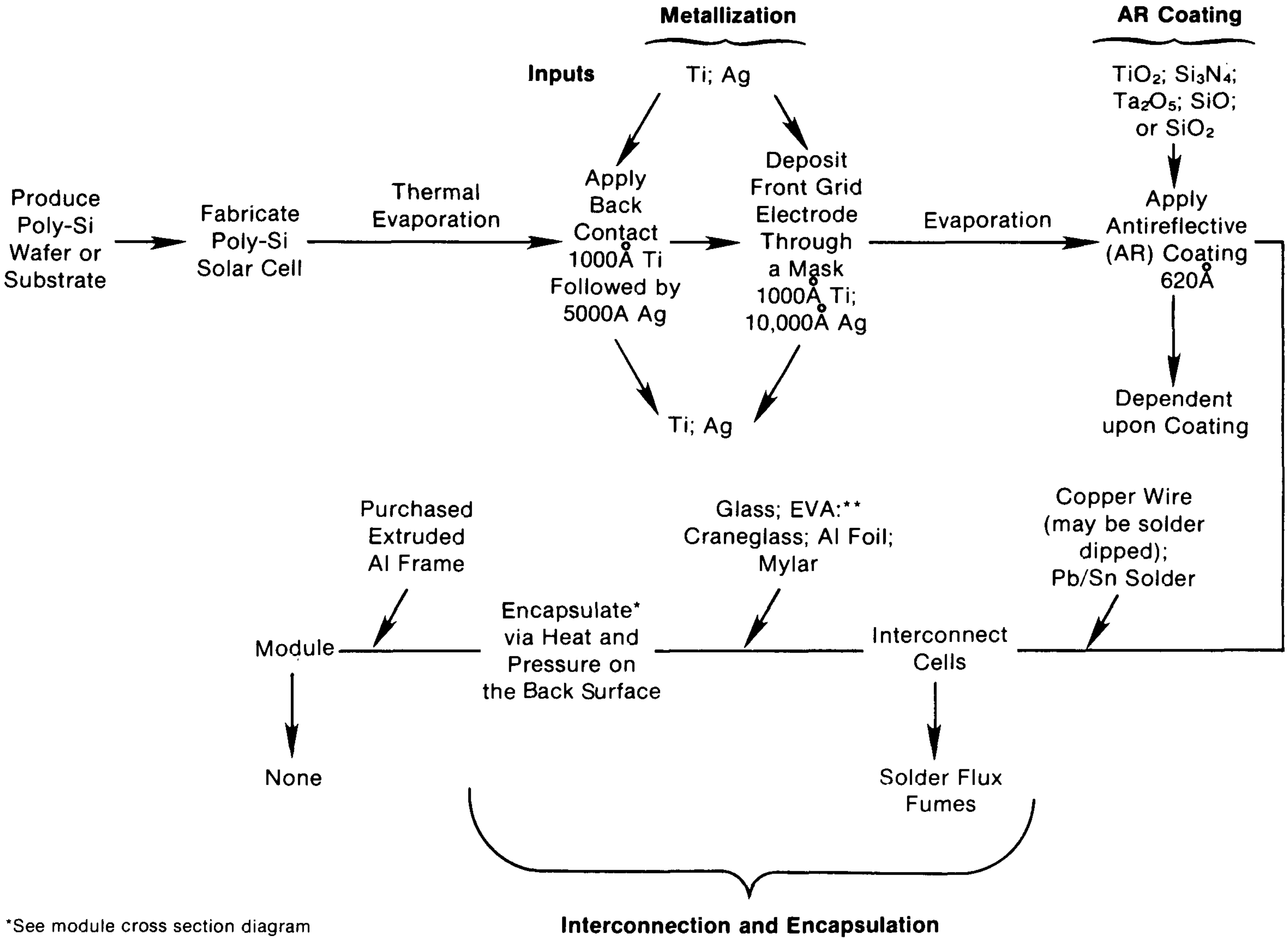
Reactor exhaust gases if the dopant is $POCl_3$: H_2 containing SiO_2, HCl, Cl_2, and various phosphorus compounds such as P_2O_5

Process Alternatives:

As noted, a number of process options are available for formation of the p/n junction, such as the diffused junction process. Because of more research experience, the diffusion process yields cells with 10%-13% efficiency. Cells with epitaxially formed junctions are generally 9%-11% efficient; efficiency is expected to improve as more experience is gained with the epitaxial deposition process.

Cell Processing. Cell processing comprises metallization, application of an antireflective (AR) coating if needed, interconnection, encapsulation, and module framing. Processing is assumed to be the same for all the poly-Si options. The input to cell processing is a clean poly-Si cell with a junction; i.e., the output of the previously described diffused p/n junction, spray-deposited SnO_2, and epitaxial deposition processes. The cell-processing option selected for review is schematically summarized in Fig. 2-12.

Metallization. Metal contacts must be applied to the front and back of cells to channel and collect the photovoltaic-generated electricity. The entire back of the cell is coated with 1000 Å titanium (Ti) followed by 5000 Å silver (Ag). The front grid is formed by 1000 Å Ag deposited through a shadow mask. Thermal evaporation is used for both front and back contact application.



*See module cross section diagram
**EVA = Ethylene vinyl acetate

Figure 2-12. Overview of Module Fabrication

Wastes:

Ti and Ag deposited on the walls of the evaporation chamber and the shadow mask pattern; metals probably will be reclaimed and reprocessed if economically attractive

Process Alternatives:

A number of alternatives are available for thermal evaporation of contacts. One option, screen printing, utilizes ink containing metal organic binders and glass frit. The ink is screened onto the front in the grid pattern and onto the back of the cell. Cells are baked for about 15 min at 100°-400°C (depending upon the specific ink), then fired 1-5 min at 600°C to drive off the organic binders. Screen printing is a dry process that can be automated.

Other alternatives include grid-pattern demarcation through application of a photoresist (such as discussed for metallization of the Cu_2S/CdS cell) followed by metals application via electroless plating or electroplating. Metals that have been used instead of titanium/silver include copper applied over a nickel barrier, nickel/solder, palladium/palladium nickel applied over a silicon nitride (Si_3N_4) AR coating, and titanium/palladium/silver.

Aluminum and copper are generally deposited by flash evaporation, and nickel is applied through electroless plating. For the nickel/solder option, about 300 Å of nickel is applied to the cell through flash evaporation, then cells are dipped into 60:40 lead/tin solder (Watts et al. 1979). The palladium/palladium-nickel metallization is performed by electrolytic plating, sinter, followed by a copper-plating step (Coleman et al. 1979). In the final option, evaporation is used to successively apply 40 Å titanium, 20 Å palladium, and silver to the desired thickness. The total grid thickness is about 5 μm (Watts et al. 1979).

Antireflection (AR) Coating. The poly-Si/SnO_2 option does not require application of an AR coating. As previously noted, the SnO_2 serves as both the heterojunction and the AR coating.

The diffused p-n/poly-Si and epitaxial poly-Si cell options both require an AR coating. The AR coating usually is applied after metallization. A number of compounds are suitable AR coatings: titanium dioxide (TiO_2), tantalum pentoxide (Ta_2O_5), silicon nitride (Si_3N_4), silicon oxides (SiO_2 and SiO), and TiO_2-SiO and SiO-Ta_2O_5 mixtures. The desired thickness is 600 Å to 800 Å.

The application method depends on the specific AR coating. Vacuum deposition is often utilized for oxide coatings such as SiO_x, Ta_2O_5, and SiO-Ta_2O_5. Si_3N_4 is deposited on the cells through the reaction in a 600°C hot-well, quartz-lined furnace of SiH_4 and NH_3 in a nitrogen carrier gas, or by the reaction of H_2SiCl_2 and NH_3. Other application techniques include spinning, spraying, or painting on the AR coating. For example, one approach involves placing a small amount of a titanium/silica film thinned with ethyl alcohol on the cells; the cells are then spun to achieve even distribution of the coating. Cells are successively baked at 100°C and 400°C for 15 min in air to produce a 750 Å-thick coating (D'Aiello et al. 1979). Other application techniques include sputtering and e-beam evaporation (Watts et al. 1979).

Wastes:

Depend on the specific coating

Interconnection. Interconnection of the photovoltaic cells involves soldering and will probably utilize copper foil strips, copper wire, and copper busbars. The copper may be coated in 60:40 lead/tin (Pb/Sn) solder. Additional inputs include solder flux and Pb/Sn solder.

Wastes:

Fumes from soldering

Liquid effluent from cleaning flux from the cells; cleaning may use a water spray if an aqueous flux is used

Encapsulation and Framing. Interconnected cells will probably be machine-aligned onto 4-ft x 4-ft (1.2 m x 1.2 m) panels. The packing factor (percentage of panel area covered by solar cells) will range from 85%-87% for round cells to approximately 93% for rectangular cells. The encapsulation technique selected for review is that developed within the low-cost silicon array manufacturing program at the Jet Propulsion Laboratory (Berger 1980, Sanchez 1980). The panel substrate is composed of mylar (0.001 in., 0.25 mm thick), aluminum foil (0.001 in., .025 mm thick), Craneglass (a nonwoven fiberglass, 0.005 in., .127 mm thick, used to prevent bubble formation), and white ethylene vinyl acetate (EVA—0.015 in., .381 mm thick), purchased in roll form. The EVA is used to cushion thermal expansion differences between the silicon cells and the glass. The solar cells and busbars are aligned on top of the EVA. Next, another layer of clear EVA (0.015 in., .381 mm thick) is placed on top of the cells, followed by Craneglass (0.005 in., .127 mm thick) and finally, a glass superstrate. The glass provides mechanical protection for the panel and protects the encapsulant materials from photohydrolysis. Bonding of the layers is accomplished through pressure and radiant heat (about 150°C) in a vacuum chamber. If encapsulation is not performed in a vacuum, air bubbles tend to form between layers. See Fig. 2-7 for a cross-sectional drawing of the encapsulated panel.

At present, most photovoltaics manufacturers purchase prefabricated module-framing materials. Extruded aluminum framing is most commonly used because of cost, weight, and durability factors. Encapsulated panels are slid into three assembled (by screws or a snap system) frame sides, and the fourth side is attached. Completed modules are then packaged for distribution.

Wastes:

Miscellaneous solid wastes such as EVA, mylar and aluminum foil, and glass; fumes possible from vacuum chamber

2.2.4 Summary of Manufacture Emissions, Effluents, and Solid Wastes

The fabrication processes for poly-Si solar cells are undergoing research and development. None are at the pilot-plant stage; rather, they are all small-scale laboratory processes. The process flows shown in Figs. 2-9, 2-10, and 2-11 were developed with this in mind. Attention was directed toward qualitatively identifying emissions, effluents, and solid wastes. Because considerable changes probably will occur in scaling up laboratory processes to pilot plant production flows and because there may be changes in process steps, waste streams cannot now be quantified.

Although quantitative data are not available, potential environmental, health, and safety problem areas can be identified on the basis of qualitative waste-stream data. Table 2-3 presents a summary of qualitative emissions data for poly-Si wafer and substrate production processes, the three cell fabrication approaches, and cell processing. As in Table 2-2, information is arranged by waste streams that probably will be associated with processing poly-Si solar cells, and by those that are associated with process steps which may be replaced or deleted. Environmental, health, and safety implications of the waste streams are discussed in the next section.

Table 2-3. EMISSIONS, EFFLUENTS, AND SOLID WASTES SUMMARY FOR POLY-SI CELL FABRICATION

	Probably Will Result From Cell Fabrication	Questionable: From Process Steps Which May Be Replaced or Deleted
	Poly-Si Wafer Production[a]	
Particulate and Gaseous Air Emissions	H_2 exhaust Melt furnace exhaust which will contain amorphous SiO_x and possibly Si	
Liquid Effluents	Aqueous silicon slurry from wafer slicing; contains oil lubricants and particles worn from saw blades	
Solid Wastes	Silicon cropped from the ingot; can be partially recyled or sold to steel alloying industry	
	Silicon Substrate Production[b]	
Particulate and Gaseous Air Emissions	Silicon dust from grinding MG-Si HCl and HNO_3 fumes N_2O_4, Cl_2, NO_2, and CO_2 produced from acid leach reaction Melt furnace exhausts containing amorphous SiO_x and possibly Si	
Liquid Effluents	Large amounts of water containing HF; HCl; HNO_3; Fe-, Al-, and Ca- chlorides and nitrides Aqueous silicon slurry from wafer slicing; contains oil lubricant and particles worn from saw blades	
Solid Wastes	Silicon cropped from the ingot; can be partially recycled or sold to the steel alloying industry	

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[a] Assumes use of wafer production technique shown in Fig. 2-9; wafer is suitable for use in all three poly-Si cell fabrication options.

[b] Assumes acid leach purification shown in Fig. 2-8; wafer is suitable only as a substrate for the epitaxial deposition process.

Table 2-3. **EMISSIONS, EFFLUENTS, AND SOLID WASTES SUMMARY FOR POLY-SI CELL FABRICATION** (continued)

	Probably Will Result From Cell Fabrication	Questionable: From Process Steps Which May Be Replaced or Deleted
	Diffused p-n Junction/Poly-Si Wafer	
Particulate and Gaseous Air Emissions	N_2; BCl_3 in N_2; B_2O_3 particulates and HCl in exhaust from the diffusion furnace Silicon particulates removed from wafer back surfaces following diffusion	HF-HNO_3 fumes plus small amounts of H_2 from polishing p-type wafers; use of n-type wafers is assumed
Liquid Effluents	10%HF oxide-etch solution containing SiF_4; used for substrate preparation HNO_3-H_2O etch solution containing SiO_x	HF-HNO_3 etch/polish solution containing SiF_4; used for p-type wafer Isopropyl alcohol wafer degreasing solution; probably will not be done in a commercial facility
	Deionized water rinses containing small amounts of HF and SiO_x	Cleaning solutions H_2O_2:NH_4:H_2O and H_2O_2:HCl:H_2O will probably not be needed in a commercial facility
	SnO_2/Poly-Si Wafer	
Particulate and Gaseous Air Emissions	Exhaust from spray deposition furnace, including HCl, $SnCl_4$, SnO_x, Cl, and solvent fumes; removed with a wet scrubber	
Liquid Effluents	HF-HNO_3 dip polish solution containing up to 50% of the silicon originally in the wafer as SiF_4, SiO_x, and possibly Si-N compounds	Isopropyl alcohol wafer degreasing solution; probably will not be needed in a commercial facility

Table 2-3. EMISSIONS, EFFLUENTS, AND SOLID WASTES SUMMARY FOR POLY-SI CELL FABRICATION (concluded)

	Probably Will Result From Cell Fabrication	Questionable: From Process Steps Which May Be Replaced or Deleted
	Epitaxial Deposition/Silicon Substrate[a]	
Particulate and Gaseous Air Emissions	Exhausts from epitaxial growth of the p-layer: H_2, $SiHCl_3$, SiO_2, HCl, and small amounts of B_2H_6, possibly B_2O_3 Exhausts from epitaxial growth of the n-layer: H_2, $SiHCl_3$, SiO_2, HCl, and small amounts of PH_3, P_2O_5, $POCl_3$, H_3PO_4, Cl	
Liquid Effluents	30% NaOH etch solution containing up to 50% of the silicon originally in the substrate as Na_2SiO_3	
	Cell Processing	
Particulate and Gaseous Air Emissions	TiO_x particulates from AR coating application Solder and flux fumes from cell interconnection Possibly some volatilized plasticizer fumes resulting from heat during encapsulation	
Liquid Effluents	Aqueous cleaning solution used to remove flux residues	
Solid Wastes	Miscellaneous encapsulation materials such as trimmings from mylar, Al-foil, EVA, broken glass	

[a] Assumes use of a low-cost substrate (such as MG-Si or wafers prepared by acid leach as shown in Fig. 2-8) and junction formation via epitaxial growth.

SECTION 3.0

ENVIRONMENTAL, HEALTH, AND SAFETY CHARACTERISTICS OF PROCESSING MATERIALS AND BY-PRODUCTS

As shown in Tables 2-2 and 2-3 and in the production flows in Sec. 2.0, a variety of toxic materials will appear in the waste streams that result from selected advanced material photovoltaic cell processes. The environmental, health, and safety hazards of these waste streams will depend upon their total volume, the quantities and types of compounds present, and how they are treated and handled.

Because commercialization of advanced material photovoltaic options has not yet been realized, the specific amounts of hazardous waste that will be generated is unknown. Similarly, the amounts of different chemical compounds that will be formed is also in question. To further complicate the problem of determining waste hazards to the environment, many of the chemicals used in production processes may or may not be part of future production, and decisions about chemicals to be used will have a profound effect on the content of the waste streams.

3.1 ENVIRONMENTAL, HEALTH AND SAFETY CHARACTERISTICS OF WASTE STREAMS

Some discussion of the properties of individual compounds that may be found in waste streams will not only help determine some of the hazards manufacturers will face in commercializing photovoltaic cells, but will also help them make decisions about which particular chemicals to use when choices are available.

The chemical compounds discussed here were identified from production processes discussed in Sec. 2.0. Compounds are grouped into two categories: those associated with the front-wall Cu_2S/CdS cell fabrication process and those associated with the three poly-Si cell fabrication processes. (As noted, only one approach for production of Cu_2S/CdS cells and three approaches for production of poly-Si cells were selected for study.)

Several specific areas need to be investigated to determine the relative environmental hazards of the chemical compounds. These areas include the effects of the compounds on land use and terrestrial life, on water quality and aquatic life, and on occupational health and safety. Air pollution is another area of concern, but under normal operating conditions (i.e., installation of the air pollution control equipment necessary to meet local, state, and federal standards), the production of photovoltaic cells should have little impact on air pollution levels. Disposal of certain wastes by incineration, or the possibility of a system malfunction or accident that causes a fire or overheating, may result in the generation of some toxic gases and may require special preventive precautions. However, under normal operations, most gases produced can be controlled or safely vented and dispersed into the air. See Part II of this report for a more detailed examination of air quality regulations and their applicability to Cu_2S/CdS and poly-Si process waste streams.

3.1.1 Overview of Hazardous Properties

Wide disparities exist in degrees of hazard among chemical compounds found in alternative PV cell manufacturing processes. For instance, nitrogen is a waste product of all the processes but, except in high concentrations in which it would act as an asphyxiant, it should cause no adverse effects. At the same time, hydrofluoric acid is found in the waste stream of polycrystalline silicon processes and hydrogen sulfide is found in the waste stream of cadmium sulfide/copper sulfide processes. Both of these compounds can be extremely hazardous and need to be used, treated, and disposed of with care.

Tables 3-1 through 3-4 display and summarize particular characteristics of the various compounds. Toxicity, explosiveness, flammability, and reactivity have been chosen to illustrate the relative hazards of different compounds because these same characteristics are used by the EPA to distinguish hazardous and nonhazardous waste streams. If these characteristics are present in the waste stream, the EPA considers the stream hazardous; it must be handled and disposed of under the rules and regulations set forth by the Resource Conservation and Recovery Act of 1976 (RCRA). See Part II for a more detailed discussion of RCRA and its potential applicability to Cu_2S/CdS and poly-Si waste streams. While it does not necessarily follow that a waste stream will possess the same characteristics, or those characteristics to the same degree, as its individual components (the quantity of various components and the ability of some compounds to ameliorate or possibly intensify negative impacts of others affects properties exhibited by the whole waste stream), the tables can help identify the relative hazards of individual components. Suspected or confirmed carcinogens are also noted.

The compounds that are considered highly toxic are described in greater detail in Tables 3-5 and 3-6; the tables show how injury may occur. The following definitions apply in these two tables:

> Acute—Used in the medical sense to mean "of short duration." Applied to materials that are inhaled or absorbed through the skin, it refers to a single exposure of a duration measured in seconds, minutes, or hours. As applied to materials that are ingested, it refers to a single quantity or dose.
>
> Chronic—Used to mean "of long duration." Applied to materials that are inhaled or absorbed through the skin, it refers to prolonged or repeated exposures of a duration measured in days, months, or years. As applied to materials that are ingested, it refers to repeated doses over a period of days, months, or years.
>
> Local—Refers to the site of action of an agent; the action takes place at the point of contact. The site may be the skin; mucous membranes of the eyes, nose, mouth, or throat; or anywhere along the respiratory or gastrointestinal system.
>
> Systemic—Refers to a site of action other than the point of contact, presupposing that absorption has taken place. It is possible, however, for toxic agents to be absorbed through a channel (skin, lungs, or intestines) and produce later effects on one of those channels that are not a result of the original direct contact. Thus, it is possible for some agents to produce harmful effects on a single organ or tissue as a result of both "local" and "systemic" actions (Sax 1975).

Table 3-1. SOME DANGEROUS PROPERTIES OF WASTE STREAM COMPOUNDS

Copper Sulfide/Cadmium Sulfide Cells

Chemical Compound	Symbol	Toxicity	Explosiveness	Flammability
Ammonium Chloride	NH_4Cl	Moderate		
Ammonium Fluoroborate	NH_4BF_4	High		
Cadmium Chloride[b]	$CdCl_2$	High		
Chromium Compounds[a,b]		High		
Copper Chloride	CuCl	Low		
Gold	Au	Low		
Hydrochloric Acid	HCl	High		
Hydrogen Sulfide	H_2S	High	Moderate	High
Methanol	CH_3OH	Moderate to High	Moderate	High
Nickel[b]	Ni	Moderate to High	Moderate	Slight
Nitrogen	N_2			
Phosphorus Detergent		High	Moderate	High
Silicon Monoxide	SiO	Unknown		
Sodium Chloride	NaCl	Low		
Tantalum Oxide	Ta_2O_5	Low		
Zinc Fluoroborate	$ZnBF_4$	High		

Toxicity:

High:	May cause death or permanent injury after very short exposure to small quantities.
Moderate:	May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.
Low:	Cause readily reversible changes which appear after end of exposure.

[a] EPA-classified compound which, if found in sufficient quantities in the waste stream, automatically characterizes the stream as "hazardous."

[b] Suspected or confirmed carcinogen.

Source: N. Irving Sax, Dangerous Properties of Industrial Materials. 1979.

Table 3-2. SOME DANGEROUS PROPERTIES OF WASTE STREAM COMPOUNDS

Polycrystalline Silicon Cells

Chemical Compound	Symbol	Toxicity	Explosiveness	Flammability
Aluminum Chloride	$AlCl_3$	High		
Aluminum Nitride	AlN	None		
Arsine*	AsH_3	High	Moderate	Moderate
Boron Oxide	B_2O_3	Low		
Boron Trichloride	BCl_3	High		
Calcium Chloride	$CaCl_2$	Low		
Calcium Nitride	Ca_3N_2	Low		
Carbon Dioxide	CO_2	Low		
Chlorine	Cl_2	High	Slight	Moderate
Diborane	B_2H_6	High	Slight	High
Ethyl Acetate*	$CH_3COOC_2H_5$	Low to Moderate	Moderate	High
Ferric Chloride	$FeCl_3$	Low		
Fluorine	F_2	High		High
Hydrochloric Acid	HCl	High		
Hydrofluoric Acid*	HF	High		
Hydrogen	H_2	None	High	High
Hydrogen Peroxide	H_2O_2			
Isopropyl Alcohol	$CH_3CHOHCH_3$	Low to Moderate	Moderate	High
Metal Silicides		Varies	Moderate	Moderate
Nitric Acid	HNO_3	High	Slight	Moderate
Nitrogen	N_2			
Nitrogen Dioxide*	NO_2	High		
Nitrogen Tetroxide*	N_2O_4	High		
Phosphine*	PH_3	High	Moderate	High
Phosphoric Acid	H_3PO_4	Moderate		
Phosphorus Oxychloride	$POCl_3$	High		
Phosphorus Pentoxide	P_2O_5	High		High
Silane	SiH_4	High	Moderate	High
Silicon	Si	Unkown		Moderate
Silicon Chloride	$SiCl_4$	High		
Silver*	Ag			Moderate
Sodium Hydroxide	$NaOH$	Moderate to High		
Sodium Silicate	Na_2SiO_3	Low		
Stannic Chloride	$SnCl_4$	High		Slight
Tin Oxide	SnO_x	Low		
Titanium	Ti		Moderate	Moderate

Toxicity:
High: May cause death or permanent injury after very short exposure to small quantities.
Moderate: May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.
Low: Cause readily reversible changes which appear after end of exposure.

*EPA-classified compound which, if found in sufficient quantities in the waste stream, automatically characterizes the stream as "hazardous."

Source: N. Irving Sax, Dangerous Properties of Industrial Materials. 1979.

Table 3-3. REACTIVITY CHARACTERISTICS OF WASTE STREAM COMPOUNDS
Copper Sulfide/Cadmium Sulfide Cells

Chemical Compound	Reactivity	Reactive Agent(s)	Reaction Outcomes
Ammonium Chloride	Dangerous	Heat or Acid	Toxic Fumes
Ammonium Fluoroborate	Dangerous	Heat or Acid	Toxic Fumes
Cadmium Chloride[a]	Dangerous	Heat or Acid	Toxic Fumes of Chloride
Chromium Compounds[a,b]	Dangerous	Dependent on Compound	Varies
Copper Chloride	Dangerous	Heat or Acid	Toxic Fumes of Chloride
Gold (Powdered)	Moderate	Heat	Explosion
Hydrochloric Acid	Dangerous	Water or Steam	Toxic and Corrosive Fumes
Hydrogen Sulfide[a]	Dangerous	Heat or Oxidizing Materials	Explosion and Toxic Fumes of Oxides of Sulfur
Methanol[a]	Dangerous	Heat or Oxidizing Materials	Explosion and Fire
Nickel (Powdered)[a,b]	Moderate	Heat	Explosion
Nitrogen			
Phosphorus Detergent	Dangerous	Dependent on Compound	Toxic Fumes of Oxides of Phosphorus
Silicon Monoxide			
Sodium Chloride	Slight	Heat	Irritating Vapors
Tantalum Oxide			
Zinc Fluoroborate	Dangerous	Heat or Acid	Toxic Fumes

[a] EPA-classified compound which, if found in sufficient quantities in the waste stream, automatically characterizes the stream as "hazardous."

[b] Suspected or confirmed carcinogen.

Source: N. Irving Sax, Dangerous Properties of Industrial Materials. 1979.

Table 3-4. REACTIVITY CHARACTERISTICS OF WASTE STREAM COMPOUNDS
Polycrystalline Silicon Cells

Chemical Compound	Reactivity	Reactive Agent(s)	Reaction Outcome
Aluminum Chloride	Dangerous	Water or Steam	Heat, Toxic and Corrosive Fumes
Aluminum Nitrate	Slight	Water or Steam	Toxic and Corrosive Fumes
Arsine*	Dangerous	Heat or Oxidizing Material	Toxic Fumes of Arsenic
Boron Oxide			
Boron Trichloride	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Calcium Chloride			
Calcium Nitride	Slight	Water	Ammonia
Carbon Dioxide	Slight		
Chlorine	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes of Hydrochloric Acid
Diborane	Dangerous	Heat, Water, Steam, or Oxidizing Material	Explosion, Hydrogen, and Toxic Fumes of Boron Oxides
Dinitrogen Tetroxide	(see Nitrogen Dioxide)		
Ethyl Acetate*	Dangerous	Heat or Oxidizing Material	Explosion and Fire
Ferric Chloride	Dangerous	Heat, Water	Toxic and Corrosive Fumes of Hydrochloric Acid
Ferric Nitride			
Fluorine	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Hydrochloric Acid	Dangerous	Water or Steam	Toxic and Corrosive Fumes
Hydrofluoric Acid*	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes of Fluoride
Hydrogen	Dangerous	Heat or Oxidizing Material	Explosion and Fire
Isopropyl Alcohol	Dangerous	Heat or Oxidizing Material	Explosion and Fire
Metal Silicides	Moderate	Water, Steam, or Acid	Hydrogen and Toxic Fumes
Nitric Acid	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Nitrogen			
Nitrogen Dioxide*	Dangerous	Heat, Water, Steam, or Reducing Material	Corrosive Fumes
Phosphine*	Dangerous	Heat or Oxidizing Material	Toxic Fumes of Oxides of Phosphorus

Table 3-4. REACTIVITY CHARACTERISTICS OF WASTE STREAM COMPOUNDS (concluded)
Polycrystalline Silicon Cells

Chemical Compound	Reactivity	Reactive Agent(s)	Reaction Outcome
Phosphoric Acid	Dangerous	Heat	Toxic Fumes of Oxides of Phosphorus
Phosphorus Oxychloride	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Phosphorus Pentoxide	Dangerous	Water, Steam, or Reducing Material	Heat, Fire, and Toxic Fumes
Silanes	Dangerous	Heat	Explosion, Fire, and Toxic Fumes
Silicon	Dangerous	Oxidizing Material or Heat with Water or Steam	Hydrogen Gas
Silicon Chloride	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Silver (Powder)*	Moderate	Heat	Explosion
Sodium Hydroxide	Dangerous	Water	Heat and Will Attack Living Tissue
Sodium Silicate			
Stannic Chloride	Dangerous	Heat or Water	Toxic and Corrosive Fumes of Hydrochloric Acid
Tin Oxide			
Titanium (Powder)	Moderate	Heat	Explosion

*EPA-classified compound which, if found in sufficient quantities in the waste stream, automatically characterizes the stream as "hazardous."

Source: N. Irving Sax, Dangerous Properties of Industrial Materials. 1979.

Table 3-5. TOXICITY CHARACTERISTICS OF WASTE STREAM COMPOUNDS
Copper Sulfide/Cadmium Sulfide Cells

Chemical Compound	Acute Local	Acute Systemic	Chronic Local	Chronic Systemic
Ammonium Fluoroborate	High	High	Low	High
Cadmium Chloride[a]	High	High		High
Chromium Compounds[a,b]	High		High	High
Hydrochloric Acid	High	High	Moderate	
Hydrogen Sulfide[a]	High	High		High
Methanol	Moderate	High		High
Zinc Fluoroborate	(see Ammonium Fluoroborate)			

Toxicity:

High:	May cause death or permanent injury after very short exposure to small quantities.
Moderate:	May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.
Low:	Cause readily reversible changes which appear after end of exposure.

[a] EPA-classified compound which, if found in sufficient quantities in the waste stream, automatically characterizes the stream as "hazardous."

[b] Suspected or confirmed carcinogen.

Source: N. Irving Sax, Dangerous Properties of Industrial Materials. 1979.

Table 3-6. TOXICITY CHARACTERISTICS OF WASTE STREAM COMPOUNDS

Polycrystalline Silicon Cells

Chemical Compound	Acute Local	Acute Systemic	Chronic Local	Chronic Systemic
Aluminum Chloride	High			
Arsine*	High	High		High
Chlorine	High			
Diborane	High	High		
Fluorine	High	High	High	High
Hydrochloric Acid	High	High	Moderate	
Hydrofluoric Acid*	High	High	Moderate	High
Nitric Acid	High	High	Moderate	
Nitrogen Dioxide*	High	High		Moderate
Phosphine*	Moderate	High		High
Phosphorus Oxychloride	(see Hydrochloric Acid)			
Silane	High			
Silicon Chloride	High			
Stannic Chloride	(see Hydrochloric Acid)			

Toxicity:

High:	May cause death or permanent injury after very short exposure to small quantities.
Moderate:	May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.
Low:	Cause readily reversible changes which appear after end of exposure.

*EPA-classified compound which, if present in sufficient quantities in the waste stream, automatically characterizes the stream as "hazardous."

Source: N. Irving Sax, Dangerous Properties of Industrial Materials. 1979.

3.1.2 Potential Effects on Water Quality

Many chemicals and chemical waste streams are disposed of by discharging them into bodies of water or even into municipal sewage systems. It is, therefore, necessary to look at the effects of the waste components on water quality. Water quality is a broad term that can refer to effects on human consumption, effects on fresh water and marine life forms, and effects on the aesthetics and on recreational use of our water resources.

The effect of a waste stream on water quality is influenced by a number of factors: flow rate, temperature, pH level, salinity, turbidity, presence of other waste compounds, etc. These factors will affect the allowable discharge limits of various chemicals at any given time. In addition, there are restrictions on water characteristics as well as specific chemicals so that stating criteria for allowable amounts of a particular compound can be misleading or even erroneous. For example, the EPA has specific criteria for the allowable level of cadmium in the domestic water supply. At the same time, limits are given for allowable levels for dissolved solids. Even if the allowable cadmium levels have been met, further reductions in the discharge level of cadmium may be required to meet all water criteria if dissolved solids levels exceed their allowable levels. See Part II for a more detailed examination of federal water quality regulation and its applicability to waste streams from each cell process.

EPA has published a document containing permissible quality criteria for water (EPA 1976). In this document, permissible levels are given for such materials as ammonia, arsenic, boron, cadmium, chlorine, chromium, copper, iron, nickel, phosphorus, silver, and zinc. Also, information is included on allowable limits for the alkalinity, the dissolved oxygen and other gases, the hardness, the pH, the dissolved solids and salinity, the suspended solids and turbidity, and the temperature of the water.

Besides the standards set by EPA, every state and municipality has its own rules and regulations covering the discharge of substances to bodies of water and to local sewage systems. Table 3-7, for example, shows the limits for certain chemicals that have been established by the Commonwealth of Massachusetts. These limits pertain to discharges into bodies of water. The Metropolitan District Commission (MDC) is a regional agency in charge of regulating discharges into the sewage system of Boston and its surrounding communities (Metropolitan District Commission 1979). Criteria have been set by the MDC that include such chemicals and compounds as ammonia, arsenic, boron, cadmium, chlorides, chromium, copper, iron, nickel, sulfates, sulfides, silver, tin, and zinc. All state concentration limits must be at least as strict as federal standards, and all local limits must be at least as strict as both state and federal permissible concentrations.

Some information on the effects of hazardous compounds on water quality also can be obtained from Water Quality Characteristics of Hazardous Materials by W. Hahn and P. Jensen. In Table 3-8, aquatic toxicity ratings from this document are given for some of the compounds found in the waste stream from the production of photovoltaic cells. The ratings give an indication of the toxicity of the compounds to aquatic life.

3.1.3 Occupational Health and Safety Hazards of Waste Streams

Early environmental, health and safety studies indicate that occupational health and safety risks will be greatest during preparation of semiconductor materials and cell manufacture, and will result from worker exposure to hazardous substances (EDP 1979, BNL 1980, Briggs and Owens 1979). Both chronic low-level exposure and acute exposure to certain materials may affect workers' health, causing such health problems as respiratory diseases or even acute poisoning.

Table 3-7. CONCENTRATION LIMITS FOR CERTAIN POLLUTANTS IN WATER

	Daily Avg. (mg/L)	Daily Max. (mg/L)
TSS[a]	20.00	30.00
Cyanide (dest. by Cl_2)	0.10	0.20
Cyanide (total)	0.25	0.65
Fluoride	20.00	40.00
Aluminum	1.50	2.00
Barium	2.00	4.00
Cadmium	0.50	1.00
Chromium (+6)	0.10	0.25
Chromium (total)	1.50	3.00
Copper	1.50	3.00
Iron	2.00	3.00
Lead	0.40	0.80
Manganese	2.00	4.00
Nickel	1.80	3.60
Silver	0.15	0.30
Tin	2.00	4.00
Zinc	1.50	3.00
pH	6.0-9.5 (range)	

Note:

Daily Avg.--Value refers to an eight grab composite collected over a normal operating day.

Daily Max.--Value refers to an individual grab sample.

Metal concentrations represent total metal limits (i.e., sum of dissolved and suspended forms).

Source: Commonwealth of Massachusetts, Department of Environmental Quality Engineering, Division of Water Pollution Control, Industrial Waste Section; January 1980.

[a] TSS: Total suspended solids.

Table 3-8. AQUATIC TOXICITY RATING FOR SOME COMPOUNDS

Chemical Compound	Aquatic Rating (TLm96)[a] (ppm)
Polycrystalline Silicon Cells	
Acetic Acid	100-10
Calcium Chloride	Over 1000
Chlorine	Under 1
Ethyl Acetate	Over 1000
Isopropyl Alcohol	1000-100
Nitric Acid	100-10
Nitrogen Tetroxide	1000-100
Sodium Hydroxide	100-10
Phosphorus Oxychloride	100-10
Silicon Chloride	100-10
Stannic Chloride	1000-100
Cadmium Sulfide/Copper Sulfide Cells	
Cadmium Chloride	100-under 1
Methanol	Over 1000
Silica	Over 1000
Sodium Chloride	Over 1000

[a] TLm96 is as the 96-hour static or continuous flow standard protocol. The toxicity ranges result from the variety of species that were investigated.

Source: Registry of Toxic Effects of Chemical Substances, National Institute for Occupational Safety and Health. 1977 edition.

In the production of polycrystalline silicon cells, for instance, inhalation of silica dust is known to cause respiratory disease. Inhalation may occur during several phases of silicon cell production—primarily, during mining of quartz and sandstone, and second, during silicon refining. Deposition of silicon-containing particles in the lungs may result in fibrosis and eventually in silicosis. Another possible result of inhalation or ingestion, for which there is currently only limited evidence, is accumulation in the kidney, followed by development of systemic hypertension.

Toxic gases resulting from doping silicon with boron, phosphorus or arsenic may also be dangerous to workers in the production of poly-Si cells.* Doping silicon with boron involves using boron trichloride at high temperatures. The dissolution of boron trichloride and diffusion of boron into the silicon vent undetermined amounts of chlorine and boron trichloride. Chlorine gas is irritating to the eyes and respiratory tract and may result in pulmonary edema. Boron trichloride is extremely toxic, having a lowest reported lethal concentration (LCLo) for inhalation of 20 ppm for rats, and, therefore it presents a serious threat in cases of accidental leakage. Doping with phosphorus is also a concern since phosphine, phosphorus oxychloride, and phosphorus pentoxide are used as the diffusing agents. Phosphine is a highly toxic gas with an LCLo for human inhalation of 8 ppm. Chronic exposure to phosphine may result in gastrointestinal damage, anemia, and nervous system disorders.

In the production of copper sulfide/cadmium sulfide cells, inhalation of toxic cadmium compounds during the material production phases presents some serious concerns about workers' health, even to the possibility of lethal acute poisoning. For example, cadmium is extracted from zinc ore and, while breathing equipment is usually used, accidental exposure to escaped emissions during equipment maintenance or throughout the material production is quite possible. Inhalation of dust or fumes generally affects the respiratory tract, but the inhaled product also becomes concentrated in and may damage kidneys. Acute exposure may result in changes in the lungs—similar to those found with bronchopneumonia—accompanied by severe chest pain, coughing, severe dyspnea, and death. Since onset of these symptoms does not occur until several hours after exposure, workers can be subjected to very high levels of contamination before they are alerted to leave the area.

Potentially, cadmium sulfide fumes and dust are the most hazardous pollutants to workers in copper sulfide/cadmium sulfide cell production. The relative toxicity of cadmium sulfide compared with cadmium oxide and elemental cadmium has not been clearly established. Comparing data for the same route of administration to the same species, cadmium sulfide appears to be as toxic as cadmium oxide and between one-third to one—half as toxic as elemental cadmium. Cadmium sulfate seems to be from 3-45 times more toxic than the sulfide, and the chloride is about 20-35 times more toxic than the sulfide (NIOSH 1977.) However, other researchers have indicated that cadmium sulfide appears to be about 10 times less toxic than cadmium dust or soluble salts (data cited in Briggs and Owens 1979). Regardless, cadmium compounds can pose a serious threat to workers' health, being a suspected carcinogen. (Nickel is also a recognized carcinogen, and chromium is suspected. Although cadmium sulfide is not a confirmed carcinogen, along with cadmium nitrate, it is at the top of the list of 102 compounds recommended by the National Toxicological Program for investigation in FY 1981 for possible carcinogenicity.) The cadmium sulfide used in the production of photovoltaic cells comes in a

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*For an additional discussion of dopants and other compounds used in production of photovoltaic cells, see BNL (1980a).

powdery form and could become entrained in the air within the plant. "Safe" levels of exposure to carcinogens are not established.

Tables 3-9 and 3-10 give information on occupational health and safety exposure limits for some of the chemical compounds used in the production of poly-Si and Cu_2 S/CdS photovoltaic cells. The threshold limit values (TLV) are the American Conference of Governmental Industrial Hygienists (ACGIH) recommended time-weighted average (TWA) concentrations to which most workers can be exposed without adverse effects. The OSHA standards refer to standards promulgated under the Occupational Health and Safety Act of 1970. See Part II for a discussion of OSHA standard setting as it may influence poly-Si and Cu_2S/CdS cell production. Also, Tables 3-4 and 3-5 provide useful information on the type of health hazards that workers may be subject to under certain conditions of production.

3.2 WASTE STREAM TREATMENT METHODS AND RESULTANT EFFLUENTS

As shown in the previous section, fabrication of Cu_2S/CdS and poly-Si solar cells will produce gaseous and liquid waste streams and solid wastes. In commercial or pilot-scale cell production plants, these wastes will have to be treated and properly disposed of to meet current local, state, and federal environmental regulations. Quantities and concentrations of compounds in waste streams are not currently available, because fabrication processes are still in the research stage. However, general methods of waste treatment and disposal can be discussed qualitatively.

3.2.1 Waste Treatment Methods and Effluents

Treatment methods for individual waste compounds have been proposed based on readily available literature; they are listed in Tables 3-11 through 3-16. The treatment methods are described briefly in the Appendix to Part I. It appears that, in general, the treatment methods for each individual compound are compatible with those for other compounds in the same waste stream. However, more detailed information on the concentrations of each of the waste stream compounds, stream flow rates, temperatures, and pressures must be obtained before exact treatment methods can be specified.

Similarly, it appears that mixing of waste streams for each manufacturing process will probably not produce "exotic" problems in terms of waste treatment. Mixed waste streams are expected to call for environmental control requirements similar to those of the semiconductor industry. Predicting the cost-effectiveness and overall environmental impact of mixing waste streams must also await further research; exact specification of waste treatment processes based on systems analysis are needed, as more data become available. In general, for the aqueous waste stream, removing heavy metals and neutralizing of acids are the main waste treatment concerns for all of the production processes. Treatment of gaseous waste streams is geared heavily toward industrial hygiene and acid neutralization.

A commercial silicon cell production process utilizes ion exhange to remove heavy metals for aqueous wastes and follows this with acid neutralization. Water is then discharged to the local municipal waste water treatment system. Solids and spent ion exchange columns are trucked to facilities for further treatment and landfill disposal. Two unique waste treatment processes were developed to treat other (proprietary) waste chemicals.

Table 3-9. WORKER EXPOSURE LIMITS TO CERTAIN WASTE STREAM COMPOUNDS

Copper Sulfide/Cadmium Sulfide Cells

Chemical Compound	Threshold Limit Value	OSHA Standards
Ammonium Chloride	10 mg/m^3	
Cadmium Chloride		TWA 0.2 mg/m^3 as (Cd) CL 0.6 mg/m^3
Chromium Compounds	Salts: 0.5 mg/m^3 Acids: 0.1 mg/m^3	
Copper Chloride		TWA 1 mg/m^3 as (Cu II)
Hydrochloric Acid		CL 5 ppm
Hydrogen Sulfide	10 ppm	CL 20 ppm
Methanol	200 ppm*	TWA 200 ppm[a]
Nickel	0.1 mg/m^3	TWA 1 mg/m^3
Phosphorus Detergent	0.1 mg/m^3 as (P)	TWA 0.1 mg/m^3 as (P)
Tantalum Oxide		TWA/m^3 as (Ta)

[a] Significant additional exposure from skin absorption may be possible.

ppm - parts per million parts of air

mg/m^3 - milligrams per cubic meter

TWA - time-weighted average concentration

CL - ceiling value

Source: National Institute for Occupational Safety and Health. Registry of Toxic Effects of Chemical Substances. 1977 edition.

Table 3-10. WORKER EXPOSURE LIMITS TO CERTAIN WASTE STREAM COMPOUNDS

Polycrystalline Silicon Cells

Chemical Compound	Threshold Limit Value	OSHA Standards
Arsine	0.2 mg/m^3	TWA 0.05 ppm
Boron Oxide	10 mg/m^3	TWA 15 mg/m^3
Carbon Dioxide	5000 ppm	TWA 5000 ppm
Chlorine	1 ppm	TWA 1 ppm
Diborane	0.1 ppm	TWA 0.1 ppm
Dinitrogen Tetroxide	See Nitrogen Dioxide	
Ethyl Acetate	400 ppm	TWA 400 ppm
Ferric Chloride	1 mg/m^3 as (Fe)	
Fluorine	1 ppm	TWA 0.1 ppm
Hydrochloric Acid	5 ppm	CL 5 ppm
Hydrofluoric Acid	3 ppm	TWA 3 ppm
Nitric Acid	2 ppm	TWA 2 ppm
Nitrogen Dioxide	5 ppm	TWA 5 ppm
Phosphine	0.3 ppm	TWA 0.4 mg/m^3
Phosphoric Acid	1 mg/m^3	TWA 1 mg/m^3
Silane	0.05 ppm	
Silver	0.01 mg/m^3	TWA 0.01 mg/m^3
Sodium Hydroxide	2 mg/m^3	TWA 2 mg/m^3
Stannic Chloride		TWA 2 mg/m^3 as (Sn)
Tin Oxide		TWA 2 mg/m^3 as (Sn)

ppm - parts per million parts of air

mg/m^3 - milligrams per cubic meter

TWA - time-weighted average concentration

CL - ceiling value

Source: National Institute for Occupational Safety and Health. Registry of Toxic Effects of Chemical Substances. 1977 edition.

3.2.2 Hazardous Properties of Waste Treatment Effluents

The products of interest here that result from possible treatment methods of individual chemicals in waste streams are listed in Tables 3-11 through 3-16 in the column titled "Probable Effluents." Not all products of reaction are shown in these tables—only the most potentially toxic. Those not shown are generally salts resulting from neutralization and are obvious from the reactants shown. In this section information is given on the toxicity, explosiveness, flammability, and reactivity of these treatment products.

Tables 3-17 and 3-18 summarize briefly toxicity, explosiveness, and flammability characteristics. Reactivity characteristics are shown in Tables 3-19 and 3-20. Additional toxicity information is given in Tables 3-21 and 3-22. The dangerous properties listed in these tables should be interpreted in light of the concentrations and the degree of isolation of the chemicals that could greatly reduce the danger levels. For example, for most chemicals, explosiveness is a factor only in very narrow concentration ranges for gases or only under specific environmental conditions for liquids or solids. The disposed wastes resulting from the treatment process under consideration here are highly unlikely to pose explosive hazards since gases are dispersed, solvents are recovered or burned, etc. Also, some wastes listed in Tables 3-17 and 3-18 may be recycled as indicated in Tables 3-11 through 3-16 and would therefore pose minimal disposal hazards.

Some toxic solid wastes, such as $Cr(OH_3)$ and CaF_2, are insoluble or only slightly soluble and must be placed in a chemical landfill that does not permit runoff and movement in soil. Also, the effects of acid rain on metal leachability and of airborne dust from landfills should be monitored carefully. Thus, these toxic compounds should be isolated from humans, animals, and vegetation.

In general, the danger levels of the treatment products listed in Tables 3-17 through 3-22 should be interpreted as those resulting from worst case conditions but not expected to result from proper disposal methods. Dangers could be present, though, in failures of one kind or another of the waste treatment and disposal system. Thus, there is some environmental risk associated with these products.

3.2.3 Disposal of Waste Streams and Effluents

Wastes, either treated or untreated, from the production of photovoltaic cells will be disposed of ultimately into a body of water (e.g., lake or stream), into the local sewage system, or into land. The most common methods of land disposal are landfilling or incineration (the residue is landfilled). Some possible disposal methods for process effluents are shown in the final columns of Tables 3-11 through 3-16. These methods are representative; however, there may be other disposal methods not listed that can be used. The specific disposal method utilized by a photovoltaic cell manufacturer will depend on a number of factors, including distance to disposal facilities, existing or future environmental regulations, development of new waste treatment technologies, and cost. Three basic options for waste disposal are: (1) discharge to water; (2) landfill of solid/sludge/ash wastes; and (3) dispersion to the atmosphere. All atmospheric emissions must meet air quality standards. Control is generally achieved by using various scrubbers and collectors. Atmospheric release of wastes from photovoltaic cell fabrication plants is not viewed as a major problem area and will not be discussed in detail here. However, potential releases of submicron-sized particles of Si and SiO from production of silicon in electric arc furnaces may present an environmental, health, and safety problem. Further area research is needed to assess whether a problem indeed exists.

Table 3-11. COPPER SULFIDE/CADMIUM SULFIDE FRONT-WALL PROCESS WASTE STREAM TREATMENTS

Process Step/Waste	Possible Treatment	Probable Effluents	Disposal
1. Substrate Preparation			
Chromate Coating	Lower pH with H_2SO_4, add agent (SO_2), reduce Cr^{+6} to Cr^{+3}, add lime (Patterson 1975, Sittig 1976) or ion exchange w/recycle (Patterson 1975)	$Cr(OH)_3$	Landfill
Oakite 91 and 91A (phosphorus detergent)	Biological, activated sludge, municipal or lime treatment and anaerobic digestion (Callely 1976)	Precipitate (insoluble)	Landfill
2. Zinc Plating			
$ZnBF_4$	Add Ca^{++}, raise pH (Yehaskel 1979)	CaF_2, $Zn(OH)_2$, H_3BO_3	Landfill
NH_4Cl	Add NaOH (Powers 1976)	NaCl; NH_3	Water to sewer (dilute if needed)
NH_4BF_4	Add Ca^{++} (Yehaskel 1979)	CaF_2, H_3BO_3	Landfill
Licorice root solution	Activated carbon		Recycle (?)
HCl (to pH 3 to 4)	Raise pH with $Ca(OH)_2$(Powers 1976)	$CaCl_2$	Water to sewer or treat
CH_3OH (methanol)	Solvent extraction, fluidized bed, activated carbon (Ross 1968, Powers 1976)		Recycle or incinerate
3. CdS Deposition and Etch			
HCl(g)	Liquid absorption and neutralization (ammonia) (Stern 1977)	NaCl	Discharge to sewer (dilute if needed)
$CdCl_2$	Add lime (Sittig 1976); lime and $FeSO_4$ (Patterson 1975)	$Cd(OH)_2$ (insoluble); $Fe(OH)_2$	Landfill; water to sewer
H_2S(g)	Liquid absorption (ammonia) (Stern 1977)	$(NH_4)_2S$	Recycle
4. Cu_2S Barrier Formation			
NaCl	Ion exchange if concentration excessive	NaCl	Discharge to sewer
CuCl	Add lime (Sittig 1976; Patterson 1975)	$Cu(OH)_2$	Landfill
H_2S(g)	Liquid absorption (ammonia) (Stern 1977)	$(NH_4)_2S$	Recycle
$CdCl_2$	Add lime (Sittig 1976); or lime and $FeSO_4$ (Patterson 1975)	$Cd(OH)_2$; $Fe(OH)_2$	Landfill
HCl(g)	Liquid absorption (+ ammonia?) (Stern 1977)	NH_4Cl	Discharge to sewer
N_2(g)	Vent	N_2	Vent

Table 3-11. COPPER SULFIDE/CADMIUM SULFIDE FRONT-WALL PROCESS WASTE STREAM TREATMENTS (concluded)

Process Step/Waste	Possible Treatment	Probable Effluents	Disposal
4a. Alternate Cu_2S Formation			
CdCl	Add lime (Sittig 1976); or lime and $FeSO_4$ (Patterson 1975)	$Cd(OH)_2$; $Fe(OH)_2$	Landfill
CuCl	Add lime (Sittig 1976, Patterson 1975)	$Cu(OH)_2$	Landfill
5. Grid			
Au	Ion exchange		Recover
Ni	Add lime (Sittig 1976, Patterson 1975)	$Ni(OH)_3$	Landfill or recycle
Cu Plating Bath	Add lime (Sittig 1976, Patterson 1975)	$Cu(OH)_2$	Landfill or recycle

Table 3-12. POLYCRYSTALLINE SILICON INITIAL PROCESS WASTE TREATMENTS

Waste Stream		Possible Treatment	Probable Effluents	Disposal
Acid Leach Purification of MG-Si[a]				
Si Dust		Bag filters	Si	Recycle or landfill
HCl(g)	Fumes and Air Emissions	Liquid absorption (and neutralize with lime) (Stern 1977, Powers 1976)	HCl (or $CaCl_2$)	Recycle (or dilute and discharge)
HNO_3(g)		Liquid absorption (and neutralize with lime) (Stern 1977, Powers 1976)	HNO_3 (or $CaNO_3$)	Recycle (or discharge)
Cl_2 (g)		Fiber mist eliminator (Stern 1977)	Cl ions, probably present as a salt, depending upon pH	Recycle or landfill
NO_2(g)		Molecular sieve absorption (Stern 1977)	HNO_3 (upon regeneration)	Recycle
CO_2(g)		Vent		Vent
SiO_x dust (in inert gas)		Filter	SiO_x	Recycle or landfill
HF	Aqueous Stream	Add lime (Patterson 1975)	CaF_2	Landfill
HCl		Add lime (Powers 1976)	$CaCl_2$	Treat further or discharge to sewer (dilute if needed)
HNO_3		Add lime (Powers 1976)	$CaNO_3$	Discharge to sewer (dilute)
$FeCl_3$		Add lime (Patterson 1975)	$Fe(OH)_3$	Landfill
Fe_2N		Add lime	$Fe(OH)_3$	Landfill
$AlCl_3$		Add lime	$Al(OH)_3$	Landfill
Al_2N_2		Add lime	$Al(OH)_3$	Landfill
$CaCl_2$		Add Na_2CO_3 (soda ash) (Powers 1976)	$CaCO_3$ (insoluble); NaCl	Landfill; dilute and discharge to sewer
Ca_3N_2		Add Na_2CO_3	$CaCO_3$	Landfill; discharge
Si slurry		Settle out fines	Si	Recycle or landfill
Wafer Production from $SiCl_4$[b]				
$SiCl_4$		Recycled within process		Recycle
H_2(g)		Burn or vent	H_2O	Vent
Si slurry		Settle out fines	Si	Recycle or landfill

Table 3-12. POLYCRYSTALLINE SILICON INITIAL PROCESS WASTE TREATMENTS (concluded)

Waste Stream		Possible Treatment	Probable Effluents	Disposal
Wafer Production by the Seimens Process[c]				
$H_2(g)$		Burn or vent	$H_2O(g)$	Vent to atmosphere
Si Dust		Bag filter	Si	Recycle or landfill
$SiCl_4$[d]		Add slaked lime ($Ca(OH)_2$) (Powers 1976) for liquid	$CaCl_2$; SiO_2	Landfill
Silanes (g)[d] (SiH_4, etc.)[d]	Fumes and Air Emissions	Separate and recycle or vent with inert gas to prevent combustion (Briggs 1980)		Recycle or vent
$SiCl_4(g)$[d]		Liquid sorption; add lime (Powers 1976)	$CaCl_2$, SiO_2	Landfill
HCl(g)	Gas Stream	Liquid absorption (and neutralize with lime) (Stern 1977, Powers 1976)	HCl (or $CaCl_2$)	Recycle (or treat further)

[a] See Sec. 2.0, Fig. 2-8.

[b] See Sec. 2.0, Fig. 2-10.

[c] See Sec. 2.0, Fig. 2-9.

[d] Probably will be recycled within the process if gaseous streams are not contaminated with other waste products.

Table 3-13. POLYCRYSTALLINE SILICON p/n DIFFUSION PROCESS WASTE TREATMENTS

Process Step/Waste	Possible Treatment	Probable Effluents	Disposal
2b. Degrease[a]			
$(CH_3)_2CHOH$	Fluidized bed of activated carbon (Ross 1968)	$(CH_3)_2CHOH$ (sorbed)	Recover and reuse
3b. Etch			
HF (dilute)	Add lime (Patterson 1975)	CaF_2	Landfill
SiF_4 (small amount)	Add lime for SiF_4 in solution (soluble in acid); if gas liberated, may form H_2SiF_6(g) and HF (Briggs 1980) which would require further treatment if not at very low levels	CaF_2; SiO_2 Very low levels of HF(g);H_2SiF_6(g)	Landfill Vent if at very low levels
4b. Clean (same as Etch)			
5b. Diffusion			
B_2O_3(g)	Cool and use liquid absorption	B_2O_3	Solids to landfill liquid to sewer
HCl(g)	Liquid absorption and neutralization (CaO) (Stern 1977)	$CaCl_2$	Landfill
6b. Etch			
HNO_3	Add lime (Powers 1976)	$CaNO_3$ (soluble)	Discharge to sewer
SiO_x	Settle out	SiO_x	Landfill
N_2(g)	Vent	N_2 (dispersed)	Vent
7b. Clean			
HNO_3 (trace)	Add lime (Powers 1976)	$CaNO_3$ (soluble)	Discharge to sewer
8b. Etch			
HF (dilute)	Add lime (Patterson 1975)	CaF_2	Landfill
SiF_4 (dilute)	Add lime; if gas liberated, may form H_2SiF_6 and HF (Briggs 1980) (See 3b.)	CaF_2; SiO_2	Landfill; vent

[a] Process step may not be necessary in an integrated plant where MG-Si is purified, formed into ingots, and sliced into wafers on site if time between process steps and handling is minimized.

Table 3-14. POLYCRYSTALLINE SILICON TIN OXIDE SPRAY PROCESS WASTE TREATMENTS

Process Step/Waste	Possible Treatment	Probable Effluents	Disposal
2a. Degrease[a]			
$(CH_3)_2CHOH$ (isopropyl alcohol)	Fluidized bed of activated carbon (Ross 1968)	$(CH_3)_2CHOH$	Recover and reuse
3a. Etch and Polish			
HF	Add lime (Patterson 1975)	CaF_2	Landfill
HNO_3	Add lime (Powers 1976)	$CaNO_3$	Discharge to sewer (dilute)
Si	Settle out fines	Si	Recycle or landfill
SiF_4 (small amounts)	Add CaO	CaF_2, SiO_2	Landfill
SiO_2 (small amounts)	Settle out	SiO_2	Recycle or landfill
$N_2(g)$ (small amounts)	Vent	N_2	Vent to atmosphere
4a. Rinse and Dry	Same as in Etch and Polish step above, without Si cuttings		
5a. Spray Deposition			
$HCl(g)$	Liquid absorption and neutralization	NaCl	
$SnCl_4$	Cool and treat with lime in solution	SnO_x or $Sn(OH)_2$	Landfill
SnO_x	Cool and collect	SnO_x (insoluble)	Landfill
Cl_2	Fiber mist eliminator (Stern 1977)	Cl_2 or HCl	Recycle
$CH_3CO_2C_2H_5(g)$ (ethyl acetate)	Adsorption with carbon or resin; incinerate (Powers 1976)		Incinerate

[a] Process step may not be necessary in an integrated plant where MG-Si is purified, formed into ingots, and sliced into wafers on site if time between process steps and handling is minimized.

Table 3-15. POLYCRYSTALLINE SILICON EPITAXIAL DEPOSITION PROCESS WASTE TREATMENTS

Process Step/Waste		Possible Treatment	Probable Effluents	Disposal
2c. Etch				
NaOH		See 3c below		
Na_2SiO_3		See 3c below		
3c. Rinse				
NaOH		Neutralize solution (?)		
Na_2SiO_3		Neutralize solution (?) and settle out solid	Na_2SiO_3 (insoluble)	Landfill
4c. Epitaxial Deposition				
Dopant in H_2				
B_2H_6:	$B_2H_6(g)$[a]	Water scrubber (Briggs 1980)	$B_2H_6(g)$ or O_3BH_3 (?)	Discharge water
or AsH_3:	$AsH_3(g)$[a]	Water scrubber (Briggs 1980); lime treatment	$AsH_3(g)$ or AsO_3	Long-term storage in weather-proof containers
or PH_3 or $POCl_3$	$P_2O_5(g)$[a] in gas carrier	Water scrubber (Briggs 1980); forms H_3PO_4; reuse or neutralize	Phosphate	Biological treatment
	$POCl_3(l)$[a] in gas carrier	Water scrubber (Briggs 1980); decomposes in H_2O; neutralize (CsO)	phosphate	Biological treatment
	$H_3PO_4(l)$[a] in gas carrier	Water scrubber (Briggs 1980); recycle or neutralize	phosphate	Biological treatment (municipal)
5c. p/n Junction Diffusion		Same as Table 3-13, 5b		
6c. Etch		Same as Table 3-13, 6b		
7c. Clean		Same as Table 3-13, 7b		
8c. Etch		Same as Table 3-13, 8b		

[a] May be vented if emissions are at very low levels.

Table 3-16. POLYCRYSTALLINE SILICON CELL PROCESSING WASTE TREATMENTS

Process Step/Waste	Possible Treatment	Probable Effluents	Disposal
9. Grid Deposit			
Ti	Collect on Filter	Ti	Recycle
Ag	Collect on Filter	Ag	Recycle
10. Coating			
Depends on coating			
11. Cell Connection			
Solder flux, fumes	Vent	Fumes	Vent
12. Encapsulate	None		

Table 3-17. SOME DANGEROUS PROPERTIES OF POTENTIAL WASTE TREATMENT EFFLUENTS

Copper Sulfide/Cadmium Sulfide Cells

Chemical Compound	Symbol	Toxicity	Explosiveness	Flammability
Ammonia	NH_3	High	Moderate	Moderate
Cadmium Hydroxide	$Cd(OH)_2$	High		
Calcium Chloride	$CaCl_2$	Low		
Calcium Fluoride	CaF_2	High		
Chromous Hydroxide	$Cr(OH)_3$	High		
Copper Hydroxide	$Cu(OH)_2$	Moderate		
Ferrous Hydroxide	$Fe(OH)_2$			
Nickelous Hydroxide	$Ni(OH)_2$	Moderate		
Phosphate	xPO_4	Varies		
Sodium Chloride	NaCl	Low		
Sulfur	S	Low	Moderate	Slight
Sulfuric Acid	H_2SO_4	High		Moderate
Zinc Hydroxide	$Zn(OH)_2$	Low		

Source: From Sax 1979.

Table 3-18. SOME DANGEROUS PROPERTIES OF POTENTIAL WASTE TREATMENT EFFLUENTS

Polycrystalline Silicon Cells

Chemical Compound	Symbol	Toxicity	Explosiveness	Flammability
Aluminum Hydroxide	$Al(OH)_3$	Unknown		
Arsenic Oxide	As_2O_3	High		
Arsine	AsH_3	High	Moderate	Moderate
Boric Acid	H_3BO_3	Moderate		
Boron Oxide	B_2O_3	Low		
Calcium Carbonate	$CaCO_3$	Low		
Calcium Chloride	$CaCl_2$	Low		
Calcium Fluoride	CaF_2	High		
Chlorine	Cl_2	High	Slight	Moderate
Diborane	B_2H_6	High	Slight	High
Ferric Hydroxide	$Fe(OH)_3$			
Formaldehyde	HCHO	High	Low	Moderate
Hydrochloric Acid	HCl	High		
Hydrofluoric Acid	HF	High		
Hydrofluosilicic Acid	H_2SiF_4	High		
Isopropyl Alcohol	$CH_3CHOHCH_3$	Low to Moderate	Moderate	High
Nitric Acid	HNO_3	High	Slight	Moderate
Nitrogen	N_2			
Phosphates	xPO_4	Varies		
Phosphoric Acid	H_3PO_4	Moderate		
Phosphorus Oxychloride	$POCl_3$	High		
Phosphorus Pentoxide	P_2O_5	High		
Silicon	Si			Moderate
Silicon Chloride	$SiCl_4$	High		
Silicon Oxides	SiO_x	Unknown		
Silver	Ag			Moderate
Sodium Chloride	$NaCl_4$	Low		
Stannic Hydroxide	$Sn(OH)_3$			
Stannic Oxide	SnO_4	Low		
Titanium	Ti		Moderate	Moderate

Source: From Sax 1979.

Table 3-19. REACTIVITY CHARACTERISTICS OF POTENTIAL WASTE TREATMENT EFFLUENTS

Copper Sulfide/Cadmium Sulfide Cells

Chemical Compound	Reactivity	Reactive Agent(s)	Reaction Outcome
Ammonium	Moderate	Heat	Toxic Fumes
Cadmium Hydroxide			
Calcium Chloride			
Calcium Fluoride	Dangerous	Heat or Acid	Toxic Fumes
Chromous Hydroxide			
Copper Hydroxide			
Ferrous Hydroxide			
Nickelous Hydroxide			
Phosphate	Dangerous	Heat	Toxic Fumes
Sodium Chloride	Slight	Heat	Irritating Vapors
Sulfur	Dangerous	Heat or Oxidizing Material	Toxic Fumes of Oxides of Sulfur
Sulfuric Acid	Dangerous	Heat, Water, Steam, Oxidizing Materials, or Reducing Materials	Heat and Toxic Fumes
Zinc Hydroxide	Moderate	Heat of Zinc	Toxic Fumes of Oxides

Source: From Sax 1979.

Table 3-20. REACTIVITY CHARACTERISTICS OF POTENTIAL WASTE TREATMENT EFFLUENTS

Polycrystalline Silicon Cells

Chemical Compound	Reactivity	Reactive Agent(s)	Reaction Outcome
Aluminum Hydroxide			
Arsenic Oxide	Dangerous	Heat or Acid	Toxic Fumes of Arsenic
Arsine	Dangerous	Heat or Oxidizing Material	Toxic Fumes of Arsenic
Boric Acid			
Boron Oxide			
Calcium Carbonate			
Calcium Chloride			
Calcium Fluoride	Dangerous	Heat or Acid	Toxic Fumes
Chlorine	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes of Hydrochloric Acid
Diborane	Dangerous	Heat, Water, or Steam, or Oxidizing Material	Explosion, Hydrogen, and Toxic Fumes
Ferric Hydroxide			
Formaldehyde	Moderate	Air	Irritating Vapors
Hydrochloric Acid	Dangerous	Water or Steam	Toxic and Corrosive Fumes
Hydrofluoric Acid	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes of Fluorides
Hydrofluosilicic Acid	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes of Fluorides
Isopropyl Alcohol	Dangerous	Heat or Oxidizing Material	Explosion and Fire
Nitric Acid	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Nitrogen			
Phosphates	Dangerous	Heat	Toxic Fumes
Phosphoric Acid	Dangerous	Heat	Toxic Fumes of Oxides of Phosphorus
Phosphorus Oxychloride	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Phosphorus Pentoxide	Dangerous	Water, Steam, or Reducing Material	Heat, Fire, and Toxic Fumes
Silicon	Dangerous	Oxidizing Material or Heat with Water or Steam	Hydrogen Gas
Silicon Chloride	Dangerous	Heat, Water, or Steam	Toxic and Corrosive Fumes
Silicon Oxide			
Silver (Powder)	Moderate	Heat	Explosion
Sodium Chloride	Dangerous	Heat or Acid	Toxic Fumes
Stannic Hydroxide			
Stannic Oxide			
Titanium (Powder)	Moderate	Heat	Explosion

Source: From Sax 1979.

Table 3-21. TOXICITY CHARACTERISTICS OF POTENTIAL WASTE TREATMENT EFFLUENTS
Copper Sulfide/Cadmium Sulfide Cells

Chemical Compounds	Acute Local	Acute Systemic	Chronic Local	Chronic Systemic
Ammonia	High		Low	
Cadmium Hydroxide	High	High		High
Calcium Fluoride	High	High	Low	High
Chromous Hydroxide	High		High	High
Sulfuric Acid	High		Moderate	

Source: From Sax 1979.

Table 3-22. TOXICITY CHARACTERISTICS OF POTENTIAL WASTE TREATMENT EFFLUENTS
Polycrystalline Silicon Cells

Chemical Compound	Acute Local	Acute Systemic	Chronic Local	Chronic Systemic
Arsenic Oxide	High	High	Moderate	High
Arsine	High	High		
Calcium Fluoride	High	High	Low	High
Chlorine	High			
Diborane	High	High		
Hydrochloric Acid	High	High	Moderate	
Hydrofluoric Acid	High	High	Moderate	High
Hydrofluosilicic Acid	High	High		High
Nitric Acid	High	High	Moderate	
Phosphorus Oxychloride		See Hydrochloric Acid		
Silicon Chloride	High			

Source: From Sax 1979.

3.2.3.1 Discharge to Water—Aqueous Wastes

Generally, it is easiest and most convenient to dispose of aqueous wastes into a body of water or a local sewage system. However, in recent years regulations have greatly curtailed the amount of untreated wastes that can be discharged into either of these places. The EPA has set water quality criteria that have limited the disposal of such substances as ammonia, boron, cadmium, chlorine, chromium, iron, nickel, phosphorus, and silver into bodies of water (EPA 1976). Many states have issued concentration limits for certain pollutants. Restrictions on the disposal of chemicals into a municipal sewage system usually fall under the jurisdiction of local authorities; each limits the release of those substances with the greatest local environmental impacts.

For almost all industrial aqueous wastes, some type of treatment can be used that either breaks up the regulated contaminants into lower concentrations or changes the character of the agents so that they may be discharged safely into the environment, either directly into a body of water or indirectly through a municipal system. Table 3-23 shows some of the general limiting values for a municipal sewage system and some of the treatment methods used to achieve these values. Table 3-24 lists some chemical compounds that may be disposed of (after pretreatment in some cases) by stream discharges. The problem that ultimately restricts the disposal of aqueous waste in these ways is the cost of treatment, which often makes other disposal options economically more attractive. However, some types of waste from the production of photovoltaics (e.g., ammonia, calcium chloride, calcium nitrate, hydrochloric acid, sodium chloride, and sulfuric acid after necessary dilution or neutralization) will be disposed of by these two methods. Laboratory and/or field studies will be necessary to determine exactly the allowable quantities and types of treatment.

3.2.3.2 Landfill of Solid, Sludge, and Ash Wastes

With the enactment of stricter water discharge regulations in the 1970s, more wastes are being deposited in landfills. Rules and regulations regarding the disposal of wastes in landfills have been set by the EPA under the authority of the Resource Conservation and Recovery Act. EPA also may classify wastes as "hazardous" or "nonhazardous." Solid wastes in both categories can be disposed of in landfills, although additional precautions must be taken with hazardous wastes.

Laboratory tests are generally required to identify the characteristics of industrial wastes properly. According to the EPA, the waste stream of an industrial generator is considered hazardous if the stream possesses corrosive, ignitable, reactive, or toxic characteristics, and the generator produces quantities in excess of 1000 kilograms per calendar month. There may be cases in which a company may find it more economical to assume its waste to be hazardous rather than to spend the money to prove otherwise. Because advanced material photovoltaic cells are currently in various stages of development and there are uncertainties about the quantities of waste in the waste streams, it is not possible to describe in detail their hazardous or nonhazardous nature.

However, the presence of some compounds (400 presently specified by the EPA) automatically places a waste in the hazardous category. The quantity of waste is again crucial, since small-volume waste generators may be exempt from special requirements. Compounds on the EPA list which may result from the selected advanced material photovoltaic processes include: arsine, cadmium compounds, chloride, chromium compounds, ethyl acetate, fluorine, hydrofluoric acid, hydrogen sulfide, formaldehyde, nickel compounds, nitrogen dioxide, nitrogen tetroxide, phosphine, and silver.

Table 3-23. INDUSTRIAL CONTAMINANTS AND THEIR GENERAL LIMITING VALUES FOR DISCHARGE INTO MUNICIPAL SEWAGE SYSTEMS

Contaminant:	Concentration generally limiting for municipal sewage systems:	Reason for limitation:	If contaminant is excessive, the acceptable pretreatment generally required is:
1. Flow	50% of municipal sewage flow	Causes sewage treatment system to react differently from its normal pattern as designed for municipal sewage. Unequalized or unproportioned industrial flow is especially troublesome	1. Equalization and proportioning 2. Recirculation and reuse within industry to reduce flow 3. Redesign sewage treatment plant to react more specifically to industrial waste
2. BOD 5,220° C	300 ppm	Exerts a disproportionately high percentage of oxygen-demanding organic matter to municipal wastewater	1. Change in industrial manufacturing process 2. Equalization 3. Biological pretreatment plant
3. Color	Visible in dilutions of 4 parts sewage to 1 part industrial waste	Color is normally not removed by domestic sewage treatment plants, will appear in the combined, treated effluent, will be readily detected and visually undesirable from an aesthetic standpoint	1. Change in industrial manufacturing process 2. Chemical pretreatment to remove color 3. Equalization and/or proportioning
4. Suspended solids	350 ppm	Overload disproportionately normal domestic sewage treatment plants	1. Change in industrial manufacturing process 2. Equalization 3. Sedimentation pretreatment plant
5. pH	5.5-9	Corrosion of sewers and treatment plant equipment causes a diminution or a malfunctioning of biological treatment units	1. Equalization 2. Neutralization 3. Change in industrial manufacturing process

Table 3-23. INDUSTRIAL CONTAMINANTS AND THEIR GENERAL LIMITING VALUES FOR DISCHARGE INTO MUNICIPAL SEWAGE SYSTEMS (continued)

Contaminant:	Concentration generally limiting for municipal sewage systems:	Reason for limitation:	If contaminant is excessive, the acceptable pretreatment generally required is:
6. Grease	100 ppm	Interferes with plant operating equipment—including aeration, primary sedimentation, etc. Overloads sludge-handling treatment units such as scum collection, digestion, and sludge-drying beds	1. Change in industrial manufacturing process 2. Install grease traps or remove pretreatment units
7. Heavy metals Cr, Sn, Pb, Zn, Hg, Cu, Ni, etc.	1 ppm Cu, Cr 5 ppm Zn, Ni	Inhibit biological action in municipal sewage units, such as activated sludge, trickling filters, and especially sludge digesters	1. Equalization 2. Chemical pretreatment and sedimentation pretreatment
8. Inorganics and other toxic chemicals	None so as to be toxic to bacteria serving the treatment plant or people or animals working in or near the sewage plant	Exhibit toxicity toward biological treatment units and cause health hazard to man and animals	1. Change industrial plant process 2. Use of advanced pretreatment wastewater techniques
9. Inflammable liquids, foaming agents, rags, solidifiable greases, ashes, metals, cinders, mud, straw, glass, feathers, tar, plastics, wood, chicken, manure, etc.	None in such quantities that will cause either a hazard to the environment or a nuisance to the operation of the plant	Cause a nuisance and interfere with the normal operation of the domestic sewage treatment plant	Removal by process change or physical means, such as screening

Table 3-23. INDUSTRIAL CONTAMINANTS AND THEIR GENERAL LIMITING VALUES FOR DISCHARGE INTO MUNICIPAL SEWAGE SYSTEMS (concluded)

Contaminant:	Concentration generally limiting for municipal sewage systems:	Reason for limitation:	If contaminant is excessive, the acceptable pretreatment generally required is:
10. Temperature	150°F	Hastens corrosion, drives out dissolved oxygen, volatilizes hazardous gases such as H_2S	1. Change in industrial process 2. Use of cooling water systems
11. Storm water	None resulting from direct connections or faulty sewer construction	Occupies valuable volume capacity of domestic and industrial sewers	1. Construct separate sewer 2. Use better construction procedures
12. Refractory organic matter	None	Contaminates the municipal sewage plant effluent for possible reuse downstream for water supplies	1. Change in industrial manufacturing process 2. Carbon adsorption pretreatment
13. Refractory mineral matter	Boron 0.7 ppm NaCl 1000 ppm	Contaminates the municipal sewage plant effluent for possible reuse for irrigation waters	1. Change in industrial manufacturing process 2. Pretreat industrial plant wastewater by membrane separation or distillation

Source: N. L. Nemerow, Industrial Water Pollution. 1978.

Table 3-24. SOME CHEMICAL COMPOUNDS THAT MAY BE DISPOSED OF BY STREAM DISCHARGE

Compound	Treatment
Ammonium Chloride:	Pretreatment involves addition of sodium hydroxide to liberate ammonia and form the soluble sodium salt. The liberated ammonia can be recovered and sold. After dilution to the permitted provisional limit, the sodium salt can be discharged into a stream or sewer.
Boron Chloride:	Pretreatment involves addition of soda ash-slaked lime solution to form the corresponding sodium and calcium salt solution. This solution can be safely discharged after dilution.
Calcium Chloride:	Pretreatment involves precipitation with soda ash to yield the insoluble calcium carbonate. The remaining brine solution, when its sodium chloride concentration is below 250 mg/l, may be discharged into sewers and waterways.
Hydrochloric Acid:	Soda ash-slaked lime is added to form the neutral solution of chloride of sodium and calcium. This solution can be discharged after dilution with water.
Nitric Acid:	Soda ash-slaked lime is added to form the neutral solution of nitrate of sodium and calcium. This solution can be discharged after dilution with water.
Phosphorus Oxychloride:	Decompose with water forming phosphoric and hydrochloric acids. Neutralize acids and dilute if necessary for discharge into the sewer system.
Silicon Tetrachloride:	Pretreatment involves addition of soda ash-slaked lime solution to form the corresponding sodium and calcium salt solution. This solution can be safely discharged after dilution.
Potassium Fluoride:	Pretreatment involves reaction with an excess of lime, followed by lagooning, and either recovery or landfill disposal of the separated calcium fluoride. The supernatant liquid from this process is diluted and discharged to the sewer.

Source: Philip W. Powers, How to Dispose of Toxic Substances and Industrial Wastes. Noyes Data Corporation; 1976.

If the waste stream is determined to be nonhazardous, either with or without treatment, it can be disposed of into a conventional sanitary landfill. The Resource Recovery and Conservation Act regulations for operating a sanitary landfill must be followed. For instance, the solid waste must be deposited and compressed in a prepared trench, which is then covered daily with six inches of compacted soil. When the landfill reaches its capacity, two additional feet of soil are placed over it. As long as land is available, a properly designed and operated conventional sanitary landfill is an effective means of solid waste disposal.

If a waste stream is classified as hazardous, a sanitary landfill can be modified to make it legally acceptable for receipt of hazardous materials. Taken together, these modifications result in a "chemical waste landfill." In general, such operations can protect surface and subsurface waters from hazardous waste deposits and prevent hazards to public health and the environment for an extended period of time. To do so, the sites must be located or engineered to avoid direct hydraulic continuity with surface and subsurface waters, generated leachates need to be contained, and subsurface flow into the disposal area must be eliminated. In addition, federal regulations require that incompatible wastes be separated to prevent dangerous reactions, that operators of facilities obtain special operating permits, and that site owners monitor and maintain closed chemical waste landfills for 30 years to be sure the wastes do not leak into the environment.

Some hazardous wastes will require treatment or prepreparation before disposal in chemical waste landfills. Such treatment or preparation is designed to protect public health and the environment by limiting leaching of the waste. Some common treatment methods include: (1) chemical fixation, solidification; (2) detoxification; and (3) encapsulation.

In chemical fixation, specific chemicals are mixed with the waste sludges, and the resulting mixture is pumped onto the land, where solidification occurs some time between a few days and a few weeks (depending on the process). Chemical fixation processes can be broken down into four major categories: cement-based techniques, pozzolanic or lime-based techniques, thermoplastic binders, and organic binders. No company has a solidification process that can handle everything, but there are claims that at least one process can be selected and tailored to handle anything. Although the resulting solidified waste-sludges are expected to cause less environmental damage than if the wastes were deposited on land "as is," the main problem with the different techniques is that they have not received enough testing under actual field conditions to determine their long-term resistance to deterioration and leaching.

Detoxification prior to landfill disposal can often be accomplished by thermal, chemical, or biological processes. Included are such techniques as ion exchange, pH adjustment or neutralization, oxidation-reduction, pyrolysis, incineration, activated sludge, aerated lagoons, waste stabilization ponds, and trickling filters (see the Appendix). The primary advantage of these techniques is that the hazardous waste is "destroyed," so there is no further need for containment or monitoring. The chief disadvantage is that these methods are applicable to only a limited percentage of hazardous wastes.

Those wastes that are not amenable to detoxification or solidification may be encapsulated in some permanent material before disposal. Available materials include concrete, molten asphalt, and plastics (e.g., polyurethane or polyethylene). Leachable heavy metals are examples of wastes that may require encapsulation before disposal into the land. In some cases, the resulting encapsulated wastes will require casting in drums before disposition in the landfill. The purpose of encapsulation is to limit leaching of potentially toxic materials by containment from water contact with the hazardous substances or their immediate containers.

Because the new hazardous waste regulations require special precautions for disposal of hazardous waste in landfills, and thus increase the cost of disposal, other land disposal options are being used more frequently. Correspondingly, incineration of the waste stream to reduce its volume—popular before the 1970s and then curtailed because complying with the air pollution regulations made it economically unattractive—is once again being relied on.

Incineration is a controlled process that uses combustion to convert a waste to a less bulky, less toxic, or less noxious material for land disposal. The principal products of incineration with regard to volume are carbon dioxide, water, and ash; the products of primary concern because of their environmental effects are compounds containing sulfur, nitrogen, and halogens. When the combustion products from an incineration process contain undesirable compounds, a secondary treatment—such as afterburning, scrubbing, or filtration—is required to lower concentrations to acceptable levels before release into the atmosphere. The solid and liquid effluents from the processes may also require treatment before their ultimate disposal.

Incineration can be used in the disposal of both organic and inorganic wastes, although organics are usually more combustible and thus more cheaply and efficiently disposed of. Organic chemicals that may be subject to ultimate disposal in concentrated forms by incineration include acetic acid, ethyl acetate, formaldehyde, and methanol. Inorganics often require some type of pretreatment before incineration. For instance, fluorine must be pretreated by reaction with a charcoal bed. The product of the reaction is carbon tetrafluoride, which is usually vented. Residual fluorine can then be combusted by a fluorine-hydrocarbon air burner followed by a caustic scrubber and stack.

An alternative to landfills (with or without waste incineration) currently receiving some attention is deep-well injection. Deep-well injection involves pumping liquid waste into porous sandstone and limestone formations 3,000-10,000 ft below the earth's surface where they are permanently stored. Although this technique has been used since the 1920s, it is being criticized increasingly by EPA and others. Deep-well injection has been used for several of the waste streams that may result from advanced photovoltaic cell processes: sodium chloride, caustic and acidic wastes, ammonia, hydrogen chloride, and detergents.

3.2.3.3 Energy Recovery and Recycling

The rising costs of waste disposal (see Appendix) are causing industry to investigate energy recovery and materials recycling. These options both decrease the volume of the waste stream and yield a resource. For example, two of the potential wastes from polycrystalline silicon cell production, sodium fluoride (NaF) and hydrofluoric acid (HF), have very small markets and pose environmental and health problems in their handling and disposal. As an alternative, they are used to manufacture synthetic cryolite (Na_3AlF_6) which is used extensively for electroreduction of aluminum from alumina.

Examples of cell fabrication process effluents that can be recycled include gold, silver, titanium, and such acids as hydrochloric acid, nitric acid, and sulfuric acid. Feasibility will depend heavily on recycling costs versus the costs of purchasing new materials, the costs of waste disposal, the markets for the recycled materials, and their concentrations in the waste stream.

SECTION 4.0

ENVIRONMENTAL, HEALTH, AND SAFETY EFFECTS OF INSTALLATION, OPERATION AND MAINTENANCE, AND DECOMMISSION

The potential for both positive and negative environmental health and safety effects occurs throughout a photovoltaic system's lifetime. Effects can result from direct physical changes in the environment, such as those that occur during mining or deployment site preparation, or from indirect changes associated with the release of fabrication pollutants or with the system's physical presence (e.g., shading). The previous section presented the pathways (air emissions; solid and liquid waste streams; waste disposal) by which environmental, health, and safety effects can occur from the selected advanced photovoltaic cell fabrication processes. This section is a summary of potential effects resulting from installing, operating and maintaining, and decommissioning photovoltaic systems composed of polycrystalline silicon and copper sulfide/cadmium sulfide solar cells. Discussions are based primarily on past research conducted for single-crystal silicon photovoltaic cells. Areas where the effects of poly-Si and Cu_2S/CdS production and use may differ from those of single-crystal silicon cells are also discussed.

4.1 EFFECTS OF INSTALLATION

Solar energy systems applications can be divided into three major categories: residential; commercial, industrial, intermediate load; and central station. Remote applications such as supplying power to ocean buoys, agricultural pumping, microwave repeater stations, etc., are not addressed in this report since their total market size is relatively small compared with the three major applications.

Installation involves site preparation (if necessary); mounting of the array into some kind of physical support (for example, a roof or anchored metal support bars); and electrical connection with the utility grid network energy storage, or back-up system. As noted, energy storage is assumed to be supplied by the utility grid network. Electrical interconnection of poly-Si and Cu_2S/CdS systems will involve using the same methods as for single-crystal silicon photovoltaic systems. As a result, this section discusses only site preparation and mounting of arrays.

The amount of site preparation required depends on both the application and the specific site. Site preparation requirements for poly-Si and Cu_2S/CdS will be like those for single-crystal silicon systems. Arrays will be shipped from the factory in prefabricated form; i.e., encapsulated, wired and framed, probably with extruded aluminum molding. For residential and intermediate load applications, arrays will probably be mounted on rooftops if adequate areas are available. For retrofit, arrays will require attachment to support structures, such as aluminum braces. New construction may orient roof angles and allow enough roof area to permit the photovoltaic system to function as the roof itself in addition to supplying the structure with electricity. A typical residential system will be about 8 kW and have an area of 500-1200 ft^2 (46.5 m^2 x 111.5 m^2), depending upon local insolation. If the roof area is not adequate for placement of the photovoltaic system, arrays may be mounted nearby at ground level. Wood or metal vertical array supports will have to be ground mounted. Depending on the site [e.g., public access; frequency of high winds; surface characteristics (asphalt, concrete, or compacted soil)], concrete pads may be required for placement of the vertical array supports.

Few, if any, ecological or public health effects will result from installing roof-mounted photovoltaic systems. Most residential and intermediate load sites are already highly disrupted ecologically. Some fugitive dust (causing nose, lung, and eye irritation) may be released if ground-mounted arrays are necessary.

The principal risks of installing roof-mounted residential and intermediate load systems will be to workers. Risks to rooftop installers will be similar to risks in the general roofing business and will primarily involve falls. In addition, a shock risk also exists during electrical interconnection of the arrays with the use center and the utility grid. However, the occupational hazards from installing poly-Si and Cu_2S/CdS systems should not differ from those associated with flat-plate single-crystal silicon systems.

Installation of central station photovoltaic systems differs markedly from residential and intermediate load applications. Central station applications will require commitment of large tracts of land, much of which previously may have been undisturbed. Land use estimates vary considerably, but a representative estimate is 2 hectares per MW_e for photovoltaic flat-plate systems (Turner 1980). This estimate translates to 7.72 mi^2 per installed GW_e. Although it is unlikely that a GW_e-scale installation will occur at one site, installations in the size range of 100 MW_e are possible and would require a little less than a square mile (about 2.5 km^2) of land. The institutional issues (e.g., availability of a properly zoned site with acceptable insolation, slope, and access characteristics) of acquiring a one-square-mile (2.59 km^2) site must be considered for each installation and should not be discounted. In some areas, the Endangered Species Act may be a key factor in whether large tracts of land can be procured. In addition, local and state environmental regulations must be complied with. Often, these are stricter and more numerous than federal regulations (Turner 1980).

The aesthetic acceptability of a photovoltaics installation may have an effect on whether a particular site may be utilized. However, aesthetic reactions to photovoltaic systems must be balanced against the aesthetic aspects of competing energy technologies. For example, although siting of a 1000-MW_e photovoltaic system will require far more land than a 1000-MW_e coal facility, the environmental (including land use), health, and safety effects of mining coal for 30 years will not occur in connection with the photovoltaics system.

Because of favorable insolation levels and a large number of clear, sunny days, deserts are viewed as favorable deployment sites for central station photovoltaic systems. However, the characteristics that make deserts attractive sites for photovoltaic systems also make them ecologically fragile. The major environmental impacts of installing photovoltaic systems on desert sites are associated with site clearing and preparation and result from soil compaction, dust, and potential spillage of toxic materials such as oil, lubricants, gasoline, etc. The site itself will contain interconnected photovoltaic arrays; roads to provide access to the site and to individual panels for servicing and cleaning; power conditioning facilities; maintenance, control, and office buildings; and transmission lines.

Much of the field data available on the environmental effects of desert installations have been collected at the solar thermal electric central receiver test site near Barstow, California. Most of this data is readily applicable to deployment of central station photovoltaic systems in a desert, but probably represents a worst-case situation since the Barstow site was totally cleared of vegetation, graded, and compacted. In some cases, the deployment site for small installations may require little or no grading if it is fairly level or has only a gentle slope. In this instance, soil compaction would be greatly reduced compared with Barstow.

However, for large installations, such as a 100-MW_e photovoltaic facility (which would require about 200 hectares of land), grading and clearing probably will be required. In this instance, soil destabilization will occur and be accompanied by fugitive dust and erosion problems if control measures are not implemented.

Soil compaction and dust problems result from worker and construction vehicle activity. The surface area of many previously undisturbed desert sites is covered with desert crust or desert pavement that protect the underlying surfaces from wind and water erosion. Desert crust, a layer of fine materials up to 6 mm thick, appears to form slowly from the compaction associated with rainfall, but the exact mechanism of formation is unknown. Desert pavement is a fairly densely packed layer of pebbles and stones ranging in size from 0.5-20.0 cm. Desert pavement forms as water carries off fine sand, silt, and clay, leaving the larger pebbles and stones encrusted (cemented) with various salts, gypsum, lime, and silicates (Davidson and Grether 1977, Patten 1978). Both are fragile and easily broken by the weight of workers and construction vehicles. As a result, wind and water erosion will increase in these areas.

At some installations, the site may be totally cleared of vegetation. When the Barstow site was cleared, graded and compacted, wind erosion was severe. An estimated 160 MT of sand blew downwind from the 53-hectare site. Small dunelets within 100 m of the site increased in size by up to 18 cm (Turner 1980). The large downwind transport of sand also impaired the growth of surrounding vegetation. Complete clearing also destroys the site's ecosystem and drastically decreases the number and kinds of organisms. If the site is oiled or paved to suppress further wind erosion, the immediate area will become essentially lifeless (Romney et al. 1979).

The use of heavy construction vehicles causes compaction of the soil. In addition, vehicle tracks may cause gulleys to form by stimulating erosion. Soil compaction will drastically affect burrowing species and the infiltration of water, which then affects plant growth, runoff, and subsurface geohydrology (Patten 1978, Davidson and Grether 1977). Some ecologists believe soil compaction is potentially serious; at some sites it may be irreversible (S. Smith in Patten 1978).

The degree of soil compaction will be influenced greatly by the site (e.g., soil structure and presence of access roads) and the number and weight of construction vehicles. With care, soil compaction, wind erosion, and runoff can be minimized by limiting construction activity and site clearing to only what is absolutely necessary.

The occupational hazards of installing central station photovoltaic systems have not been addressed in detail. However, most occupational risks will closely approximate those of any large construction activity and will not differ for single-crystal silicon, poly-Si, or Cu_2S/CdS photovoltaic systems. The possibility of electrical shock exists for all application and system types. Photovoltaic systems produce direct current (DC) which is generally (except in the case of some remote applications) converted to alternating current (AC). Although DC presents less of a shock hazard than AC, levels of direct current are sufficient to warrant worker caution for all application types (EEA 1980).

4.2 EFFECTS OF OPERATION AND MAINTENANCE

The 20-30 years' operation and maintenance lifetime for photovoltaic systems is environmentally attractive for a number of reasons. There is no consumptive water use by the photovoltaic systems selected for study, with the possible exception of periodic panel washing at some installations. Air pollutants are not released except in atypical events such as fires or outgassing of toxic gases should the system overheat. Cooling systems are not required for polycrystalline silicon and copper sulfide/cadmium sulfide designs; thus, the thermal pollution of cooling water and the effects of cooling tower drift (containing biocides, etc.) will not occur. Noise pollution is negligible to nonexistent, depending upon the application, and there will be no releases of ionizing radiation. The photovoltaic panels are sealed during encapsulation so that entry of cell materials into the environment should not occur unless panels are cracked or broken. These benefits of photovoltaic-generated electricity are substantial and continual throughout system operation. However, this does not imply that operation and maintenance (O&M) of poly-Si and Cu_2S/CdS photovoltaic systems are without any ecological, health, and safety effects.

4.2.1 Residential, Commercial/Industrial, and Intermediate Load Applications

As discussed, residential, commercial/industrial, and intermediate load systems generally will be installed at ecologically disturbed sites, precluding significant additional ecological effects from operating and maintaining these systems. However, health and safety risks must be considered and may be of more importance for residential installations than for central power station applications. Because residential systems are sited in more densely populated areas than central station systems, they entail a higher potential for site access and thus for greater exposure hazards to more people in the event of releases of toxic materials. In addition, roof-mounted systems present hazards to maintenance personnel that ground-mounted systems do not. The potential health and safety effects of residential, commercial/industrial, and intermediate load applications follow.

Building occupants experience a risk if roofs are not structurally sound enough to accommodate the weight of roof-mounted photovoltaic systems, especially during extreme loading situations (such as heavy snowfall). This is a potential problem for all photovoltaic systems regardless of cell-type (e.g., single-crystal silicon, poly-Si, or Cu_2S/CdS). The structural integrity of roofs in newly constructed buildings fitted with photovoltaic systems will probably be assured through some sort of minimum property standards. These standards would probably be similar to those suggested for flat-plate solar heating systems (see, for example, DOE 1980) and may require consideration of wind, hail, and snow loads in roof design. Ensuring proper loading of roofs in retrofit installations may be accomplished through building permit issuance procedures.

Breakage of photovoltaic panels could present health and safety risks in two ways: (1) fragments of broken glass and (2) release of toxic materials. Encapsulation of both poly--Si and Cu_2S/CdS cells requires glass. Glass breakage could occur during inclement weather (e.g., hail or high winds) or because of vandalism. Fragments of broken glass would present hazards to children, especially in residential applications, and to personnel repairing or replacing damaged panels. Hazards from broken glass can be minimized two ways. First, access to the site can be restricted with fences; they may also reduce vandalism problems. Site access restriction appears feasible for most commercial/industrial and intermediate load installations (EEA 1980). The second option is to use heat—tempered glass for panel encapsulation. Tempered glass "beads" when broken, presenting a lower risk of cuts and lacerations than normal glass fragments do.

Cracking of encapsulant materials or breakage of panels, or both, may allow cell contents to enter the environment; this poses health and safety risks. The hazard for poly-Si panels is minimal because of the stability and low toxicity of silicon. Silicon will not leach until water has a pH of 2-3, a condition not found in environmental conditions, even acid rain. Breakage of Cu_2S/CdS photovoltaic panels presents a greater hazard because of the toxicity of cadmium. Cadmium sulfide is relatively immobile, but leaching will occur at pH 4.5 or lower (BNL 1980b). It is possible that some cadmium may leach from cracked panels subjected to acid rain, or from cell fragments released from broken panels. However, the potential for health hazards is very small because (1) broken panels will probably be replaced before any appreciable leaching can occur, and (2) it is unlikely that rain or other water affecting the panels will be acidic enough to mobilize significant amounts of the cadmium present in the cells. To fully assess this hazard, however, data are needed on whether acid rain does in fact leach cadmium, and, if so, the chemical form and concentration of cadmium in the leachate must be examined. Cell fragments from broken Cu_2S/CdS panels may present a poison hazard if they are ingested by children or animals. The hazard of severe poisoning is remote, however, because cell fragments will be sharp and therefore difficult to ingest; cadmium in large doses is an emetic (Esmen et al. 1973); and panels will probably be replaced soon after they are damaged. One study has estimated that if a child ate 0.09 m^2 (1 ft^2) of Cu_2S/CdS cells in which the CdS was 10 μm thick, a total of 4.55 gm (0.01 lb) CdS would have been ingested (ERDA 1977). Although the toxic effect of a single dose this large is unknown, it is certainly an extreme-case calculation which has little likelihood of occurring. Esmen et al. suggested also that a child would have to eat 5 cm^2 of Cu_2S/CdS cells (in which the CdS layer was 30 μm thick) before experiencing a severe reaction. As mentioned, the likelihood of this occurring is extremely remote, first because cadmium is an emetic and next because cell fragments would be too sharp to swallow.

Release of toxic air pollutants from poly-Si and Cu_2S/CdS panels will not occur except under conditions such as system overheat (resulting in offgassing of volatile compounds) and fire. Release of toxic gases and flammability are highly influenced by the encapsulate monomer. For a panel using methyl methacrylate as an encapsulant, the following was observed: "In one test of silicon cell arrays, cutting an interconnect wire resulted in arcing, smoking and occasional flames" (Briggs and Owens 1979, as cited in EEA 1980). The encapsulation method discussed for poly-Si cell approaches utilize ethylene vinyl acetate (EVA). The amounts of EVA present in the panels currently meet fire codes for plastics in roof-mounted structures. However, to ensure that fire-related hazards are minimal, panel module design are undergoing fire testing by Underwriters Laboratories (UL) under the sponsorship of the Jet Propulsion Laboratory (JPL). Encapsulation techniques for Cu_2S/CdS panels have not been firmly established; thus, all fire hazards cannot be fully assessed at this time.

Fire hazards are probably greatest for roof-mounted systems because external flames could cause fires and combustible materials are close by. Materials present in poly-Si panels should exhibit the same hazard potentials as single-crystal silicon array materials. Silicon and most encapsulant materials (e.g., glass, aluminum) are relatively inert and should remain in the ash formed during the fire. Dopant levels (ppm levels) in cells are extremely low and should not present a health hazard to firefighters or to clean-up crews. As previously noted, amounts of EVA present in panels currently comply with fire codes.

The theoretical health hazard of fires involving Cu_2S/CdS photovoltaic systems has been addressed for panels mounted on a one-story, single-family, wood frame house (Esmen et al. 1973). The roof-mounted Cu_2S/CdS system was assumed to have 225 m^2 of panels. The CdS layer was designated to be 30 μm thick, yielding a total of 28 kg of CdS per house. Fire conditions were assumed to be as follows: (1) ample oxygen was present to convert all the CdS to the more toxic cadmium oxide (CdO), (2) burning was rapid and uniform, (3) the ash would contain only 70% of all CdO, and (4) all the CdO had an aerodynamic equivalent size of 1 μm. Under these conditions, the calculated upper bound concentration of CdO at ground level adjacent to the fire was 184 $\mu g/m^3$. Although this level is excessive, it is unlikely that anyone would be this near to the fire without adequate respiratory protection. (For example, toxic levels of carbon monoxide, estimated to be 2500 ppm, would be expected and presumably protected against.) To generate a more realistic estimate, the authors calculated that CdO levels 25 m downwind (a reasonable distance for unprotected persons to be) would be 1.96 $\mu g/m^3$, or about three times the maximum ambient concentrations of cadmium. In summary, the authors concluded that (1) there would be little public health danger from a fire involving Cu_2S/CdS cells, (2) health hazards would exist for firefighters but could be controlled using proper respirators, (3) at least 90% of the CdO would probably end up in the ash in a form combined with other materials, and therefore would not be an air contaminant; and (4) atmospheric cadmium emissions from fires could be controlled through proper building design.

Fire hazards thus can be minimized if design and installation precautions are followed, such as those outlined in the recent Programmatic Environmental Assessment for photovoltaic systems (EEA 1980): (1) flammability testing of all materials used in panels; (2) careful circuit design and component selection; (3) use of devices to detect potential fire-causing failures; (4) proximity of adequate fire extinguishers: (5) use of an automatic or passive firefighting system (may be practical only for commercial/industrial or intermediate load applications); (6) emergency procedures; and, possibly, (7) component separation or size limitations, or both.

A shock hazard exists for all known photovoltaic systems and would not be unique for the poly-Si or Cu_2S/CdS options. This hazard will probably be reduced through building and electrical codes which will ensure use of safe and adequate methods for insulation, grounding, mounting techniques, and access restriction (if necessary). Shock hazard is a function of both current and voltage. Voltage must be at a high enough level to cause a current to pass through a person. Suggested voltages for residential and commercial applications are 200-250 volts. Current is the factor that causes injury from an electrical shock (EEA 1980). Photovoltaic systems produce direct current at levels sufficient to cause electrical shock. The DC is generally converted to AC, which has a higher shock hazard (EEA 1980). This conversion will probably not be effected at the point where wires exit the panels, which limits the shock hazard generally for panel maintenance workers. Hazards can be further minimized by convenient location of breaker switches (EEA 1980). Electrocution and shock hazards associated with photovoltaic systems are being investigated by UL with the support of JPL (BNL 1980a).

Maintenance workers may have contact with hot, dangerous surfaces. However, this should not occur if panels are properly designed and free from wiring defects. Maintaining roof-mounted panels may involve fall hazards. However, these hazards should be no greater than those for maintaining flat-plate solar heating panels. The risk of falls can be reduced by worker training and panel deployment configurations that allow easy access (EEA 1980).

4.2.2 Central Station Applications

Central station photovoltaic systems will require a 20-30 year commitment of large tracts of land that may be previously undisturbed. Many initial installations will probably be located in desert sites because of favorable insolation conditions. The physical site changes associated with installation (e.g., site clearing and grading) and the presence of the photovoltaic panels themselves will produce a number of abiotic changes which will in turn induce changes in the number and diversity of plant and animal populations. Thus, ecological changes are of concern for central station photovoltaic systems, especially in fragile and slow-to-recover locations such as deserts.

Health and safety considerations for central station applications will be similar to residential, commercial/industrial, and intermediate load applications. However, central station applications will probably employ only ground-mounted panels that are not as near to combustible materials as roof-mounted panels. Central station systems will probably be located in fairly remote locations, minimizing the potential of exposing a large numer of people to toxic gases in case of fire, etc. In addition, access to central station facilities will probably be limited. The hazards of shock and of contact with hot surfaces will be the same as for residential applications. Voltages for utility applications are much higher than for residential applications; the range recommended in building codes is 1500-2000 volts (EEA 1980). As noted, the fire hazard will probably be lower for central station than for residential applications.

The ecological effects of poly-Si and Cu_2S/CdS photovoltaic systems will be the same as for systems using single-crystal silicon cells. Effects will be due to biotic reactions (big plants and animals) to abiotic changes brought on by the physical presence of the panels, past site preparation techniques, and by the methods used for site stabilization. The abiotic changes will affect microclimate, which will in turn affect plant and animal species.

Installation activities based upon site clearing will force the emigration of mobile species, destroy sessile species, create fugitive dust problems, and compact the soil. The site will have to be stabilized to alleviate resulting erosion, runoff, and dust problems. Stabilization can be achieved by two principal methods: (1) paving or graveling the area under the panels or (2) using plants. Paving will control fugitive dust, but will be expensive and may create runoff problems for adjacent land areas and will eliminate deep water drainage which may have occurred in the past. Graveling will stabilize the soil under panels (i.e., decrease runoff erosion) but may create additional dust problems. In addition, paving or graveling will make the site essentially lifeless and may induce significant changes in albedo (EEA 1980, Romney et al. 1979).

For long-term ecological and soil stability, using plants to reduce runoff, erosion, and dust problems appears superior to the paving or graveling method of site stabilization. Initial invading species will probably be weeds, e.g., tumbleweeds, which will not sufficiently stabilize the site. Plants selected for site stabilization will probably be non-irrigated, cultivated types, such as arid adapted shrubs and grasses. Users of vegetation for site stabilization must consider carefully the limitations imposed by the microclimate within and outside the field (i.e., in full sun, shade, and shade/sun regimes), plant growth height to avoid panel shading and possible later use of vegetation suppression techniques, and ease of plant establishment (i.e., plants requiring extensive care would be too costly for selection). Plants, the primary producers in the food chain, are the driving force of an ecosystem. What affects their diversity and density ultimately affects all other species. The presence of photovoltaic panels and past site preparation activities will produce a variety of microclimates at the site due to shading, wind deflection, and soil compaction. Soil erosion and albedo will intitially be high due to vegetation removal and soil compaction produced by installation of the central photovoltaic power station. Panel shading and wind deflection will produce microclimatic changes supporting plant growth, and plant species will begin invading the site if it is not paved. Microclimatic changes will include (1) decreased air, surface and soil temperature during the day in shaded areas and smaller diurnal fluctuations in temperature; (2) decreased evaporation in shaded areas resulting in an increase in soil moisture; (3) decreased long-wave radiation loss from the ground at night, resulting in warmer nighttime temperatures under panels in the open desert; and (4) decreased wind speed within the panel field resulting in lowered advective moisture losses to the surrounding desert air and decreased evaporation, which together increase relative humidity and soil moisture (Patten 1978b).

Changes in the microclimate will produce conditions favorable for plant growth under the panels. Initially established plants (i.e., invader species) will probably be ephemeral and weedy. In some locations, weed control may become a problem—especially if water input (for example, from panel washing) is increased. As plant succession continues, primary production and photosynthesis within the field (especially in areas intermittently shaded by panels) will increase and annual weeds, forbs, and grass species will become more common and dense. Because climatic, especially moisture, stresses will be less under panels than in the open desert, plant density within the field will be relatively greater as the post-rain seasons progress. As plant food sources become more plentiful, the density (and possibly composition) of animal species near and in the field may change. If human activity at the site is not extensive, the density and diversity of animals, plants, insects, soil microorganisms, nematodes, arthropods, and burrowing species will be more numerous than in the open desert. Some animals may find panel-shaded areas to be favorable habitats during periods of intense heat or cold, resulting in a temporary influx of open desert species (Patten 1978a, Patten 1978b). However, immigration of all but very small mammals, birds, and invertebrates will not occur if the site is fenced. The abiotic changes and their resultant microclimatic and ecosystem effects are summarized in Table 4-1.

4.3 EFFECTS OF DECOMMISSION

The activities associated with decommissioning a photovoltaic system will be influenced by several factors: total installed capacity, the lifetime and obsolescence of individual components, the cell materials utilized, the type of application, available recycle and disposal options, and the intended use of a retired system site. In addition, solid wastes associated with panel breakage or obsolescence will require disposal at various stages during the 20-30 years of system operation and maintenance.

Decommissioning all application types will require environmentally sound disposal methods for various solid wastes. Site reclamation may or may not be required. Damaged, broken, or obsolete photovoltaic panels may be replaced and a central station site used for electricity generation for more than 20-30 years. In this case, only the panels would require disposal. Alternatively, an entire central station site may be decommissioned, requiring disposal of panels and support structures, and site reclamation.

Solid wastes can be recycled or disposed of, depending upon the specific material. Panel support structures and frames probably will be made of metals such as aluminum or steel, and these can be recycled. Materials within the panels may be recycled, depending on economic conditions, environmental regulations, and available technology. For example, if supplies of polycrystalline silicon are production-capacity constrained, it may be economically attractive to reuse poly-Si solar cells. Methods of cadmium reclamation have been developed in response to environmental regulations. Although there has been no research on specific techniques for cadmium reclamation from Cu_2S/CdS cells, such a technology may be developed if used extensively and there is pressure or incentive to recycle Cu_2S/CdS cells.

Table 4-1. SUMMARY OF THE ECOLOGICAL EFFECTS OF CENTRAL STATION PHOTOVOLTAIC SYSTEMS

Abiotic Change	Microclimate Effect	Biotic Response
Soil Compaction	Increased bulk density and penetration resistance of soil	Reduced root penetration and soil aeration causing loss of perennial plants and inhibiting establishment of ephemerals
	Decreased soil macropore space and water infiltration rate	
	Decreased diffusiveness in wet soils but not in dry	Decreased density and diversity of soil organisms
Shading	Decreased surface and soil temperature in shade; possible decrease in air temperature	Increase in primary producers (plants) which will lead to an increase in secondary producers (animals)
	Decreased evaporation rate leading to increased soil moisture and relative humidity in the shade	Possible effect on plant behavior; stomates may remain open longer
	Less diurnal temperature fluctuation; cooler days and warmer nights under panels	Possible influx of animals to the cooler day/ warmer night microhabitat under panels
Wind Deflection	Decreased wind speed and advective moisture loss to drier surrounding desert air leading to an increase in soil moisture	Less dessication and higher soil moisture will probably lead to increased photosynthesis and, therefore, primary production in plants receiving alternate shade and sunlight
	Possible increase in air and soil temperature in unshaded areas within the field	Plants should exhibit greater stomatal opening throughout the day, potentially resulting in increased photosynthesis
		Increase in density of animal species due to higher plant production and presence of mesic microhabitat relative to open desert

Source: Table developed based on Patten 1978a and Patten 1978b.

If solid wastes are not recycled, they will be disposed of using current handling methods for solid refuse. As noted, the principal method of solid waste disposal is landfilling (i.e., direct shipment to sanitary landfills, pulverization followed by landfill, incineration followed by landfill of lower volume ash, or sealing of toxic materials followed by landfill).

Poly-Si photovoltaic panels (as is the case for single-crystal silicon panels) can be landfilled with little or no environmental, health, or safety hazards. Glass and most plastics—such as the EVA encapsulant—can be sent to sanitary landfills while meeting current environmental regulations. Silicon is a relatively nontoxic immobile element which occurs widely in the environment. Silicon is the second most common element in the earth's crust, and an essential mineral for some plants (Horst and Marschner 1978). Silicon will not leach from photovoltaic cells until pH is 2-3 (extremely acidic conditions), and then it rapidly binds the soil nutrients (BNL 1980b). The possibility of silicon entering into groundwater is therefore extremely remote. In summary, no environmental, health, or safety problems are envisioned for poly-Si panels disposed in sanitary landfills.

Disposal of Cu_2S/CdS panels will require greater care than poly-Si because of cadmium's higher toxicity, persistence, and mobility. As noted, landfill of all solid wastes, including cadmium and silicon, is regulated by the EPA under the Resource Conservation and Recovery Act of 1976. Cadmium-containing wastes are generally classified as hazardous, and must be treated accordingly. Cu_2S/CdS (if not recycled) can be disposed of in modified sanitary landfills, termed "chemical waste landfills." Chemical waste landfills are designed to protect the quality of surface and subsurface waters, the environment, and public health. They are located or engineered (1) to avoid direct hydraulic continuity with surface and subsurface waterways, (2) to contain leachates if they form, and (3) to eliminate subsurface water flow into the area.

Some wastes, including heavy metals such as cadmium, are sealed before landfill to prevent leaching. Because cadmium can be leached by water with pH 4.5 or lower (BNL 1980b), proper disposal of Cu_2S/CdS is important to assure that cadmium does not become a ubiquitous environmental pollutant. Although cadmium is not an essential element, it is taken up and accumulated by numerous species. Plants take up cadmium from soil and water and thereby it enters the food chain. Cadmium is readily absorbed and accumulated by molluscs and crustaceans, and, to a lesser degree, by fish. The acute toxicity of cadmium to aquatic species (expressed as a LC_{50} value) is in the mg/l range, but the chronic toxicity is high.

Air is generally not a major route of cadmium exposure to humans and animals except at sources such as zinc and cadmium refineries. Smokers are exposed to larger than normal amounts of airborne cadmium from the tobacco smoke. Diet is actually the principal route of cadmium exposure to humans and domestic animals. Humans absorb about 6% of the cadmium ingested. Because the biological half-life of cadmium is long (10 years or more), cadmium accumulates in the body and is stored mostly in the kidneys. Accumulation of large amounts of cadmium results in renal tubule dysfunction; in addition, cadmium is a suspected carcinogen (NRC 1978, EPA 1975.) Therefore, entry of cadmium into the environment, and thus into the food chains, must and can be controlled through either recycling of Cu_2S/CdS cells or disposal in EPA-approved landfills.

Residential, commerical/industrial, and intermediate load applications will not undergo dramatic ecological changes if the site is totally decommissioned and no longer used for power production. It is possible that central power stations may be decommissioned and the site retired; in this case, site reclamation will be required. Many of the impacts of site decommissioning will result in effects similar to installation; i.e., heavy machinery and associated noise, fugitive dust, and erosion problems. If site stabilization is achieved through paving, removal of the asphalt and landfill of the solid waste would be required and it would be expensive. Panel removal from plant-stabilized sites will produce a dramatic and rapid ecological shift from a cooler, more moist and shady microhabitat to the conditions of the open desert. Many shade-tolerant species that may have populated the area under the panels for 20-50 years will die, and sun-tolerant species will invade the area.

If plant loss is extensive, large machinery destruction of stabilized soil surfaces is extreme, or if the site was paved, revegetation will be required to prevent severe soil loss from runoff and erosion. Field studies on the revegetation of desert sites are being conducted as part of the Barstow Solar Thermal Central Receiver Research Program. This information is directly applicable to revegetation of photovoltaic central station sites in similar desert locations. The revegetation studies are designed to understand the biotic and abiotic processes influencing revegetation, and to experiment with techniques to promote the growth and reestablishment of native plants. The initial revegetation studies at Barstow indicated that water was the most important factor in governing plant response in the desert ecosystem. The behavior of animals also has a significant effect on seedling and plant survival. In addition, many desert plants exist as local ecotypes highly adapted to the local climatic and edaphic environment; thus, revegetation stock must often come from the area (Romney et al. 1979). Reclamation and revegetation of desert sites may be expensive (e.g., if fencing and supplemental water is needed) and time consuming. Therefore, extreme care should be exercised during decommissioning to minimize disturbance of plants and stabilized soil surfaces.

SECTION 5.0

CONCLUSIONS, PART I

Polycrystalline silicon (poly-Si) and copper sulfide/cadmium sulfide (Cu_2S/CdS) photovoltaic systems are two of several systems that may develop into commercial products with widespread applications. Normal operation of the systems will not produce air or water pollutants, thermal pollution, or bothersome noise. These benefits are substantial because they will occur throughout the 20 to 30 years of system operation. However, some potential environmental, health, and safety (EH&S) effects from manufacturing, installing, operating, and decommissioning poly-Si and Cu_2S/CdS systems do exist.

Environmental, health, and safety effects for selected poly-Si and Cu_2S/CdS cells generally are controllable given currently available pollution abatement and waste disposal techniques and industrial experience, since all of the required material inputs are used in other industries. For example, the semiconductor industry has a successful environmental, health, and safety record relative to its use of silicon compounds and dopants. In addition, smaller quantities of materials will be used to produce poly-Si and Cu_2S/CdS photovoltaic cells in the future. Advanced option photovoltaic cell concepts must meet U.S. Department of Energy cost goals to achieve large-scale deployment. One of the many ways to reduce cell costs is to improve the efficiency of materials used (both those within the cells—silicon, cadmium, etc.—and those used for manufacture—acids, etchants, etc.). As materials efficiency improves, there will be environmental benefits: fewer wastes and effluents that must meet regulatory standards for pollution control and waste disposal.

Environmental, health, and safety risks are highly dependent upon system life-cycle phases; i.e., materials acquisition and cell fabrication, installation, operation and maintenance (O&M), and decommission. Materials acquisition and cell fabrication pose relatively high occupational health and environmental risks because of the toxicity of the materials used. Mining and processing the primary materials required for manufacture of poly-Si and Cu_2S/CdS solar cells (silicon and cadmium) entail environmental degradation and occupational hazards (for example, inhalation of Si, SiO_x and cadmium particulates). However, net increases in adverse effects from the photovoltaic industry initially will be small to imperceptible, especially in the raw materials sector; e.g., production of metallurgical-grade (MG) silicon and cadmium recovery at zinc smelters. For example, only about 1% of the projected year 2000 production of MG silicon would be required to fabricate 1 GW of polycrystalline silicon photovoltaic cells (Watts 1980). Some of the industries producing secondary materials, especially polycrystalline silicon, may have to increase capacity to meet the demands of the photovoltaic industry. In this case, there may be a net increase in environmental, health, and safety risks associated with expanding the industries. However, the significance of such an increase will have to be evaluated in terms of the life-cycle effects of photovoltaic-generated electricity compared with the electricity or other energy source that is displaced.

Some potential environmental, health, and safety effects are common to all photovoltaic systems, regardless of cell type. Some are unique to the selected poly-Si and Cu_2S/CdS cell options that are the focus of this report. A summary of both the common and the unique key effects for each life-cycle phase follows.

SUMMARY OF LIFE-CYCLE EFFECTS

Unique Effects of Raw Materials Acquisition and Cell Fabrication

- Environmental emissions of cadmium, primarily a by-product of zinc refining, have decreased because of a cutback in zinc production and regulatory pressures to control cadmium releases. Regulatory pressures for cadmium release control are expected to continue and possibly increase in the future.
- Waste products of cadmium production must be disposed of in an environmentally sound manner (e.g., in approved landfills) to minimize dispersion by wind-blown particles, runoff, or leaching by acidic waters.
- The principal health risks of cadmium processing are occupational and result from inhalation of cadmium-containing particles. These risks should be controllable by using respirators or other worker protection devices.
- Environmental and health hazards from disposing of solid wastes from MG silicon production appear minimal because of the stability and low toxicity of silicon.
- Atmospheric emissions of submicron-sized silicon-containing particulates from electric arc furnaces (used to produce MG silicon) need to be analyzed to determine emission levels and size ranges before occupational and public health risks can be assessed.

Installation

- Residential, commercial/industrial, and intermediate load photovoltaic applications will probably be located at highly disturbed sites. Ecological effects of their installation are expected to be small to nonexistent.
- The major ecological effects of central-station photovoltaic applications include (1) soil compaction, (2) fugitive dust, (3) erosion due to wind and water runoff, and (4) destruction of some to all of the wildlife in the immediate area. These effects are common to all large-scale construction activities. Their severity, however, will be highly influenced by the site—its ecological fragility, amount of grading and clearing, accessibility, etc.
- The occupational health and safety hazards to installers are greater for roof-mounted systems (because of the risk of falls) than for central station and other ground-mounted applications. All application types include shock and general construction activity risks. The probability of falls can be minimized by training workers adequately and designing systems that assure easy access.

Operation and Maintenance

- Acquiring large tracts of land for deployment of central-station photovoltaic systems (independent of cell type) could be difficult in some areas, especially if the area is relatively pristine. The Endangered Species Act may be a key consideration in some site acquisitions.
- Fugitive dust and erosion begun during system installation can continue to be a problem if the site is not stabilized. Using native plants is the most ecologically sound technique for site stabilization.

- The presence of photovoltaic panels can produce microclimate changes which will, in turn, affect the diversity and density of the biotic community, if the site is not paved or graveled. Photosynthesis and primary plant production in intermittently shaded areas increases with time, and probably will result in an increase in animal and insect populations.
- Health and safety hazards to system maintenance workers could include shock; contact with hot surfaces; and, for roof-mounted systems, falls. Shock hazards can be minimized through adherence to electrical codes. Properly designed and wired systems will have no dangerously hot surfaces.
- Public health risks may result in atypical events, such as outgassing or fire. The risk is greater for residential and commercial/industrial applications because they generally are located in more densely populated areas. In addition, these systems are often mounted directly onto combustible materials, like roofing materials. Outgassing should not occur if systems are properly designed and tested before sale. Poly-Si panels should pose relatively few hazards in case of fire because of the low toxicity of most panel materials. Hazardous levels of cadmium compounds could be released if Cu_2S/CdS panels are burned. However, dilution by the outdoor air of any toxic fumes will help to mitigate health hazards.
- Entry of toxic materials into the environment from cracked or broken panels is not expected to be a problem for poly-Si options. It is possible that acid rain (if pH is below 4.5) could leach cadmium from damaged Cu_2S/CdS panels, but this is not likely because damaged panels probably will be rapidly replaced. However, the feasibility of entry by this route has not been determined, nor its significance, if any, analyzed.

Decommission

- The materials used in the selected photovoltaic systems can be disposed of in an environmentally safe manner. Metals used for array supports and panel framing can be recycled. Plastics (used for panel encapsulation) can be used for landfill.
- It is possible that an industry to reclaim and recycle the materials in poly-Si and Cu_2S/CdS panels may develop if incentives are provided (e.g., the cost of new materials versus recycled ones, materials availability, or environmental regulations).
- If poly-Si panels are not recycled, they can be crushed and disposed of in ordinary landfills.
- Disposal of unrecycled Cu_2S/CdS panels will require care and also will probably require the use of landfills approved for heavy metals by the U.S. Environmental Protection Agency (EPA). Cu_2S/CdS cells may require encapsulation or sealing before disposal to assure that cadmium is not leached under conditions of acidic drainage.
- If a central-station photovoltaic facility (regardless of cell type) is fully decommissioned and retired, the site will have to be reclaimed. Site reclamation should be examined at the onset of the facility's construction to minimize difficulties (e.g., reclamation of a paved or highly disturbed site will be far more difficult and costly than one stabilized with plants during O&M). Reclamation of highly disturbed desert sites can be time consuming, expensive and labor intensive, especially if extensive plant management and additional water are required.

RECOMMENDATIONS

Overall, the environmental, health, and safety risks of a photovoltaic industry based on poly-Si or Cu_2S/CdS cells appear to be acceptable and controllable, given current knowledge. However, there are too few data in several area to fully evaluate EH&S risks; some of these areas appear to need further investigation. These are summarized below.

- If use of a silicon wafer technology continues for the poly-Si cell fabrication options (i.e., if wafers are not replaced by ribbons or sheets), large amounts of silicon wastes will be generated during wafer slicing. Unrecycled wastes (mostly saw kerf) are currently stockpiled or sold to the metal alloying industry. Attention should be directed toward developing cost-effective methods for recycling or disposing of the saw kerf.
- As cell fabrication techniques are defined in greater detail, attention should be directed toward quantifying wastes and identifying techniques to treat mixed-waste streams.
- Research is needed to determine whether cadmium reclamation techniques used by other industries can be applied to cell processing waste streams and decommissioned Cu_2S/CdS panels.
- Cadmium is known to be leached from mine tailings, etc., by acid drainage. Research should be conducted to determine whether acid rain leaches cadmium from Cu_2S/CdS cells, what the leaching rate and concentrations are, and what makes up the chemical composition of the leachate. Such information is critical in accurately assessing whether cadmium in damaged or improperly disposed Cu_2S/CdS panels can be mobilized under environmental conditions.
- Inadequate health-effect information exists for some cell compounds and potential waste streams (e.g., submicron particulates of Si, SiO, and CdS). These should be determined to properly evaluate their occupational and public health risks.

APPENDIX TO PART I

OVERVIEW OF WASTE STREAM TREATMENT METHODS AND THEIR COSTS

A.1 TREATMENT METHODS

The common treatment methods for aqueous wastes are described briefly in this section. Other, more detailed processes are described in the references cited. The descriptions below are taken from DeRenzo (1978).

A.1.1 Adsorption—Carbon

A large variety of organic solutes, and a more limited number of inorganic solutes, can be removed from aqueous waste streams by adsorption into activated carbons with a high adsorptive surface area (500-1500 m^2/g). Adsorption of organic solutes is commonly followed by thermal regeneration of the carbon and simultaneous destruction of the adsorbates. In a few cases, the carbon may be regenerated and the adsorbate recovered by treatment with an acid, a base, steam, or a solvent.

Energy requirements include electricity for pumps and fuel for the regeneration furnace. Energy costs may be about 25% (or higher) of the total operating costs where concentrated waste streams are being treated and the carbon is regenerated thermally. Energy may constitute no more than 5% of total operating costs if regeneration is accomplished by nonthermal means.

If spent carbons are not regenerated, a disposal problem can arise. If they are regenerated thermally, the regeneration furnace will usually require an afterburner, a scrubber, and perhaps a dust filter.

A.1.2 Adsorption—Resin

Resin adsorption can use synthetic resins (which may vary significantly in their chemical and physical nature) to extract and recover dissolved organic solutes from aqueous waste streams. Resins with either (or mixed) hydrophobic or hydrophylic natures are available and can be used to extract hydrophobic or hydrophylic solutes, respectively. Resins are chemically regenerated. When organic solvents are used as the regenerant, solute recovery is accomplished generally through distillation.

Energy requirements are small when the regenerant is not recycled. When both solvent and solute are recovered, the steam requirements for distillation (requiring up to three stills) will be significant. If the regenerant is not recycled, it must be disposed. If the regenerant is recycled (e.g., by distillation), the still bottoms must be disposed.

Capital costs are moderately large; while no furnace is needed for regeneration (an expensive item with carbon systems), resins costs are high. Operating costs may be below $1/1000 gal. in some applications, but may reach $5-$20/1000 gal. when concentrated waste streams are treated and the solute recovered.* Credit for recovered solute can allow a system to operate at a profit in favorable cases.

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*The waste disposal and waste treatment industries currently use gallon or ton measurements. To convert gallons to litres, multiply the number of liquid gallons by 3.785, or dry gallons by 4.404.

A.1.3 Biological Treatment: Activated Sludge

Aqueous organic waste streams having less than 1% suspended solids have flocculated, biological growth continuously circulated, and contacted in the presence of oxygen. Since the process was introduced at the turn of the century, it has been modified through improved methods of maintaining aerobic conditions under varying organic loadings.

The process involves an aeration step, followed by solids-liquid separation, recycling a portion of the solids. The basic system has an open tank for mixing the active biomass with influent wastewater and air, followed by a clarifier. Bacteria in activated sludge systems serve to perform hydrolysis and oxidation reactions.

The activated sludge system is energy-intensive, with over 10% of total operating cost based on energy needed for pumping, aeration, and clarification. The system is basically environmentally sound; natural degradation takes place and no chemicals are added.

A.1.4 Filtration

Filtration is a well-developed liquid/solid separation process currently applied to the full-scale treatment of many industrial wastewaters and waste sludges. For the treatment of hazardous wastes, filtration can be used to perform two distinctly different functions:

(1) Removal of suspended solids from a liquid (usually aqueous) waste stream to produce a purified liquid.

(2) Increasing the solids concentration, and thereby reducing the volume, of a high concentration liquid/solid mixture (sludge) by removing liquid from the mixture ("sludge dewatering").

As a wastewater treatment process, filtration is usually most applicable when it follows some form of flocculation and/or sedimentation. As a sludge dewatering process, filtration is usually technically and economically competitive with other dewatering processes.

Filtration is a physical process whereby particles suspended in a fluid are separated by forcing the fluid through a porous medium. As the fluid passes through the medium the suspended particles are trapped on the surface of the medium and/or within the body of the medium. Filter media can be a thick barrier of a granular material, such as sand, coke, coal, or porous ceramic; a thin barrier, such as a filter cloth or screen; or a thick barrier composed of a disposable material such as powdered diatomaceous earth or waste ash. The pressure differential to move the fluid through the medium can be induced by gravity, positive pressure, or vacuum. The intended application has a great influence on both the type of filter and its physical features.

Energy requirements for filtration are relatively low. A vacuum filtration system capable of dewatering 36,000 gal./day of sludge containing 6 tons of solids will have a power requirement of only 25 hp.

A.1.5 Flocculation, Precipitation, and Sedimentation

Flocculation is the process whereby small particles that do not settle readily and are suspended in a liquid are made to agglomerate into larger particles that will settle. Precipitation is a physiochemical process where some or all of a substance in solution is removed from the solution and transformed into a second (usually solid) phase. Sedimentation is a purely physical process whereby particles suspended in a liquid are made to settle by means of gravitational and inertial forces acting on both the particles suspended in the liquid and the liquid itself.

Energy consumption is very low compared to other processes. The processes produce a waste sludge, which can often present a serious disposal problem.

A.1.6 Ion Exchange

Ion exchange involves the interchange of ions between an aqueous solution and a solid material (the "ion exchanger"). After removal of the solution, the exchanger is then exposed to a second aqueous solution of different composition which removes the ions picked up by the exchanger. The process is most frequently carried out by pumping the solutions through one or more fixed beds of exchanger. Energy requirements are low, consisting primarily of electricity for pumping solutions.

The dilute purified product stream can be discharged into sewers. The regenerant stream requires further treatment for recovery or disposal. Minor amounts of exchange materials will require disposal occasionally.

A.1.7 Neutralization

Neutralization is a liquid-phase chemical reaction between an acid and a base which produces a neutral solution. It may be carried out in batch or continuous flow. It requires reaction tanks, agitators, monitoring and control capability, pumps, ancillary equipment for handling solids and/or liquids, and storage facilities. The treated stream undergoes no change in physical form, other than solids dissolution (or precipitation) or gas evolution. The process can be used on aqueous and nonaqueous liquids, slurries, and sludges.

Energy requirements are primarily for electricity used to run pumps and stirrers. Treated streams may contain precipitated solids that require additional handling. The solids must be recovered or sent for disposal as solid waste. There is the possibility of toxic gas being involved, particularly if sulfides or cyanides are present in the waste stream. Capital investment requirements are highly variable, depending on the size of the stream to be treated. Operating costs range from \$0.20/1000 gal. to \$4.00/1000 gal.

A.2 TREATMENT METHOD COSTS

A valid comparison of waste treatment costs of the four cell-production methods can be made only after more quantitative information is available on the size of waste streams and the chemicals in them; detailed specifications of treatment processes must be made first. Nevertheless, some preliminary cost comparisons can be made of the individual treatment methods that might be used in the production processes.

In general, possible gaseous waste treatment processes are relatively straightforward and inexpensive compared with water treatment methods. For example, venting and liquid adsorption (which then require water treatment methods) are relatively inexpensive. Costs of protecting workers from gases may be substantial, however. These industrial hygiene techniques are beyond the scope of this study. Briggs and Owens (1979) treat industrial hygiene issues in detail.

Costs of several water treatment methods relative to solar cell production appear in Table A-1. Capital and operating costs for water treatment vary from method to method. These per-gallon costs may also vary considerably depending on the capacity of the treatment facilities, types of chemicals used, etc. (DeRenzo 1978, Sittig 1975). If the typical individual treatment method costs are taken into account for each of the four production processes, there appear to be no striking differences among the methods. However, the tin oxide spray process for polycrystalline silicon cell production (using the Union Carbide process [see Fig. 2-10] for wafer purification) appears to require less expensive associated waste treatment methods. This conclusion is tentative and is based on preliminary information, however; relative cost estimates could change drastically once detailed designs are completed.

One factor that could make some difference in overall treatment cost is the availability of municipal sewage treatment systems. The process steps for these systems vary from municipality to municipality, but all involve sedimentation and biological oxidation. Some also include anaerobic treatment to reduce nitrates, sulfates, etc. Detailed discussions of various biological treatment systems are included under "Activated Sludge" in this appendix and in various references (see, e.g., Callely 1976, De Renzo 1978, and Yehaskel 1979). Some biological treatment may have to be at least begun at the cell manufacturing facility if no municipal treatment system is available.

Table A-1. WATER TREATMENT METHODS—TYPICAL RELATIVE COSTS

Process	Capital Costs (per gpd) For "Typical" Size ($)	Operating Costs ($) (per 1000 gal)
Neutralization	1.05	2.00-3.00
Sedimentation		0.10-0.50
Precipitation	0.75	1.00-2.00
Ion Exchange	5.00	4.00-6.00
Carbon Adsorption	12.00	5.00-20.00 (upper limit with regeneration)
Solvent Extraction	4.00	4.00-6.00

Source: A. D. Little and Co., in DeRenzo (ed.) 1978.

PART II

ENVIRONMENTAL, HEALTH, AND SAFETY REGULATORY PROGRAMS APPLICABLE TO ADVANCED PHOTOVOLTAIC MATERIAL OPTIONS

SECTION 1.0

AN OVERVIEW OF FEDERAL LEGISLATION, REGULATIONS, AND GUIDELINES

Commercial-scale production of the advanced photovoltaic material options examined in Part I of this report 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 used. Federal regulatory programs will apply to waste streams generated in photovoltaic cell production in much the same way as they apply to a variety of other industrial activities. This part of the report examines the major federal environmental, health, and safety programs that apply to photovoltaic cell manufacture, use, and disposal.

This section describes significant legislation applicable to photovoltaic production waste streams. Programs and regulations developed under these environmental, health and safety statutes are highlighted in Table 1-1 (EPA 1979a). In Sec. 2.0, the specific waste streams identified in Part I are examined in the context of the regulatory programs noted in Table 1-1. In Sec. 3.0 we explore the trends in regulatory control over waste streams linked to advanced photovoltaic material options. This analysis will help forecast possible future regulatory constraints for a developing photovoltaics industry.

Photovoltaic cell production and utilization has six discrete stages. In Sec. 2.0, each stage will be addressed separately, from a regulatory perspective. The first stage covers the extraction of minerals and materials utilized in cell production under each advanced process. Mineral and material processing is examined in the second stage, with greater emphasis on metal and mineral inputs used in photovoltaics production than on conventional chemical inputs.*

Waste streams from photovoltaic cell and module fabrication characterize the third stage. As the potential environmental, health, and safety impacts expected from this stage are in some degree unique to the photovoltaics industry, a detailed regulatory analysis is provided. It is at this stage that choices between various process alternatives, posing substantially different environmental impacts, can be made. The fourth and fifth stages outline the waste streams generated by photovoltaic system installation/operation/maintenance and decommissioning. Impacts associated with the transportation of materials, processing inputs, and wastes at each of the five previous stages are examined in the sixth stage.

1.1 THE FEDERAL REGULATORY PROCESS

The major federal programs in environmental, health, and safety regulation are both procedurally and substantively complex. Coordination in program implementation among a number of federal agencies is often required, as both complementary and competing

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*Research conducted for the Department of Energy by the Battelle Memorial Institute has identified the material supply characteristics of photovoltaic systems development. Interest in the processing and extraction stages from a regulatory perspective has been supported by materials research at Battelle. Battelle Memorial Institute. The Evaluation of Critical Materials for Five Advanced Design Photovoltaic Cells with an Assessment of Indium and Gallium. PNL-3319. May 1980.

Table 1-1. MAJOR ENVIRONMENTAL, HEALTH, AND SAFETY REGULATORY PROGRAMS DEVELOPED UNDER FEDERAL LEGISLATION

Legislation	Programs or Regulations Established
Clean Air Act	National Ambient Air Quality Standards National Emissions Standards for Hazardous Air Pollutants New Stationary Source Performance Standards
Federal Water Pollution Control Act (Clean Water Act)	Water Quality Criteria National Pollutant Discharge Elimination System Point Source Effluent Standards Toxic Pollutant Effluent Standards Pretreatment Standards Oil and Hazardous Substance Regulations
Safe Drinking Water Act	National Interim Primary Drinking Water Regulations National Secondary Drinking Water Regulations Underground Injection Control Regulations
Occupational Safety & Health Act	Limitations for Toxic and Hazardous Substances in Workplace Air
Toxic Substances Control Act	Establishment of Interagency Testing Committee Compounds Recommended for Testing
Resource Conservation and Recovery Act	Hazardous Waste Regulations Solid Waste Regulations

responsibilities exist.* When state agencies assume control of many federal regulatory programs, already complex legislation can become even more complicated. The environmental, health, and safety regulations applicable to an emerging photovoltaics industry must be considered within such a framework.

Generally, two types of regulations and guidelines are intended to address the environment, health, and safety: those that are performance-based and those that are technology-based. The predominant type of regulatory standard is that which establishes some level or threshhold that effluents, exposures, or behavior may not exceed. Theoretically, the method of compliance with such a threshhold is left to the party being regulated. In actual practice, a regulatory agency such as the Environmental Protection Agency (EPA) is active in the development of technologies acceptable in the control of waste-stream effluents.** Thus, the second type of regulation, technology-based standards, is also used in environmental control strategies. Requirements in most environmental programs mandate the use of "best available control technology" to help achieve specific emission limits from a given pollutant source.[¶]

The federal regulatory process is often as complex as the resulting regulations. By means of legislation, Congress assigns agencies the responsibility for implementing certain environmental, health and safety programs. Legislation usually extends authority to an agency to issue regulations designed to achieve the goals of the statute. While program guidance is often provided to an agency in the language of a statute, considerable discretion often is left to agency personnel to fulfill the legislative mandates. As an example, Congress may not define the universe of hazardous materials to be controlled in a solid waste disposal program yet may give EPA the flexibility to add substances and prescribe treatment methods as necessary.[¶¶] Such a mandate is relatively open-ended, and regulations implementing the statute may be amended frequently.

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*The Environmental Protection Agency has primary federal responsibility in most environmental areas, including 72% of total 1980 federal outlays for pollution control and abatement. However, 18 other agencies share in the federal environmental responsibility. These agencies include the U.S. Departments of Labor, Commerce, Agriculture, Transportation and Energy, the Tennessee Valley Authority, the Consumer Product Safety Commission, and others. Charlotte Garvey. "Highlights of the Federal Environmental Effort." EPA Journal. September 1980.

**EPA efforts at pollution control technology are perhaps best illustrated by the research directed at sulfur oxides. EPA has advanced research into flue gas desulfurization (FGD) as a principal means of reducing steam electric power plant SO_x emissions. Compliance with Clean Air Act standards is the driving force behing FGD research. Other waste treatment technology options are being supported by EPA in the areas of water pollution control and solid waste management. U.S. Environmental Protection Agency. Sulfur Emission: Control Technology and Waste Management. EPA 600/9-79-019. May 1979.

[¶] Under the Clean Water Act, there are variations in the requirements for adoption of best available control technology depending on the nature of the pollutant being regulated. Control of conventional water pollutants may be achieved using "best conventional pollutant control technology" while unconventional and toxic pollutants require the more stringent "best available technology." U.S. EPA, A Handbook of Key Federal Regulations and Criteria for Multimedia Environmental Control. August 1979. pp. 58, 59.

[¶¶] EPA may list types of solid waste as hazardous if it has reason to believe that individual components within the type of solid waste are hazardous as defined in § 1004 (5) of the Resource Conservation and Recovery Act of 1976. P. L. 94-580, October 1976.

Throughout the following discussion of regulatory programs, certain acronyms will be used to facilitate both preparation and utilization of the analysis. A list of these acronyms is provided at the beginning of this section. Legislation and accompanying regulatory programs follow the order established in Table 1-1.

1.2 THE CLEAN AIR ACT

The Clean Air Act (CAA) amendments of 1970 greatly expanded the Federal Government's role in regulating the nation's air quality (amended P.L. 95-95, 1977). Under these and subsequent amendments, regulatory programs were created to develop air quality criteria and standards and to establish emission limits for air pollutant discharges from several categories of industrial sources. The authority for administration and enforcement of the CAA rests with EPA. Many important CAA programs may apply to industrial activities associated with one or more stages of the photovoltaic cell manufacturing process.

CAA provisions that are expected to both directly and indirectly influence the production of advanced material photovoltaic cells are:

(1) national primary and secondary ambient air quality standards, for air pollutants for which air quality criteria exist (P.L. 95-95, 1977, § 109);

(2) performance standards for new industrial sources that generate air pollutants covered by a national standard (P.L. 95-95, § III);

(3) emission limitations for discharge of hazardous air pollutants for which no national standard exists (P.L. 95-95, § 112); and

(4) standards for the prevention of significant deterioration of air quality (P.L. 95-95, §§ 160-168).

The framework for achievement of CAA goals is based in part on the existence of 247 Air Quality Control Regions (AQCRs).* These AQCRs have been established nationwide to allow regional variations in meteorology, industrial activity, and land-use priorities to influence federal and state responses to CAA objectives. EPA has given state air pollution control agencies the authority in many cases to administer and enforce the standards and emissions limits listed above. In some instances, however, EPA retains that authority. The mechanism generally used in the administration of the program is a permit issued by the regulatory agency to an actual or potential air pollution source.

1.2.1 National Primary and Secondary Ambient Air Quality Standards

National ambient air quality standards (NAAQS) for certain major air pollutants have been established by EPA under authority of the CAA (40 CFR Part 50). Primary standards have been set at levels considered sufficient for the protection of public health. Secondary standards have been set to protect the public welfare from any known or

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*Section 107 of the amended Clean Air Act authorizes the Administrator of EPA to designate air quality control regions as deemed necessary by EPA.

anticipated adverse effects of a pollutant. Public welfare as defined by the CAA includes, but is not limited to, effects on soils, water, crops, vegetation, wildlife, climate, property value, and personal comfort and well being.

Pollutants for which NAAQS have been established are referred to as "criteria pollutants." These pollutants are substances that can reasonably be expected to endanger public health or welfare and that are released into the air by numerous or diverse sources. The NAAQS promulgated under the 1970 amendments to the CAA address particulate matter, sulfur dioxide, carbon monoxide, hydrocarbons (nonmethane), nitrogen dioxide, and photochemical oxidants. Standards for lead were added at a later date and the standards for photochemical oxidants are now incorporated in the ozone standards. Table 1-2 summarizes these standards (40 CFR Part 50).

The EPA has granted the states authority to promulgate regulations and issue permits to control point source air pollution in AQCRs within state borders to achieve ambient air quality standards. State regulations must be as stringent as necessary to meet the federal standards. Each state must submit to EPA a State Implementation Plan (SIP) specifying the manner in which the NAAQS will be achieved and maintained. States that fail to adopt regulations that meet federal criteria or fail to enforce the regulations surrender their authority to the EPA.

1.2.2 New Source Performance Standards (NSPS)

Section 111 of the CAA requires EPA to publish a list of categories of stationary sources judged to cause or contribute significantly to air pollution and that may be reasonably foreseen to endanger the public health or welfare (see also P.L. 95-95, § III). Once a specific source is added to the list, proposed regulations applicable to it must be published within 120 days. Public comment precedes final adoption of each NSPS. States must then submit plans for establishing and implementing standards that are at least as stringent as the NSPS. The NSPS apply to the owner or operator of any regulated stationary source, the construction or modification of which began after publication of applicable standards (Clean Air Act, § III (a)(2)). The control level for emissions of air pollutants established by the NSPS must reflect the degree of emission limitation that can be achieved by applying the best system of emission reduction which EPA determines is available at a reasonable cost and time.

At present, NSPS exist for 26 industrial source categories (40 CFR Part 60). The individual NSPS are not directly formulated to achieve national ambient air quality goals, but rather, they are formulated to reflect the best technology available for each individual source. The overriding long-term goal of the body of standards is to prevent new air pollution problems from arising. To help achieve this, the standards provide an incentive for changes in control technology.

Current NSPS regulations are of three types. Most of the regulations establish allowable emission limitations for a given source category. Other regulations require the achievement of a specified percentage reduction in emissions, while in other cases where it is not feasible to prescribe a specific standard, the EPA has promulgated designs, equipment, operation standards, work practices, or any combination thereof which reflects the best environmental control (EPA 1979a, p. 34).

Table 1-2. NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS

Pollutant	Type of Standard	Averaging Time	Frequency Parameter	Concentration $\mu g/m^3$	Concentration ppm
Carbon monoxide	Primary and secondary	1 hr	Annual maximum[a]	40,000	35.00
		8 hr	Annual maximum	10,000	9.00
Hydrocarbons (nonmethane)	Primary and secondary	3 hr (6 to 9 a.m.)	Annual maximum	160[b]	0.24[b]
Nitrogen dioxide	Primary and secondary	1 yr	Arithmetic mean	100	0.05
Particulate matter	Primary	24 hr	Annual maximum	260	—
		24 hr	Annual geometric mean	75	—
	Secondary	24 hr	Annual maximum	150	—
		24 hr	Annual geometric mean	60[d]	—
Sulfur dioxide	Primary	24 hr	Annual maximum	365	0.14
		1 hr	Arithmetic mean	80	0.03
	Secondary	3 hr	Annual maximum	1,300	0.03
Lead	Primary	90 day		1.5	—
Ozone	Primary and secondary	1 hr		235	0.12
Photochemical oxidants[c]	Primary and secondary	1 hr	Annual maximum	160	0.08

[a] Not to be exceeded more than once per year.

[b] As a guide in devising implementation plans for achieving oxidant standards.

[c] Expressed as ozone by the Federal Reference Method.

[d] As a guide to be used in assessing implementation plans for achieving the annual maximum 24-hr standard.

Note: See 40 CFR Part 50.

1.2.3 National Emission Standards for Hazardous Air Pollutants

Section 112 of the CAA requires the EPA to establish National Emission Standards for Hazardous Air Pollutants (NESHAPs). These standards are intended to limit emissions of very hazardous pollutants from specific industrial source categories. Pollutants that have been shown to cause or contribute to an increase in human mortality or to an increase in serious irreversible or incapacitating reversible illness are classified by EPA as hazardous. The standards are designed to provide an ample margin of safety to protect the public health. If a specific standard is not practical either in prescription or enforcement, the EPA may promulgate designs, work practices, operational standards, equipment, or a combination thereof, to protect public health (EPA 1979a, p. 34). Enforcement authority may be delegated to states whose approved plan has been accepted by EPA.

Current NESHAPs apply to asbestos, beryllium, mercury, and vinyl chloride (40 CFR Part 61). The EPA recently added arsenic to the list of NESHAPs, but specific standards have not yet been developed. Industrial activities for which the EPA intends to develop standards for controlling arsenic emissions include glass manufacturing and copper, lead, and zinc smelters (45 Federal Register 37886).

1.2.4 Prevention of Significant Deterioration

The 1977 amendements to the CAA instituted a new program to help achieve and maintain NAAQS. The amendments required states to submit by December 6, 1977, for each AQCR, a report on the attainment status of each pollutant addressed by NAAQS (EPA 1979a, p. 36). AQCRs for which the air quality is cleaner than that specified by NAAQS for SO_2 or for particulates are designated a Prevention of Significant Deterioration (PSD) area for that pollutant (40 CFR Part 51.24). AQCRs in which the air quality does not meet NAAQS are designated Non-Attainment (NA) areas. It is possible for an AQCR to have PSD designation for one pollutant and NA designation for the other.

Regions designated PSD are assigned one of three clean air classifications. Class designation criteria are listed in Table 1-3 (EPA 1979a, p. 51). PSD increment limitations are specified for each of the three CAA classifications as listed in Table 1-4 (EPA 1979a, p. 52). Additional SO_2 emission allowances are permitted in Class I regions for new sources. These allowances listed in Table 1-5, are in addition to the normal limitations and are dependent upon the terrain and the stack height of the particular source involved (EPA 1979a, p. 52).

New construction of certain "major stationary sources" is subject to PSD review and permitting in areas regulated by PSD regulations. These sources are listed in Table 1-6 (EPA 1979a, p. 53). In general, "major stationary source" means any source which emits, or has the potential to emit, 250 tons or more per year of any air pollutant regulated under the CAA (40 CFR Part 51.24 (b)(1)). "Construction" means fabrication, erection, installation, or modification of a source (40 CFR Part 51.24 (b)(7)). Before construction, it must be shown that emissions from the new facility will not cause an increase in the ambient air concentrations greater than the allowed increments listed in Table 1-4, and that the ambient concentration will remain below the NAAQS. Such facilities must adopt the best available control technology (BAT) for each pollutant (40 CFR Part 51.24 (b)(10)). The PSD allowable increment applies to all sources in an AQCR for all future times, therefore, it is unlikely that an individual new or modified facility will be permitted to use an entire increment (EPA 1979a, p. 36).

Table 1-3. PREVENTION OF SIGNIFICANT DETERIORATION (PSD) CLEAN AIR REGION CLASSIFICATION CRITERIA

Class	Criteria
Class I	A. The following areas are automatically classified as Class I if they were in existence at the time of enactment of the Clean Air Act Amendments of 1977 (August 7, 1977). They may not be redesignated. ● International Parks ● National wilderness areas > 5,000 acres ● National memorial parks > 5,000 acres ● National parks > 6,000 acres
	B. All areas that were redesignated as Class I under regulations promulgated before enactment of the amendments may be redesignated.
Class II	A. All areas except those automatically designated as Class I or petitioned to Class III are Class II areas.
	B. The following areas may remain Class II or may be redesignated as Class I only. ● National monument > 10,000 acres ● National primitive area > 10,000 acres ● National preserve > 10,000 acres ● National recreation area 10,000 acres ● National wild and scenic river area > 10,000 acres ● National wildlife refuge > 10,000 acres ● National lakeshore or seashore > 10,000 acres ● National park or wilderness area > 10,000 acres established after enactment of amendments (August 7, 1977)
	C. Indian reservations may be designated only by the appropriate Indian governing body.
Class III	Designation as a Class III area is achieved by petition and public hearing and requires approval from the Governor of the State, consultation with the legislature and local governments representing the affected residents. A Class III redesignation must not contribute to concentrations of a pollutant that exceed the maximum allowable increase in another area.

Table 1-4. PREVENTION OF SIGNIFICANT DETERIORATION PERMITTED INCREMENTS

(Allowed increase over baseline concentration in $\mu g/m^3$)

Pollutant	Averaging Time	Class I	Class II	Class III	NAAQS
SO_2	Annual	2	20	40	80
	24-hour[a]	8	91	182	365
	3-hour[a]	25	512	700	1,300 (S)[c]
TSP[b]	Annual	5	19	37	7,560 (S)[c]
	24-hour[a]	10	37	75	260,150 (S)[c]

[a] All 24-hour and 3-hour values may be exceeded one per year.

[b] TSP is total suspended particulate.

[c] (S) indicates secondary standard.

Table 1-5. ADDITIONAL ALLOWANCES FOR CLASS I

(SO_2 increment limits for 18 exceeding days/yr)

Time	High Terrain (900 ft above stack base)	Low Terrain
24-hour maximum	62 $\mu g/m^3$	36 $\mu g/m^3$
3-hour maximum	221 $\mu g/m^3$	130 $\mu g/m^3$

Table 1-6. SELECT MAJOR STATIONARY SOURCES SUBJECT TO PSD REVIEW

Charcoal production facilities
Coal cleaning plants
Chemical process plants
Coke oven batteries
Glass fiber processing plants
Hydrofluoric acid plants
Iron and steel mill plants
Lime plants
Municipal incinerators
(>250 tons/day)
Power plants
(>250 million Btu/h)
Primary aluminum ore reduction plants
Primary copper smelters
Primary lead smelters
Primary zinc smelters
Secondary metal production facilities
Sintering plants
Specific sources
(>100 tons/yr any pollutant)
Sulfur recovery plants
Sulfuric acid plants
Any other source
(>250 tons/yr any pollutant)

Industrial growth in AQCRs not meeting NAAQS for a specific pollutant is regulated by NA rules. New construction or modification of major stationary sources in NA regions are subject to EPA's emission offset policy as established in the 1977 CAA amendments (EPA 1979a, p. 37). This policy requires expanding facilities to reduce emissions at their own facility to the lowest levels possible and to obtain emission reductions from other plants in the affected AQCR so that the net ambient pollution levels resulting from facility expansion are lowered. New facilities must also attain an emission level that is the Lowest Achievable Emission Rate (LAER). Variances may be authorized (40 CFR Part 52.21 (q)(5) through (q)(7)).

1.3 THE CLEAN WATER ACT

The Federal Water Pollution Control Act (FWPCA) of 1972 was amended in 1977 and is now referred to as the Clean Water Act (CWA), (P.L. 95-217). The responsibility for administering it rests with EPA. The principal goal of the Federal water pollution control program is to make waterways of the United States fishable and swimmable by 1983 and to achieve zero discharge of pollutants by 1985. The major regulatory vehicle for accomplishing these goals is the National Pollutant Discharge Elimination System (NPDES). Under this program, the states are given the authority to issue permits to point source dischargers, provided that the discharger assures that the following standards will be met:

- Source-specific effluent limitations guidelines (including New Source Performance Standards),
- Toxic pollutant regulations (for specific substances regardless of source), and
- Regulations applicable to oil and hazardous substances liability.

1.3.1 The 1983 Water Quality Goal

The EPA has required each state to adopt water quality standards that meet or exceed federal water quality criteria to achieve the 1983 goal of fishable and swimmable waters. Water quality standards formulated by the states are used as the basis for both point source-based effluent limitation guidelines (see Sec. 1.3.3) and toxic pollutant limitations used in issuing NPDES permits.

1.3.2 National Pollutant Discharge Elimination System

The CWA has established a National Pollutant Discharge Elimination System (NPDES) program (P.L. 95-217, §§ 318, 402, and 405(a)). This program regulates the discharge of pollutants from point sources into the waters of the United States. All point source discharges are unlawful without an NPDES permit. Discharges must be in compliance with all applicable terms and conditions of an NPDES permit.

The NPDES permit system has recently been combined with several other permit programs administered by EPA.* There are few substantive changes to the NPDES program as a result of this permit consolidation. Program modifications are largely procedural.**

Each NPDES permit application made by an existing manufacturing, commercial mining, and silvicultural discharger must include the location of the effluent-receiving water, a water intake and discharge accounting, average effluent flow, effluent treatment description, and effluent characteristics (45 Federal Register 33443 (1980)). There are varying requirements with respect to the detail of quantitative data for effluent characterization based on the nature of the discharge.

Primary industries subject to the NPDES program are listed in Table 1-7. Permit applicants within these categories must provide quantified data for a lengthy list of organic, toxic pollutants according to fraction of volatile, acid, base/neutral and pesticide. The industrial categories, testing requirements, toxic pollutants, and fractions are detailed in Tables C-1 and C-2 in Appendix C. Permit applicants who are not within the primary industry categories must provide quantitative data for pollutants (see Table C-1), but not by fraction. All permit applicants must report quantitative data for the toxic pollutants listed in Table 1-8, and for conventional and nonconventional pollutants listed in Table 1-9 if those are expected to be present in the discharge. Every NPDES permit applicant must also indicate whether any hazardous pollutant listed in Table C-3 is expected to be present (45 Federal Register 33452-33455 (1980)).

Each NPDES permit applicant must also meet the effluent limitation guidelines of the CWA (§ 301), the pretreatment standards (§ 307(b)), new source performance standards (§ 306), any toxic pollutant effluent standards (§ 307), any hazardous substance regulation (§ 311), and any more stringent state standard, limitation, or compliance requirement established in accordance with the CWA (§ 301(b)(1)(c)). The technical aspects of these standards and regulations are discussed in subsequent sections.

EPA regulations establish requirements for state assumption of the NPDES program (40 CFR Part 123)). As of April 1980, thirty-three states had assumed legal responsibility for the NPDES program within their jurisdictions. EPA regulations also establish general program requirements for NPDES decision-making procedures (40 CFR Part 124)). EPA has set the criteria and standards for the NPDES program by defining the type of control technology required for certain discharges and by defining standards for best management practices (40 CFR Part 125). For purposes of effluent limitation guidelines and NPDES permits, EPA has classified water pollutants as conventional,

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*On May 19, 1980, the Environmental Protection Agency (EPA) issued regulations establishing a consolidated permit program that governs the Hazardous Waste Management (HWM) program under the Resource Conservation and Recovery Act (RCRA), the Underground Injection Control (UIC) program under the Safe Drinking Water Act (SDWA), the National Pollutant Discharge Elimination System (NPDES) program and State Dredge or Fill ("404") programs under the Clean Water Act (CWA), and the Prevention of Significant Deterioration (PSD) program under the Clean Air Act (CAA). The consolidated permit regulations are basically procedural in nature. They do not affect the technical criteria used in establishing permit conditions. Each program has additional regulations governing these technical requirements.

**The consolidated permit program is codified at Title 40 of the Code of Federal Regulations, Parts 122 through 125.

Table 1-7. **NPDES PRIMARY INDUSTRY CATEGORIES**

Industry Category
Adhesives and sealants
Aluminum forming
Auto and other laundries
Battery manufacturing
Coal mining
Coil coating
Copper forming
Electrical and electronic components
Electroplating
Explosives manufacturing
Foundries
Gum and wood chemicals
Inorganic chemicals manufacturing
Iron and steel manufacturing
Leather tanning and finishing
Mechanical products manufacturing
Nonferrous metals manufacturing
Ore mining
Organic chemicals manufacturing
Paint and ink formulation
Pesticides
Petroleum refining
Pharmaceutical preparations
Photographic equipment and supplies
Plastics processing
Plastic and synthetic materials manufacturing
Porcelain enameling
Printing and publishing
Pulp and paper mills
Rubber processing
Soap and detergent manufacturing
Steam electric power plants
Textile mills
Timber products processing

Table 1-8. OTHER TOXIC POLLUTANTS; METALS, CYANIDE, AND PHENOLS

Antimony, total	Arsenic, total
Beryllium, total	Cadmium, total
Chromium, total	Copper, total
Lead, total	Mercury, total
Nickel, total	Selenium, total
Silver, total	Thallium total
Zinc, total	Cyanide, total
Phenols, total	

Table 1-9. CONVENTIONAL AND NON-CONVENTIONAL POLLUTANTS THAT MUST BE TESTED BY EXISTING DISCHARGERS IF PRESENCE IS SUSPECTED

Bromide	Chlorine, total residual
Color	Fecal coliform
Fluoride	Nitrate-nitrite
Nitrogen, total organic	Oil and grease
Phosphorus, total	Radioactivity
Sulfate	Sulfide
Sulfite	Surfactants
Aluminum, total	Barium, total
Boron, total	Cobalt, total
Iron, total	Magnesium, total
Molybdenum, total	Manganese, total
Tin, total	Titanium, total

toxic, and nonconventional (44 Federal Register 44501 (1979)). The five pollutants listed in Table 1-10 are the conventional pollutants designated to date under the CWA (44 Federal Register 44503 (1979)).

Sixty-five compounds have been designated toxic under the CWA (§ 307). These compounds are listed in Table C-4 (EPA 1979a, p. 66). All pollutants regulated by effluent limitations and not designated conventional or toxic are classified as nonconventional pollutants.

Currently, NPDES permit applicants must limit effluent discharges by applying the best practical control technology currently available (BPT). On July 1, 1984, discharges of conventional pollutants must reflect application of the best conventional pollution control technology (BCT). BCT will consider the cost of control in relation to the effluent reductions achieved. On the same date, discharges of toxic and nonconventional pollutants will require best available control technology (BAT). Waivers from BAT are available for nontoxic, nonconventional pollutants. Waivers from BCT are not available for conventional pollutants.

1.3.3 Source-Based Effluent Limitation Guidelines, Pretreatment Standards, and New Source Performance Standards

Under authority of the CWA, EPA is responsible for the establishment of point source effluent limitation guidelines for municipal waste water discharges, industrial discharges, industrial uses of municipal treatment works and for all toxic discharges for each specific industry. EPA has issued effluent limitation guidelines for twenty-one industries (see Table 1-11; EPA 1979a, p. 67). Selected effluent limitation guidelines are presented in Table C-5 (see also EPA 1979a, pp. 68-77). New source performance standards are incorporated within the guidelines in each industrial category and apply to discharges made directly into receiving bodies of water. These limitations are incorporated into the NPDES permits received by a discharger. A list of pollutants and water quality characteristics addressed by effluent limitation guidelines is found in Table 1-12 (EPA 1979a, p. 80).

Pretreatment standards apply to waste streams from these same sources that are sent to publicly owned treatment works. EPA has issued pretreatment standards for most of the twenty-one industrial categories for which effluent guidelines exist. These regulations have been issued to protect the treatment works from any materials that would either harm the treatment facility or pass through untreated. Table C-6 lists selected pretreatment standards (EPA 1979a, pp. 78-80).

1.3.4 Toxic Pollutant Effluent Standards

The EPA is required to publish a list of toxic pollutants under the CWA and may issue an "ambient water criterion" or effluent standard for each. Such a criterion should be a concentration level of a toxic pollutant in U.S. waters that, based on available data, will not result in an adverse impact on important aquatic life or on consumers of such aquatic life.

The concentration level should also not result in significant adverse health risks for large concentrations of human populations. Source categories to which these standards apply are specified in EPA's regulations. Compounds initially designated toxic pollutants under

Table 1-10. CONVENTIONAL POLLUTANTS

1. Biological oxygen (BOD)
2. Total suspended solids (nonfilterable) (TSS)
3. pH
4. Fecal coliform
5. Oil and grease

Table 1-11. INDUSTRY CATEGORIES COVERED BY EFFLUENT LIMITATION GUIDELINES

1. Timber products processing
2. Steam electric power plants
3. Leather tanning and finishing
4. Iron and steel manufacturing
5. Petroleum refining
6. Inorganic chemicals manufacturing
7. Textile mills
8. Organic chemicals manufacturing
9. Nonferrous metals manufacturing
10. Paving and roofing materials (tars and asphalt)
11. Paint and ink formulation and printing
12. Soap and detergent manufacturing
13. Auto and other laundries
14. Plastic and synthetic materials manufacturing
15. Pulp and paperboard mills, and converted paper products
16. Rubber processing
17. Miscellaneous chemicals
18. Machinery and mechanical products manufacturing
19. Electroplating
20. Ore mining and dressing
21. Coal mining

Table 1-12. POLLUTANTS AND WATER QUALITY CHARACTERISTICS ADDRESSED BY EFFLUENT LIMITATION GUIDELINES

Aluminum
Ammonia
Ammonia (as N)
Arsenic
Asbestos
Barium
Cadmium
Chlorine (free available)
Chrome
Chromium; total
Chromium; dissolved
Chromium VI
Copper
Copper; dissolved
Cyanide (total)
Cyanide (amenable to (chlorination)
Fluorides
Fluoride (as F)
Gold
Iridium
Iron
Iron; dissolved
Iron; filtrable
Lead
Manganese
Mercury
Nickel
Nickel; dissolved
Nitrate
Nitrate (as N)
Organic nitrogen (as N)
Osmium
Palladium
PCB compounds
Phenol
Phenolic compounds
Phosphorus
Phosphorus (as P)
Phosphorus; elemental
Platinum
Radium^{226}; total
Radium^{226}; dissolved
Rhodium
Ruthenium
Selenium
Silver
Sulfate
Uranium
Zinc

BOD$_5$
COD
pH
TKN
TSS
Color
Debris
Fecal coliform
Oil and grease
Settleable solids
Suspended solids
Drilling muds & cuttings
Water
Sand
Deck drainings

the FWPCA are presented in Table 1-13.* Additional toxic pollutants are listed in Table C-4. To date, only nine chemicals have been regulated as toxic pollutants.

1.3.5 Hazardous Substances Regulations

The discharge of hazardous substances is regulated by the EPA under § 311(b)(4) of the Clean Water Act. EPA has developed a list of hazardous substances and classified them into categories of acute toxicity to aquatic organisms (40 CFR Part 116). "Reportable quantities" of 1, 10, 100, 1000, and 5000 pounds have been assigned to each category. For convenience, EPA has coded the categories "X," "A,", "B," "C," and "D." A discharge of any quantity of one of the listed substances that equals or exceeds the reportable quantity must be reported to the EPA. Table C-7 lists selected hazardous substances and their assigned reportable quantities (44 Federal Register 50766 (1979)).

Hazardous substances may be regulated in an NPDES permit or on a case-by-case basis. A facility is excluded from meeting a reportable quantity requirement if it has a valid NPDES permit allowing discharge of a hazardous substance in a quantity equal to or greater than that established under § 311 of the Act.

1.4 THE SAFE DRINKING WATER ACT

The Safe Drinking Water Act (SDWA) of 1974 intends to assure that the public is provided with nonhazardous drinking water (amended to P.L. 95-190, 1977). Under the law, primary and secondary drinking water regulations have been issued by EPA. These specify maximum levels for certain contaminants in public drinking water and apply to utilities that supply municipalities with drinking water. These levels serve as indicators as to the quantity of a pollutant that can be discharged into receiving waters.

The SDWA also established an underground injection control (UIC) program designed to protect underground sources of drinking water. EPA has developed minimum UIC requirements states must adopt to protect underground drinking water sources from endangerment by the subsurface emplacement of fluids through well injection (40 CFR Parts 122, 123, and 124). All states require an EPA-approved UIC program. Once a state program is established, all underground injections are unlawful and subject to penalties unless authorized. Owners or operators of wells that inject hazardous waste within the meaning of the Resource Conservation and Recovery Act (RCRA) (see Sec. 1.8) must achieve "interim" status under the hazardous waste management program of that Act even though such injection practices will be ultimately controlled under state UIC programs.

Under EPA's UIC requirements, five classes of injection wells have been established. Class I wells are those used to inject industrial, nuclear, and municipal wastes beneath the deepest stratum containing an underground drinking water source. These wells could

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*A consent decree between EPA and various environmental groups (June 7, 1976) resulted in the listing of 65 compounds for which EPA agreed to develop and issue effluent limitation guidelines. The terms of the consent decree also required EPA to add these 65 compounds to the list of toxic pollutants initially designated under § 307(a) of the Clean Water Act if effluent limitation guidelines failed to achieve water quality criteria. See also EPA 1979, pp. 56, 60.

Table 1-13. **COMPOUNDS INITIALLY DESIGNATED TOXIC POLLUTANTS UNDER SECTION 307(a) OF THE FWPCA**[a]

Aldrin/dieldrin[b]
Benzidine[b]
Cadmium
Cyanide
DDT, (DDD, DDE)[b]
Endrin[b]
Mercury
PCBs[b]
Toxaphene[b]

[a] 65 pollutants listed in the Settlement Agreement were designated to be toxic pollutants and added to the initial list under the Clean Water Act Amendments of 1977. See Table C-4.

[b] Regulations adopted in 1977.

Table 1-14. **OSHA STANDARDS ESTABLISHING WORKPLACE AIR CONTAMINANT LEVELS**[a]

Contaminant	Standard	Ceiling
Asbestos	2 fibers/cc air	10 fibers/cc
Coke oven emissions	150 $\mu g/m^3$ - 8-hour day	——
Cotton Dust		
Slashing and weaving	750 $\mu g/m^3$ - 8-hour day	
Others	500 $\mu g/m^3$ - 8-hour	
Vinyl Chloride	1 ppm-8-hour day	5 ppm
Benzene[b]	1 ppm	5 ppm
Acrylonitrile	2 ppm TWA	10 ppm
Carcinogens (14)[c]		
Lead	50 $\mu g/m^3$	
Inorganic arsenic	5 $\mu g/m^3$	10 $\mu g/m^3$

[a] Regulations for these contaminants also include rules covering personal protective equipment, work practices, environmental monitoring, medical surveillance, record keeping, etc.

[b] Revoked by court action.

[c] These are discussed in Sec. 1.5.2 and listed in Table 1-15.

inject dangerous fluids and will have to meet strict construction, operating, and monitoring requirements (40 CFR Part 146, subpart B). Class II and Class III wells involve fluid disposal related to oil and natural gas production or storage, and in situ coal and oil shale processing. Class IV wells are used by generators of hazardous wastes or by owners and operators of hazardous waste management facilities to inject into or above strata that contain underground drinking water sources. Class V wells encompass all wells not contained in Classes I through IV.

EPA's underground injection control regulations became effective on July 24, 1980. States have 270 days in which to develop UIC programs and submit them to EPA for approval.

1.5 THE OCCUPATIONAL SAFETY AND HEALTH ACT

The Occupational Safety and Health Act of 1970 authorized standards to assure safe and healthful working conditions; assistance to the states in similar efforts; and the development of information research, education, and training in the field of occupational safety and health (P.L. 91-596). The Act created the Occupational Safety and Health Administration (OSHA) within the Department of Labor. OSHA is charged with the regulatory responsibility to protect workers from the hazards of the workplace. The act also created the National Institute for Occupational Safety and Health (NIOSH). NIOSH is responsible for recommending regulatory standards for OSHA establishment.

OSHA has issued both safety and health regulations. Safety regulations include handling, labeling, posting warning requirements, and implementing safety precautions such as protective gear for workers. Health regulations include establishing employee health record requirements and setting contaminant exposure limits and maximum contaminant levels for workplace air. Recommendations for new regulations or for changes in existing regulations are made to OSHA by NIOSH, its scientific advisory body, and by other recognized standard-setting organizations, including the American National Standards Institute (ANSI) and the American Conference of Governmental and Industrial Hygienists (ACGIH).

1.5.1 OSHA Regulations for Occupational Exposure to Specific Chemicals

OSHA has issued regulations that establish levels of certain pollutants acceptable for workplace air (29 CFR Part 1910). These levels are "time weighted averages" (TWA) based on 8 hours per day or 40 hours per week of exposure. They reflect the recommended Threshold Limit Values (TLVs^R) published first by ACGIH in 1968 and subsequently adopted by the ANSI. Selected TWA exposure levels are listed in Table C-8 (29 CFR Part 1910.1000 (1979)). Additionally, OSHA has set standards requiring workers to take special precautions and/or to wear protective equipment against other air contaminants that may be encountered in the workplace. Table 1-14 lists selected examples.

As noted in footnote "b" in Table 1-14, OSHA standards for benzene were revoked recently in a court action. Under the decision, the Labor Department must provide more conclusive justification for its job safety and health rules for benzene than it did in 1977.

1.5.2 Substances Regulated as Carcinogens

OSHA regulates several chemical contaminants designated to be carcinogens. These are listed in Table 1-15 (EPA 1979a, p. 127). Special handling, protective devices, and minimum contact regulations have been adopted concerning these compounds. OSHA recently has issued additional regulations for the identification, classification, and control of potential occupational carcinogens (29 CFR Part 1990). These regulations provide for the classification of these potential carcinogens into two categories based on the nature and extent of available scientific evidence.

Table 1-15. SUBSTANCES REGULATED BY OSHA AS CARCINOGENS

2-Acetylamino fluorine
Acrylonitrile
4-Aminodiphenyl
Asbestos
Benzene 4-Nitrobiphenyl
Benzidine
bis-Chloromethyl ether
Coke oven emissions
3,3-Dichlorobenzidine (and its salts)

4-dimethylaminoazobenzene
Ethyleneimine
Methyl chloromethyl ether
α,β-Naththylamine

n-Nitrosodimethylamine
β -Propiolactone
Vinyl chloride

Workers' exposure to Category I, Potential Carcinogens, must be reduced to the lowest feasible level. Exposure to Category II, Potential Carcinogens, must be reduced as appropriate and consistent with statutory requirements. OSHA has recently issued a list of substances, referred to as the "Candidate List," which are reported to be present in any U.S. workplace and which, on the basis of scientific evidence, may be considered candidates for regulation as Category I or II Potential Carcinogens. This is discussed in greater detail in Sec. 3.0 of this report (see 3.1.4).

1.5.3 Recommended Contaminant Limits for Workplace Air

Recommendations for contaminant limits in workroom air are made by NIOSH, ANSI, and ACGIH. NIOSH is the research arm of OSHA, responsible for developing criteria for setting occupational standards. These recommendations are generally developed for a specific substance, although recently they have been formulated for a specific process such as coke ovens emissions (EPA 1979a, p. 105). Results of NIOSH research are published in criteria documents.

ANSI is a federation of national trade, technical labor and consumer organizations, government agencies, and private companies. The group coordinates a voluntary standardization system intended to protect consumer and industrial workers. Among the standards endorsed by ANSI are those for acceptable concentrations of toxic dusts and gases (EPA 1979a, p. 107).

ACGIH is composed of professionals in government agencies or educational institutions who are engaged in occupational safety and health programs. This group publishes an annual list of Threshold Limit Values that prescribes recommended levels of chemical substances for workroom air (EPA 1979a, p. 106).

1.6 THE TOXIC SUBSTANCES CONTROL ACT

The Toxic Substances Control Act (TSCA) of 1976 delegates to the EPA the authority to secure information on all new and existing chemical substances and to control any of these substances determined to cause unreasonable risks to public health or the environment (P.L. 94-469). The substances controlled under these regulations are those that are not controlled by other federal legislation such as the CAA, CWA, or RCRA. If EPA determines that a substance can be controlled by the enforcement of an existing regulation then that program will be utilized rather than by issuance of new regulations under TSCA.

An Interagency Testing Committee was created to help carry out the provisions of TSCA. The agencies represented on the Committee are EPA, OSHA, the Council on Environmental Quality (CEQ), the National Institute of Environmental Health and Safety, the National Cancer Institute, the National Science Foundation, and the Department of Commerce. This committee makes recommendations to EPA on substances that require testing. The committee developed a "Candidate List" of all chemicals from which all drugs, food additives, pesticides, and noncommercial chemicals were eliminated. This list was reduced by eliminating all chemicals already regulated, all chemicals characterized as hazardous or inert, and natural products that would be difficult to test. A list of 300 priority compounds was then formed by ranking according to human and environmental exposure levels. From this list, 100 compounds were selected for detailed study. Additional compounds have been added to the priority testing list. The tests are to assess the environmental risks and the technological and economic factors involved in order to determine what action might or should be taken with respect to regulation (EPA 1979a, p. 155).

To facilitate the ranking of chemical compounds, EPA required manufacturers, importers, and processors of chemical substances for commercial purposes to submit certain information to the agency. Manufacturers and importers must continue to report information to EPA concerning new chemical substances not included in the master inventory file of chemical substances and which they intend to manufacture or import. To date only two substances have been regulated under TSCA: polychlorinated biphenyls (PCBs) and fully halogenated chlorofluoroalkanes (EPA 1979a, p. 156).

On July 11, 1980, EPA proposed new recordkeeping rules for toxic substances (45 Federal Register 47008 (1980)). The rules would require all persons who manufacture or process chemical substances or mixtures and all distributors of chemical substances and mixtures, except retailers, to keep records of every significant adverse reaction to health or the environment alleged to have been caused by the substances or mixtures. These proposed regulations are in addition to § 8(e) of TSCA, which requires that persons must inform the EPA if they have information to support the conclusion that a chemical substance poses a substantial risk of injury to public health or to the environment (see 43 Federal Register 11110).

1.7 THE HAZARDOUS MATERIALS TRANSPORTATION ACT

The Hazardous Materials Transportation Act (HMTA) of 1975 delegates to the U.S. Department of Transportation (DOT) the authority to protect against risks to life and property which are inherent in the transportation of hazardous materials in commerce (P.L. 93-633). DOT has issued regulations for the classification of hazardous materials and for their packaging, marketing, labeling, and conditions for shipping. The regulations make it unlawful for persons to offer or accept a hazardous material for transportation in commerce in the United States if it does not meet the DOT requirements (49 CFR Parts 172-177). Section 1803 of the Act directs DOT to designate those hazardous materials that may pose an unreasonable risk to health and safety or property. Table 1-16 is a selected list of materials designated by DOT as hazardous for purposes of transportation. Shipping requirements, as well as regulations for transport by rail, aircraft vessel, and on public highways have been issued by DOT.

1.8 THE RESOURCE CONSERVATION AND RECOVERY ACT

The Resource Conservation and Recovery Act (RCRA) of 1976 amended the Solid Waste Disposal Act; it is the legislative basis for federal solid waste regulations (P.L. 94-580). The legislative intent is to safeguard the public health and welfare by providing guidelines to protect the quality of groundwater, surface water, and ambient air from contamination by solid waste. EPA is the agency responsible for achieving these basic goals of RCRA. The principal means for attaining the goals include establishing environmentally sound solid waste disposal practices, including proper hazardous waste disposal, and encouraging resource conservation and recovery. These programs are to be carried out through a cooperative effort among federal, state, and local governments and the private sector (44 Federal Register 53438 (1979)). EPA has determined that the problem of nonhazardous solid waste disposal is primarily a state and local government problem and has proposed criteria to assist the states in developing regulations to assure environmentally safe disposal of such wastes. The problem of hazardous waste disposal is viewed as more severe and, therefore, one that warrants more stringent federal regulations (EPA 1979a, p. 169).

1.8.1 The Solid Waste Management Program

EPA's regulations for solid waste disposal provide criteria that states must follow in implementing their solid waste management programs. Guidelines for thermal processing of solid waste list the requirements and recommended practices for facilities that process fifty tons or more per day of nonhazardous municipal solid waste (40 CFR Part 240). General requirements for land disposal of nonhazardous solid wastes delineate minimum levels of performance required of any solid waste land disposal site operation. They are designed to ensure that construction and operation of both existing and future sites meet the health and environmental standards for the area in which they are located. Guidelines for the storage and collection of residential, commercial, and institutional nonhazardous solid waste have been issued by EPA, but these guidelines do not apply to industrial, mining, construction, or agricultural solid wastes (40 CFR Part 243).

On July 31, 1979, EPA issued a final rule which contains guidelines for the development and implementation of state solid waste management plans (44 Federal Register 45068 (1979)). Under RCRA, states are eligible to receive financial assistance if their plans have been approved by EPA. The rule establishes the requirements for state plans and recommends methods and procedures to meet those requirements. Under RCRA, the state plan must provide for the identification of state, local, and regional responsibilities for solid waste management, the encouragement of resource recovery and conservation, and the application and enforcement of environmentally sound disposal practices. State plans will prohibit the establishment of open dumps and provide for the closing of all existing open dumps.

Table 1-16. SELECTED SUBSTANCES CONSIDERED HAZARDOUS BY THE U.S. DEPARTMENT OF TRANSPORTATION

Acetaldehyde
Acetic acid
Acetone
Acid, liquid
Alcohol
Aluminum, powder and dross
Ammonia
Ammonium hydroxide
Antimony
Arsenic, dust and compounds
Arsine
Batteries
Blasting caps
Borontrichloride
Borontrifluoride
Calcium chlorite
Calcium oxide
Carbon dioxide
Carbon monoxide
Charcoal
Chromic acid
Coal
Coke
Copper chloride
Etching acid N.O.S.[a]
Explosive, mine
Ferric chloride
Flue dust, poisonous
Formaldehyde
Hydrochloric acid
Hydrogen chloride
Hydrogen
Hydrogen fluoride
Hydrogen peroxide
Hydrogen sulfide
Lead dross
Lead scrap
Lime
Methane
Mine explosives
Mining reagents
Nitric acid
Nitric oxide
Nitrogen
Nitrogen dioxide
Nitroglycerin
Oxygen
Phosphine
Phosphorus trichloride
Phosphorus pentachloride
Potassium fluoride
Road oil
Sodium hydroxide
Stannous chloride
Sulfuric acid
Sulfur dioxide
Titanium metal, powder

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[a] The abbreviation N.O.S. signifies those members of the general class "not otherwise specified" by name in this listing.

Final rules issued by EPA on September 13, 1979, set the criteria for classification of waste disposal facilities and practices. The regulation contains minimum criteria for determining what solid waste disposal facilities and practices pose a reasonable probability of adverse effects on health or the environment. Those facilities that violate the criteria are "open dumps" for purposes of the state solid waste management plan. The criteria are designed to protect ground and surface water sources, control disease vectors, safeguard environmentally sensitive areas, maintain air quality, protect food chain crops and endangered species, and promote conditions that ensure human safety. The criteria also partially fulfill the requirement of the CWA to provide guidelines for the disposal and utilization of waste water treatment plant sludges from publicly owned facilities (40 CFR Part 257).

1.8.2 The Hazardous Waste Management Program

On May 19, 1980, EPA issued interim final rules under RCRA which regulate the management of hazardous wastes by implementing the Hazardous Waste Management (HWM) program. These rules became effective November 19, 1980, and will control hazardous wastes from the point of generation through transportation, storage, and ultimate disposal. When fully and finally implemented, this program will provide "cradle-to-grave" management of hazardous waste.*

The centerpiece of the HWM system is the requirement that EPA issue regulations that identify the characteristics of hazardous waste and list solid wastes that, under the system, must be managed as hazardous wastes (40 CFR Part 261). The regulations define the terms "solid waste" and "hazardous waste," identify those wastes excluded from regulation under the HWM system, and establish special management requirements for hazardous waste produced by small quantity generators and hazardous waste that is used, reused, recycled or reclaimed (40 CFR Part 261, subpart A). The regulations state that a material not identified as a hazardous waste is still hazardous for purposes of the HWM system if it may cause, or significantly contribute to an increase in mortality or to an increase in illness or may pose a substantial hazard to human health or the environment when improperly treated, stored, transported or disposed. This classification is taken from the definition of hazardous waste in RCRA (§ 1004(5)).

The EPA will list a solid waste as a hazardous waste only upon determining that it meets one of the following criteria: it exhibits any of the characteristics of hazardous waste identified in regulations issued under RCRA; it has been found fatal to humans in low doses, or in the absence of data on human toxicity, it has been shown in animal studies to have a listed toxicity or is otherwise capable of causing or significantly contributing to an increase in serious illness [wastes listed in accordance with this criterion will be designated Acute Hazardous Waste (H)]; or it contains any of the toxic constituents listed in Table 1-17 [wastes which meet this criterion will be designated Toxic Wastes (T)] (45 Federal Register 33082, 33132 (1980)). Additionally, EPA may list classes or types of solid waste as hazardous if it has reason to believe that individual wastes, within the type or class of waste, typically or frequently are hazardous as defined in RCRA (45 Federal Register 33084, 33121 (1980)).

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*The technical requirements of the program are found in 40 CFR Parts 260 through 265. Procedural requirements are incorporated in EPA's consolidated permit program at 40 CFR Parts 122-124.

Table 1-17. TOXIC CONSTITUENTS LISTED BY EPA UNDER RCRA

Acetaldehyde
Antimony and compounds, N.O.S.[a]
Arsenic and compounds, N.O.S.
Arsenic acid
Arsenic pentoxide
Arsenic trioxide
Barium and compounds, N.O.S.
Benzene
Cadmium and compounds, N.O.S.
Calcium chromate
Calcium cyanide
Chromium and compounds, N.O.S.
Copper cyanide
Fluorine
Formaldehyde
Hydrocyanic acid
Hydrogen sulfide
Lead and compounds, N.O.S.
Mercury and compounds, N.O.S.
Nickel and compounds, N.O.S.
Nitric oxide
Nitrogen dioxide
Nitroglycerine
Phosphine
Potassium cyanide
Selenium and compounds, N.O.S.
Silver and compounds, N.O.S.
Zinc cyanide

[a] The abbreviation N.O.S. signifies those members of the general class "not otherwise specified" by name in this listing.

EPA requires that a hazardous waste be identified by testing to determine if it possesses any one of four characteristics. Three of the characteristics produce acute effects likely to cause immediate damage, while the fourth creates chronic effects likely to appear over a longer period (EPA 1980a, p. 12). The four characteristics are: ignitability (I), corrosivity (C), reactivity (R), and EP toxicity (E). Ignitability identifies wastes that pose a fire hazard during routine management. Corrosivity identifies wastes requiring special containers because of their ability to corrode standard materials, or requiring segregation from other wastes because of their ability to dissolve toxic contaminants. The characteristic of reactivity identifies waste that, during routine management, tend to react spontaneously, to react vigorously with air or water, to be unstable to shock or heat, to generate toxic gases, or to explode. EP toxicity refers to an extraction procedure test method used to identify waste that, when improperly managed, may release toxicants in sufficient quantities to pose a substantial hazard to human health or the environment. If a solid waste has a concentration greater that that of any of the contaminants specified in Table C-9, it is considered by EPA to be a hazardous waste having the characteristic of EP toxicity (45 Federal Register 33084, 33122 (1980)).*

The regulations also list hazardous wastes from specific and nonspecific sources on the basis of the characteristics listed above. Detailed justification for listing each hazardous waste is contained in specific background documents (45 Federal Register 33084, 33113 (1980)). Table C-10 lists hazardous wastes from nonspecific sources (45 Federal Register 33084, 33123 (1980)). Table C-11 lists selected hazardous wastes from specific sources (45 Federal Register 33084, 33123 (1980)). Table C-12 identifies for each EP toxic (E) waste and toxic waste (T) the constituent which caused EPA to list the waste as such (45 Federal Register 33084, 33131 (1980)). The hazard codes are the abbreviations for

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*EPA's EP toxicity test procedure requires a representative 100 gram sample of waste to be crushed to a specific particle size, to which 16 times the sample weight of deionized water is added. From this solution, a sample is extracted and analyzed for the presence of suspected contaminants.

each characteristic. The regulations also list additional materials and items that are hazardous wastes when they are discarded or intended to be discarded. These materials and items include certain chemical products or intermediates having generic names listed in Tables 1-18 and 1-19, or any container or liner used to hold the listed chemicals. Table 1-18 lists the chemical products or intermediates identified as acute hazardous wastes (H) and Table 1-19 lists such chemicals identified as toxic wastes (T).

EPA has also set standards for generators of hazardous waste (40 CFR Part 262). EPA regulations are intended to ensure proper recordkeeping and reporting, the use of a manifest system to track shipments of hazardous waste, the use of proper labels and containers, and other pretransport requirements. Generators of hazardous waste must obtain an EPA identification number (40 CFR Part 262). These same regulations require that a generator of hazardous waste prepare a manifest that permits one facility to handle the waste described on the manifest and one alternative facility. Pretransport requirements have been established that regulate packaging, labeling, marking, placarding, and the length of time a generator may accumulate hazardous waste without obtaining a permit to function as a storage facility. This period has been set by EPA at 90 days.

Regulations require that each transporter of hazardous waste obtain an EPA identification number, comply with the established manifest system, deliver the entire quantity of hazardous waste to the designated treatment, storage, or disposal facility, and keep records of the transportation of hazardous waste (40 CFR Part 263).

Regulations also have been established to be used in issuing permits for hazardous waste treatment, storage, and disposal facilities (40 CFR Part 264). Included are requirements covering preparedness for and prevention of hazards, contingency planning and emergency procedures, the manifest system for tracking waste from one person to another, and recordkeeping and reporting. Also included are general requirements for identification numbers, required notices, waste analysis, security at facilities, inspection of facilities, and personnel training.

Additional EPA regulations establish requirements applicable during the interim period after an owner or operator applies for a permit, but before final disposition of the application (40 CFR Part 265). These regulations cover preparedness for, and prevention of hazards, contingency planning and emergency procedures, the manifest systems, recordkeeping and reporting, ground water monitoring, facility closure and postclosure care, and the design and operation of tanks, surface impoundments, waste piles, and other storage and disposal means.

1.8.3 Resource Conservation and Recovery

RCRA also provides legislative initiative for the encouragement of recycling by municipalities and private enterprises. The specific resources identified as suitable for recycling are paper, beverage containers, corrugated boxes, tires, and energy from solid waste. EPA has issued various regulations directed toward resource conservation and recovery, including resource recovery facilities guidelines, guidelines for source separation of materials, and guidelines for procurement of products that contain recycled materials (40 CFR Parts 244, 246, and 247).

Table 1-18. SELECTED CHEMICAL PRODUCTS OR INTERMEDIATES IDENTIFIED AS ACUTE HAZARDOUS WASTES (H).

Hazardous Waste No.	Substance
P006	Aluminum phosphide
P010	Arsenic acid
P011	Arsenic pentoxide
P012	Arsenic trioxide
P021	Calcium cyanide
P030	Cyanides
P055	Ferric cyanide
P056	Fluorine
P063	Hydrocyanic acid
P074	Nickel cyanide
P076	Nitric oxide
P078	Nitrogen dioxide
P079	Nitrogen peroxide
P081	Nitroglycerine
P096	Phosphine
P104	Silver cyanide
P106	Sodium cyanide
P121	Zinc cyanide

Table 1-19. SELECTED CHEMICALS AND INTERMEDIATES IDENTIFIED BY EPA AS TOXIC WASTES (T)

Hazardous Waste No.	Substance
U001	Acetaldehyde
U002	Acetone
U032	Calcium chromate
U054	Cresylic acid
U112	Ethyl acetate
U122	Formaldehyde
U123	Formic acid
U134	Hydrofluoric acid
U135	Hydrogen sulfide
U144	Lead acetate
U145	Lead phosphate
U146	Lead subacetate
U151	Mercury
U154	Methanol
U205	Selenium sulfide

1.9 THE FEDERAL METAL AND NONMETALLIC MINE SAFETY ACT

The Federal Metal and Nonmetallic Mine Safety Act of 1966 provides the legislative initiative for health and safety standards for metal and nonmetallic mining (P.L. 89-577). The Mine Safety and Health Administration has issued health and safety standards for open pit mining, regulations for sand, gravel, and crushed stone operations, and regulations for underground mines. These regulations prescribe standards for the protection of life and the prevention of accidents. Standards apply to ground stabilization control, fire prevention, air quality for worker health safety, drilling, blasting, equipment usage, worker safety, loading and hauling, travelways and escapeways, and materials storage.

The air quality regulations provide that worker exposure to airborne contaminants shall not exceed the threshold limit values adopted by the American Conference of Governmental Industrial Hygienists. This regulation does not list the standards, but rather incorporates them by reference as published in the ACGIH booklet, "TLVs Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1973" (30 CFR Part 55.5). Table 1-20 lists selected TLVs.

1.10 THE NATIONAL ENVIRONMENTAL POLICY ACT

The National Environmental Policy Act (NEPA) of 1969 requires the preparation of an environmental impact statement (EIS) on all major federal actions significantly affecting the quality of the human environment (P.L. 91-190). Regulations issued by the Council on Environmental Quality establish minimum procedures for federal agency implementation of NEPA's EIS mandate. Agencies must develop EIS regulations specific to their individual assignments (i.e., permit issuance, research and development, licensing) and their respective decision processes.

Federal actions such as those mentioned—plus activities such as guarantee of loans, project construction, rate/tariff establishment, and grants—may have significant impact on the quality of the human environment. Should an agency decide that one of its proposed actions is so classified, it must apply its EIS preparation regulations to the proposal before taking action. Agency NEPA regulations allow public contribution to development of the EIS as well as opportunity for review and comment upon agency issuance of the document. NEPA regulations are enforced by the respective federal agencies and by the courts.

Table 1-20. SELECTED THRESHOLD LIMIT VALUES FOR CHEMICAL SUBSTANCES AND PHYSICAL AGENTS IN THE WORKROOM ENVIRONMENT

Substance	ppm[a]	mg/m^3[b]
Arsenic and compounds	—	0.5
Cadmium (metal dust and salts)	—	0.2
Cadmium oxide fume	—	0.1
Carbon dioxide	5,000	9,000
Carbon monoxide	50	55
Copper fume dusts and mists	—	1
Fluoride (as F)	—	2.5
Fluorine	1	2
Hydrogen sulfide	10	15
Lead, inorganic fumes and dusts	—	0.15
Nitric oxide	25	30
Nitrogen dioxide	5	9
Oil mist, particulate	—	5
Silicon	—	10
Sulfur dioxide	5	13
Zinc oxide	—	5

[a] Part of vapor or gas per million parts of contaminated air by volume at 25°C and 760 mm Hg. pressure.

[b] Approximate milligrams of substance per cubic meter of air.

SECTION 2.0

THE APPLICABILITY OF REGULATORY PROGRAMS TO PHOTOVOLTAICS PROCESSING

This section focuses on how the regulatory programs outlined in Sec. 1.0 apply to the photovoltaics (PV) production processes for both copper sulfide/cadmium sulfide (Cu_2S/CdS) and polycrystalline silicon (poly-Si) cell material options. These programs will be examined in terms of the regulations and standards that may be applied to the treatment, storage, transport, and disposal of waste stream by-products generated during six stages of photovoltaic cell production and utilization: extraction, processing, fabrication, installation/operation/maintenance, decommissioning, and transportation.

2.1 EXTRACTION OF MATERIAL INPUTS

U.S. extraction industries handle large volumes of different materials in a wide range of process steps. For purposes of this analysis, extraction is defined as the mining and milling of minerals normally conducted at a mine site. It is important to note that U.S. extraction industries have been operating and are expected to continue operating irrespective of PV commercialization. Preliminary indications are that demand on the extraction industries attributable to widespread PV development is not expected to critically stress extraction capacity for needed materials (see Battelle Memorial Institute, PNL-3319 (1980)).

2.1.1 Air, Water, and Solid Waste By-Products From Extraction

2.1.1.1 Atmospheric Emissions

Air emissions associated with extraction industries consist of gases and particulates, some of which may be health hazards. Mining emissions result from fuel combustion, explosives and transportation. Open-pit mining generally contributes more particulate matter to the atmosphere than underground mining, while underground activity results in more fumes and gases being vented from mine shafts.

Milling operations also emit atmospheric contaminants. Crushing and grinding, initial milling steps in the preparation of mined ore for additional beneficiation, create large quantities of dust via a wet milling operation. In dry milling operations, dust emissions can be controlled with baghouses or other filtration devices. Crushing and grinding can also result in the release of various rock gases. Roasting and calcining milling steps release fumes and particulates. These emissions may be controlled by baghouses, electrostatic precipitators, or wet scrubbers (Nerkervis and Hallowell 1976, pp. 8-10).

2.1.1.2 Liquid Effluents

Groundwater is frequently encountered in mining operations and may become contaminated with mine chemicals. The major effluent problem associated with open-pit mining is acid mine drainage. This results when the surrounding rock gives up chemicals to the natural drainage system because of earth disturbances. Underground mining may also give rise to acid mine drainage, and sulfide ores are the most frequent source of acid. Control of acid discharge to local water systems is accomplished easier in open-pit conditions than in underground mines. In the latter case, control is both difficult and expensive. Placer mining consumes large quantities of water and results in silting of discharges. Using explosives in all mining operations contributes to high nitrogen content in mine water discharges.

Crushing activity in milling operations may entail dry or wet processing. If wet scrubbers are used, water usually passes through and discharges its waste burden into tailings ponds. Some portion of the mined ore is discharged to the tailing pond in this process. In due course, the pond may discharge to the local drainage areas.

Conditioning chemicals may be added in the grinding step of milling operations and may also be discharged to tailing ponds. Various ore concentration steps result in high effluent discharges. Gravity concentration processes utilize heavy compounds, such as ferrosilicon, which are eventually discharged to ponds. Flotation processes result in numerous chemical reagents being partially discharged into ponds or lost by accidental spills (Nerkervis and Hallowell 1976, pp. 10-16).

2.1.1.3 Solid Wastes

Mining operations can generate voluminous amounts of waste rock and overburden. Milling operations produce significant quantities of tailings. The composition of the solid waste is dependent on the characteristic host rock type. Generally, the solids are not toxic, but may be hazardous to health in other respects or may become a source for toxic emissions as they weather.

Open-pit mining results in small mountains of overburden being stored next to the pit. Environmental problems range from aesthetics to habitat destruction. Overburden can be a source of toxic emissions to air and water as the material alters chemically over time. Underground mining typically has less waste rock than open-pit mining, as little overburden is removed. Solid wastes from placer mining are usually less than those from open-pit or underground activities. However, the spoil banks left from placer dredging can change the character of water sources via acid and heavy metal drainage (Nerkervis and Hallowell 1976, pp. 15-20).

2.1.2 The Applicability of Environmental Regulations to the Extraction of Materials for the Copper Sulfide/Cadmium Sulfide Material Option

The production of Cu_2S/CdS cells is described in Part I of this report. For purposes of this analysis, materials inputs to probable and alternative Cu_2S/CdS processes are examined collectively, and any regulatory impacts are specifically noted. Inputs for both the probable and alternative processes are listed in Table 2-1. From this listing, certain material inputs are examined in terms of regulatory impact upon their extraction. These materials were selected because they represent some of the major cell constituents. The regulatory programs that apply are representative of programs applicable to extraction of other material inputs.

Table 2-1. MATERIAL INPUTS FOR Cu_2S/CdS CELL PRODUCTION

Adhesive
Ammonium chloride (NH_4Cl)
Ammonium fluoroborate
Cadmium sulfide (CdS)
Chromate coating[a]
Copper foil
Cuprous chloride (Cu_2Cl_2)
Deionized water
Glass
Gold
Hydrochloric acid (HCl)
Hydrogen sulfide (H_2S)
Ink[b] (conducting)
Licorice root solution
Methanol
Nickel
Nitrogen
Oakite 91 and 91a, phosphate detergent, degreasant[a]
Photoresist
Polyvinyl butyrol
Silicon monoxide
Sodium chloride (NaCl)
Tantalum pentoxide (TaO_5)
Water
Zinc
Zinc fluoroborate

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[a] Proprietary process.

[b] Not yet developed.

2.1.2.1 Copper

Copper is one of the principal material inputs to the Cu_2S/CdS cell process. Next to aluminum, copper is the leading nonferrous metal consumed in the United States. The United States is practically self-sufficient in meeting its copper requirements, providing 95% of domestic needs. The most important copper ore type is the porphyry copper deposits which are ususally mined by open-pit methods. Copper concentrations are frequently found with other metals—most commonly lead, zinc, gold, and silver (Nerkervis and Hallowell 1976, p. 57). The extraction of copper deposits by either open-pit or underground mining produces waste streams similar to those discussed in Sec. 2.1.1.

Atmospheric Emissions. Atmospheric emissions associated with copper mining are particulates and fugitive dust, generated by ore removal, milling, and waste dumping, and gases emitted by use of blasting explosives. Milling operations, such as crushing and grinding, give rise to large quantities of dust and possibly to lesser amounts of rock gases.

There are no air pollution regulations that are specific to mining or milling operations. However, these industries will have to meet the general program requirements of the Clean Air Act as they apply. As noted, particulates constitute the major air pollutant generated by copper mining and milling. Particulate matter is one of the "criteria pollutants" for which EPA has issued a NAAQS. Non-Attainment (NA) rules and PSD review are the major programs designed to achieve the NAAQS. These programs apply to new stationary sources or sources that have undergone major modifications. Mining and milling activities are not specifically listed by EPA as "major stationary sources" subject to PSD review or NA rules. The only other way a specific source can be subject to these regulations (as a major stationary source) is if it emits greater than 250 tons per year of any regulated pollutant (40 CFR Part 51.24(b)(1)).

It is estimated that open pit mining emits approximately 1.02 pounds of particulate matter per short ton of ore mined (Nerkervis and Hallowell 1976, p. 9). A new or modified excavation site would need to produce roughly 500,000 tons of ore per year in order to generate 250 tons of particulate matter per year. As it is estimated that the entire U.S. copper industry produces 2.3 million tons per year and that 90% of that is provided by the 25 leading mines (Nerkervis and Hallowell 1976, p. 57), it is unlikely that any one copper facility would qualify as a major stationary source. However, regulations issued under the CAA that specify the requirements for State Implementation Plans (SIPs) recognize the adverse effects of fugitive dust on air quality and require the application of water or chemicals to roads, stockpiles, and other surfaces to control airborne dust (PEDCo 1979a, p. 216).

New Source Performance Standards have not been issued by EPA for the extraction industry. None of the pollutants generated by the mining or milling of copper are regulated under the NESHAP program.

The Mine Safety and Health Administration has issued health and safety standards that apply to metal and nonmetallic mining (30 CFR Part 55). Included in the standards are regulations pertaining to air quality. These regulations incorporate by reference the threshold limit values for airborne contaminants established by the American Conference of Governmental Industrial Hygienists (ACGIH). Standards that apply to copper extraction include cadmium, copper fume, lead, and zinc oxide (see Table 2-2).

Table 2-2. MATERIAL INPUTS FOR POLY-SI CELL PRODUCTION

Aluminum foil
Ammonia
Arsine (AsH_3)
Boron trichloride (BCl_3)
Coke
Copper catalyst
Copper wire
Diborane (B_2H_6)
Ethyl acetate ($CH_3COOC_2H_5$)
Ethyl vinyl acetate
Glass
Hydrochloric acid (HCl)
Hydrogen
Hydrogen fluoride (HF)
Hydrogen peroxide (H_2O_2)
Ion amine catalyst
Isopropyl alcohol [$(CH_3)_2$ CHOH]
Mylar
Nitric acid (HNO_3)
Nitrogen
Oil lubricant
Phospine (PH_3)
Phosphorus trichloride ($POCl_3$)
Quartz, silica
Silicon
Silicon dioxide (SiO_2) (quartz, sand)
Si_3N_4
Silicon trioxide (SiO_3)
Silicon tetrachloride ($SiCl_4$)
Silver
Solder, lead/tin
Sodium hydroxide (NaOH)
Stannic chloride (tin tetrachloride)
Sulfuric acid (H_2SO_4)
Tantalum pentoxide (Ta_2O_3)
Titanium
Titanium dioxide (TiO_2)
Trichlorosilane ($SiHCl_3$)
Water

Liquid Effluents. Water effluents associated with copper extraction are similar to the general extraction liquid effluents discussed in Sec. 2.1.1 above. The major problems appear to be waste water runoff from mining and milling operations, slurries from milling, and acid mine drainage.

Effluent waste streams are regulated by the NPDES program outlined in Sec. 1.3.2. This program requires all point source discharges, such as copper excavation operations, to obtain an NPDES permit. Operators of all new copper mines must submit an application which includes a Best Management Plan (BMP) at least 180 days before operations are to begin. For NPDES permit renewals, existing commercial copper mining operations must provide detailed information about the location of the effluent receiving water, a water intake and discharge accounting, effluent treatment description, and effluent characteristics. See Sec. 1.3.2 for a more detailed discussion.

Copper mining is a subcategory of ore mining, which is listed as a primary industry category by EPA. This activity, therefore, requires testing for toxic pollutants by the fractions specified by EPA. Further, the NPDES application must contain quantitative data for the applicable metals discharged for conventional and nonconventional pollutants, and must list any other hazardous pollutants discharged.

Each copper mining and milling operation must also meet the effluent limitation guidelines issued by EPA if discharge is made directly into a receiving water (40 CFR Part 440). The effluent guidelines are specific to ore mining and milling. Copper ore extraction standards apply to base and precious metals. These guidelines regulate the maximum allowable discharge concentration for total suspended solids (TSS), copper, zinc, lead, and mercury and establish the allowable pH range. Copper milling operations that utilize leaching and flotation processes for the beneficiation of the ores are subject to effluent guidelines that limit the dischargeable concentration of the same pollutants cited for mining, but also include discharge limitations for cadmium (40 CFR Part 440).

No pretreatment standards or NSPS have been specifically promulgated for ore mining and milling, but industries must meet the general pretreatment regulations for existing and new sources of pollution (40 CFR Part 403).

Copper and several other metals found in copper mining and milling waste waters were designated toxic pollutants for which EPA will issue effluent standards. To date, standards have been issued for nine of the compounds, none of which appear to be applicable to copper ore extraction.*

Certain process wastes resulting from copper extraction are listed as hazardous substances under the CWA. Discharge of these substances is limited to the reportable quantity unless an effluent limitation guideline established in the NPDES permit allows a greater discharge (see the discussion in Sec. 1.3.5). Flotation and leaching processes may utilize reagents, such as sodium cyanide or calcium hydroxide, regulated as hazardous substances (Nerkervis and Hallowell 1976, p. 16). Discharge of these reagents with the tailings or by accidental spill are limited to the reportable quantity.

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*Toxic pollutant effluent standards have been developed for aldrin/dieldrin, DDT, DDE, DDD, toxaphene, benzidine, and polychlorinated biphenyls. See EPA 1979a, pp. 86, 87.

If deep well injection is used to dispose of the liquid effluents resulting from copper extraction, the injections must fulfill the requirements of the UIC program as discussed in Sec. 1.4. Additionally, the SDWA could affect mining operations that contaminate wells or other sources of drinking water protected by the Act (Pedco 1979a, p. 97).

Solid Wastes. Solid wastes are generated at an approximate ratio of 2.5 tons of waste for every ton of copper ore extracted (Nerkervis and Hallowell 1976, p. 16). Most mining solid wastes are nonhazardous, consisting of glacial till, silts, clays, sand and gravel, and broken rock (Pedco 1979a, p. 88). These wastes are regulated mainly by state and local law, since the federal Solid Waste Management (SWM) program's scope does not include mining wastes (see Sec. 1.8.1).

Other extraction solid wastes may be regulated under the Hazardous Waste Management (HWM) program outlined in Sec. 1.8.2. The HWM program excludes only overburden intended for return to the mine site (40 CFR Part 261.4(b)(3)). Tailings, leach piles, gangue, and other wastes are considered hazardous wastes if they are intended to be discarded and are listed as a hazardous waste by EPA; they are a mixture of a solid waste and a listed hazardous waste or toxic constituent; or if they exhibit the characteristic of ignitability, corrosivity, reactivity, or EP toxicity.

The majority of the hazardous wastes associated with copper extraction are generated by beneficiation steps in the form of tailings. Copper tailings consist of sand, silt, and clay-sized particles. Although the chemical composition of copper tailings varies with location, most are basically a siliceous material with trace amounts of copper and heavy metals and trace amounts of reagents (PEDCo 1979a, p. 97). The presence of the heavy metals may cause the tailings to exhibit characteristic of EP toxicity if they are present in high enough concentrations.

Heavy metals in copper tailings are silver, lead, and cadmium. Most often, however, these metals are recovered if they are present at high concentrations. Tailings from flotation processes and the bath solutions are classified as a hazardous waste by the HWM program. Reagents utilized in copper beneficiation—such as sodium cyanide, cresylic acid, and hydrogen sulfide—are classified as hazardous wastes. These compounds, flotation tailings, and the compound containers must be stored, treated, transported, and disposed of in compliance with the HWM program regulations discussed in Sec. 1.8.2.

Worker Safety and Health. Safety and health considerations, other than air quality, are regulated by the Mine Safety and Health Administration. These regulations, discussed in Sec. 1.9, apply to the copper extraction industry.

2.1.2.2 Cadmium, Zinc, and Lead

Cadmium, like copper, is one of the major material inputs in the production of Cu_2S/CdS cells. It is mined as a component of greenockite ore but, more importantly, is recovered as a by-product of metal refining (Department of the Interior 1976, p. 914). Cadmium production is discussed in greater detail in Part I of this report.

Some cadmium is recovered from the flue dust of lead and copper smelters, but most is recovered from zinc smelting. Therefore, wastes from cadmium extraction are examined association with zinc extraction. Zinc also may be utilized for the production of Cu_2S/CdS cells in several alternative process steps. Zinc and lead occur in major ore bodies in such intimate mixtures that they must be mined together. Lead also may be used in Cu_2S/CdS cell production as solder for the grid connections.

In contrast to the major open-pit operations of the copper industry, almost all zinc and lead ores are mined by underground techniques. The ores are concentrated after initial crushing and grinding, using two general methods—gravity and flotation. The waste streams discussed in Sec. 2.1.2.1 are typical of the waste streams generated by zinc and lead extractions.

Atmospheric Emissions. Atmospheric emissions generated by zinc and cadmium mining are mainly airborne dust and gases emitted from mine explosives. Milling operations also give rise to particulates as well as to lesser quantities of rock gases.

As noted in the discussion on copper extraction, there are no air pollution regulations under the Clean Air Act specific to zinc extraction operations. As with copper extraction, the amount of particulate matter generated by a single zinc or lead extraction facility is probably insufficient to classify it as a major stationary source subject to PSD review. These facilities may have to meet the regulations requiring application of water or chemicals in order to control fugitive dust, and would be subject to general requirements of State Implementation Plans.

New Source Performance Standards have not been promulgated for the zinc extraction industry and none of the pollutants regulated under the NESHAP program appear to be generated by the extraction of zinc and lead.

Air quality standards promulgated by MSHA to safeguard worker health are applicable to the extraction of zinc and lead. Applicable standards include zinc oxides, lead, copper fumes, and cadmium.

Liquid Effluents. Water effluents resulting from zinc and lead mining, and thereby from the extraction of cadmium, are similar to those associated with the mining of copper ores. Since zinc and lead extraction operations are point source dischargers they must be issued an NPDES permit. Under the CWA, operators of new mines must submit a Best Management Plan at least 180 days before operations begin, while renewal permit applications by owners of existing operations must provide the detailed effluent information already described for copper operations. Lead and zinc extraction are included in the ore mining category, listed as a primary industry category in Table 1-7. The effluents generated therefore require testing for toxic pollutants by the specified fractions, testing of discharge waters for the presence of the metals listed in Table 1-8, including cadmium, lead, and zinc, for conventional and nonconventional pollutants, and the hazardous pollutants specified in Table C-3.

Mining and milling operations must also meet guidelines for effluent limitation issued by EPA if discharges are made directly into receiving water. Effluent standards for zinc and lead extraction have been issued with the other base and precious metals. The effluent guidelines set the maximum allowable discharge concentration for TSS, copper, zinc, lead, and mercury, and establish an allowable pH range. The major effluent problems associated with the mining of lead and zinc ores are the discharge of suspended solids from blasting and the excessive alkalinity of the discharge waters (Nerkervis and Hallowell 1976, p. 160). Flotation processes for the beneficiation of lead and zinc ores are regulated by effluent guidelines that limit the discharge concentration of TSS and heavy metals and establish an allowable pH range.

No pretreatment standards or new source performance standards have been issued by EPA for ore extraction processes. However, the industry must meet the general pretreatment standards that apply to all existing and new discharge sources.

Cadmium, lead, zinc, and other metals associated with lead and zinc extraction were designated as toxic pollutants for which EPA has issued effluent standards. No toxic pollutant standards issued to date appear to apply to the extraction of lead or zinc ores.

Certain extraction wastes, such as zinc sulfate, which result from milling processes (Nerkervis and Hallowell 1976, p. 164), are listed as hazardous substances under the CWA. Discharge of these substances is generally limited to the reportable quantity.

If deep well injection is utilized to dispose of liquid effluents, the injection program has to meet the applicable regulations established by the UIC program discussed in Sec. 1.4.

Solid Wastes. Lesser quantities of solid wastes are generated in the extraction of lead and zinc ores than copper ores, since most lead and zinc ores are mined by underground methods (Nerkervis and Hallowell 1976, p. 16). Most of the mining solid wastes are nonhazardous host rock consisting of pyrite (FeS_2), fluorite (CaF_2), and barite ($BaSO_4$) (Pedco 1979a, pp. 90, 92). These nonhazardous solid wastes are regulated by state programs because the federal Solid Waste Management Program specifically excludes mining wastes (see Sec. 1.8.1). Those solid wastes resulting from mining and milling regarded as hazardous are regulated and defined by the HWM program outlined in Sec. 1.8.2.

Overburden from lead and zinc mining intended for return to the mine site is excluded from regulation. Tailings, gangue, waste rock not intended for reclamation, slurries, and other solid wastes are considered hazardous waste if they are to be discarded and are listed as hazardous wastes by EPA, if they are a mixture of a solid waste and a listed hazardous waste or toxic constituent, or if they exhibit characteristics of ignitability, corrosivity, reactivity, or EP toxicity.

The majority of the hazardous wastes associated with excavation of zinc, lead, and copper are generated by milling operations. The chemical composition of tailings recovered from lead and zinc milling operations varies with local geology. Generally, they contain pyrite or calcium and magnesium oxides along with traces of lead, zinc, cadmium, copper, iron, nickel, selenium, and antimony (PEDCo 1979a, pp. 99, 100). The tailings also contain reagents added during beneficiation. The presence of the heavy metals may cause the tailing piles to be considered hazardous wastes if they are present in high enough concentrations to exhibit EP toxicity.

2.1.3 The Applicability of Environmental Regulations to the Extraction of Materials for the Polycrystalline Silicon Material Option

Production of polycrystalline silicon cells is described in Part I of this report. Module fabrication is discussed in terms of various possible alternatives for most production steps. For purposes of this section, material inputs are examined collectively; any significant differences in regulatory impact are specifically noted. The inputs are listed in Table 2-2. From this listing, silicon extraction is examined in terms of regulatory impacts. The regulatory programs that must be met for the extraction of silica depict the programs that apply to the extraction of other major material inputs.

Silicon is the main material input for the production of polycrystalline silicon (poly-Si) cells. Silicon is one of the more abundant minerals in the earth's crust. Silicon metal does not occur in nature, but is formed by carbothermic reduction of silica. Most silica is mined by open-pit mining of vein quartz or gravel deposits (Dept. of Interior 1976, p. 992). The extraction of silica ores produce waste streams typical of those discussed in Sec. 2.1.1 above.

2.1.3.1 Atmospheric Emissions

Atmospheric emissions associated with silica mining are particulates and fugitive dust generated by ore removal, milling, and waste dumping, and gases emitted by the use of blasting explosives. Milling operations, such as crushing and grinding, give rise to large amounts of particulates and fugitive dust. There are no air pollution regulations under the Clean Air Act specific to silica extraction operations. As with copper, zinc, and lead extraction, the amount of particulate matter emitted by silica extraction operations is probably insufficient to classify such facilities as major stationary sources subject to the PSD program. These facilities do have to meet regulations promulgated under the CAA that require the application of water or chemicals to roads, stockpiles, and other surfaces to control airborne dust, and facilities must meet the applicable SIP.

New Source Performance Standards have not been established for the silica extraction industry and none of the pollutants regulated under the NESHAP program appear to be generated by the extraction of silica.

Air quality standards promulgated by MSHA apply to silica extraction. These standards limit workers' exposure to air contaminants, including silicon dusts.

2.1.3.2 Liquid Effluents

Water effluents resulting from silica extraction are similar to those associated with the mining of other ores. Silica extraction operations are point source dischargers which must obtain an NPDES permit. New mines must submit a Best Management Plan at least 180 days before operations begin. Existing facilities making renewal applications must provide detailed effluent information as described for copper operations. Mining silicon ore is one of the primary industry categories listed by EPA. EPA requires that effluents generated by silica extraction be tested for toxic pollutants, metals, conventional and nonconventional pollutants, and hazardous pollutants.

No effluent limitation guidelines have been issued by EPA for the extraction of silica, nor have any pretreatment standards or new source performance standards been issued for ore mining and milling. However, these industries must meet general pretreatment standards if they discharge into publicly owned treatment facilities.

None of the toxic pollutant standards appear to be applicable to silica extraction. Nor do any of the hazardous substances listed under the authority of the CWA appear to be generated by the extraction of silica ores. Milling operations are limited generally to crushing and grinding; thus, no flotation associated waste problems occur.

If deep well injection is used to dispose of liquid wastes, the injection program must meet the requirements of the UIC program established under the authority of the SDWA, as discussed in Sec. 1.4. Additionally, the SDWA could affect mining operations that contaminate wells or other sources of drinking water protected by the Act (PEDCo 1979a, p. 216).

2.1.3.3 Solid Waste

Small quantities of solid wastes are generated by silica extraction—which consists mainly of blasting and cutting the host rock, crushing and grinding to reduce the size of the stone, and then transporting it to the processing locations. The disposal of solid waste overburden is regulated mainly by state programs. Negligible amounts of tailings are produced by stone mining operations such as the extraction of silica (PEDCo 1979b, p. 3). There appear to be no waste streams generated that would be considered hazardous for purposes of the HWM program.

2.1.3.4 Worker Safety and Health

Silica extraction operations also must meet the safety and health regulations promulgated by MSHA as outlined in Sec. 1.9.

2.2 PROCESSING OF MATERIALS

2.2.1 Introduction

Once the necessary materials have been extracted, most require some additional upgrading, such as refining, before they can be used in PV cell and module fabrication. In the case of metals, the initial processing steps are accomplished at the extraction site. Therefore, an analysis of their processing was addressed initially in the preceding section. Further refining steps, such as smelting, are necessary; these are examined in the following sections. Processing of chemical inputs will also be examined briefly to provide a representation of regulations applicable to the chemical processing industry.

2.2.2 Materials Processing for Copper Sulfide/Cadmium Sulfide Cell Production

The production of Cu_2S/CdS cells is described in Part I of this report. A list of material inputs for the selected processes is contained in Table 2-1. From this list, certain major inputs are examined in terms of the regulatory impacts upon process waste streams. The regulatory programs and standards that must be met for these inputs apply to the processing of the other inputs.

2.2.2.1 Copper

Copper, as noted in Sec. 2.1.2.1, is one of the main material inputs to the production of Cu_2S/CdS cells. Once the copper ore is mined and milled, it must be further upgraded for commercial applications. Smelting is the processing method used to upgrade copper ore. This is accomplished by melting the ore in one of several different types of furnaces and pouring off the molten copper. Certain chemical gases may be introduced into the furnace to reduce the impurities.

There are two broad categories of smelters: primary smelters, which process copper ores, upgrading them to copper metal, and secondary smelters, which process scrap or recycled copper into copper metal. Differences in the waste streams from these smelters will be noted and examined with respect to applicable environmental regulations.

Atmospheric Emissions. The major atmospheric emissions generated by smelters are particulates, sulfur oxides, nitrogen oxides, metallurgic fumes, gases, and fugitive dusts (Umlauf and Wayne 1977, ch. 4) The composition of particulates emitted from primary smelters is not available. However, the composition of particulates resulting from secondary copper smelters consists largely of heavy metal oxides—commonly, zinc, copper, lead, and tin. The detailed composition of the particulate matter is related to the composition of the material charged into the furnace. Further, the type of furnace used, the operational procedures, the rate of heating, and the temperature attained all affect the rate and composition of particulate emissions (Umlauf and Wayne 1977, pp. 4-20).

Sulfur oxides are a major problem with primary smelters because the sulfur content of recycled materials charged into secondary smelters is generally low (Umlauf and Wayne 1977, pp. 5-7). The principal sulfur oxide emitted is sulfur dioxide. Additional gases emitted from smelting facilities include nitrogen oxides and carbon monoxide. Metallurgic fumes generated by smelters can include arsenic trioxide, antimony trioxide, lead oxide, and zinc oxide. Additionally, secondary smelters may emit smoke from oily or insulation covered scrap. Dusts, which arise during charging, slag removal, metal pouring, and air lancing, include zinc oxide, ferric oxide, magnetite, and alumina (Umlauf and Wayne 1977, ch. 5).

Unlike extraction, there are air quality regulations specific to the industry under the CAA for both primary and secondary production facilities. Particulates, sulfur dioxide, nitrogen dioxide, and carbon monoxide are criteria pollutants for which NAAQS have been promulgated. Copper smelting facilities must meet the pollution control requirements developed in applicable State Implementation Plans (SIP) unless the facilities qualify for a Nonferrous Smelter Order (NSO).*

The major federal programs designed to meet the NAAQS for particulates and sulfur dioxide are PSD review and NA rules. As copper smelting operations are considered a "major stationary source," new construction (or modification of existing facilities) is subject to PSD review if it is within a PSD area or to NA rules if it is within an NA area. Facilities within PSD areas must adopt the best available control technology (BAT) for control of both sulfur dioxide and particulates, while copper smelters within NA areas must attain the lowest achievable emission rate (LAER) for each pollutant. Emissions from a new or modified facility within a PSD area must not cause an increase in the ambient air concentration greater than allowed increments.

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*EPA rules established at 40 CFR Part 57 include criteria for deciding whether a smelter is eligible for a Nonferrous Smelter Order (NSO). NSOs may be granted to smelters by EPA or a state to allow use of intermittent control technology in combination with dispersion techniques to maintain the NAAQS for SO_2. Under EPA regulations, a smelter is eligible if its owner cannot afford the control equipment necessary to meet its SIP emission limitation for SO_2. The regulations apply to primary copper, lead, and zinc smelters in existence and operating on August 7, 1977.

Expansion of copper smelters in an NA area must meet EPA's emission offset policy by reducing emissions to the lowest possible level and obtaining emission reductions from other plants in the affected AQCR so that net ambient air pollution levels are lowered.

New Source Performance Standards have been issued for primary copper smelters. These standards apply to all primary copper smelters that were constructed or modified after the standards were published.

Copper smelters must also meet the NESHAP standards if they emit asbestos particles or mercury. Arsenic, which also may be emitted by copper smelters, has been added by EPA to the list of NESHAPs, but standards have not yet been developed.

Worker safety and health standards regulating air quality have been issued by OSHA and directly affect copper smelting operations. The levels for specified pollutants limit the time workers can be exposed during an 8-hr day or a 40-hr workweek. Standards applicable to copper smelting include those developed for airborne copper dust and mists, iron oxide, sulfur dioxide, cadmium dust, and zinc oxide.

Liquid Effluents. Water is used in copper smelting operations for both smelting and cooling. Major effluents are suspended solids, heavy metals, and oil and grease. Waste waters from smelting operations are stored in impoundments, discharges from which are regulated under the authority of the NPDES program (40 CFR Part 421). Owners of all new copper smelters must submit an NPDES application that includes a Best Management Plan at least 180 days before operations begin. NPDES permit renewal applications by operators of existing facilities must provide detailed information about the location of effluent receiving waters, a water intake and discharge accounting, effluent treatment description, and effluent characteristics.

Copper smelting is included in the nonferrous metals manufacturing category, one of the primary industry categories listed by EPA. Effluents generated by copper smelters must be tested for toxic pollutants, metals, conventional and nonconventional pollutants, and hazardous pollutants.

The smelters must also meet the effluent limitation guidelines issued by EPA (40 CFR Part 421). These rules regulate the allowable discharges from waste water impoundments for primary copper smelters. Standards apply to the maximum allowable concentration of TSS, arsenic, copper, lead, cadmium, selenium, and zinc and establish an allowable pH range. These discharges may only be made under certain rainfall conditions, otherwise no discharge of process waste water is allowed. Secondary copper smelting is covered by standards for the discharge of TSS, copper, zinc, and oil and grease, and sets an allowable pH range. These discharges are also limited to certain rainfall conditions, otherwise no discharge is allowed. The effluent guidelines apply to discharges made directly into U.S. waters.

No separate NSPS have been issued for copper smelting operations. Primary copper smelters must meet the general pretreatment standards if they discharge into publicly owned treatment facilities. Specific pretreatment standards have been established for existing secondary copper smelters which regulate discharges made directly into publicly owned wastewater treatment facilities. Pollutants that may create a fire hazard, cause corrosive structural damage, have a pH of less than 5.0, or cause obstructions are not allowed to be discharged into such facilities. Regulations also set effluent limitations for oil and grease, copper and cadmium.

Copper and several of the metals found in smelting waste waters were designated toxic pollutants by EPA. To date, EPA has issued effluent guidelines for nine of the compounds, none of which appear applicable to by-product wastes from copper smelting.

Certain metallurgic compounds produced as by-products of copper smelting, such as arsenic trioxide and antimony trioxide, are listed as hazardous substances under the CWA. Discharge of these substances is generally limited to the reportable quantity. If liquid effluents are intended to be disposed of by deep well injection, the injections must meet the requirements of the applicable UIC program.

Solid Wastes. Solid wastes generated by copper smelting are primarily ash and waste rock. Nonhazardous solid waste disposal is regulated by state and local law, since the federal Solid Waste Management program excludes industrial wastes.

Some of the solid wastes generated by copper smelting qualify for regulation under the HWM program. Wastes that contain any of the toxic constituents listed by EPA are considered hazardous if they are intended to be discarded. Cadmium, antimony, arsenic, lead, and compounds containing these metals, are listed as hazardous and may be found in copper smelting ash. If other wastes exhibit any of the four characteristics of a hazardous waste, they are considered hazardous for purposes of the HWM program. A concentration of arsenic, lead, cadmium, or mercury in the smelting process solid waste, at or above concentrations specified, would give the waste the characteristic of EP toxicity. The slurries and sludges resulting from copper processing are listed as specific sources of hazardous wastes. Arsenic pentoxide and arsenic trioxide and mercury are listed as hazardous wastes. These compounds may be present in the solid wastes generated by smelting. All hazardous wastes must be treated, stored, transported, and disposed of in compliance with the HWM program regulations outlined in Sec. 1.8.2.

Worker Safety and Health. Safety and health regulations issued by OSHA are applicable to the copper processing industry. In addition to the air quality standards already discussed, OSHA regulations pertain to such areas as job safety, handling, labeling, and warning requirements, and protective clothing and gear for workers.

2.2.2.2 Cadmium and Cadmium Sulfide

Cadmium is another of the major materials utilized in the production of Cu_2S/CdS cells. Once cadmium is collected from the flue dust of zinc, lead, and copper smelters, or from cadmium sponge (a by-product of zinc refining), it must be refined. The production of cadmium is described in Part I of this report; a summary follows.

The cadmium-bearing fume is roasted, crushed, leached, and purified. Cadmium is then precipitated by one of several processes. After precipitation, the cadmium may be oxidized to produce cadmium oxide. Other alternative processes may be used to generate cadmium sulfate. Cadmium sulfide is then produced by dissolving the cadmium oxide in dilute sulfuric acid or by dissolving the cadmium sulfate in water. These processes both produce cadmium sulfate in solution, which is further purified to remove heavy metals and subjected to hydrogen sulfide gas to precipitate the cadmium sulfide.

Atmospheric Emissions. The major atmospheric emissions resulting from the refining of cadmium and the production of cadmium sulfide are particulates, dusts, metallurgic fumes, hydrogen sulfide, sulfates, and other volatile contaminants (see Part I of this report). Particulates are one of the criteria pollutants for which NAAQS have been issued. Cadmium metal production facilities and cadmium sulfide chemical processing operations must meet the requirements of the applicable SIPs, as discussed in Sec. 1.2.1. Chemical processing plants are listed as major stationary sources and therefore are subject to PSD review or NA rules under the Clean Air Act. These rules apply to the construction of new facilities or the modification of existing facilities which emit, or have the potential to emit, 100 tons or more of particulates per year. Such facilities within PSD areas must adopt the BAT for control of particulates and must not cause an increase in the ambient air concentration greater than allowed increments. Facilities within NA areas must attain LAER for each pollutant and must meet EPA's emission offset policy. NSPS have not been developed for cadmium metal production or cadmium sulfide processing.

If either cadmium metal production or cadmium sulfide production emit mercury, the NESHAPs issued to control such emissions must be met. Arsenic, which may also be emitted, has been added to the NESHAP list by EPA, but standards have not yet been developed (see Sec. 3.1.1.3).

OSHA air quality standards limit workers' exposure to atmospheric cadmium fumes and dusts and hydrogen sulfide. These standards specify maximum exposure levels for workers for an 8-hr day or a 40-hr week.

Liquid Effluents. Usually, H_2SO_4 or water is used in the leaching step of cadmium metal production and may be used in the processing of cadmium sulfide. In the case of cadmium metal production, the effluents are leaching reagents and heavy metals. Other liquid wastes from both cadmium metal and cadmium sulfide production include sulfuric acid, hydrogen sulfate and heavy metals. Cadmium metal and cadmium sulfide production facilities are point source discharges subject to the NPDES program of the Clean Water Act. Under EPA's Consolidated Permit regulations, all new facilities must submit an NPDES application that includes a Best Management Plan at least 180 days before beginning operations. Renewal applicants must provide the detailed effluent information described in Sec. 1.3.2.

Cadmium metal production is included in the nonferrous metals manufacturing category, and cadmium sulfide production is included in the inorganic chemicals manufacturing category, both of which are primary industry categories under the CWA. Effluents generated by both operations must undergo preapplication testing for toxic pollutants, metals, conventional and nonconventional pollutants, and hazardous pollutants.

No effluent limitation guidelines have been issued specific to cadmium metal production or cadmium sulfide processing, nor have NSPS or pretreatment standards been issued for either industry. However, the industry must meet general pretreatment standards for new and existing point sources. Cadmium and its compounds have been designated as toxic pollutants, but none of the toxic pollutant standards promulgated to date by EPA apply to these pollutants. Hydrogen sulfide and sulfuric acid are listed as hazardous substances. Discharge of these process wastes is generally limited to reportable quantities. Any deep well disposal of liquid effluents generated by either cadmium metal or cadmium sulfide production must meet the requirements of the applicable UIC program.

Solid Wastes. The solid wastes generated by cadmium metal and cadmium sulfide production are filter cakes, leach residues, and heavy metals. Filter cakes contain compounds such as lead sulfate, copper sulfide, iron with impurities, and copper with impurities. The heavy metals include cadmium, zinc, lead, and copper, while leach residues consist of heavy metals along with traces of leaching reagents, such as hydrogen sulfide, calcium hydroxide, sodium carbonate, and sulfuric acid.

The disposal of nonhazardous solids is regulated by state and local laws. Some of the solid wastes generated are hazardous under the HWM program. Wastes containing any of the toxic constituents listed in Table 1-17 are hazardous if they are intended to be discarded. Therefore, the leach cakes that contain cadmium, arsenic, or lead are hazardous solid wastes. Also, if any of the wastes exhibit any of the characteristics of a hazardous waste, such as EP toxicity, they are hazardous for purposes of the HWM program. These wastes must be treated, stored, transported, and disposed of in compliance with the HWM regulations.

Worker Safety and Health. In addition to the air quality standards, OSHA has promulgated other regulations which address worker safety and health. These regulations apply to the cadmium metal and cadmium sulfide production industries and are discussed in Sec. 1.5.

2.2.3 Materials Processing for Polycrystalline Silicon Cell Production

The production of silicon cells is described in Part I of this report. A list of the material inputs for the selected processes is contained in Table 2-2. Representative inputs will be examined in this section in terms of regulatory impacts upon the process waste streams. The regulatory impact upon the processing of material inputs examined is representative of the impact upon the processing of other materials used in poly-Si cells.

2.2.3.1 Silica

The processing of silica begins at the mine site with the crushing and grinding of the quartzite and sandstone. This material must then be refined into metallurgical-grade (MG) silicon. The MG-Si is prepared by the carbothermic reduction of silica in submerged electric arc furnaces. The carbon source is usually supplied in the form of coke, although charcoal or wood chips can be used. This process is discussed in greater detail in Part I. The MG-Si must be upgraded further to semiconductor-grade silicon. This processing will be discussed in the section on cell module fabrication (2.3).

Atmospheric Emissions. The major wastes generated by the upgrading of silica to MG-Si are atmospheric emissions of particulates and carbon monoxide. The particulates are 85%-95% silicon dioxide (SiO_2) which is formed when silicon and silicon monoxide contact the atmosphere. Both pollutants are criteria pollutants for which NAAQS have been issued (see Table 1-2). The silica processing facility must meet the requirements of the applicable SIP, as discussed in Sec. 1.2.1. If MG-Si production operations are considered secondary metal production facilities, a listed major stationary source, then construction or modification of such facilities is subject to PSD review and NA rules. Such rules apply to these facilities if they emit, or have the potential to emit, 100 tons or more of particulates per year. Qualifying MG-Si production facilities located within a PSD area for particulates must adopt the BAT and must not cause an increase in the ambient air concentration of particulates greater than allowed increments. Facilities situated within NA areas must attain LAER for particulates and must comply with EPA's offset policy.

New source performance standards have not been developed for MG-Si production operations. None of the air pollutants regulated by NESHAP appear to be emitted by the production of MG-Si. OSHA air quality standards limit workers' exposure to atmospheric carbon monoxide, hydrogen chloride, and silicon dusts. These standards specify maximum exposure levels for workers for an 8-hr workday or a 40-hr workweek (Table 2-1).

Liquid Effluents. Water is not used in the processing of MG-Si either as an input or as a cooling agent. The discharge of wastes either directly into a body of water or to a publicly owned treatment facility must comply with requirements of the NPDES permit program as discussed for cadmium metal processing. Similarly, any deep well disposal of liquid wastes must meet the requirements of the applicable UIC program.

Solid Wastes. The solid wastes generated by MG-Si production consist of filter cakes from furnace stacks, ash, and various metal oxides produced by reaction with gases pumped into the process chamber to remove impurities. The oxides include aluminum oxide, magnesium oxide, calcium oxide, and titanium oxide.

The disposal of the nonhazardous solid waste is regulated by state and local laws. It does not appear that any of the wastes exhibit any of the criteria for hazardous wastes under the HWM program. However, if such wastes occur they must be treated, stored, transported, and disposed of in compliance with HWM regulations.

Worker Safety and Health. Worker safety and health standards issued by OSHA are applicable to the MG-Si processing industry, as discussed in Sec. 1.5.

2.2.3.2 Hydrofluoric Acid

Hydrofluoric acid (HF) is a material input that may be used at several stages of poly-Si module fabrication. It has been selected to represent the type of regulatory controls that apply to the manufacture of the numerous chemical inputs used in poly-Si cells and Cu_2S/CdS cell production.

Atmospheric Emissions. There are very few sources of air emissions in an HF manufacturing plant. The majority of emissions consist of fugitive dust, particulates, HF gas, sulfur dioxide, and silicon tetrafluoride (Boscak 1978, p. 38). HF manufacturing plants must meet any applicable SIP and, as chemical process plants, are considered major stationary sources for PSD purposes under the Clean Air Act.

Construction or modification of HF production facilities is subject to both PSD review and NA rules. PSD rules apply if the plants emit, or have the potential to emit, 100 tons or more of particulates per year. Plants located within a PSD area for particulates must adopt the BAT and must not cause an increase in ambient air concentration of particulates greater than allowed increments. Facilities in NA areas must attain LAER for particulates and meet EPA's offset policy.

New source performance standards have not been established for HF production plants. The only chemical manufacturing plants applicable to the PV processes examined, for which NSPS have been promulgated, are sulfuric and nitric acid plants.

None of the pollutants regulated by NESHAP appear to be emitted by HF production facilities. Applicable OSHA air quality standards limit worker exposure to atmospheric fluoride, hydrogen fluoride, silicates, and sulfur dioxide (see Table C-8).

Liquid Effluents. Water is used in HF manufacturing to scrub the HF gas after it has been produced for cooling purposes and may also be used in plant stack scrubbers. Water used in the stack scrubbers to remove both soluble fluoride and silicon tetrafluoride as a slurry is then transferred to gypsum ponds after treatment with caustic or soda ash and lime. Sulfuric acid, calcium fluoride (CaF_2), silicon dioxide and $CaSO_4$ are also discharged to the pond system (Boscak 1978, pp. 38-40).

HF manufacturing plants are point source dischargers subject to the NPDES program. Under EPA's Consolidated Permit regulations, all new HF manufacturing facilities must submit an application which includes a Best Management Plan at least 180 days before beginning operations. Renewal applicants must provide the detailed effluent description information described in Sec. 1.3.2. HF manufacturing is included in the inorganic chemicals manufacturing industry, one of EPA's primary industry categories. Effluents generated by these industries must undergo preapplication testing for toxic pollutants, conventional and nonconventional pollutants, and hazardous pollutants.

EPA intends to develop effluent limitation guidelines for HF manufacturing, but no such standards presently exist.* Specific pretreatment standards and new source performance standards have not yet been developed for HF manufacturing. However, the industry must meet general pretreatment standards if plants discharge into publicly owned treatment facilities. Effluent guidelines and specific pretreatment standards have been developed for other subcategories of the chemical manufacturing industry, some of which may be applicable to the PV manufacturing processes. None of the toxic pollutant standards issued to date apply to HF manufacturing processes.

Sulfuric acid is listed as a hazardous substance under the CWA. Discharge of sulfuric acid and other hazardous substances that may be generated by HF manufacturing is generally limited to reportable quantities specified by the EPA.

Any disposal of liquid effluents by deep well injection must be in compliance with the UIC program discussed in Sec. 1.4.

Solid Waste. The solid wastes generated by HF manufacturing processes consist mainly of waste spar, spent filters, and precipitates (Boscak 1978, pp. 38-50). The disposal of nonhazardous solid wastes is regulated by state and local law. It is uncertain after a review of the literature whether any of these solid wastes exhibit criteria for designation as hazardous waste under the HWM program.

Worker Safety and Health. Safety and health standards issued by OSHA for workers' protection are applicable to the chemical manufacturing industry, as discussed in Sec. 1.5.

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*Subpart G of 40 CFR Part 415 has been reserved for HF manufacturing plants.

2.3 CELL AND MODULE FABRICATION

2.3.1 Introduction

This section examines regulatory impacts on the fabrication of Cu_2S/CdS and poly-Si cells and modules. The fabrication process for both cell types involves several process steps. Some of these process steps can be accomplished by various alternative methods. For purposes of this section, the waste stream generated by the steps and their alternatives will be examined collectively. Different impacts resulting from different process steps will be noted.

2.3.2 Copper Sulfide/Cadmium Sulfide Cell and Module Fabrication

The fabrication of Cu_2S/CdS cells is outlined in Part I. The process involves the deposition of a CdS layer on a substrate over which a Cu_2S layer is deposited to form a barrier, which is then covered with a metallic grid and encapsulated. Individual cells are next interconnected to form the module. These process steps can be accomplished by various alternative methods all of which produce waste streams.

2.3.2.1 Atmospheric Emissions

The fabrication of Cu_2S/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. Cells are interconnected by soldering, which emits various acid fluxes, such as zinc chloride, ammonium and stannous chlorides, lead suboxides, and formaldehyde and fluorine fumes (Briggs and Owens 1979). Hydrocarbons are produced during the degreasing done in the substrate preparation stage; however, these can be controlled with ventilation hoods and activated carbon or other absorbing methods.

The particulates emitted in AR coating and the hydrocarbons produced by degreasing are both criteria pollutants for which NAAQS have been issued. The Cu_2S/CdS cell manufacturing operations would have to meet SIP requirements for these pollutants.

These manufacturing facilities are not classified as a major stationary source by EPA and therefore do not automatically qualify for PSD review or NA rules. Nor does it appear that such facilities would emit greater than 250 tons per year of a regulated pollutant. Cu_2S/CdS cell manufacturing plants, therefore, would probably not be subject to PSD review or NA rules without the creation of a new stationary source category by EPA. Additionally, there are no NSPS that apply to such manufacturing facilities nor do any of the NESHAPs appear to be applicable to Cu_2S/CdS cell manufacturing.

The worker health and safety standards regulating air quality issued by OSHA are applicable to a Cu_2S/CdS cell manufacturing industry. Standards for workplace exposure have been developed for many of the atmospheric contaminants generated by the production of the cells.

2.3.2.2 Liquid Effluents

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 step; cadmium sulfide and hydrogen chloride from deposition processes; cadmium chloride and hydrogen chloride from etching; sodium, copper, and cadmium chlorides generated during barrier formation; and gold, nickel, and copper bath solutions used in the metalization step.

These liquid effluents may be discharged into receiving waters or into publicly owned treatment works, or they may be stored and treated as solid wastes. If they are discharged, the cell manufacturing facility may be considered a point source subject to the NPDES program as modified in EPA's Consolidated Permit regulations. Manufacturing operations producing the Cu_2S/CdS cells may be considered a primary industry source under the electronic component manufacturing category. The effluents generated must undergo preapplication testing for toxic pollutants for metals, conventional and nonconventional pollutants, and hazardous pollutants.

No effluent limitation guidelines have been issued specific to Cu_2S/CdS cell or module manufacturing operations. However, there are effluent guidelines which apply to electroplating and etching operations performed during cell manufacturing processes (40 CFR Part 413). Plating operations may be used for substrate preparation and grid application during metallization. The 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 on the size of the regulated facility, the volume of discharge water, and the number of plant employees. Regulations also control discharges resulting from the electroplating of precious metals such as gold in the metallization step. These standards establish an allowable pH range and set the quantity of gold which may be discharged after application of BAT. Economics will result in almost complete recycling of this metal after use. There are pretreatment standards which limit effluent discharges made into publicly owned treatment facilities. Effluent standards exist for discharges resulting from chemical etching of nonferrous materials and pretreatment standards apply (see also 40 CRF Part 413).

There are no NSPS developed for the Cu_2S/CdS cell manufacturing industry, nor for any of the specific process steps involved. Additionally, none of the toxic pollutant effluent standards issued to date by EPA appear to be applicable to the manufacture of these cells.

Some of the liquid effluents generated by the manufacture of the Cu_2S/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 to the reportable quantities. Deep well disposal of any liquid effluent produced during the manufacture of Cu_2S/CdS cells must be in compliance with applicable UIC programs.

2.3.2.3 Solid Wastes

The solid wastes generated by the manufacture of Cu_2S/CdS modules basically consist of any of the liquid effluents discussed in the previous section that are stored and disposed of on land.

Disposal of nonhazardous wastes is regulated by state programs established under RCRA. Some of the wastes generated by the production of the cells qualifies for regulation under the HWM program if disposed of on land or if stored for treatment preceding eventual discharge. If any of the wastes contain any of the toxic constituents listed by EPA, they are considered hazardous wastes. Wastewater treatment sludges, spent bath solutions, bath sludges, and spent stripping and cleaning bath solutions from electroplating operations, and certain spent solvents used in degreasing operations are all listed by EPA as hazardous wastes.

Additionally, if any of the wastes exhibit any of the four characteristics of hazardous waste, discussed in Sec. 1.8.2, they are considered hazardous for purposes of the HWM program. Such wastes must be treated, stored, transported, and disposed of in compliance with HWM program regulations.

2.3.2.4 Worker Safety and Health

In addition to the air quality standards discussed in the section on atmospheric emissions, OSHA has issued safety and health regulations that establish job safety, handling, labeling, and warning requirements, and protective gear for workers. These regulations are applicable to the manufacture of Cu_2S/CdS cells.

2.3.3 Polycrystalline Silicon Cell and Module Fabrication

The fabrication of silicon modules is outlined in Part I. The process begins with the refinement of the MG-Si to substrate quality polycrystalline silicon. Three alternative refinement processes are examined. The next step involves fabrication of the silicon wafer, which may be accomplished by one of three alternative procedures depending on the method used for silicon refinement in the preceding step. These wafers are then metalized—during which the grid is applied—and are coated with an AR compound, encapsulated, and interconnected to form the module. These process steps all produce waste streams (outlined in Part I) and are discussed collectively in terms of regulatory impact in following subsections.

2.3.3.1 Atmospheric Emissions

The fabrication of silicon cells generates various atmospheric contaminants. Silicon purification produces silicon and silicon oxide particulates, hydrogen chloride, nitric acid, chlorine, nitrogen dioxide, and carbon dioxide fumes if the acid leach method is used; silicon particulates and hydrogen gas if the silicon tetrachloride method is used; and silicon and silicon oxide particulates, hydrogen chloride fumes, silicones, silicon chlorides, and hydrogen gas if the Siemens process is used.

Cell fabrication generates boride compounds, hydrogen chloride, and nitrogen and hydrogen gases if the diffused P/N junction alternative is used; hydrogen chloride, chlorine, nitrogen and hydrogen gases, nitric and hydrofluoric acid fumes, and tin oxide and chloride particulates if the tin oxide spraying deposition alternative is used; and dopant gases, such as hydrogen, phosphorous pentoxide, and phosphorus trichloride if phosphine is the dopant used, and silicon oxide particulates if the epitaxial deposition alternative is used. The application of an AR coating may emit particulates depending on the coating and encapsulation may emit ethyl vinyl acetate fumes. Interconnection of the cells involves soldering—which emits various gases, such as zinc chloride, ammonium and stannous chlorides, lead suboxides, and formaldehyde and fluorine fumes (Briggs and Owens 1979).

The particulates, generated in several process steps, and the nitrogen dioxide, emitted in one alternative purification step, are criteria pollutants for which NAAQS have been issued. Therefore, the manufacturing operations will have to meet the applicable SIP requirements for these pollutants.

Since the silicon module manufacturing industry is not classified as a major stationary source, the facilities do not automatically qualify for PSD review or NA regulations. Nor does it appear likely that such facilities would emit greater than 250 tons per year of a regulated pollutant. Therefore, silicon cell or module manufacturing operations would probably not be subject to PSD review or NA rules without the creation of a new stationary source category by EPA. Additionally, there are no NSPS which would apply to silicon cell or module manufacturing facilities nor do any of the NESHAPs appear to be applicable to the industry.

Several of the air contaminants generated during cell and module manufacturing are regulated by OSHA air quality standards. Standards limit workers' exposure to chlorine, carbon dioxide, fluoride, hydrogen chloride, hydrogen fluoride, nitric acid, nitrogen dioxide, silicon dusts and fumes, inorganic tin compounds, phosphorus trichloride, phosphine, and zinc chloride.

2.3.3.2 Liquid Effluents

Water is used during several of the process steps as an input, solvent, or rinse and thereby becomes contaminated with metals, oils, acids, and suspended salts. Silicon purification discharges include hydrogen fluoride, hydrogen chloride, nitric acid, nitric oxides, iron, aluminium, and calcium chlorides and nitrides, and a slurry which contains an estimated 50%-70% of the silicon wafer.

Similar to the effluents generated by Cu_2S/CdS cell manufacturing, the silicon cell effluent streams may be discharged into a receiving water or into public treatment works, or they may be stored and treated as solid wastes. If they are discharged, the cell manufacturing operation is a point source subject to the NPDES program as modified by EPA's Consolidated Permit program.

Manufacturing operations producing the silicon modules may be considered a primary industry source under the electronic component manufacturing category. If they are considered under this category, the effluents generated must undergo pre-application testing for toxic pollutants, metals, conventional and nonconventional pollutants, and hazardous pollutants.

No effluent limitation guidelines apply to the silicon module manufacturing industry as a whole, nor do any of the specific guidelines appear to be applicable to any of the process steps. Additionally, no pretreatment standards or NSPS have been issued that are applicable to the silicon module manufacturing operations. However, the facilities must comply with general pretreatment standards if any discharges are made into public treatment works. None of the toxic pollutant effluent standards issued to date appear to apply to the manufacturing of silicon cells.

Some of the effluents generated are listed as hazardous substances under the CWA. Hydrochloric, hydrofluoric, and nitric acids and ferric chloride generated during acid leach purification of silicon, and sodium hydroxide and ammonia generated during cell fabrication processes are listed as hazardous wastes. The discharge of these effluents is generally limited to reportable quantities. Any disposal of a liquid effluent by deep well injection must be in compliance with the applicable UIC program.

2.3.3.3 Solid Wastes

The solid wastes generated by the manufacture of silicon cells and modules consist of any of the liquid effluents discussed in the previous section that are stored and disposed of on land. Additionally, silicon dust collected from silicon purification processes, waste titanium and silver metals from metallization steps, and waste glass, plastics, and aluminum foil resulting from encapsulation procedures make up the solid wastes. Furthermore, the silicon tetrachloride by-product produced during Siemens purification of silicon may be a solid waste if no suitable resale market exists.

Disposal of nonhazardous wastes is regulated by state land disposal programs established by RCRA. Some of the wastes generated during production of silicon cells and modules may qualify for regulation as hazardous wastes under the HWM program if disposed of on land or if stored for treatment preceding eventual discharge. If any of the wastes contain any of the toxic constituents listed in Table 1-17 they are considered hazardous. Certain spent solvents used in degreasing operations are listed as hazardous waste in Table C-10.

If any of the solid wastes exhibit any of the four characteristics of hazardous waste discussed in Sec. 1.8.2, they are considered hazardous wastes. All hazardous wastes generated by silicon module fabrication must meet HWM program requirements for storage, treatment, transport, and disposal.

2.3.3.4 Worker Safety and Health

Manufacturers of silicon modules must comply with OSHA safety and health regulations pertaining to job safety, handling, labeling, and warning requirements, and protective gear and garments for workers (see Sec. 1.5).

2.4 INSTALLATION, OPERATION, AND MAINTENANCE

This section examines briefly the environmental concerns associated with the installation, operation, and maintenance of the PV systems using Cu_2S/CdS and poly-Si cells materials. The regulatory programs already discussed in Sec. 1.0 will not affect this stage of either of the PV materials options at very many points. Rather, this stage of the system life cycle for both Cu_2S/CdS and poly-Si cells systems is affected more by state and local statutes and ordinances.

Both PV materials options will be collectively examined in terms of centralized and decentralized systems. For purposes of this discussion, centralized systems are large, greater than 100 MW, utility-owned central stations that supply power to regional electric grids; decentralized systems are residential and intermediate load center systems located at or near their end uses.

2.4.1 Centralized Systems

The installation of centralized PV systems will produce various environmental impacts. Large amounts of land will be needed for these facilities. The land requirements for a 100-MW silicon cell facility that has a 15% cell efficiency and a 10% overall efficiency is estimated at 2 to 3 km^2 (Mintzer 1980, p. 23). These facilities would most likely be constructed in the arid lands of Southwest states.

Construction of these systems will disturb the local ecosystem. Soils will be disturbed and compacted, animal species will be displaced, and habitat destroyed by array installations that could involve paving large amounts of the total area used. Installations can cause increased erosion which could lead to siltation of local streams and lakes. Increased erosion also produces increased levels of fugitive dust, as do construction activities themselves (Energy and Environmental Analysis [EEA] 1980, pp. 1-29).

No emissions are expected during routine operation of PV systems; however, overheating of the units may cause volatilization and offgassing of either or both cell or encapsulant materials. This may present a potentially severe accident problem when concentrating collectors are used (Mintzer 1980, pp. 5-36). Fires also can result in offgassing of cell materials; however, the likelihood of fires involving large areas of a central station plant is slight, with the possible exception of systems located in areas where vegetation would be capable of sustaining large fires. Fires, earthquakes, and other accident conditions are more of a concern with Cu_2S/CdS cells since cadmium and cadmium sulfide are highly toxic and tend to remain in the soil and to bioaccumulate in animals (EEA 1980, pp. 5-24).

Silicon cells tend to remain chemically stable and biologically inert during all plausible accident conditions (Mintzer 1980, p. 50). Microclimate impacts, changes in weather patterns, temperatures, and humidity conditions near the ground, can be caused by central station systems. It is not possible to predict at what scale and concentration of PV central station deployment mesoscale climate changes, such as increased cloud formation and rainfall, will occur; however, large-scale deployment of such systems could affect regional weather patterns (EEA 1980, pp. 5-15).

Maintenance of centralized PV stations can have various minor environmental impacts. Central stations may use significant amounts of water for array surface cleaning. This may be an environmental problem in arid regions, where such facilities are likely to be situated. If detergents such as phosphates are used, runoff may pollute local water supplies. Vegetation will have to be controlled so as not to interfere with systems' operation and maintenance. This may be accomplished by herbicide treatment, paving, or mowing. Herbicides may get carried into local water systems and may endanger local wildlife. Paving causes habitat destruction and leads to increased erosion (EEA 1980, pp. 5-12). Vegetation suppression may cause fugitive dust if it results in bare soil and in increased erosion and siltation of local water supplies. Finally, accidental electric shocks of workers may occur during maintenance procedures.

2.4.2 Decentralized Systems

The installation of decentralized systems appears to produce fewer environmental impacts than the installation of central stations. Because residential units are likely to be roof mounted, they will not require appreciable land area. Ground-mounted systems will have largely the same disruptive ecological effects as central stations, but of a much smaller magnitude per location. The installation of decentralized systems should not have any major impacts on water or air quality (EEA 1980, pp. 1-5). There may be a greater incidence of installation-related worker injuries associated with residential roof-mounted systems. Additional concerns unique to the installation of decentralized systems include problems of structure design, solar access protection, and roof-overloading. These problems may be avoidable through the enactment of local ordinances.

No atmospheric emissions are expected during routine operation of these systems; however, overheating of the units may cause volatization and offgassing of either or both cell or encapsulant materials to occur (EEA 1980, pp. 5-36). Offgassing would also occur during fires. Residential roof-mounted systems present a greater hazard because of the proximity of flammable materials and dense population (EEA 1980, pp. 1-6). Fires and other accident conditions present a greater hazard for Cu_2S/CdS systems because of the toxicity of cadmium compounds when compared with relatively stable silicon compounds. However, it is likely that a variety of natural and synthetic materials in typical residences will produce more significantly hazardous emissions in the event of a fire than residential-size quantities of PV cadmium compounds.

The operation of residential systems should not result in appreciable microclimate impacts. Decentralized systems are not expected to have any significant effects on the mesoclimate.

Maintenance of decentralized systems should result in fewer environmental impacts than central station maintenance. Residential systems will require minor amounts of water for array cleaning. Vegetation suppression would only be necessary for ground mounted systems. The danger of electric shocks or burns from handling hot units may be greater for decentralized residential units than central stations if handled by inexperienced workers.

2.4.3 Applicable Regulatory Programs

As mentioned in the introduction to this section, most of the regulatory effects on PV system installation, operation, and maintenance impacts will arise from state laws and local ordinanaces. Federal programs may apply in some areas, however.

Installation of central PV stations may be affected by federal land management programs, particularly in the southwest United States. The utilization of federal land must be in conformance with the Federal Land Policy and Management Act, the National Forest Management Act, and NEPA. State and local land-use controls will affect installation of central stations (Mintzer 1980, p. 35). If installation threatens the habitat of an endangered or threatened species, the requirements of the Endangered Species Act would apply (EEA 1980, pp. 5-33). Installation practices must comply with applicable worker safety and health standards developed by OSHA. The installation of decentralized systems will be influenced largely by the adequacy of solar access protection laws. Local building and electrical codes will apply to installation of the systems.

System operation may also be affected by federal and state regulations. It does not appear that any of the substances emitted during offgassing are regulated by NESHAP; however, OSHA air quality standards may apply to central-station workers. Any chemical spills that occur would be regulated under RCRA's HWM program if such chemicals were hazardous.

Discharges from array cleaning operations that utilize chemicals may have to be pretreated under the conditions of an NPDES permit if such facilities are considered point sources. The use of herbicides to suppress vegetation may be regulated by state or federal pesticide control programs.

2.5 DECOMMISSIONING

Decommissioning of spent PV cell, module, and array components will generate various solid wastes. Assuming a 20-year lifetime, the quantity of spent components generated during the first 10 years of a system will be relatively small; an increase in the waste stream will occur toward the end of the design lifetime. Decommissioning of an entire array, particularly for a large central station, will probably be rare unless radically new PV technology makes replacement of an entire array economical (EEA 1980, pp. 5-42).

Disposal of spent components will probably be by means of landfills. Incineration would be a less likely disposal method, because toxic offgassing could occur. With residential applications, the individual homeowner may well discard either a failed module or an entire array. In the absence of enforceable guarantees, waste cells disposed of by homeowners could easily end up in municipal incinerators. However, if incineration were used knowingly, the incinerators would have to meet the NSPS issued under the authority of the CAA. Most of the solid wastes generated during decommissioning would be nonhazardous. Disposal of these wastes have to meet state regulatory programs set up under the federal SWM program of RCRA. Some of the spent modules, particularly the Cu_2S/CdS materials, would require an approved hazardous waste disposal site before landfill (EEA 1980, pp. 5-35). Cadmium and copper in the wastes could mandate their designation as EP-toxic under the HWM program.

The amount of land required for disposal sites depends on the technological and economic feasibility of recycling. The extent of government regulatory effort under RCRA to encourage materials recycling will also be a factor (EEA 1980, pp. 5-35). Silicon systems present less of a disposal problem than do Cu_2S/CdS systems because silicon is relatively stable and inert.

In general, centralized systems may present more opportunities for recycling materials than would decentralized systems, since larger quantities of materials would be available at one place and time. Recycling of decentralized system components could be done through businesses that service and maintain the systems (EPA 1979a, p. 16). The value of materials within the spent components will determine the extent of this practice.

2.6 TRANSPORTATION

Transportation is needed at all stages of PV cell production. Inputs, end products, and, sometimes, wastes must be transported to and from each process operation. The major area of concern for purposes of this report is the transport of hazardous substances. The U.S. Department of Transportation (DOT), under the authority of the HMTA, has designated certain materials as hazardous if transported in commerce. DOT has issued regulations pertaining to packaging, marking, labeling, and conditions for shipping. Table 1-16 lists selected substances DOT has classified as hazardous. Additionally, transport of all wastes considered hazardous under RCRA is regulated by standards issued by EPA as part of th HWM program.

Certain extraction inputs, such as mining explosives and beneficiation reagents, are regulated as hazardous by DOT. Tailings, spent reagents, and heavy metal wastes are hazardous wastes. Their transport to treatment or disposal facilities is regulated by the HWM program. Some mined ores and minerals are regulated by DOT as hazardous substances, including arsenic, coal, and titanium.

Material processing inputs, such as acids, alcohols, ammonia, borax trifluoride, coke, copper chloride and others are hazardous substances subject to DOT regulations. Certain processing wastes, such as ashes or filter cakes containing heavy metals would be regulated under the HWM program if transported for treatment or disposal. Others may be regulated under DOT regulations. Additionally, some process products, particularly chemicals, are considered hazardous under DOT regulations.

Many of the regulated processing products are module fabrication inputs and therefore their transport to the manufacturing operation is also regulated. Certain wastes, such as plating bath sludges, stripping solutions, plating bath solutions, and degreasants must meet the transportation requirements of the HWM program. Other wastes, such as methanol, copper chloride, and assorted acids, are regulated by DOT.

The installation, operation, and maintenance process stage generally produces no wastes that would be transported. Certain inputs required for initial installation may be regulated by DOT, but it does not appear likely, because processed materials most often will be used. Road oil which may be used to control dust and certain pesticides used for vegetation control would be regulated by DOT. Any hazardous wastes generated during decommissioning would be regulated by the HWM program transportation requirements.

2.7 SUMMARY

The applicability of various environmental, health, and safety regulatory programs on the production, installation, operation and maintenance, and decommissioning of both copper sulfide/cadmium sulfide and polycrystalline silicon PV materials options is presented in Table 4-1. The table roughly illustrates which stages and processes are influenced by which regulatory programs. The magnitude of an impact can only be understood through an analysis of the applicable program and from the discussions in the text.

Note that, where no federal regulations apply, there still may be applicable state regulations. These state programs are often, but not always, constructed to meet the goals and objectives of the federal acts and policies discussed in this report.

The degree to which a particular process stage is influenced by regulation will depend on the waste disposal options and pollution-control technologies chosen. This analysis makes no attempt to distinguish among these, especially in Table 4-1. The assumption is made that a waste will be disposed of in all possible media so that each potentially applicable regulatory program may be identified.

It is worth noting again that only certain wastes, material inputs, and processes were examined for each stage of PV production. The ones chosen serve as examples of how the several regulatory programs apply. This type of analysis requires greater detail for more of the material inputs and waste streams, particularly quantitative measures, before comprehensive PV development and industry policy decisions can be made.

Finally, the energy used at each process stage of PV production will have a set of environmental impacts subject to regulatory controls not considered in this report. Within this environmental, health, and safety regulatory framework, it is possible to explore emerging developments in regulatory control that could influence advanced PV material options in the future. Section 3.0 provides an outline of these regulatory trends as they may apply to Cu_2S/CdS and poly-Si PV materials.

SECTION 3.0

REGULATORY TRENDS

The two preceding sections of this report have identified the range of federal environmental, health, and safety regulatory programs that probably will be applicable to one or more stages of Cu_2S/CdS and poly-Si photovoltaic cell development. This analysis has been limited, in part, because of the strictly qualitative information available on materials inputs and waste stream by-products of the two PV material options. There has been no attempt (nor is it indeed possible to make one) to indicate whether regulatory compliance uncertainties surround any stage of PV development. At best, the analysis can indicate the potential applicability of regulatory programs.

As noted in Part I of the report, alternative manufacturing processes may be used at future stages of technology development. This could easily result in the addition or subtraction of regulatory programs from the set identified in Part I. Changes in the regulatory framework may modify this analysis similarly. 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; 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.

It is possible, however, to achieve at least some indication of regulatory modifications before their actual occurrence. Regulatory programs already legislated but not yet implemented by the administering agencies can be identified relatively easily. New legislative initiatives can be tracked from the day of introduction in Congress, if not earlier, through administration or congressional statements of intent. Where agencies have been given discretionary authority to publish rules and guidelines, it is somewhat more difficult to determine either the content or time frame of regulatory proposals. However, as environmental, health, and safety standards generally fix numerical limits on pollutant emissions, worker exposure, etc., such standards require an adequate foundation in health effects and ecological research. The identification of current and planned research agendas can serve as a surrogate measure of agency interest in further regulatory proposals.

This section of the report will attempt to identify some of the major regulatory proposals, legislative initiatives, and research efforts that could eventually lead to rulemaking applicable to Cu_2S/CdS and poly-Si photovoltaic cell development. While regulatory trends may be identified, the true intent and actual impact of specific proposals must await future events.

3.1 AUTHORIZED REGULATORY PROGRAMS

Regulatory programs authorized under federal environmental, health, and safety legislation are subject to a variety of implementation time frames. In some instances, enabling legislation requires agency action to establish procedures and set standards within discrete time periods. Some programs, though, give agencies more leeway and time to develop rules. Accelerated regulatory implementation schedules generally reflect the legislative priority assigned to a particular environmental issue. Agency staff, resource, and data shortcomings often result in program delays, despite the best intentions. The regulatory process itself presents a variety of opportunities for delay in program implementation. Table 3-1 is an illustration of the regulatory flowchart associated with EPA's development of a new source performance standard under the Clean Air Act (EPA 1979a, p. 16).

Table 3-1. REGULATORY FLOW: A NEW SOURCE PERFORMANCE STANDARD DEVELOPED BY EPA

Clean Air Act Transmitted to EPA
↓
Standard Development
↓
1. Source Priority Determination
2. Industry Survey
3. Pollution Control Technology Survey
4. Issues Analysis

↓
Regulation Proposed and Published in the Federal Register
↓
Public Comment
↓
Regulation Becomes Final
↓
Implementation

3.1.1 The Clean Air Act

3.1.1.1 Prevention of Significant Deterioration

EPA is presently considering whether to propose regulations providing guidelines for states to develop plans that limit emissions of carbon monoxide, nitrogen dioxides, lead, hydrocarbons, and ozone in PSD areas (EPA 1980b, p. 44114). These regulations are mandated in the Clean Air Act. EPA's tentative timetable calls for a notice of proposed rulemaking in August 1981 and final PSD rules by April 1982. The potential applicability of these proposed rules on one or more stages of PV development will be similar to that discussed for particulates and SO_2 in Sec. 2.0 of this part.

3.1.1.2 New Source Performance Standards

EPA is developing new source performance standards to control emissions from a number of additional industries. Table 3-2 lists the industries of potential significance to one or more stages of PV development and the timetable tentatively established by EPA for NSPS rulemaking for each (EPA 1980b, pp. 44109-44112). The proposed NSPS for nonmetallic mineral operations and electric arc furnaces would apply at the materials extraction stage of PV cell development. The proposed NSPS for organic solvent cleaners would apply at the fabrication stage.

Table 3-2. SELECTED INDUSTRIAL CATEGORIES FOR WHICH NSPS ARE BEING DEVELOPED

Industrial Category	NSPS Proposal	Timetable
Nonmetallic mineral operations	Control of particulate emissions from quarrying and related facilities	Final rule: 4/81
Organic solvent cleaners	Control of evaporative emissions from metal cleaning and degreasing operations	Final rule: 1/81
Electric air furnaces in ferrous foundries	Control of particulate emissions from electric air furnaces	Final rule: 7/81

Source: 45 Federal Register No. 127, pp. 44109-44112.

3.1.1.3 National Emission Standards for Hazardous Air Pollutants

EPA is required under the Clean Air Act to develop NESHAPS for emissions that cause or contribute to air pollution which results in an increase in mortality or in serious or incapacitating illness. NESHAPS under consideration by EPA with potential applicability to PV development include arsenic (from glass manufacturing and from copper, zinc, and lead smelters) (EPA 1980b, p. 44113) and coke oven emissions (EPA 1980b, p. 44113).

3.1.1.4 National Ambient Air Quality Standards

Currently under EPA review for possible revision are the NAAQS for carbon monoxide, nitrogen dioxide, sulfur dioxide, and particulates (EPA 1980b, p. 44108). Updated criteria documents are being prepared that will review the health basis for the current standards. Final rules reflecting these NAAQS reviews are expected to be complete by late 1981. The revised NAAQS will apply at every stage of PV development, for each of the two materials options.

3.1.2 The Clean Water Act

3.1.2.1 Effluent Limitation Guidelines and Pretreatment Standards

EPA currently is working on regulations to control the discharge of toxic and other substances from different industries. Regulatory mechanisms principally involve the development of effluent limitation guidelines and pretreatment standards for both new and existing sources which discharge into municipal waste treatment systems. Table 3-3 lists the industries for which effluent guidelines and pretreatment standards are being developed. Applicability to PV development will be at the extraction and processing stages for each materials option.

3.1.2.2 Water Quality Standards

EPA is considering a revision of its water quality standards regulations. As described by EPA, the regulation

> may require States to adopt Water Quality Standards for some toxic pollutants covered by ambient water quality criteria. One effect of this will be that dischargers, both municipal and industrial, may have to install treatment technology beyond that required by Best Practical Waste Water Treatment Technology (BPWTT) or Best Available Technology (BAT) guidelines. (EPA 1980b, p. 44135)

A notice of proposed rulemaking was expected in late 1980, and final regulatory action was projected for May 1981. There could be several stages of PV development at which this proposal would apply. The most direct impact could occur during the processing and fabrication stages, where toxic pollutants may most likely enter a liquid waste stream. See Sec. 2.0 for a discussion of specific toxic pollutants associated with the respective stages of PV development.

Table 3-3. SELECTED INDUSTRIAL CATEGORIES FOR WHICH EFFLUENT LIMITATION GUIDELINES AND PRETREATMENT STANDARDS ARE BEING DEVELOPED

Industry	Tentative EPA Timetable	
Iron and steel manufacturing	Proposed rule Final rule	12/80 6/81
Nonferrous metals manufacturing	Proposed rule Final rule	5/81 12/81
Ink formulation	Final rule	4/81
Ore mining and dressing (point source)	Proposed rule Final rule	10/80 7/81
Inorganic chemicals manufacturing	Final rule	2/81
Plastics and synthetics	Proposed rule Final rule	6/81 5/82
Miscellaneous chemicals: adhesives and sealants	Proposed rule	2/81
Electroplating	Proposed rule Final rule	4/81 11/81
Copper forming	Proposed rule Final rule	2/81 9/81
Aluminum forming	Proposed rule Final rule	3/81 9/81
Nonferrous metals forming	Proposed rule Final rule	11/82 6/83

Source: EPA 1980b, p. 44131-44134.

Table 3-4. REGULATORY PROPOSALS FOR HAZARDOUS SUBSTANCE DESIGNATIONS UNDER THE CLEAN WATER ACT

Rulemaking Action	Summary Description	EPA Timetable	
Designation of carcinogens as hazardous substances	The regulation identifies substances that pose a threat of cancer to people who drink from water sources which contain discharges of hazardous substances	Final rule	12/80
Designation of human acute toxicants as hazardous substances	The regulation identifies additional toxic substances that, when discharged into drinking water sources, pose a threat to people	Proposed rule	10/80
Determination of reportable quantities for carcinogen hazardous substances	The regulation provides the reporting requirements necessary for carcinogen substances designated as hazardous	Proposed rule Final rule	10/80 6/81

Source: EPA 1980b, pp. 44136-44137.

3.1.2.3 Toxic Pollutants

EPA is proposing to add ammonia to its list of toxic substances developed under § (307)(a) of the Clean Water Act. Final rulemaking was expected in September 1980 (EPA 1980b, p. 44136).

3.1.2.4 Hazardous Substances

As discussed, the CWA requires that EPA regulate hazardous substances by, among other measures, identifying such substances and establishing reporting requirements for spills. Table 3-4 outlines the major hazardous substance control regulations now in the rulemaking process at EPA. Once in effect, the hazardous substance designations will add to the list of those chemicals for which testing and reporting must be done before discharging effluents. These designations are likely to affect the processing and fabrication stages of PV development.

3.1.3 The Safe Drinking Water Act

The deep well injection of hazardous wastes is intended by EPA to be regulated under state underground injection control programs. Recently published EPA rules require states to devise UIC plans consistent with EPA standards. In the absence of such plans, EPA will enforce its own program. States have been given six months to phase out wells that discharge toxic, corrosive, or other hazardous waste.*

3.1.4 The Occupational Safety and Health Act

3.1.4.1 Substances Regulated as Carcinogens

In an action having no immediate regulatory effect but which could signal future carcinogen determinations, OSHA recently listed 107 substances as candidates for further review as potential occupational carcinogens (U.S. DOL 1980). Placement of these 107 substances on OSHA's list is part of an initial screening of more than 2,000 substances with some evidence of carcinogenicity. At this moment, listing does not represent a scientific determination of carcinogenicity nor is it a preclassification warning. Rather, it will serve as one of the primary sources for the development of priority lists of Category I and Category II potential carcinogens (see Sec. 1.5.2).** The candidate list does not differentiate the substances as Category I or Cataegory II Potential Carcinogens.

OSHA will be considering a variety of factors in individual rulemaking procedures on occupational carcinogen determinations. Among these will be:

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*The regulations were issued in the Federal Register of June 24, 1980, and took effect July 24, 1980.

**EPA's Carcinogen Assessment Group has developed a list of approximately 150 substances it considers to show substantial evidence of carcinogenicity.

- the estimated number of exposed workers;
- the estimated levels of workers' exposure;
- the molecular similarity of the substance to a known carcinogen; and
- the availability of safer substitute substances.

There is a clear potential for OSHA-designated potential carcinogens to affect the development of Cu_2S/CdS and poly-Si photovoltaic cells. Only a few of the 107 substances recently listed are used as material inputs or created as waste by-products in the two cell options. However, a number of substances on an earlier preliminary list of Category I carcinogens are prominent in the two cell processes. Among these are cadmiun, cadmium oxide, cadmium sulfate, cadmium sulfide, sulfuric acid, nickel, ammonium, chromium, and other chromium compounds.

Under the terms of OSHA's Cancer Policy, a streamlined set of procedures and scientific assumptions have been established ("OSHA Develops New Cancer Policy" 1980). These rules will apply to the rulemaking proceedings in which all future workplace carcinogens will be controlled. A substance qualifying under OSHA's rules of evidence for carcinogenicity will trigger regulation at "lowest feasible" levels. 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 may be banned. Suspected carcinogens that do not meet OSHA's rules of evidence may still be regulated in the workplace at less stringent levels.

Finally, OSHA has noted the "special circumstances" of research laboratories and will entertain exemptions for them during the standard-setting process for each chemical (Lehner 1980).

3.1.4.2 Occupational Exposure Regulations

Perhaps the most significant development with respect to OSHA's occupational exposure regulations occurred in July 1980 when the U.S. Supreme Court struck down the 1977 exposure standard for benzene (Lehner 1980). The Court ruled that OSHA must provide more justification for its health rules than it did in developing the benzene standard. Specifically, OSHA's benzene standard (reduced from 10 ppm to 1 ppm) was ruled not "reasonably necessary" as required in the statute, unless the then-existing level (10 ppm) was found to be unsafe (Cooper 1980, p. A15). OSHA had not determined that the 10-ppm level presented a significant risk.

OSHA's rationale for failing to pursue such a finding was embodied in its "safe-level" policy for exposure to carcinogens. OSHA policy holds that there is no such thing as a "safe level" for exposure to carcinogens. Thus, once a substance has been demonstrated to cause cancer at any level of exposure, as benzene had, OSHA would require reduction of exposure to the lowest feasible levels (Lehner 1980). The benzene ruling is significant for all future OSHA carcinogen standards. Determinations of "significant risk" probably will have to precede establishment or modification of occupational exposure regulations. Substances used or produced in PV cell production processes will be affected accordingly.

3.1.5 Toxic Substances Control Act

EPA is curently developing regulations under several sections of TSCA which will apply to or affect different stages of PV cell production (EPA 1980b, pp. 44127-44130).

3.1.5.1 Reporting and Record Keeping

EPA is preparing a series of three reporting regulations on chemicals for which regulatory controls are being developed. Chemical processors will be required to supply information on their products regarding exposures, by-products, and toxicity. The regulations being proposed largely apply to chemical manufacturers and processors and will assist EPA in identifying chemicals for possible regulation. Final rules on reporting and recordkeeping are scheduled for the end of calendar year 1981 (EPA 1980b, p. 44129).

Under TSCA, "processors" include the electrical component industry, which may handle chemicals in preparing its products. EPA notes that its reporting rules will complement those already issued by OSHA on recordkeeping for occupational injuries and immediate health hazards ("Proposed New Toxic Rules . . ." 1980). EPA proposals will also require notification and record keeping for allegations of adverse reaction to health or the environment from the use of toxic chemicals.

3.1.5.2 Specific Control Actions

Chemical hazard warning labels will be required under rules EPA is expected to issue in mid-1981. As one in a series of specific chemical control actions required by TSCA, the labels rules will require chemical manufacturers to affix warning labels to containers distributed in commerce. The labels would inform industrial users of hazardous chemical substances about health and safety hazards, including control of exposure and remedial actions. Final labeling rules are expected in July 1981.

Both the reporting/recordkeeping and labeling regulations would apply to the processing and fabrication stages of industrial PV activity, where hazardous chemicals probably will be handled or controlled most frequently.

3.1.6 The Resource Conservation and Recovery Act

3.1.6.1 Hazardous Waste Criteria—Identification and Listing

Phase IA of EPA's hazardous waste identification and listing programs became effective in November 1980 (EPA 1980c, pp. 33084-33137). These regulations define wastes slated for control under the national HWM system. Phase IB of the EPA rules defines additional hazardous wastes, while Phase II addresses a variety of administrative and procedural issues related to the HWM program. Wastes identified by EPA in Phase II could apply at each stage of PV production as could the procedural regulations. Phase III, a 1980-1990 effort, will list and delete additional hazardous wastes (EPA 1980d).

3.1.6.2 Treatment, Storage and Disposal Standards

EPA rules issued in May 1980 established general regulations and interim standards that apply to the generation, transport, storage, and disposal of hazardous wastes. Phase II regulations, authorizing final EPA permit procedures for this program, were expected in late 1980. From 1980-1990, EPA will develop tailored industry and waste industry standards (EPA 1980d). While the fabrication stage of PV production, particularly for the Cu_2S/CdS option, is not likely to result in long-term storage of hazardous chemical by-products, the on-site retention time for such substances could qualify a PV cell production facility as a "storage" site for hazardous waste. In such instances, the full spectrum of EPA rulemaking directed to hazardous waste storage facilities could apply. Public opposition to final storage and disposal sites for hazardous wastes could complicate the process of legal disposal of hazardous substances from a variety of industries (EPA 1979b). Public opposition to even temporary storage facilities could complicate PV plant siting.

3.2 LEGISLATIVE INITIATIVES

The pace and substance of legislative proposals, particularly in the area of environmental regulation, are difficult to forecast. Many environmental laws have been the product of public and congressional concern over specific health and ecological episodes. High pollutant levels in Louisiana public water supplies helped focus support for the Safe Drinking Water Act of 1974 just as the Love Canal pollution disclosures prompted accelerated regulatory action in the area of control of toxic and hazardous substances.

While most of the major environmental and public health media appear to have been covered by federal legislation (air, water, underground water supplies, waste disposal, drinking water, pesticides, radiation, and occupational health), in the future, amendments to existing law could add to, or subtract from, the current degree of regulatory control over industrial and municipal activities. One advance notice of such action, of course, is the legislative calendar for each Congress. The Administration can call directly for legislative action by means of executive and cabinet-level statements. Indirect endorsement of new programs can arise from presidential commissions and advisory committees. Two examples of possible legislative action in environmental regulation are examined here.

3.2.1 Hazardous Waste Containment Act

At the time of this writing, Congress had a bill under serious consideration that was directed to strengthening existing hazardous waste management programs. The House of Representatives passed the Hazardous Waste Containment Act of 1980 on September 23, 1980. The Senate is considering similar legislation; it is likely that a hazardous waste bill will be passed before adjournment of the 96th Congress ("Measure Creating Superfund to Clean up Chemical Wastes. . ." 1980). The Senate measure would result in the imposition of fees on sales of petrochemical products, inorganic materials, and crude oil. The limit on fees from the sale of inorganic material, such as arsenic, lead, and mercury, would be $10 per ton. Fees would go into a "superfund" to pay to clean up potentially hazardous waste dumps across the United States. The potential applicability of such legislation to PV production and utilization would be economic, although the relatively small amounts of hazardous substances expected in PV processing and fabrication could effectively limit the cost burden from such fees. A more telling analysis awaits final legislative and regulatory action.

3.2.2 Toxic Chemicals Control

In mid-1980, President Carter's Toxic Substances Strategy Committee released a report assessing problems and shortcomings in the federal toxic chemicals research and regulatory efforts (Toxic Substances Strategy Committee 1980). The report recommended new legislation and other steps to address the problem of toxic chemicals in the environment, the workplace, and the home. Reflecting the work of an 18-agency committee, the report called for new efforts to improve federal agency coordination in toxic substances control, a government-wide data network to ensure ready access to information about chemical substances, and a variety of approaches to speed the issuance of fair, cost-effective regulations. Should these recommendations be subsequently incorporated in legislation or regulation, there may be additional procedural requirements placed on the use of chemical substances required in PV development.

3.3 ENVIRONMENTAL, HEALTH, AND SAFETY RESEARCH

Analytical techniques used in various research efforts often are more sophisticated than the regulatory frameworks available to respond to environmental and health concerns ("Health and the Environment" 1979). As a result, the direction and effort of environmental research can serve as a barometer of future regulatory and legislative activity. In FY 1980, pollution control and abatement expenditures of the federal government (including health standards development and research) totaled $2.8 billion ("The Federal Effort" 1980). A brief examination of EPA's multimedia program will help illustrate the focus of federal environmental research and point toward possible areas of future regulatory action.

3.3.1 Atmospheric Emissions

EPA's research effort into the effects of cadmium and heavy metal substances has a multimedia focus. Within the general category of atmospheric emissions and biological uptake, the current health effects research agenda includes the following studies (EPA 1980e):

- An Investigation into the Metabolism of Inhaled Trace Metal Effluents From Combustion Processes (completion date 7/82);
- Animal Health Effect Studies of Inhaled Particulates (completion date 10/81); and
- Impact of Proximal Living to Lead, Copper, and Zinc Smelters on Trace Metal Burden (completion date 1980).

3.3.2 Liquid Effluents

EPA's research efforts in the area of liquid effluents, biological uptake, and general water quality as a result of trace metal releases/exposures include (EPA 1980e):

- A Determination of the Toxic Effects of Selected Inorganic Pollutants on Western Aquatic Species (completion date 9/82);

- Relationships of Cadmium Complexation to Toxicological Responses of Aquatic Life (initial research completed; proposal for two-year support under review);
- Development of an Activated Carbon Process for the Removal of Cadmium from Industrial Waste Waters (multiyear effort);
- The Susceptibility of Metals to Treatment in Combined Industrial-Municipal Systems (multiyear effort); and
- Energy Model and Analysis of a Cadmium Stream with a Correlating Embodied Energy and Toxicity Effect (multiyear effort).

Recently completed EPA research into hazardous material spills and responses has collected data which may be used to assess possible changes in NPDES and pretreatment requirements (EPA 1980f).

3.3.3 General Health Effects Research

EPA's general health effects research related to cadmium, cadmium compounds, and other trace metal substances includes a wide range of studies. Some of the active research efforts representative of this category are (EPA 1980e):

- Identification of Levels of Cadmium Exposure Indicators in the United States (multiyear effort);
- Effect of Environmental Pollutants in Relation to Age and Dietary Influence—Toxic Trace Elements (completion date—1980);
- Human Cadmium Exposure and Cancer (completion date—1980);
- Saliva as an Indicator of Exposure to Toxicants (active research);
- The Effects of Heavy Metals on Neurotransmitter Translocation (active research);
- Influence of Diet on Gastrointestinal Absorption of Cadmium (completion date—9/81); and
- Measurement of Ingestion of Cadmium, Lead, Zinc, and Calcium in Selected Populations in the United States (completion date—7/81).

3.3.4 Land and Soil Effects

EPA is also examining the nature of land and soil transport mechanisms with respect to trace toxic metal loadings (EPA 1980e). Specific research includes:

- Studies of Existing Land Application Systems (Soil profiles analysis; downward movement and accumulation of Cd, Zn, Cu, and Ni) (completion date—1/82);
- Effect of Soil Properties and Previous Metal Additions on the Solubility of Metals (completion date—10/81);
- A Survey of Concentration of Metals in Soils and Crops (completion date—2/83); and
- Heavy Metal Bioavailability in Sludge-Amended Soils (completion date—1980).

The above research projects represent only one element of EPA's overall regulatory interest in cadmium and heavy metals control. Research that may be sponsored by EPA's RCRA and Toxic Substances programs in this area has not yet been identified. NIOSH research in support of OSHA's regulatory responsibilities has also not been specified. However, details of the EPA research program provided above leave little doubt over the continuing concern of the Federal Government with respect to the environmental impact of cadmium and other heavy metals. The steady flow of findings from this research effort will provide input to the established regulatory programs described in Sec. 1.0 of this part. Implications for one or more stages of photovoltaic production using advanced material options will await both the conclusion of research and future regulatory decisions. A continued tracking of this activity should accompany PV technology development.

SECTION 4.0

CONCLUSIONS, PART II

This part of the report examined major environmental, health, and safety regulatory programs that may apply to the manufacture, use, and disposal of photovoltaic cells developed with Cu_2S/CdS and poly-Si materials. In Table 4-1, summaries of programs that appear to apply to one or more PV production stages are shown. The analysis was based on qualitative information about the characteristics of waste streams expected from each of the two PV materials options. Without quantitative data on waste stream components, discharge rates, selected waste stream control options, and discharge sites, regulatory compliance reviews specific to array sites cannot be performed.

Based on the qualitative review of regulations and on the explanation of waste-stream control options presented in Part I, it is possible to identify the three most significant regulatory programs affecting PV that should receive continuing and more detailed study. The regulatory programs that 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.

There are no current effluent limitation guidelines under CWA regulations that specifically apply 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 that triggers standards specific to the industry. At other stages in the production process for PV cells, manufacturing, mining, and processing activities are common enough to be addressed by existing regulations affecting specific industries (i.e., electroplating, glass manufacture, and inorganic chemicals manufacturing) (see Appendix A).

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 that must be controlled in the work environment, regardless of the industrial category affected. A stringent cadmium exposure standard for the workplace will have implications for a variety of industries besides PV cell production.

Under RCRA, a tight regulatory program will be developed for the "cradle-to-grave" tracking and monitoring of hazardous wastes. To the extent that the PV materials options examined here include the use or disposal of hazardous chemicals, regulatory responsibilities will have to be maintained. In the absence of air or water quality standards or workplace exposure limits specific to the industry, no federal regulatory programs addressing environment, health, or safety exist that are unique to the PV industry under either materials option.

Some of the more established PV materials options have already been the focus of environmental research by industry. The data bases being developed in such efforts should facilitate the analysis of quantitative environmental effects and regulatory forecasts of PV materials options now in early research and development processes.

Table 4-1. **SUMMARY OF ENVIRONMENTAL, HEALTH AND SAFETY REGULATORY PROGRAMS APPLICABLE TO Cu$_2$/S/CdS AND POLY-Si PHOTOVOLTAIC SYSTEMS**

Photovoltaic Production and Utilization Stages	Federal Legislation, Regulations, and Guidelines																	
	Clean Air Act					Clean Water Act						RCRA		OSHA		SDWA	HMTAFMNSA	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Extraction																		
Cu$_2$S/DcS																		
Cu	x	-	?	?	-	x	x	-	x	-	x	-	x	/	/	x	x	x
Cd	x	-	?	?	-	x	x	-	x	-	x	-	x	/	/	x	x	x
Zn	x	-	?	?	-	x	x	-	x	-	x	-	x	/	/	x	x	x
Poly-Si																		
Si	x	-	?	?	-	x	-	-	x	-	-	-	x	/	/	x	x	x
Processing																		
Cu$_2$S/CdS																		
Cu	x	x	x	x	x	x	x	-	x	-	x	-	x	x	x	x	x	/
Cd	x	?	?	?	-	x	-	-	x	-	x	-	x	x	x	x	x	/
CdS	x	?	?	?	-	x	-	-	x	-	x	-	x	x	x	x	x	/
Poly-Si																		
Silica	x	-	x	x	-	-	-	-	-	-	-	-	-	x	x	-	?	/
HF	x	-	x	x	x	x	x	x	x	-	?	-	?	x	x	x	x	/
Fabrication																		
Cu$_2$/S/CdS																		
substrate preparation	x	-	?	?	-	x	x	-	x	-	x	-	x	x	x	x	x	/
deposition	-	-	?	?	-	x	-	-	x	-	-	-	-	x	x	x	x	/
etching	-	-	?	?	-	x	x	-	x	-	-	-	-	x	x	x	x	/
barrier	-	-	?	?	-	x	-	-	x	-	x	-	-	x	x	x	x	/
metallization	-	-	?	?	-	x	x	-	x	-	-	-	x	x	x	x	x	/
AR coating	?	-	?	?	-	-	-	-	-	-	-	-	-	x	x	x	x	/
encapsulation	-	-	?	?	-	-	-	-	-	-	-	-	-	x	x	x	x	/
interconnection	x	-	?	?	-	-	-	-	-	-	-	-	-	x	x	x	x	/
Poly-Si																		
silicon purification																		
(a) acid leach	x	-	?	?	-	x	-	-	x	-	x	-	?	x	x	x	x	/
(b) SICI$_4$	x	-	?	?	-	x	-	-	x	-	-	-	?	x	x	x	x	/
(c) Selmens	x	-	?	?	-	x	-	-	x	-	-	-	?	x	x	x	x	/
cell fabrication																		
(a) diffused p/n	x	-	?	?	-	x	-	-	x	-	x	-	?	x	x	x	x	/
(b) spray	x	-	?	?	-	x	-	-	x	-	x	-	?	x	x	x	x	/
(c) epitaxial	x	-	?	?	-	x	-	-	x	-	x	-	?	x	x	x	x	/
metallization	x	-	?	?	-	x	-	-	x	-	-	-	?	-	x	x	x	/
AR coating	x	-	?	?	-	-	-	-	x	-	-	-	?	-	x	x	x	/
encapsulation	x	-	?	?	-	-	-	-	x	-	-	-	?	-	x	x	x	/
interconnection	x	-	?	?	-	-	-	-	x	-	-	-	?	x	x	x	x	/
Installation	-	-	-	-	-	-	-	-	-	-	-	x	x	-	x	-	-	/
Operation	?	?	?	?	-	-	-	-	-	-	-	-	-	x	x	-	-	/
Maintenance	-	-	-	-	-	?	-	-	?	-	?	?	x	x	x	-	?	/
Decommissioning	?	?	?	?	?	-	-	?	-	?	x	x	?	x	-	x	/	
Transportation	/	/	/	/	/	/	/	/	/	/	/	x	x	?	?	/	x	/

Legend to Table 4-1

x = Regulatory impact
x = No regulatory impact
? = Possible impact (depends on production factors)
/ = Not applicable

Clean Air Act
1. NAAQS
2. NESHAP
3. PSD
4. NA
5. NSPS

Clean Water Act
6. NPDES
7. Effluent Limitation Guidelines
8. NSPS
9. Pretreatment
10. Toxic
11. Hazardous

Resource Conservation and Recovery Act
12. SWM
13. HWM

Occupational Safety and Health Act
14. Air standards
15. Worker Safety

Safe Drinking Water Act
16. UIC

Hazardous Materials Transportation Act (17)

Federal Metal and Non-Metallic Mine Safety Act (18)

One of the conceptual issues which should be discussed further concerns the extent to which regulatory analyses of PV materials options should address repeatedly the "front-end" waste streams from materials extraction. If the PV industry were to develop more extensively than expected, basic input materials could represent a significant percentage of industry output. However, it is unlikely that the PV cell fabrication industry would experience the direct regulatory responsibility for such pollutant burdens. Should tighter environmental regulatory controls be applied outside the cell fabrication stage of PV development, alternative material input sources, if not alternate materials themselves, may limit the effects of such controls on advances in the technology.

In summary, then, the extent to which Cu_2S/CdS and poly-Si materials options will be affected by environmental, health, and safety regulations depends on three major determinants:

- the modifications that may occur within waste-generating processes at all stages of PV development and use;
- the changes, either more or less restrictive in quantitiative environmental, health, and safety standards (see Appendix B); and
- the specific quantitative dimensions of waste streams, control options, and discharge sites to be employed.

As more progress is achieved in PV materials R&D and as forecasts are made of the quantitative dimensions of the PV cell production process, more conclusive findings as to regulatory compliance potential and associated costs may be reached. The qualitative regulatory review presented here can help guide the direction of subsequent research into these important issues.

APPENDICES TO PART II

APPENDIX A TO PART II

Table A-1. INDUSTRIES RELATED TO PV CELL PRODUCTION SPECIFICALLY ADDRESSED BY FEDERAL ENVIRONMENTAL REGULATIONS

Industry	Regulatory Programs					
	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 snythetics manufacturing			X			

APPENDIX B TO PART II

Table B-1. **SUMMARY OF QUANTITATIVE ENVIRONMENTAL, HEALTH, AND SAFETY STANDARDS OF POTENTIAL APPLICABILITY TO DISCHARGES FROM ADVANCED PV CELL PRODUCTION**

Pollutant	Medium	Recommendation, Regulation or Criteria	Value
Lead and compounds	Air	NAAQS	$1.5\ \mu g/m^3$
		NIOSH	$0.15 \mu g/m^3$
		OSHA	$50\ \mu g/m^3$
	Water	Interim Primary Drinking Water Standards	0.05 mg/ℓ
		Water Quality Criteria	0.05 mg/ℓ
		Effluent Standard (iron and steel manufacturing, vacuum degassing)	0.100 mg/ℓ
		Pretreatment (Inorganic chemicals manufacturing, lead monoxide production	1.0 mg/ℓ
		Hazardous Substances (Lead fluoride)	454 kg
Nitrogen oxides, nitrates	Air	NAAQS	$0.100\ mg/m^3$
		NIOSH	$1.8\ mg/m^3$
		OSHA	$9\ mg/m^3$
		NSPS (Fossil fuel fired steam electric power generator using gaseous fossil fuels)	86 mg/joule heat input
	Water	Interim Primary Drinking Water Standards	10 mg/ℓ
		Water Quality Criteria	10 mg/ℓ
		Effluent Standard (Iron and steel manufacture [open hearth])	0.0094 kg/kkg product

Table B-1. SUMMARY OF QUANTITATIVE ENVIRONMENTAL, HEALTH, AND SAFETY STANDARDS OF POTENTIAL APPLICABILITY TO DISCHARGES FROM ADVANCED PV CELL PRODUCTION (Continued)

Pollutant	Medium	Recommendation, Regulation or Criteria	Value
Cadmium and compounds	Air	NIOSH	0.040 mg/m^3 TWA
		OSHA	0.1 mg/m^3
	Water	Interim Primary Drinking Water Standards	0.010 mg/ℓ
		Water Quality Criteria	0.010 mg/ℓ
		Effluent Standard (Ore mining and dressing [base and precious metals])	0.05 mg/ℓ
		Pretreatment Standard (Nonferrous metal manufacture)	0.2 mg/ℓ
		Hazardous Substances (Cadmium acetate, bromide, chloride)	45.5 kg
Chromium and compounds	Air	NIOSH	1 µg/m^3
		OSHA	100 µg/10
	Water	Interim Primary Drinking Water Standards	0.05 mg/ℓ
		Water Quality Criteria	0.05 mg/ℓ
		Effluent Standard (Iron and steel manufacturing, hot coatings-galvanizing)	0.0026 mg/ℓ
		Pretreatment Standard (Electroplating)	0.09 mg/ℓ
		Hazardous Substances	454 kg
Ammonia	Air	NIOSH	50 ppm
		OSHA	50 ppm
	Water	Water Quality Criteria	100 mg/ℓ

Table B-1. SUMMARY OF QUANTITATIVE ENVIRONMENTAL, HEALTH, AND SAFETY STANDARDS OF POTENTIAL APPLICABILITY TO DISCHARGES FROM ADVANCED PV CELL PRODUCTION (Continued)

Pollutant	Medium	Recommendation, Regulation or Criteria	Value
Ammonia (cont'd)		Effluent Standard (Ore mining and dressing, uranium, radium, and vanadium ores)	100 mg/ℓ
		Pretreatment	100 mg/ℓ
		Hazardous Substances	45.4 kg
Carbon monoxide	Air	NAAQS	10 mg/m^3
		NIOSH	35 ppm
		OSHA	50 ppm
Chlorine, chloride	Air	NIOSH	0.5 ppm
		OSHA	1 ppm
	Water	Water Quality Criteria	2.0 μg/ℓ
		Effluent Standard (Steam electric power generating [generating unit])	0.2 μg/ℓ
		Hazardous Substances	4.54 kg
Copper and compounds	Air	OSHA (Fume)	0.1 mg/m^3
	Water	Water Quality Criteria	1.0 mg/ℓ
		Effluent Standard (Ore mining and dressing [base and precious metals])	0.15 mg/ℓ
		Pretreatment Standard (Inorganic chemicals manufacturing, copper sulfate production, nonferrous metals, secondary copper)	0.5 mg/ℓ
		Hazardous Substances	4.54 kg
Hydrocarbons	Air	NAAQS	160 μg/m^3
		NIOSH	350 mg/m^3

Table B-1. SUMMARY OF QUANTITATIVE ENVIRONMENTAL, HEALTH, AND SAFETY STANDARDS OF POTENTIAL APPLICABILITY TO DISCHARGES FROM ADVANCED PV CELL PRODUCTION (Continued)

Pollutant	Medium	Recommendation, Regulation or Criteria	Value
Hydrocarbons (cont'd)		OSHA (Pentane)	1000 ppm
		OSHA (n-Heptane, octane, n-hexane)	500 ppm
Silver and compounds	Air	OSHA	0.01 mg/m^3
	Water	Interim Primary Drinking Water Standards	0.05 mg/ℓ
		Water Quality Criteria	0.05 mg/ℓ
		Pretreatment Standard	0.34 mg/ℓ
Zinc and compounds	Air	NIOSH (Zinc oxide)	5 mg/m^3
		OSHA (Zinc oxide)	5 mg/m^3
	Water	Effluent Standard (Iron and steel manufacturing, vacuum degassing)	0.100 mg/ℓ
		Pretreatment Standard (Inorganic chemicals, aluminum sulfate production)	2.5 mg/ℓ
		Hazardous Substances (Zinc cyanide)	4.54 kg
Nickel and compounds	Air	NIOSH	0.15 mg/m^3
		OSHA	1 mg/m^3
	Water	Effluent Standard (Ore mining and dressing, mercury ore)	0.1 mg/ℓ
		Hazardous Substances (Nickel hydroxide)	454 kg
Sulfur dioxide	Air	NAAQS	80 μg/m^3(1 yr)
		NIOSH	0.5 ppm
		OSHA	5 ppm

Table B-1. SUMMARY OF QUANTITATIVE ENVIRONMENTAL, HEALTH, AND SAFETY STANDARDS OF POTENTIAL APPLICABILITY TO DISCHARGES FROM ADVANCED PV CELL PRODUCTION (Concluded)

Pollutant	Medium	Recommendation, Regulation or Criteria	Value
Sulfuric acid	Air	NIOSH	1 mg/m^3 TWA
		OSHA	1 mg/m^3 TWA
		NSPS (Sulfuric acid plants)	0.075 kg/kkg acid produced
	Water	Hazardous Substances	454 kg

APPENDIX C TO PART II

SELECTED POLLUTANTS AND POLLUTANT LEVELS REGULATED BY EPA AND OSHA

Table C-1. NPDES TESTING REQUIREMENTS FOR ORGANIC TOXIC POLLUTANTS BY INDUSTRIAL CATEGORY FOR EXISTING DISCHARGERS

Industrial Category	GC/MS fraction[a]			
	Volatile	Acid	Base/ Neutral	Pesticide
Adhesives and sealants	(*)	(*)	(*)	——
Aluminum forming	(*)	(*)	(*)	——
Auto and other laundries	(*)	(*)	(*)	(*)
Battery manufacturing	(*)	——	(*)	——
Coal mining	(*)	(*)	(*)	(*)
Coil coating	(*)	(*)	(*)	——
Copper forming	(*)	(*)	(*)	——
Electric and electronic components	(*)	(*)	(*)	(*)
Electroplating	(*)	(*)	(*)	——
Explosives manufacturing	——	(*)	(*)	——
Foundries	(*)	(*)	(*)	——
Gum and wood chemicals	(*)	(*)	(*)	(*)
Inorganic chemicals manufacturing	(*)	(*)	(*)	——
Iron and steel manufacturing	(*)	(*)	(*)	——
Leather tanning and finishing	(*)	(*)	(*)	(*)
Mechanical products manufacturing	(*)	(*)	(*)	——
Nonferrous metals manufacturing	(*)	(*)	(*)	(*)
Ore mining	(*)	(*)	(*)	(*)
Organic chemicals manufacturing	(*)	(*)	(*)	(*)
Paint and ink formulation	(*)	(*)	(*)	(*)
Pesticides	(*)	(*)	(*)	(*)
Petroleum refining	(*)	(*)	(*)	(*)
Pharmaceutical preparations	(*)	(*)	(*)	——
Photographic equipment and supplies	(*)	(*)	(*)	(*)
Plastic and synthetic materials manufacturing	(*)	(*)	(*)	(*)
Plastic processing	(*)	——	——	——
Porcelain enameling	(*)	——	(*)	(*)
Printing and publishing	(*)	(*)	(*)	(*)
Pulp and paper mills	(*)	(*)	(*)	(*)
Rubber processing	(*)	(*)	(*)	——
Soap detergent manufacturing	(*)	(*)	(*)	——
Steam electric power plants	(*)	(*)	(*)	——
Textile mills	(*)	(*)	(*)	(*)
Timber products processing	(*)	(*)	(*)	(*)

[a] The toxic pollutants in each fraction are listed in Table C-2.

*Testing required

Table C-2. ORGANIC TOXIC POLLUTANTS IN EACH OF FOUR FRACTIONS IN ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROPHOTOMETRY (GC/MS)

Volatiles

IV	acroelein
2V	acrylonitrile
3V	benzene
4V	bis (chloromethyl)ether
5V	bromoform
6V	carbon tetrachloride
7V	chlorobenzene
8V	chlorodibromomethane
9V	chloroethane
10V	2-chloroethylvinyl ether
11V	chloroform
12V	dichlorobromomethane
13V	dichlorodifluoromethane
14V	1,1-dichloroethane
15V	1,2-dichloroethane
16V	1,1-dichloroethylene
17V	1,2-dichloropropane
18V	1,2-dichloropropylene
19V	ethylbenzene
20V	methyl bromide
21V	methyl chloride
22V	methylene chloride
23V	1,1,2,2-tetrachloroethane
24V	tetrachloroethylene
25V	toluene
26V	1,2-transdichloroethylene
27V	1,1,1-trichloroethane
28V	1,1,2-trichloroethane
29V	trichloroethylene
30V	trichlorofluoromethane
31V	vinyl chloride

Acid Compounds

1A	2-chlorophenol
2A	2,4-dichlorophenol
3A	2,4-dimethylphenol
4A	4,6-dinitro-o-cresol
5A	2,4-dinitrophenol
6A	2-nitrophenol

Acid Compounds (cont'd.)

7A	4-nitrophenol
8A	p-chloro-m-cresol
9A	pentachlorophenol
10A	phenol 2,4,6-trichlorophenol
11A	2,4,6-trichlorophenol

Base/Neutral

1B	acenaphtene
2B	acenaphthylene
3B	anthracene
4B	benzìdine
5B	benzo(a)anthracene
6B	benzo(a)pyrene
7B	3,4-benzofluoranthene
8B	benzo(ghi)perylene
9B	benzo(k)fluoranthene
10B	bis(2-chloroethoxy)methane
11B	bis(3-chloroethyl)ether
12B	bis(2-chloroisopropyl)ether
13B	bis(2-ethylhexyl)phthalate
14B	4-bromophenyl phenyl ether
15B	butylbenzyl phthalate
16B	2-chloronaphthalene
17B	4-chlorophenyl phenyl ether
18B	chrysene
19B	dibenzo(a,h)janthracene
20B	1,2-dichlorobenzene
21B	1,3-dichlorobenzene
22B	1,4-dichlorobenzene
23B	3,3-dichlorobenzidine
24B	diethyl phthalate
25B	dimethyl phthalate
26B	di-n-butyl phthalate
27B	2,4-dinitrotoluene
28B	2,6-dinitrotoluene
29B	di-n-octyl phthalate
30B	1,2-diphenylhydrazine (as azobenzene)
31B	fluoranthene
32B	fluorene
33B	hexachlorobenzene

Base/Neutral (cont'd.)

34B	hexachlorobutadiene
35B	hexachlorocyclopentadiene
36B	hexachloroethane
37B	indeno(1,2,3-cd)pyrene
38B	isophorone
39B	naphthalene
40B	nitrobenzene
41B	N-nitrosodimethylamine
42B	N-nitrosodi-n-propylamine
43B	N-nitrosodiphenylamine
44B	phenanthrene
45B	pyrene
46B	1,2,4-trichlorobenzene

Pesticides

1P	aldrin
2P	α-BHC
3P	β-BHC
4P	γ-BHC
5P	δ-BHC
6P	chlordane
7P	4,4-DDT
8P	4,4-DDE
9P	4,4-DDD
10P	dieldrin
11P	α-endosulfan
12P	β-endosulfan
13P	endosulfan sulfate
14P	endrin
15P	endrin aldehyde
16P	heptachlor
17P	heptachlor epoxide
18P	PCB-1242
19P	PCB-1254
20P	PCB-1221
21P	PCB-1232
22P	PCB-1248
23P	PCB-1260
24P	PCB-1016
25P	toxaphene

Table C-3. TOXIC POLLUTANTS AND HAZARDOUS SUBSTANCES REQUIRED TO BE IDENTIFIED BY EXISTING DISCHARGERS IF EXPECTED TO BE PRESENT

Toxic Pollutants

Asbestos

Hazardous Substances

Acetaldehyde
Allyl alcohol
Allyl chloride
Amyl acetate
Aniline
Benzonitrile
Benzyl chloride
Butyl acetate
Butylamine
Captan
Carbaryl
Carbofuran
Carbon disulfide
Chlorpyrifos
Coumaphos
Cresol
Crotonaldehyde
Cyclohexane
2,4-D (2,4-dichlorophenoxyacetic acid)
Diazinon
Dicamba
Dichlobenil
Dichlone
2,2-Dichloropropionic acid
Dichlorvos
Diethyl amine
Dimethyl amine
Dinitrobenzene
Diquat
Disulfoton
Diuron
Epichlorohydrin
Ethanolamine
Ethion
Ethylene diamine
Ethylene dibromide
Formaldehyde
Furfural

Hazardous Substances (cont'd.)

Guthion
Isoprene
Isopropanolamine
Kelthane
Kepone
Malathion
Mercaptodimethur
Methoxychlor
Methyl mercaptan
Methyl methacrylate
Methyl parathion
Mevinphos
Mexacarbate
Monoethylamine
Monomethylamine
Naled
Naphthenic acid
Nitrotoluene
Parathion
Phenolsulfanate
Phosgene
Propargite
Propylene oxide
Pyrethrins
Quinoline
Resorcinol
Strontium
Strychnine
Styrene
2,4,5-T (2,4,5-Trichlorophenoxy acetic acid)
TIDE (Tetrachlorodiphenylethane)
2,4,5-TP [2-(2,4,5-Trichlorophenoxy) propionic acid]
Trichlorofon
Triethylamine
Trimethylamine
Uranium
Vanadium
Vinyl acetate
Xylene
Xylenol
Zirconium

Table C-4. TOXIC POLLUTANTS

Acenapthene
Acrolein
Acrylonitrile
Aldrin/Dieldrin
Antimony and compounds[a]
Arsenic and compounds
Asbestos
Benzene
Benzidine
Beryllium and compounds
Cadmium and compounds
Carbon tetrachloride
Chlordane (technical mixture and metabolites)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)
Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
Chlorinated naphthalene
Chlorinated phenols (other than those listed elsewhere; includes trichlorphenols and chlorinated cresols)
Chloroform
20-Chlorophenol
Chromium and compounds
Copper and compounds
Cyanides
DDT and metabolites
Dichlorobenzenes (1,2- 1,3-, and 1,4-dichlorobenzenes)
Dichlorobenzidine
Dichloroethylenes (1,1- and 1,2-dichloroethylene)
2,4-Dichlorophenol
Dichloropropane and dichloropropene
2,4-Dimethylphenol
Dinitrotoluene
Diphenylhydrazine
Endosulfan and metabolites
Endrin and metabolites
Ethylbenzene
Fluoranthene
Haloethers (other than those listed elsewhere: includes chlorophenylphenyl ethers, bromophenylphenyl ether, bis(dichloroisopropyl)ether, bis-(chloroethoxy) methane and polychlorinated diphenyl ethers)
Halomethanes (other than those listed elsewhere: includes methylene chloride, methylchloride, methylbromide, bromoform dichlorobromomethane, trichlorofluoromethane, dichlorodifluoromethane)
Heptachlor and metabolites
Hexachlorobutadiene
Hexachlorocyclohexane (all isomers)
Hexachlorocyclopentadiene
Isophorone
Lead compounds
Mercury and compounds
Naphthalene
Nickel and compounds
Nitrobenzene
Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
Nitrosamines
Pentachlorophenol
Phenol
Polychlorinated biphenyls (PCBs)
Polynuclear aromatic hydrocarbons (including benzanthracene, benzopyrenes, benzofluorathene, chrysenes, dibenzanthracenes, and indenopyrenes)
Selenium and compounds
Silver and compounds
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)
Tetrachloroethylene
Thallium and compounds
Toluene
Toxaphene
Trichloroethylene
Vinyl chloride
Zinc compounds

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[a] As used throughout this table, the term "compounds" shall include organic and inorganic compounds.

Table C-5. SELECTED EPA EFFLUENT LIMITATION GUDELINES

Category	Subcategory	Basis	Pollutant or Effluent Characteristic	Maximum of Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Cement manufacturing [Expressed in kg/kkg of product]	Leaching	BPT,BAT	TSS	0.005 (of dust leached) NSPS	
	Materials storage piles runoff	NSPS	No discharge of process wastewater pollutants to navigable waters		
			pH	6.0-9.0	
			Temperature	3°C rise above inlet temperature	
Electroplating [Expressed as mg/liter] Note: all previous standards have been revoked/suspended	All subcategories—Plants discharging more than 40,000 gals/day of process wastewater	Pretreatment standards	Cyanide Amenable to Chlorination	0.20	0.08
			Total Cyanide	0.64	0.08
			Hexavalent chromium	0.25	0.09
			pH	7.50	10.00
Inorganic chemicals manufacturing [Expressed in kg/kkg of product] Note: For many of the subcategories, standards have been temporarily revoked. Many others are in "reserved" status.	For thirty-three subcategories	NSPS, BAT	No discharge of process wastewater pollutants to navigable waters		

Table C-5. SELECTED EPA EFFLUENT LIMITATION GUDELINES (continued)

Category	Subcategory	Basis	Pollutant or Effluent Characteristic	Maximum of Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Plastic and synthetics manufacturing Note: All standards have been revoked/suspended					
Nonferrous metals manufacturing [Expressed in kg/kkg of product]	For six subcategories	BPT,BAT NSPS	No discharge of process wastewater pollutants to navigable waters.		
	Primary aluminum smelting	NSPS	Fluoride	0.05	0.025
			TSS	0.1	0.05
	Primary zinc	BAT	TSS	0.28	0.14
			Arsenic	1.1×10^{-8}	5.4×10^{-4}
			Cadmium	5.4×10^{-3}	2.7×10^{-3}
			Selenium	0.054	0.027
			Zinc	0.054	0.027

Table C-5. SELECTED EPA EFFLUENT LIMITATION GUDELINES (continued)

Category	Subcategory	Basis	Pollutant or Effluent Characteristic	Maximum of Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Ferroalloy manufacturing [Expressed in kg/kkg of product]	Open electric furnaces with wet air pollution control devices	BAT, NSPS	TS	0.024	0.012
			Total chromium	0.0008	0.0004
			Hexavalent chromium	0.00008	0.00004
			Total manganese	0.008	0.0039
			pH	6.0	9.0
	Covered electric furnaces and other smelting operations with wet air pollution control devices	BAT, NSPS	Total cyanide	0.0005	0.0003
			Phenols	0.0004	0.0002
Glass manufacturing [Expressed in kg/kkg of product]	For four subcategories	BAT, NSPS	No discharge of process wastewater pollutants to navigable waters.		
	Float glass	BAT, NSPS	TSS	0.70	0.70
			Oil	1.40	1.40
			Phosphorus	0.05	0.05
			pH	6.0 to 9.0	
Ore mining and dressing [Expressed in mg/ℓ]	Base and precious metals	BPT	TSS	30.0	20.0
			Copper	0.30	0.15
			Zinc	0.4	0.2
			Lead	0.6	0.3

Table C-5. SELECTED EPA EFFLUENT LIMITATION GUDELINES (continued)

Category	Subcategory	Basis	Pollutant or Effluent Characteristic	Maximum of Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
			Mercury	0.0002	0.0001
			Cadmium	0.10	0.05
			Cyanide	0.2	0.1
			pH	6.0	9.0
	Bauxite	BPT	Iron	1.0	0.5
			Aluminum	2.0	1.0
	Ferroalloy ores	BPT	Arsenic	1.0	0.5
	Uranium, radium, and vanadium ores	BPT	Uranium	0.40	2.0
			Radium^{226} (dis.)	10.0	3.0
			Radium^{226} (total)	30.0	10.0
			COD	200.0	100.0
			Ammonia	—	100.0
	Mercury ore	BPT	Nickel	0.2	0.1
Mineral mining and processing [expressed in mg/ℓ]	[A through AL] Note: For seventeen subcategories standards are in "reserved" status				
	For sixteen subcategories	BPT	No discharge of process generated wastewater pollutants to waters.		
	Industrial sand	BPT	Total fluoride	0.006	0.003
	Graphite	BPT	TSS	20	10
			Total iron	2	1
			pH	6.0-9.0	

Table C-5. SELECTED EPA EFFLUENT LIMITATION GUDELINES (concluded)

Category	Subcategory	Basis	Pollutant or Effluent Characteristic	Maximum of Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Paint formulating	Oil-base solvent Wash paint	BPT,BAT, NPS	No discharge of process wastewater pollutants of navigable waters.		
Ink formulating	Oil-base solvent Wash ink	BPT,BAT NSPS	No discharge of process wastewater pollutants to navigable waters.		
Coal mining [Expressed in mg/ℓ]	All subcategories	BPT	Total Iron	7.0	3.5
		TSS		70.0	35.0
		pH		6.0 to 9.0	
Iron and steel manufacturing [Expressed in kg/kkg of product]	For three subcategories	BPT BAT,NSPS	No discharge of process wastewater pollutants to navigable waters		
	Byproduct coking	BAT,NSPS	Cyanide amenable to chlorination	0.0003	0.0001
			Phenol	0.0006	0.0002
			Ammonia	0.0126	0.0042
			Sulfide	0.0003	0.0001
			pH	6.0-9.0	
	Basic oxygen (with wet air pollution control methods)	BAT,NSPS	TSS	0.0156	0.0052
			Fluoride	0.0126	0.0042
	Open hearth furnace	BAT	Nitrate	0.0282	0.0094

Table C-6. SELECTED PRETREATMENT STANDARDS

Category	Subcategory	Basis	Pollutant Effluent Characteristic	Maximum for Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Electroplating [Expressed as mg/ℓ]	For all subcategories	Proposed for existing sources discharging <38,000 liters/day of process wastewater	Prohibited wastes [40 CFR 128.131] plus:		
			Cyanide amenable to chlorination	2.0	0.8
			Hexavalent chromium	0.25	0.09
			Lead	0.8	0.4
			Cadmium	1.0	0.5
		Proposed for existing sources discharging >38,000 liters/day of wastewater	Prohibited wastes as for plants discharging >38,000 liters/day of process wastewater plus:		
			Cyanide amenable to chlorination	0.2	0.8
			Cyanide, total	0.64	0.24
			Copper	4.6	2.0
			Nickel	3.6	1.8
			Total chromium	4.2	1.6
			Zinc	3.4	3.9
			Total metals	7.5	3.9
	Precious metals	Proposed for existing sources discharging >38,000 liters/day of wastewater	Prohibited wastes as for plants discharging >38,000 liters/day of process wastewater (all subcategories) plus:		
			Silver	1.0	0.34

Table C-6. SELECTED PRETREATMENT STANDARDS (continued)

Category	Subcategory	Basis	Pollutant Effluent Characteristic	Maximum for Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Inorganic chemicals manufacturing [Expressed as mg/ℓ]	Aluminum chloride production	Existing sources	Prohibited wastes [40 CFR 128,131] plus:		
			pH	5.0	10.0
		New sources	Prohibited wastes [40 CFR 128] plus NSPS for incompatible pollutants		
	Aluminum sulfate production	Existing sources	Prohibited wastes [40 CFR 128.131] plus:		
			Zinc	5.0	2.5
	Potasium dichromate production	Existing sources	Prohibited wastes [40 CFR 128.131] plus:		
			Hexavalent chromium	0.25	0.09
			Total chromium	3.0	1.0
	Copper sulfate production	Existing sources	Prohibited wastes [40 CFR 128.131] plus:		
			Copper	1.0	0.5
			Nickel	2.0	1.0
	Lead Monoxide production	Existing sources	Prohibited wastes [40 CFR 128.131] plus:		
			Lead	2.0	1.0
	Silver nirate production	Existing sources	Prohibited wastes [40 CFR 128.131] plus:		
			Silver	1.0	0.5

Table C-6. SELECTED PRETREATMENT STANDARDS (concluded)

Category	Subcategory	Basis	Pollutant Effluent Characteristic	Maximum for Any One Day	Average of Daily Values for 30 Consecutive Days Shall Not Exceed:
Nonferrous metal manufacturing [Expressed as mg/ℓ]	Secondary aluminum smelting	Existing sources—metal coating	Prohibited wastes [40 CFR 128.131] plus:		
			Oil and grease	100	
		Existing sources—demagging fume scrubbers	Prohibited wastes [40 CFR 128.131] plus:		
			pH	5	10
		New sources	Prohibited wastes [40 CFR 128] plus NSPS for incompatible pollutants		
	Secondary copper	Existing sources	Prohibited wastes [40 CFR 128.31] plus:		
			Copper	1.0	0.5
			Cadmium	0.4	0.2
Cement manufacturing	Nonleaching	Existing source	pH		No limitation
			Temperature		Do.
			TSS		Do.
	Leaching	Existing source	pH		No limitation
			BOD_5		Do.

Table C-7. SELECTED REPORTABLE QUANTITIES OF HAZARDOUS SUBSTANCES

Material	Category	RQ in lb (kg)
Acetaldehyde	C	1,000 (454)
Acetic acid	C	1,000 (454)
Ammonia	B	100 (45.4)
Ammonium acetate	D	5,000 (2,270)
Ammonium bifluoride	D	5,000 (2,270)
Ammonium carbonate	D	5,000 (2,270)
Ammonium chloride	D	5,000 (2,270)
Ammonium fluoborate	D	5,000 (2,270)
Ammonium fluoride	D	5,000 (2,270)
Ammonium hydroxide	C	1,000 (454)
Cadmium acetate	B	100 (45.4)
Cadmium bromide	B	100 (45.4)
Cadmium chloride	B	100 (45.4)
Calcium carbide	D	5,000 (2,270)
Calcium hydroxide	D	5,000 (2,270)
Chlorine	A	10 (45.4)
Chromic acid	C	1,000 (454)
Cupric chloride	A	10 (45.4)
Cupric nitrate	B	100 (45.4)
Cupric sulfate	A	10 (45.4)
Ferric chloride	C	1,000 (454)
Ferric nitrate	C	1,000 (454)
Ferric sulfate	C	1,000 (454)
Ferrous chloride	B	100 (45.4)
Ferrous sulfate	C	1,000 (454)
Formaldehyde	C	1,000 (454)
Formic acid	D	5,000 (2,270)
Hydrochloric acid	D	5,000 (2,270)
Hydrofluoric acid	D	5,000 (2,270)
Hydrogen cyanide	A	10 (4.54)
Hydrogen sulfide	B	100 (45,4)
Lead chloride	D	5,000 (2,270)
Lead fluoride	C	1,000 (454)
Nickel chloride	D	5,000 (2,270)
Nitric acid	C	1,000 (454)
Nitrogen dioxide	C	1,000 (454)
Phosgene	D	5,000 (2,270)
Phosphoric acid	D	5,000 (2,270)
Phosphorus	X	1 (0.454)
Phosphorus trichloride	D	5,000 (2,270)
Sodium fluoride	D	5,000 (2,270)
Sodium hydroxide	C	1,000 (454)
Sulfuric acid	C	1,000 (454)
Zinc chloride	D	5,000 (2,270)

Table C-8. SELECTED TIME-WEIGHTED AVERAGE WORKPLACE AIR CONTAMINANT LEVELS

(Subtable 1)

Substance	ppm[a]	mg/m^3[b]
Acetaldehyde	200	360
Acetic acid	10	25
Acetic anhydride	5	20
Acetone	1,000	2,400
Ammonia	50	35
Antimony and compounds (as Sb)		0.5
Arsenic organic compounds (as As)		0.5
Arsine	0.05	0.2
C Boron trifluoride	1	3
Butyl alcohol	100	300
Calcium oxide		5
Carbon dioxide	5,000	9,000
Carbon monoxide	50	55
C Chlorine	1	3
Chromium sol. chromic, chromous salts as Cr		0.5
Metal and insol. salts		1
Copper fume		0.1
Dusts and mists		1
Ethyl acetate	400	1,400
Ethyl alcohol (ethanol)	1,000	1,900
Fluoride (as F)		2.5
Fluorine	0.1	0.2
Formic acid	5	9
C Hydrogen chloride	5	7
Hydrogen peroxide (90%)	1	1.4
Iron oxide fume		10
Isobutyl alcohol	100	300
Isopropyl alcohol	400	908
Nitric acid		2
Nitric oxide		25
C Nitrogen dioxide		5
C Nitroglycerin-Skin		0.2
Phosphine		1
Phosphoric acid		0.1
Phosphorus pentachloride		1
Phosphorus trichloride	0.5	3
Silver, metal and soluble compounds		0.01
Sodium hydroxide		2
Sulfur dioxide	5	13
Sulfuric acid		1
Tantalum		5
Tin (inorganic compounds, except oxides)		2

[a] Parts of vapor or gas per million parts of contaminated air by volume at 25°C and 760 mm Hg pressure.

[b] Approximate milligrams of particulate per cubic meter of air.

Table C-8. SELECTED TIME-WEIGHTED AVERAGE WORKPLACE AIR CONTAMINANT LEVELS

(Subtable 1, concluded)

Substance	ppm	mg/m^3
Tin (organic compounds)		—
Titaniumdioxide		15
Zinc chloride fume		1
Zinc oxide fume		5

Table C-8. SELECTED TIME-WEIGHTED AVERAGE WORKPLACE AIR CONTAMINANT LEVELS

(Subtable 2)

Material	8-hr Time-Weighted Average	Acceptable Ceiling Concentration	Acceptable Maximum Peak Above the Acceptable Ceiling Concentration for an 8-hr Shift	
			Concentration	Maximum Duration
Cadmium fume	0.1 mg/m^3	0.3 mg/m^3	—	—
Cadmium dust	0.2 mg/m^3	0.6 mg/m^3	—	—
Chromic acid and chromates	—	1 mg/10m^3	—	—
Formaldehyde	3 ppm	5 ppm	10 ppm	30 min
Hydrogen fluoride	3 ppm	—	—	—
Hydrogen sulfide	—	20 ppm	50 ppm	10 min once only if no other measurable exposure occurs.
Fluoride as dust	2.5 mg/m^3	—	—	—
Mercury	—	1 mg/10 m^3	—	—

Table C-8. SELECTED TIME-WEIGHTED AVERAGE WORKPLACE AIR CONTAMINANT LEVELS

(Subtable 3)

Substance	mppcf	mg/m^3
Silica:		
Crystalline:		
Quartz (respirable	$\frac{250}{\%SiO_2 + 5}$	$\frac{10mg/m^3}{\%SiO_2 + 2}$
Quartz (total dust)		$\frac{30mg/m^3}{\%SiO_2 + 2}$
Cristobalite: Use 1/2 the value calculated from the count or mass formulae for quartz.		
Tridymite: Use 1/2 the value calculated from the formulae for quartz.		
Amorphous, including natural diatomaceous earth	20	$\frac{80 mg/m^3}{\%SiO_2}$
Silicates (less than 1% crystalline silca).		
Mica	20	
Soapstone	20	
Talc (nonasbestos limit		
Tremolite (see talc, fibrous)		
Portland cement	50	
Graphite (natural)	15	
Coal dust (respirable fraction less than 5% SiO_2)		2.4 mg/m^3 or
For more than 5% SiO_2		$\frac{10 mg/m^3}{\%SiO_2 + 2}$
Inert or Nuisance Dust:		
Respirable fraction	15	5 mg/m^3
Total dust	50	15 mg/m^3

Table C-9. MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (milligrams per liter)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10, 10-hexachloro-1,7-epoxy- 1,4,4a,5,6,7,8,8a-octahydro- 1,4-endo, endo- 5,8-dimethano naphthalene).	0.02
D013	Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer).	0.4
D014	Methoxychlor (1,1,1-Trichloro-2,2-bis [p-methoxphenyl] ethane).	10.0
D015	Toxaphene ($C_{10}H_{10}Cl_8$ Technical chlorinated camphene, 67-69% chlorine).	0.5
D015	2,4-D, (2,4-dichlorophenoxyacetic acid).	10.0
D017	2,4,5-TP Silvex (2,4,5-trichlorophenoxypropionic acid).	1.0

Table C-10. HAZARDOUS WASTE FROM NONSPECIFIC SOURCES

Industry and EPA Hazardous Waste No.	Hazardous Waste	Hazard Code
Generic		
F001	The spent halogenated solvents used in degreasing, tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and the chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations	(T)
F002	The spent halogenated solvents, tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2- trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, trichlorofluororomethane and the still bottoms from the recovery of these solvents	(T)
F003	The spent non-halogenated solvents, xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, n-butyl alcohol, cyclohexanone, and the still bottoms from the recovery of these solvents	(I)
F004	The spent non-halogenated solvents, cresols and creyslic acid, nitrobenzene, and the still bottoms from the recovery of these solvents	(T)
F005	The spent non-halogenated solvents, methanol, toluene, methyl ethyl ketone, methyl isobutyl keyton, carbon disulfide, isobutanol, pyridine and the still bottoms from the recovery of these solvents.	(I,T)
F006	Wastewater treatment sludges from electroplating operations	(T)
F007	Spent plating bath solutions from electroplating operations	(R,T)
F008	Plating bath sludges from the bottom of plating baths from electroplating operations	(R,T)
F009	Spent stripping and cleaning bath solutions from electroplating operations	(R,T)
F010	Quenching bath sludge from oil baths from metal heat treating operations	(R,T)
F011	Spent solutions from salt bath pot cleaning from metal heat treating operations	(R,T)
F012	Quenching wastewater treatment sludges from metal heat treating operations	(T)
F013	Flotation tailings from selective flotation from mineral metals recovery operations	(T)
F014	Cyanidation wastewater treatment tailing pond sediment from mineral metals recovery operations	(T)
F015	Spent cyanide bath solutions from mineral metals recovery operations	(R,T)
F016	Dewatered air pollution control scrubber sludges from coke ovens and blast furnaces	(T)

Table C-11. SELECTED HAZARDOUS WASTE FROM SPECIFIC SOURCES

Industry and EPA Hazardous Waste No.	Hazardous Waste	Hazard Code
Explosives:		
K044	Waste water treatment sludges from the manufacturing and processing of explosives	(R)
K045	Spent carbon from the treatment of wastewater containing explosive	(R)
K046	Wastewater treatment sludges from the manufacturing, formulation and loading of lead-based initiating compounds	(T)
K047	Pink/red water from TNT operations	(R)
Iron and steel:		
K060	Ammonia still lime sludge from coking operations	(T)
K061	Emission control dust/sludge from the electric furnace production of steel	(T)
K062	Spent pickle liquor from steel finishing operations	(C,T)
K063	Sludge from lime treatment of spent pickle liquor from steel finishing operations	(T)
Primary copper: K064	Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production	(T)
Primary lead: K065	Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities	(T)
Primary zinc:		
K066	Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production	(T)
K067	Electrolytic anode slimes/sludges from primary zinc production	(T)
K068	Cadmium plant leach residue (iron oxide) from primary zinc production	(T)
Secondary lead: K069	Emission control dust/sludge from secondary lead smelting	(T)

Table C-12. BASIS FOR LISTING EP TOXIC (E) AND TOXIC (T) WASTES

EPA Hazardous Waste No.	Hazardous Constituents For Which Listed
F001	Tetrachloroethylene, methylene chloride trichloroethyliene, 1,1,1-trichloroethane chlorinated fluorocarbons, carbon tetrachloride
F002	Tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, trichlorofluoromethane
F003	N.A.
F004	Cresols and cresylic acid, nitrobenzene
F005	Methanol, toluene, methyl ethyl keton, methyl isobutyl keton, carbon disulfide, isobutanol pyridine.
F006	Cadmium, chromium, nickel, cyanide (complexed)
F007	Cyanide (salts)
F008	Cyanide (salts)
F009	Cyanide (salts)
F010	Cyanide (salts)
F011	Cyanide (salts)
F012	Cyanide (complexed)
F013	Cyanide (complexed)
F014	Cyanide (complexed)
F015	Cyanide (salts)
F016	Cyanide (complexed)
K044	N.A.
K045	N.A.
K046	Lead
K047	N.A
K060	Cyanide, naphthalene, phenolic compounds, arsenic
K061	Chromium lead, cadmium
K062	Chromium, lead
K063	Chromium, lead
K064	Cadmium, lead
K065	Cadmium, lead
K066	Cadmium, lead
K067	Cadmium, lead
K068	Cadmium, lead

N.A.: waste is hazardous because it meets either the ignitability, corrosivity, or reactivity characteristic.

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