Environmental Assessment of Advanced Thin Film Manufacturing Process

Final Report

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"ENVIRONMENTAL ASSESSMENT OF ADVANCED THIN FILM MANUFACTURING PROCESS"

1.0 INTRODUCTION

BP Solar is currently introducing the Apollo[®] technology at its new Fairfield, California, production plant. This plant is designed and sized to produce the company's thin film module in high volume, on the order of 10 megawatts per annum. This commitment to high-volume production stems from BP Solar's extensive research and development program over the past ten years and the successful development and characterization of a stable CdTe product in the laboratory in limited pilot-line production. The Apollo[®] project achieved thin film CdTe efficiencies of over 8% on a 300mm x 300mm low-cost glass substrate.¹

The Apollo[®] technology is a chemical-based process for depositing semiconductor films of cadmium sulfide and cadmium telluride on conducting glass. The semiconductor films are interconnected using a proprietary back contact. The final product in this process is a monolithic photovoltaic device in a glass package. The Apollo[®] process produces by-products that require abatement to satisfy federal, state, and local regulators (see Figure 1).

BP's health, safety, and environmental goals are, simply stated, to have no accidents, to do no harm to people, and to do no damage to the environment. With these goals, BP Solar embarked on a strategy to investigate the typical waste streams from the Apollo[®] production process, with the objectives of reducing waste streams and introducing the best available control technology (BACT) to abate emissions. To implement this strategy, BP Solar worked closely with Radian International (Radian) of Walnut Creek, California, an environmental engineering consulting firm. Radian provided a highly experienced engineering team to supplement BP Solar's technology team in Fairfield, especially in the analysis of

¹J.M. Woodcock, M.E. Özsan, A.K. Turner, D.W. Cunningham, D.R. Johnson, R. J. Marshall, N.B. Mason, S. Oktik, M.H. Patterson, S. J. Ransome, S. Roberts, M. Sadeghi, J.M. Sherborne, D. Sivapathasundaram, and I.A. Walls, *Proceedings 12th E.C. Photovoltaic Solar Energy Conference* (1994), 948.

regulatory requirements and in the specification of BACT to meet those requirements. The BP Solar-Radian project was broken down into three phases:

- A) *Emissions Analysis of the Apollo® Process.* The Fairfield plant was designed for an initial 5 MW capacity per annum, with full build-out potential of 10 MW per annum. Each piece of equipment was designed for production at these levels, and has its own waste stream. The individual waste streams contribute to the overall waste loading of the plant. For this analysis, these waste streams are broken down into air, wastewater and other chemical solutions.
- B) *Regulatory Analysis.* A study was performed to identify all federal, state, and local regulations regarding waste disposal and emission limits. Working with Radian, BP Solar investigated all aspects of air and wastewater discharge permitting. The scope and details of the investigation are discussed in this document.
- C) *Alternative Abatement and Treatment Technologies.* After the waste streams were identified and quantified, BP Solar and Radian proceeded to determine the BACT options in the following areas:
- *Particulate Matter:* Mainly CdTe dust from laser and bead blasting operations.
 - *Volatile Organic Compounds: (VOCs):* These are mainly solvents used in the process.
 - *Inorganic Deposition Bath Emissions:* Evaporation taking place during cadmium sulfide deposition and subsequent cleaning operations.
 - *Wastewater streams:* The largest amount of waste by volume comes from aqueous waste. The team organized composite samples to be tested using a number of potential treatment technologies. The data obtained from these tests were used to assess and rank the alternative technologies and to choose the best available technology. BP Solar's approach will minimize the amount of aqueous waste, optimize the economics of processing, and, of course, meet as an absolute minimum all environmental laws and regulations.

2.0

EMISSIONS ANALYSIS OF APOLLO® PROCESS

To define the permitting requirements and identify suitable treatment technologies, it was important to characterize emissions of contaminants to the air and wastewater discharge from the manufacturing stations of the Apollo® process. The information came from pilot-scale process development research in the United Kingdom. The manufacturing stations in the Apollo® process that generate air and water releases are shown in Figure 1.

2.1

Quantification of Air Contaminant Emissions

Air contaminant emissions from the Apollo® process were estimated using material usage quantities from pilot-scale operations in U.K. laboratories and scaling them up to represent initial and full-scale production levels. The characteristics of the air emission streams at initial and full-scale production are shown in Table 1. The air contaminants generated by the Apollo® process include ammonia, hydrogen sulfide, CdTe dust, and a few species of VOCs.

Emission estimates for air permitting were developed conservatively (i.e., the estimates overstate likely process emissions) to ensure that compliance with air permit limits based on these estimates would be attainable. Since the local air permit application was filed, BP Solar has made process changes that will further reduce anticipated air emissions from several sources.

Emissions from the process stations using materials containing organic solvents were difficult to quantify accurately. Solvents by their nature are used as part of a cleaning process, rather than for manufacturing, so their usage is much more difficult to establish. Given uncertainties in the initial solvent usage, the emissions estimates and control technology proposed in the air permit application were based on initial (startup) production levels only. Emission estimates will be reevaluated before increasing production to full scale. By then, meaningful solvent usage data will be available to make decisions on future emissions control. In the interim, carbon adsorption was identified as the most appropriate abatement technology. Following

collection of actual emissions data, and given scale-up of manufacturing, the best available control technology (BACT) will be identified to minimize VOC emissions in the most effective manner.

2.2 Quantification of Wastewater Streams

Wastewater streams were also characterized based on pilot-scale process discharges from U.K. laboratory fabrication. Rinse waters from these processes will be treated on-site and discharged to the Fairfield-Suisun Sewer District. Once the rinse tanks had been sized and the rinse water usage estimated, wastewater discharges were scaled up to represent full-scale production levels. Wastewater contaminants include cadmium, organic compounds (responsible for biological oxygen demand [BOD] loading), and, to a lesser degree, ammonia and other ionic species. Total wastewater discharge rate in gallons per minute (gpm) was also calculated. This information helped to determine the best treatment solution and formed the basis for establishing the connection fees to the Fairfield-Suisun Sewer District.

The selection of the wastewater treatment system depended heavily on the demonstrated capability to treat this specific wastewater discharge to within acceptable levels (see table 5) for cadmium. This capability was determined through treatability studies conducted by each wastewater treatment system vendor whose technology was considered for potential application to the Apollo® process wastewater. Composite samples of Apollo® process wastewater representative of rinse discharges were prepared in BP Solar's pilot-scale laboratories in the United Kingdom and shipped to U.S. treatment system vendors for the treatability studies.

After the initial treatability study results were obtained, BP Solar found that it would be necessary to treat an additional wastewater stream: the discharge from each cadmium sulfide deposition bath. This additional stream increased the anticipated total process maximum (design) discharge rate by about 50% and increased concentrations of cadmium and organic compounds. On-site treatment offered an attractive economic route to reduce the amount of off-site waste stream treatment.

The combined wastewater was recharacterized based on the addition of the cadmium sulfide deposition bath discharges. Samples including the bath discharges were prepared in the United Kingdom and distributed again to wastewater treatment system vendors for a second round of treatability tests.

Samples were also sent to a local analytical laboratory for certified testing, including analysis of five-day biological oxygen demand (BOD₅). BOD₅ levels in the wastewater have not corresponded well with chemical oxygen demand (COD) and may be difficult to predict for BP Solar's wastewater. The analytical results are shown in Table 2. This information was crucial for evaluating the best technical and economic management of this waste stream. The key question remains: whether on-site treatment for removal of organics is the best solution. BP Solar intends to investigate treatment technologies for organics further in its NREL Thin Film Partnership program.

Figure 1: Apollo Process and Emission Streams

Table 1

BP Solar Air Emission Stream Characteristics

Process	Pollutant	Flow Rate (cfm)	Temperature (°F)	Average Uncontrolled Concentration (ppm)	% Control Proposed	Uncontrolled Emission Rate (lbs/day)	Controlled Emission Rate (lbs/day)
CdS Deposit	Ammonia	2,700	160	1,600 – 6,800	90	40	4
Tank Clean	Hydrogen sulfide	1,800	75	0.8	90	0.10	<0.01
Acid Strip	Hydrogen sulfide	1,500	75	1.6	90	0.10	<0.01
Diptank	VOC	6,000	75	NA	NA	131	NA
Cleaning Process	VOC	1,800	75	10	90	3.05	<0.31
Laser Etching (4 each)	CdTe	750	75	0.001 gr/dsef	99.99	0.14	1.2E-05
Abrasive Blasting	CdTe	1,375	75	0.001	99.97	0.19	5.6E-05
Wipe Cleaning	VOC	NA	75	NA	NA	4.4	NA

Table 2

Apollo® Process Wastewater Analysis

Analysis	Results (mg/l)
	Composite Rinses and other solutions
Ammonia	610
Cadmium (total)	150
BOD ₅	633
Suspended Solids	11
pH	10.6

3.0

REGULATORY ANALYSIS

An initial review was conducted to identify federal, state, and local regulations that would dictate the permitting and design requirements for environmental control technologies for the Apollo® process. California has some of the most stringent environmental standards in the world. These standards therefore represented a very high benchmark for BP Solar to achieve. The results of the regulatory review are summarized in Table 3, which identifies the required permits. The procedures for obtaining the air and sewer discharge permits were the most challenging. The following sections describe the strategy used to obtain each of these permits.

3.1

Air Permitting Strategy

The BP Solar Fairfield manufacturing facility is located within the jurisdiction of the Bay Area Air Quality Management District (BAAQMD). BAAQMD required BP Solar to obtain an Authority to Construct (ATC) permit prior to commencing installation and startup of any of the new manufacturing stations that emit air contaminants. A detailed permit application was completed, reviewed by BAAQMD, approved, and an ATC permit was issued to BP Solar in July 1997. A permit to operate (PTO) will be issued by the BAAQMD once the Apollo® process is fully operational and BP Solar demonstrates that all air permit conditions are satisfied.

With the purchase of the Fairfield facility, BP Solar acquired an existing PTO for a few emission sources permitted by the previous solar cell manufacturing operations. These sources included chemical vapor deposition (CVD) processes with associated baghouses, bead blasting station and wipe cleaning operations. Although BP Solar shut down and removed the CVD processes, it was able to make use of the permits for bead blasting and wipe cleaning after adopting more efficient particulate collection (HEPA filters with greater than 99.97% collection efficiency).

BP Solar's strategy for air permitting was to propose high-efficiency, reliable control equipment that would reduce air contaminant emission levels below levels of concern. Due to the

low emission levels of air contaminants from the new Fairfield facility, BAAQMD characterize it as a small facility and a minor source. This scale-up of cadmium telluride manufacturing technology is unique. Regulatory authorities compare the Apollo® process to other similar industries to define appropriate levels of control. BAAQMD therefore acknowledged the similarity of the solar cell manufacturing stations to semiconductor processes by grouping some of the process equipment together as a single source and characterizing this source as a solar cell (semiconductor) fabrication area. BP Solar was proactive in clarifying such preliminary permitting issues with BAAQMD permit engineers by holding a pre-application meeting and following up on issues as permit review progressed. As such, air permitting was straightforward, requiring less than 60 days for BAAQMD review.

With regard to special California Environmental Quality Act (CEQA) requirements, most Apollo® process sources were classified as exempt, but some sources required review as a "ministerial" project. BAAQMD required that BP Solar file an Appendix H Environmental Information Form describing the planned facility development to conduct this ministerial project review. BAAQMD found that the facility would be exempt from any further CEQA review. There is a CEQA exemption for facilities located on the same site as a replaced facility. This occurs when the reconstructed facility has substantially the same purpose and capacity as the replaced facility. The Fairfield plant was previously permitted by an amorphous silicon solar cell manufacturing company. Although the technology differences between amorphous silicon and cadmium telluride production plants are significant, an environmental review found that the proposed project caused no significant incremental impact over the previous operations. This was beneficial, however, the Apollo technology would have still been found exempt, even at a green field site. The previous permit only allowed expedition of the exemption.

The ATC permit application included an emissions assessment and a description of control technologies applied to emission sources, including BACT design requirements.² Control technology was proposed for Apollo® process sources that emit ammonia, hydrogen sulfide, CdTe dust, and VOCs. The biggest challenges were perceived to be controlling CdTe dust

² Radian International ATC Permit Application for BP Solar Inc., Fairfield, Ca," April 1997

emissions to levels of insignificant health risk and complying with BAAQMD's stringent requirements for VOCs in a cost-effective manner.

Regarding emissions of CdTe dust and other toxic compounds, the BAAQMD requires new facilities to evaluate their potential risk to public health. BAAQMD considers toxic substances emitted at amounts below certain annual risk screen trigger levels to pose a nonsignificant risk. The estimated amount of CdTe dust and other toxic substances emitted by the Apollo® process are listed in Table 4 along with their respective risk screen levels. Note that the risk screen trigger level for cadmium emissions (<0.046 lb/yr) is extremely low. Because of the efficient control technologies selected by BP Solar, none of the sources at the Fairfield facility will exceed their respective risk screen trigger levels. In this way, BP Solar was able to demonstrate that a detailed risk assessment analysis would not be needed. This would have required a more complicated permitting route that would have taken longer and involved greater cost.

The challenge of VOC control was addressed by adopting a phased approach for permitting VOC-emitting sources. The emission levels and vent stream flow rates from these sources (essentially, cleaning materials) were uncertain due to unknown solvent usage with new equipment, design, and material changes during installation and start-up. Cost-effective BACT control device selection depends on knowing stream composition and concentrations, which are best determined after start-up. Initial analysis at start-up production levels identified that there would be less than 10 lb/day of VOC emitted. A permit was sought under these conditions, meaning that a detailed BACT analysis would not be required at this stage. This approach allowed BP Solar to propose using carbon adsorption to achieve the required 90% control of organics initially and evaluate whether other technologies would be feasible or required as BACT after final flow rates and VOC concentrations can be measured.

Emissions from a solvent tank were estimated to trigger BACT requirements. The design of the solvent tank was specified to meet BAAQMD's criteria for BACT, which includes a

freeboard ratio of 0.75, a freeboard chiller, a cover, and an internal drainage facility³ The diptank is also currently vented to the carbon adsorption system. BP Solar is investigating the feasibility of replacing the solvent with an aqueous-based substitute.

3.2 Sewer District Wastewater Discharge Permit Strategy

With proper on-site pretreatment, BP Solar's Apollo® process wastewater has been permitted for discharge to the local publicly owned treatment works (POTW). Discharges from the Fairfield facility will be closely monitored for compliance with local and federal limits. There are also initial and monthly POTW fees for these discharges. BP Solar plans to maximize the potential reuse of rinse waters within the Fairfield facility, with an ultimate goal of zero-discharge, by phasing in additional wastewater treatment technologies. A "closed loop" approach is desirable as a pollution prevention measure and will have the additional benefit of reduced makeup water surcharges and discharge fees from the local regulator. To reach this stage, a significant level of investigation is required.

Process wastewater and sanitary wastewater from the Fairfield facility will be discharged to the Fairfield-Suisun Sewer District (FSSD), the local POTW. FSSD has set local standards for the quality of the wastewater that it accepts.⁵ Standards relevant to the Apollo® process wastewater discharges are shown in Table 5. These standards ensure that wastewater is compatible with FSSD's treatment system and will allow effluent from the POTW to be discharged into Suisun Bay, which is part of the San Francisco Bay. The local cadmium limit, which recently dropped to 30 ppb, is so low because FSSD's wastewater treatment outfall discharges directly to the Suisun Wetlands, the largest example of such a wetland area in the United States. Water in the wetlands is immobile and is a home to many migratory birds.

FSSD also administers federal pretreatment regulations. The Apollo® manufacturing processes were categorized as metal-finishing operations subject to Federal

³ Bay Area Air Quality management District, BAAQMD BACTITBACT Workbook; June 1995

⁴Fairfield-Suisun Sewer District, Wastewater Discharge Ordinance 91-1, adopted January 28, 1991, amended through November 27, 1995.

Pretreatment Standards (40 CFR 433) for the metal-finishing point source category. The Federal Pretreatment Standards for New Sources (PSNS) applicable to the Apollo® process wastewater are shown in Table 6.

The sewer discharge permitting process involved submitting an Industrial Pretreatment Program Baseline report to FSSD (to comply with federal requirements), and the POTW permit application. These submittals identified process wastewater discharges, average and maximum flow rates, pollutant concentration level before and after treatment, pretreatment system and capacity, plant sewer and storm drain plans, facility water sources and discharges, and other off-site liquid and sludge waste disposal. All information pertaining to wastewater characteristics and flow volumes submitted to the permitting agencies represents full-scale operation of the Fairfield facility.

From this information, FSSD developed a Wastewater Service Agreement for the Fairfield facility that establishes allowable discharge capacity and connection fees. Connection fees are established according to discharge flow rate, BOD₅, and total suspended solids (TSS) levels.

The Wastewater Service Agreement also outlines a program of self-monitoring that requires sampling and analysis of BOD₅, TSS, and ammonia by a state-certified laboratory to verify that the facility is in compliance. This information is also used as a basis for connection fees and monthly service charges. Ammonia must be determined because the amount in the process wastewater is uncertain and could be relatively high. FSSD can accept a moderate amount of ammonia, but high levels could require additional consideration. A discharge flowmeter and a flow-paced refrigerated automatic sampler are required for sample collection.

Numerous discussions and visits were arranged with FSSD to clarify their requirements, given the unique nature of the Fairfield plant and the particular local sensitivities to discharges in this area. These requirements particularly covered compliance, sampling, and monitoring. To demonstrate compliance with the local limits listed in Table 5, BP Solar must

continuously monitor pH at the combined discharge point (where treated process effluent and sanitary sewer discharges are combined). Additional 24-hour composite samples will be taken at this location twice annually by FSSD and analyzed for metals, total toxic organics, total petroleum hydrocarbons, and polynuclear aromatic hydrocarbons. To demonstrate compliance with Federal Pretreatment Standards, semiannual 24-hour composite samples will be taken at the process wastewater treatment system outlet by either FSSD or BP Solar. These samples will be analyzed for all pollutants listed in Table 6. BP Solar is implementing a toxic organic management plan. As allowed under the federal program, this plan will give the additional benefit of reducing some of the analytical costs.

FSSD has tracked the start-up of the wastewater treatment system closely and has imposed interim conditions on discharge during the start-up period as it becomes more familiar with the facility's unique operation. Before allowing continuous discharge to the sewer, FSSD has required batch treatment of wastewater and discharge only after receipt of certified analysis demonstrating that the treatment objectives for cadmium and pH have been achieved. In addition, FSSD requires continuous monitoring of pH.

Although storm water releases are permitted by the county, the sewer district administers and maintains the storm water program. The facility had a storm water permit filed by the previous owner, and this permit has been updated to include new operations. BP Solar has identified new storm water pollution prevention measures (e.g., sump level sensors and alarms, partial enclosure of wastewater treatment equipment, and relocation and secondary containment for chemical supply drums) to prevent the possibility of wastewater spills from the treatment area entering the nearby storm sewer.

Table 3

Air and Water Emission Source and General Permit Requirements

Process or Special Permit	Permit Requirement	Comments
Cadmium Sulfide Deposit	Requires new permit.	Will need control of peak NH ₃ emissions for odor.
Cadmium Sulfide Heat Treat	No Permit required.	Furnace is natural gas less than 10 MMBTU/hr
CdTe Heat Treat	No Permit required.	Furnace is natural gas less than 10 MMBTU/hr
Solvent Spray	Requires new permit.	Will require 90% control for VOC
Solvent Rinse	Requires new permit.	Will require BACT for VOC
Laser Scribe 1, 2, and 3	Requires new permit.	Requires control to level below health risk concern
Bead Blasting	Requires Permit Modification	Requires control to level below health risk concern
Laminating	Requires Permit Modification.	Update on anticipated wipe cleaning
Laboratories	No permit required.	No permit required for less than 25,000 sq. feet of lab space
Combined Discharges to Publicly Owned Treatment Works	Requires new permit from POTW	Subject to federal industrial pretreatment before discharge to POTW
CEQA Permit	No permit required.	No incremental impact and no significant health risk
Use Permit	Transfer existing "Use Permit"	Subject to review of zoning ordinance
Hazardous Materials	Requires new permit	Fire Department Hazardous Materials Permit
Underground Storage Tank	Exempt from state permitting	Verify that no city and county ordinances have requirements

Table 4

Comparison of Emissions to Toxic Air Contaminant Trigger Levels

Process	Compound	Trigger Level (lbs/yr)**	Uncontrolled Emissions (lbs/yr)	Controlled Emissions (lbs/yr)
CdS Deposit	Ammonia	19,300	14,600	1,460
CdS Deposit	H ₂ S	8,110	69	6.9
Laser Scribes	Cadmium*	0.046	130	0.013
Bead Blasting	Cadmium*	0.046	67	0.020
Wipe Cleaning	Isopropyl alcohol	444,000	1,550	1,550

*Note: The Cadmium fraction of total CdTe emissions is reported here for comparison with the toxic risk screen trigger levels.

**BAAQMD Regulation 2 (Permits), Rule 1-316.

Table 5

Local Sewer District Discharge Limits*
(FSSD Ordinance No. 91-1)**

Pollutant or Pollutant Property	Discharge Limit (ppm)
Arsenic	0.1
Cadmium	0.03**
Copper	1.3
Cyanide	0.7
Lead	0.5
Mercury	0.01
Nickel	0.9
Silver	0.2
Total Chromium	0.15
Zinc	2.3
Oil or Grease (animal, vegetable)	300
Oil or Grease (petroleum)	100
Untreatable Chlorinated Hydrocarbon	0.02
Untreatable Phenolic	1.0
Total Petroleum Hydrocarbon	50
Total BTEX	25
pH	6-11***
Temperature	<130°F

* This complete list of discharge limits does not infer the presence of these contaminants in BP Solar's wastewater.

** Pending adoption, reduced from 0.05 ppm.

*** BP Solar's case-specific limit allows pH between 6-12, with no excursions over 1 hour.

Table 6

Federal Pretreatment Standards for New Sources (PSNS)
(40 CFR Part 433.17)

Pollutant Or Pollutant Property	Maximum For Any 1 Day (mg/l)	Monthly Average Shall Not Exceed (mg/l)
Cadmium	0.11	0.07
Chromium	2.77	1.71
Copper	3.38	2.07
Lead	0.69	0.43
Nickel	3.98	2.07
Silver	0.43	0.24
Zinc	2.61	1.48
Cyanide	1.20	0.65
Total Toxic Organics	2.13	—
Alternate cyanide: amenable to chlorination	0.86	0.32

4.0

ALTERNATIVE ABATEMENT AND TREATMENT TECHNOLOGIES

BP Solar and Radian International conducted an evaluation of alternative air pollution abatement and wastewater treatment technologies for the Apollo[®] process waste streams. The abatement and treatment technologies were evaluated according to their guaranteed ability to meet specified levels of control, provide flexibility and reliable operation, and allow for potential future additional treatment (as BP Solar moves toward its zero-discharge objectives).

The selected air abatement technologies are summarized in Table 7. The selected wastewater treatment system is a cadmium scavenging ion exchange (IX) system and electrowinning system for processing IX regenerant to recover cadmium. A photograph of this wastewater treatment system is shown in Figure 2. This section summarizes the evaluation of each of the abatement and treatment technologies and alternatives considered.

4.1

Cadmium Sulfide Deposition Bath Emission Control

Cadmium sulfide deposition is a batch process that will generate emissions of ammonia during heating. Ammonia emissions are segregated from hydrogen sulfide emissions generated during cleaning for separate treatment. A single air abatement technology would not be feasible to control both pollutant types due to chemical incompatibilities. This segregation is achieved, in part, by use of a diverter valve on the deposition bath exhaust vent. This valve directs bath exhaust to the ammonia scrubber during deposition and to carbon adsorbers during the cleaning cycles.

BAAQMD regulations require that ammonia emissions are maintained below 5,000 ppmv at the stack outlet, that odor is prevented, and that levels of ammonia do not pose a toxic health risk. The health risk concern is avoided by ensuring that the amount of ammonia emitted annually does not exceed 19,300 lb/yr. Hydrogen sulfide must be controlled to low concentrations (<0.06 ppmv) at ground level and cause no odor.

Various packed tower absorption systems (scrubbers) were evaluated for ammonia abatement. A photograph of the selected scrubber installed at the Fairfield plant is shown in Figure 3. The specifications for a 4,500 cfm ammonia scrubbing system included considering water scrubbing with or without sulfuric acid addition and options for liquid blowdown disposal. Sulfuric acid addition was chosen to provide reliable, high removal efficiency and to reduce the amount of liquid blowdown. With acid addition, the blowdown will contain dissolved ammonium sulfate.

Compression, condensation, and recovery of ammonia from the vent stream was reviewed briefly as an alternative to scrubbing and as a means to recycle ammonia. This technology was only considered initially when plans involved use of a deposition solution containing high ammonia concentration. This technology was viewed as impractical.

Options for control of hydrogen sulfide in the segregated vent included caustic scrubbing or adsorption/oxidation on potassium hydroxide-impregnated carbon⁵. Because the deposition bath is a batch process, the stream flow rate will cycle from 1,500 to 3,250 cfm. Carbon adsorption was chosen due to the low cost, ease of operation, and adaptability. Two 300-pound carbon canisters provide adequate capacity. Two additional 300-pound canisters are installed in series as required by BAAQMD to prevent breakthrough emissions. Because the concentration of hydrogen sulfide is expected to be low, change-outs will be infrequent, which will keep disposal costs low. Also, the carbon loaded with reacted hydrogen sulfide is typically not a hazardous waste. The average cost for carbon change-out was estimated to be \$1,800 per year at full production capacity.⁶

4.2 CdTe Dust Collection

CdTe dust is generated at four locations in the Apollo[®] process: three laser scribe operations and a bead blasting station. For the three laser and bead blasting stations, the dust

⁵ Cameron Environmental, Inc., Quotation for Carbon Adsorption Systems, May 1997.

⁶ Personnel communication with V. Fthenakis, Brookhaven National Laboratory, Upton, NY.

collection equipment and existing permit required upgrading to handle canmium dust. The upgrades were necessary to achieve higher particulate collection efficiencies to prevent significant health risk concerns and also to reduce worker exposure to CdTe dust when disposing of collected particulate.

The bead blasting station was equipped with a cyclone separator that collects large particulate and recycles blasting beads. The cyclone seperator was followed by a baghouse and a HEPA filter that were rated between 95% and 98% efficient at particulate collection. Using the bead blasting station at full operation for the Apollo® process, particulate control efficiency >99.95% is required to ensure that CdTe emissions are below the cadmium toxic risk trigger threshold of 0.046 lb/yr. The existing baghouse and HEPA filter were replaced by new a high-efficiency cartridge HEPA dust collector rated for 1,375 acfm. Bag-in/bag-out cartridge removal capability was specified to facilitate disposal of collected dust and to reduce worker exposure to CdTe.

The existing laser scribe stations were equipped with cabinet-type dust collectors rated at 99% collection efficiency for 1 micron particles. The dust hopper in the collector was a removable open-top tray. The dust pickups on the scribe tables did not appear to provide adequate suction to clear all dust. This collection system was upgraded with new high-efficiency cartridge bag-in/bag-out HEPA dust collectors similar to those specified for the bead blast station. A particulate control efficiency of >99.9% was specified to ensure that CdTe dust emissions from each laser station remain below the cadmium toxic trigger level of 0.046 lb/yr. New dust pickup devices were designed, and the collection fan size was increased to 750 cfm to improve dust extraction.

4.3 VOC Emissions Control

Four major manufacturing steps in the Apollo® process generate organic solvent (or

VOC) emissions. The largest source of VOC emissions is the solvent cleaning station. This source is subject to specific design and operational requirements per local BAAQMD rules and BACT requirements. Each of these manufacturing steps regulated by different local rules, but in general the process will require >90% control of VOC emissions or use of aqueous-based substitute materials.

BP Solar is committed to researching the use of aqueous-based materials for several of these applications and has already implemented material changes to reduce the amount of VOC generated from the Apollo® process.

The most cost-effective treatment of VOC emissions is implemented by combining the process vent streams and routing them to a single control system. The total exhaust vent flow rate that results from combining process and curing exhausts is 6,000 scfm.

Each vent stream was evaluated individually at first to determine if there were any potential for solvent recovery and reuse. Because most of the solvent evaporation occurs during low-temperature curing (250–350°F), recovery (e.g., by condensation or adsorption) at elevated temperatures was not considered feasible. The most generally applicable options for VOC control are carbon adsorption in nonregenerable canisters and thermal oxidation processes.

Carbon canisters were selected as the initial VOC treatment technology because they are modular (thus, adjustable when flow rates are modified), easy to install and start up, low maintenance, low initial cost to rent (with purchase option) and install, and low disposal cost during start-up and initial production phases. Carbon canisters installed at BP Solar are shown in Figure 4. Two large canister drums containing 1,500 lbs of activated carbon each provide a total of 6,000 cfm capacity, and two more canisters were added to treat the ultrasonic solvent cleaner exhaust for a total of 12,000 cfm. Four additional canisters operate in series with each of the

primary treatment canisters as required by BAAQMD to control any breakthrough VOC emissions.

Carbon disposal costs depend on carbon utilization and need for change-out. Emissions of VOC during initial one-shift production are estimated to be 10 lb/day from the ultrasonic solvent cleaner and 12 lb/day from other processes. At this rate, the four primary beds would require change-out every 2.5 months at a cost of \$13,000. The beds last much longer during production start-up because VOC emissions are lower. Clearly, the cost to rent and dispose of carbon for long-term VOC control means that this technology is not a cost-effective solution. In this situation carbon canisters provide efficient VOC reduction on a temporary basis and allow BP Solar to implement process changes and improvements before specifying a permanent control technology.

Aside from material substitution, the most technically feasible and economical option for control of VOC emissions from the Apollo process is thermal oxidation. BP Solar conducted a preliminary review of several alternate thermal oxidation processes, including recuperative systems, pre-concentration, catalytic oxidation, and regenerative thermal oxidation (RTO). Each of these processes uses different techniques to reduce the high annual fuel cost required to treat dilute vent streams. The combined vent exhaust will be quite dilute, ranging from 50 to 200 ppmv VOC.

The size and cost of thermal oxidation devices depend on the vent flow rate treated. BP Solar intends to reduce the amount of exhaust requiring treatment by implementing material substitution wherever possible. For a 6,000 cfm exhaust vent, the uninstalled total capital costs for the various thermal oxidizers are estimated to range from \$200,000 to \$400,000. Annual fuel costs are lower for the more expensive treatment systems, with the payback on extra capital expected within two to five years.

The use of thermal oxidation will provide a cost savings over continual disposal of carbon once the Fairfield facility achieves full production. Besides cost savings, these thermal

oxidation devices provide high VOC removal efficiencies that can meet BAAQMD standards for BACT (should process emissions exceed 10 lb/day at full production). The disadvantage of these devices include their ongoing fuel costs and the combustion by-products, such as NO_x, that they create. Control technologies such as catalytic oxidation and RTOs have the advantage that they create very low thermal NO_x emissions. Some vendors also offer special low NO_x designs.

4.4 Wastewater Treatment Systems

BP Solar has several objectives in implementing wastewater treatment at the Fairfield facility, including:

- Treat process rinse wastewater to within POTW and federal pretreatment standards (metals and pH);
- Accommodate on-site treatment of aqueous bath wastewater for discharge to POTW (to avoid excessive waste disposal charges);
- Reduce POTW fees by adopting more economically favorable on-site treatment of organics; and
- Ultimately implement a closed-loop wastewater treatment system to achieve semiconductor-grade water specifications for reuse in processes (to reduce makeup water surcharges and sewer discharge fees).

BP Solar has put its emphasis on achieving the first two objectives, but the company intends to pursue all objectives to the maximum extent practicable. Research on achieving the final two objectives is the subject of an additional NREL-funded study (the NREL Thin Film Partnership Program, which BP Solar started on May 1, 1998).

The candidate wastewater treatment technologies for the BP Solar Fairfield facility are listed in Table 8. The selected technology is a cadmium scavenging IX system and electrowinning system for processing IX regenerant to recover cadmium. This system was chosen because of the technical merit of the proposed system, the favorable treatability results, the

performance guarantee, reasonable cost, and the production of low-volume cadmium waste that can be recycled to a smelter or recovered for reuse rather than disposed. This treatment system is limited to the removal of dissolved cadmium; the system would require additional treatment components to remove organics or handle other process wastes.

The selected technology includes a pre-filtration step for particulate cadmium removal prior to selective ion exchange (i.e., chelating IX resin) for dissolved cadmium removal. BP Solar's wastewater contains submicron cadmium precipitate that needs to be filtered effectively to guarantee compliance with effluent limitations. Ion exchange takes place across three lead-lag chelating resin beds with two tanks in service at all times. The chelating resin of the selected technology acts to break cadmium complexes.

Treatability tests were conducted on wastewater samples with 18.6 mg/L of cadmium in complexing agents. The treatability test results showed consistent removal of the cadmium from the BP Solar wastewater to levels of less than 10 ppb for over 60 bed-volumes of throughput. These tests were repeated to represent new design conditions of approximately 80 ppm (mg/L) of cadmium at a flow of 16 gpm. The electrowinner was sized for cadmium levels up to 200 ppmv.

At full production, the lead tank will be exhausted twice each day (24-hour period) and require regeneration. The regenerant from the ion exchange system is sent to electrowinning for metallic cadmium recovery. Only the concentrated portion of the regenerant (approximately 240 gallons) is sent to the electrowinner. The rinse waters are recycled back through the wastewater treatment system. The electrowinner (50 sq. ft.) will be capable of processing four batches of spent regenerant per day. The regeneration is accomplished with recyclable acid (sulfuric) from the electrowinner. Only a small amount of virgin acid is required. The process should recover approximately 7 kg/day of cadmium, which can be sold to a reclaimer. This system removes the need to handle hazardous materials.

Alternative systems

Chemical precipitation and microfiltration, followed by selective ion exchange polishing, was another proposed system that demonstrated <30 ppb cadmium during treatability tests. The effluent BOD would still be relatively high because this system would not remove all dissolved organic constituents. The main disadvantage of this process is that it generates a slurry of insoluble metal precipitates with trapped organic constituents. The slurry would be processed through a gasketed plate filter press to dewater to a 35–40% cake. If a cake dryer is also used, a final cake with a 10% moisture content is produced that can be sold to a reclaimer for the recovery of the cadmium. A cost estimate for treatment of BP Solar's wastewater in this system was not submitted.

A system that uses a special highly selective silica gel resin also demonstrated <30 ppb cadmium during treatability studies. The advantages of this resin over a chelating IX resin are (1) a greater capacity for the target metal because of a high selectivity; (2) benign alkali ions (Na^+ , K, Ca, Mg) are not retained; and (3) less regenerant is required to achieve resin renewal. The disadvantage of this resin technology is that it is not provided in complete systems for turnkey installation, and the additional engineering requirements for integration with other unit operations tend to off-set the apparent advantages.

Cadmium removal treatability studies were also conducted on systems that use electrochemical iron addition for co-precipitation of the cadmium in the BP Solar wastewater. This type of treatment is inhibited because cadmium is present as a complex ion, but <30 ppb cadmium was achieved by using pH adjustment and copious amounts of ferrous iron and polymer. The disadvantage of this technology is its large polymer requirements and the high utilization of the iron anode. This treatment also produces large amounts of hazardous (cadmium/iron) sludges.

From other treatability studies, BP Solar learned that RO treatment would require two passes and numerous elements to achieve the needed removals of cadmium and other

constituents. This technology would not be feasible to treat wastewater with the level of organic constituents found in BP Solar's wastewater. RO treatment would generate large volumes of reject wastewater, which would require additional concentration and disposal as a hazardous waste.

BP Solar reviewed another chelating-type resin, ion exchange system to remove cadmium. This system was similar in some respects to the selected treatment process, but was not selected because it included treatment steps that had not been researched thoroughly. The reuse system included selective chelating-type resin ion exchange to remove cadmium. Additional ion exchange columns would achieve deionization of process wastewater. Regenerant wastes from the various ion exchangers could be segregated to allow for the separate disposal of cadmium wastes. However, treatment system wastes would require sludge treatment and evaporation or the drying of cadmium-containing wastes for volume reduction prior to disposal. The total reuse system proposed biologically enhanced granular activated carbon (GAC) supplemented by expensive ozone treatment (if needed) for removal of organic compounds. The GAC unit was too small to remove the total amount of organics present. Treatability tests indicated that activated carbon treatment alone would not be effective in removing the organic component of BP Solar's wastewater.

BP Solar plans to further investigate both organic constituent removal and TDS removal. Options include biological treatment or chemical oxidization using hydrogen peroxide or ozone enhanced by the use of ultraviolet and visible light at optimum pH values. Chemical oxidation technology would be substantially more expensive to operate than a biological treatment system.

Once cadmium and organic constituents are removed from the wastewater, the remaining TDS can be removed by either RO or cation/anion exchange. The high cost of such a process means that further investigation will be required.

A successful and cost-effective zero discharge system at the BP Solar Fairfield facility will be a challenge that will require, among other efforts, evaluation of waste source reduction measures. Future implementation of a wastewater recycle system is still possible; this type of system can be evaluated once actual wastewater characterization and process data are assembled for the plant. Wastewater characterization and assembling process data are subjects for another, (NREL-funded study. NREL subcontract No ZAK-8-17619-27,"Apollo® Thin-Film Process Development").

Table 7

**Summary of Air Stream Abatement Technologies
for Apollo® Process**

Process	Specified Removal Efficiency	Recommendation
Bead Blast	99.99%	Upgrade Baghouse and HEPA with Bag In/Bag Out Filter
Laser Scribe	99.99%	Replace dust collectors with 3 Downflow dust collectors
CdS Deposit	99.5%	Scrub NH ₃ with H ₂ SO ₄
Acid Strip	95%	Adsorption/Oxidation of H ₂ S on Carbon
Solvent Cleaner	BACT Design	Freeboard ratio of 0.75, freeboard chiller, cover, and internal drainage. Option to vent to carbon adsorbers
Other solvent cleaning	95%	Carbon Adsorption Unit

Figure 2: Photograph of 16 gpm Ion Exchange Treatment System

Figure 3: Photograph of 4,500 cfm Ammonia Scrubber

Figure 4: Photograph of Activated Carbon Canisters for VOC Abatement

Table 8

Candidate Wastewater Treatment Technologies

Treatment Objective	Technologies Considered
Cadmium removal <30 ppb	<ul style="list-style-type: none">• Cadmium scavenging ion exchange with electrowinning of regenerant for cadmium recovery• Selective ion exchange with evaporation/drying of regenerant for cadmium waste disposal• Selective silica gel resin ion exchange• Chemical precipitation, microfiltration with selective ion exchange polish• Electrochemical iron addition with coprecipitation• Electrocoagulation• Reverse osmosis (upstream organic removal required)
Organics removal	<ul style="list-style-type: none">• Biological treatment• Enhanced granular-activated carbon• Chemical oxidation (peroxide or ozone)• UV oxidation
Deionization, TDS removal for reuse	<ul style="list-style-type: none">• Reverse osmosis• Microfiltration• Cation/anion exchange

Table 9

Comparison of Estimated Monthly VOC Abatement Costs¹

Monthly VOC Abatement Expense	Interim Operation	Full Operation¹
Carbon Adsorption		
Monthly Rental	\$2,600	\$2,600
Carbon Change out/Disposal	\$3,000	\$9,000
Total Monthly Carbon Adsorption Cost	\$5,600	\$11,600
Catalytic Incineration		
Incinerator Capital Expense ²	\$4,200	\$4,200
Fuel, Electrical, Catalyst	\$2,000	\$4,700
Total Monthly Catalytic Incineration Cost	\$6,200	\$8,900

¹ Abatement of 6,000 scfm vent stream.

² Capital cost of \$200,000 (total installed cost of \$350,000) annualized over 10 year incinerator life.

This study illustrates BP Solar's commitment to the environment and its resolve to undertake an extensive pre-production analysis of waste stream abatement at the Fairfield plant. BP Solar worked closely with Radian to address environmental control and permitting issues early in the process of specifying new equipment for the Apollo® process. During the study, numerous technologies were thoroughly evaluated. Through this approach, BP Solar was able to select systems that outperformed the stringent federal and state regulations. This approach also complied with the BP groups Operations Integrity Assurance System (OIAS) It requires that systems are in place to monitor and minimize environmental impacts by reducing wastes and emissions - wherever feasible - involving prevention, energy conservation, source reduction, recycling and re-use.

The main issues were originally perceived to be controlling cadmium compound releases to both air and wastewater to acceptable levels and adopting technologies for air and water waste streams in an efficient, cost-effective manner.

BP Solar's strategy for air permitting was to propose high-efficiency, reliable control equipment that would reduce air contaminant emission levels below levels of concern. Air permitting was straightforward, required less than 60 days for approval, and involved no public notification period.

Cadmium telluride dust is successfully controlled with high-efficiency (>99.9%) bag-in/bag-out filters, which prevent significant health risk and reduce worker exposure to cadmium dust when disposing of collected particulate.

For air abatement, carbon canisters provide efficient VOC reduction to allow BP Solar to implement its technology in a production environment. Wastewater pretreatment is required per federal pretreatment standards for the metal finishing point source category and the stringent local POTW limits for cadmium (30 ppb).

BP Solar installed a cadmium-scavenging ion exchange (IX) system and electrowinning system capable of removing cadmium to <10 ppb, while producing cadmium waste that can be recycled to a smelter or recovered for reuse.

BP Solar plans to maximize potential reuse of rinse waters (closed-loop) within the Fairfield facility (with an ultimate goal of zero-discharge) by phasing in additional wastewater treatment technologies. This is the subject of an additional NREL-funded study.

BP group's operations integrity assurance system (OIAS) continuing mandate to reduce emissions from year to year.

A successful wastewater recycle design will be a challenge at the BP Solar facility and will require, among other efforts, evaluation of waste source reduction measures and identification of a cost-effective treatment technology for organics.

Finally, the work to date has set the basic requirements for the introduction of the Apollo[®] technology. It has identified the areas that need to be revisited as production scales up to ensure that all health, safety, and environmental goals are met.

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