

RECYCLING OF CdTe PHOTOVOLTAIC MODULES: RECOVERY OF CADMIUM AND TELLURIUM

Vasilis Fthenakis¹, Paul Duby², Wenming Wang¹, Christopher Graves² & Anuta Belova²

¹. PV Environmental Health & Safety Research Center – Brookhaven National Laboratory, Upton, NY

². Center for Life Cycle Analysis – Columbia University, New York, NY

ABSTRACT: Research on recycling of CdTe PV modules and manufacturing waste aims in optimizing the separations and recovery of glass, cadmium and tellurium while minimizing life-cycle emissions and energy use, under the constraint of low cost (e.g. a few cents per watt). The major tasks of our research are: a) Cleaning of glass from the metals and recycling of glass; b) separation of Te from Cd and other metals and recovery of Te for its value; c) recovery of Cd for re-use or effective sequestration. The modules were crushed in fragments and were subjected to hydrometallurgical processing involving leaching, ion exchange separation, precipitation and electrowinning. Low concentration sulfuric acid solutions were effective in totally leaching cadmium and tellurium out of the glass matrix. We used ion exchange columns in series to separate copper and tellurium from cadmium in solution. Subsequently, we recovered Cd and Te from the corresponding solutions with electrowinning and reactive precipitation respectively. Electrowinning produced cadmium sheets of 99.5% wt purity in sizes of 2 by 4 cm and 11 by 11 cm at an estimated cost of only 0.1 cents/Wp. Precipitation of Te in metallic form was obtained by various reduction agents. Ongoing studies aim in improving the purity of the recovered cadmium metal and optimizing the recovery of tellurium.

Keywords: Photovoltaic, Recycling, CdTe

1. INTRODUCTION

Photovoltaic modules at the end of their useful life have to be decommissioned and disposed of, or re-used in some way. Environmental regulations impact the complexity and the cost of dealing with end-of life PV modules. The European Industry Association (EPIA) being proactive and in order to reuse valuable materials, recommends setting an industry-wide foundation to build the necessary infrastructure for PV module collection and recycling. Previous research at Brookhaven National Laboratory has addressed issues of collection [1] and technical feasibility of recycling PV modules [2, 3]. Furthermore, experimental research on CdTe PV manufacturing scrap, has shown a very effective separation of Te from Cd and other elements in the PV matrix. The key steps of our method are crushing the CdTe PV modules and leaching the fragments with a minerals acid (sulfuric) /hydrogen peroxide solution mixture to generate a solution that is rich in cadmium, tellurium, copper, and iron. The solution is then passed consecutively through a chelating resin column to remove copper, and a cation-exchange resin column to remove cadmium and iron; details of these operations are described elsewhere [4,5,6].

The current paper describes the subsequent recovery of Cd by electrowinning and Te by reactive precipitation.

2. RECOVERY OF CADMIUM

The cation-exchange column retaining cadmium was eluted with a mixed sulfuric acid/sodium sulfate solution to generate a cadmium-rich solution from which cadmium was recovered by electrowinning as a metal sheet. The solution contained about 15 to 30 g/L of Cd

and ppm concentrations of Al, Fe, Zn, Cu, Pb, Na and Ca.

A series of experiments were conducted in a small scale apparatus (e.g., 200 ml) to optimize current density and current efficiency for stable cadmium deposits and low operating cost. These experiments produced 2 cm by 4 cm sheets (Figure 1a). Deposit stability was rated qualitatively on a scale of 1 to 10 by visual observation, with higher scores for deposits which had fewer dendritic formations and were easy for the operator to remove from the cathodes without crumbling. Current efficiency was determined by employing Faraday's law. An experiment was made on a larger scale cell (i.e., 5 L) which produced 11 cm by 11 cm sheets (Figure 1b).

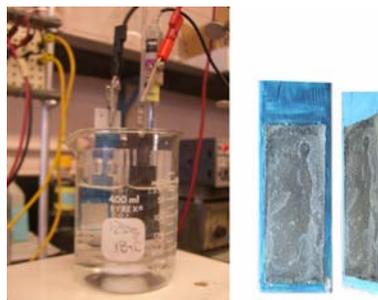


Figure 1a. Small electrowinning apparatus and Cd deposits

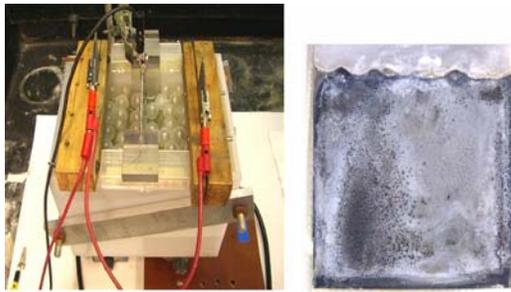


Figure 1b. Large electrowinning apparatus and Cd deposits

2.1 Characterization of Deposits

The purity of the deposits was determined by dissolving parts of them in nitric acid and measuring the concentration in solution via complexometric titration at Columbia University and via Inductively Coupled Plasma (ICP) analysis at Brookhaven National Laboratory. The uncertainty of the ICP analysis (e.g., ~3%) was too high to get accurate determination of Cd purity based on Cd analysis alone. The most accurate purity determination was obtained by measuring with ICP analysis the concentrations of all the minor elements in solution (i.e., Al, Fe, Zn, Cu, Pb, Na, Ca) and subtract them from the total. The results of this subtractive analysis was confirmed with complexometric titrations of Cd. Stable deposits were shown to be consistently composed of more than 99% cadmium and most of them had greater than 99.5% Cd purity (Figure 2).

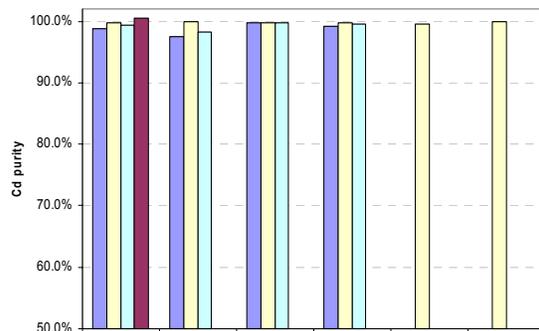


Figure 2. Cd purity analyses; various experiments

2.2 Cost Estimates

The cost of the electrochemical recovery of Cd was assessed for a facility treating about 5.7 tonnes/day of CdTe PV spent modules, equivalent to 10 MWp/yr (rated) of 9% efficient modules. This scale would produce about 4 kg of Cd per day. Automation was assumed to be too expensive for such a small scale

operation and, therefore, manual labor on a periodic cycle was assumed. The labor cost is estimated to be the highest contributor to the total operating cost; the replacement of the anodes is another significant component of the operating cost. The total amortized capital and operating cost was determined to be about \$10,000/yr translating to only 0.1 ¢/Wp (Figure 3). Both the capital cost and operating cost are supported by reference to current industrial electrowinning operations.

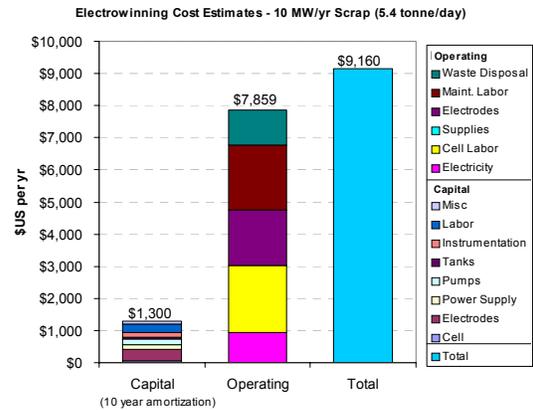


Figure 3. Cadmium Electrowinning Cost Estimates

3. RECOVERY OF TELLURIUM

The effluent solution from the ion-exchange separation contained about 1000 ppm of tellurium. To recover the tellurium from the leach solution, we explored several precipitation methods. They included (1) precipitating tellurium as tellurium dioxide using sodium hydroxide or sodium carbonate, (2) precipitating tellurium as tellurium sulfide using sodium sulfide, (3) reducing/precipitating tellurium as metallic tellurium using zinc or iron metal, and, (4) reducing/precipitating tellurium as a metallic salt using sodium metabisulfite. In all these processes, the recovered tellurium was in the form of fine powder. Elemental analysis of the aqueous solutions using an ICP spectrometer showed removal efficiencies of 60% to 100% (Figure 4).

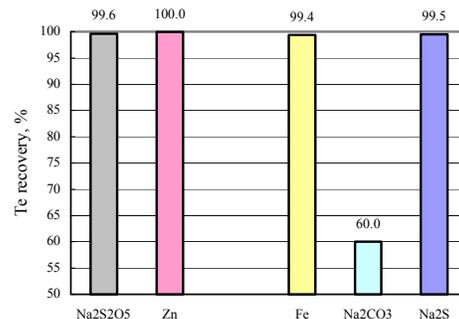


Figure 4. Recovery of tellurium by reactive precipitation

Reductions with zinc and iron carried out at low pH (<1.0) resulted in high tellurium recovery. Zinc reduction was the best of the two, reducing the tellurium concentration in the final leaching solution to less than 1.0 mg/L. It yielded a product essentially composed of only elemental tellurium, as confirmed by X-Ray Powder Diffraction (XRD) and X-Ray Spectrometry (XRF). Sodium-metabisulfite reduction must be carried out at higher pH (e.g., 3.5) to obtain a high tellurium recovery. However, a high pH precipitates tellurium dioxide, yielding a mixture of metallic tellurium and tellurium dioxide. Also, some SO₂ is produced with this method. More investigations and quantitative purity analysis are in progress.

[6] Fthenakis, V.M. and Wang, W., System and Method for Separating Tellurium from Cadmium Waste, U.S. Patent, Application Serial No. 11/421,343, May 31, 2006

4. CONCLUSION

Following a sequence of hydrometallurgical processes, cadmium was recovered by electrowinning in solid sheets of purity greater or equal to 99.5%. For manufacturing scrap equivalent to 10 MW/yr spent modules, the total capital and incremental operating cost of the electrowinning process is estimated to be only 0.1 U.S. cents/Wp. Tellurium was also quantitatively recovered by reactive precipitation.

ACKNOWLEDGEMENT

This work was funded by the Solar Technologies Program, Conservation and Renewable Energy, United States Department of Energy under contract DE-AEC02-76CH000016 and by a research grant provided by First Solar Ltd.

REFERENCES

- [1] Fthenakis V.M, Eberspacher C., and Moskowitz P.D., Recycling Strategies to Enhance the Viability of CIS Photovoltaics, *Progress in Photovoltaics: Research and Applications*; 4, 447-456 (1996).
- [2] Fthenakis V., End-of Life Management and Recycling of PV Modules, *Energy Policy Journal*, 28, 1051-1058, 2000.
- [3] Fthenakis V.M. and Wang W., Advances on Recycling of CdTe and CIGS Photovoltaic Modules, 20th EURPVSEC, Barcelona, Spain, June 6-10, 2005.
- [4] Fthenakis, V.M. and Wang, W., Extraction and Separation of Cd and Te from Cadmium Telluride Photovoltaic Manufacturing Scrap, *Progress in Photovoltaics: Research and Applications*, 2006: 14: 363-371
- [5] Wang, W. and Fthenakis, V.M., Kinetics Study on Separation of Cadmium from Tellurium in Acidic Solution Media Using Ion-Exchange Resins, *Journal of Hazardous Materials*, 2005: B125: 80-88