

HYDROMETALLURGICAL RECYCLING OF THE SEMICONDUCTOR MATERIAL FROM PHOTOVOLTAIC MATERIALS – PART TWO: METAL RECOVERY

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ABSTRACT

First Solar, Inc. is committed to the development of sustainable energy solutions based on solar technology. Part of this commitment includes the recycling of solar module manufacturing scrap and end-of-life decommissioned solar modules that contain semiconductor materials made primarily of cadmium and tellurium. SGS Minerals Services was retained by First Solar to carry out metallurgical testwork, process design and commissioning services to support the recovery and reuse of semiconductor materials. A hydrometallurgical flowsheet was established to treat the various recycling feed materials containing semiconductor materials to allow for the recovery of pay metals whilst meeting stringent environmental targets. The previous paper (part 1) describes the results of the leaching testwork, whereas the metal recovery testwork results are described in this paper (part 2).

INTRODUCTION

Part one of this paper provides details on the oxidative leaching of laminated photovoltaic scrap recycle feed that produced extractions of up to 99% for Te and Cd. Non-oxidative leaching of the waste water filter cake produced cadmium and tellurium re-leach extraction efficiencies in excess of 99% and 90%, respectively. Counter-current selective oxidative leaching of coater overspray CdTe produced 99.9% Cd extraction and 3.3 % Te co-extraction. Solution samples were produced by confirmatory bulk leaches and subjected to metal recovery testwork – the results are described below.

OBJECTIVES

The priorities of the metal recovery work were:

- Purification tests;
- Cadmium and Tellurium recovery tests;
- Elaboration of conceptual flowsheet and design criteria.

This paper presents the results available to date and with emphasis on the already commercially implemented aspects.

The results of the work currently in progress will be published at a later date.

TESTWORK RESULTS OUTLINE

BASE LINE METAL RECOVERY PROCESS CHEMISTRY CONSIDERATIONS

The cadmium and tellurium contained in the various recycle-pregnant leach solutions must be separated at a point in order to allow for their reuse.

The most robust process appeared initially to be consisting of sulphur dioxide reduction, as it has been applied for decades in the treatment of copper slimes. Preliminary testwork in this area did not produce tellurium metal with acceptable recoveries and at acceptable purity. The results of preliminary cementation tests using cadmium powder as reducing agent were equally discouraging.

A base line thermodynamics study using the HSC software revealed that direct selective reduction of Te from leach liquor containing Cd by using sulphur dioxide

(or derivatives) or by cementation on Cd itself is not possible because under the proper cementation conditions the main stable product is CdTe.

The stability domain of the Te metal is very narrow (Figure 1), being practically constrained to the low pH- near zero eH area (~ +/- 0.25 V).

Cadmium and tellurium precipitate from the PLS in presence of sodium hydroxide and this offers a temporary solution in the sense that a manageable intermediate can be produced. Unfortunately, tellurium can not be re-leached from the precipitate by adding excess of caustic soda due to formation of cadmium tellurium oxide ($Cd_2Te_2O_7$ by XRD data). Tellurium (IV) is readily soluble in sodium hydroxide, whereas Te (VI) is practically insoluble. Conversely, the telluric form is soluble in sulphuric acid, whilst the tellurous form is sparingly soluble in that medium).

Alternatively, selective tellurium precipitation from the initial PLS using lime for example is not possible unless the solution potential is maintained at practically un-attainable levels (> 1V) across the quasi-entire pH range (Figure 2).

The difficult process chemistry of separating the Te from Cd contained in the PLS was confirmed by base line testwork.

Therefore, it was concluded that the separation of tellurium from the cadmium contained in various recycle pregnant leach solutions can be done best by solvent extraction, or in case of isolated diluted streams, possibly by ion exchange.

PRECIPITATION – EQUILIBRIUM AND BULK TESTS

Equilibrium precipitation tests results

Equilibrium precipitation tests were carried out to compare the performance of the caustic soda vs. soda ash. Sodium hydroxide is known as a very effective neutralizing and precipitating agent, especially as a concentrated solution; however the final product tends to display quite difficult separability (settling/thickening /filtration). Sodium carbonate is generally a less effective neutralizing agent, especially as a diluted solution, however the reaction product tends to display improved separability.

Two equilibrium precipitation tests were carried out using 50% wt. NaOH solution (to simulate the commercial product) and 250 g/L Na₂CO₃ (to simulate the in-plant made-up solution). Both tests involved the addition of measured amounts of reagent into a reaction vessel containing 2 L of representative PLS consisting of an equal blend of laminate/laminated modules leach solutions produced during the locked cycle bulk tests.

Analytical samples were retrieved from the test-solutions at certain pH values and subjected to Te and Cd analyses. The results were interpreted as concentration vs. pH and as precipitation vs. pH.

Relevant equilibrium correlations are depicted in Figure 3 through Figure 6.

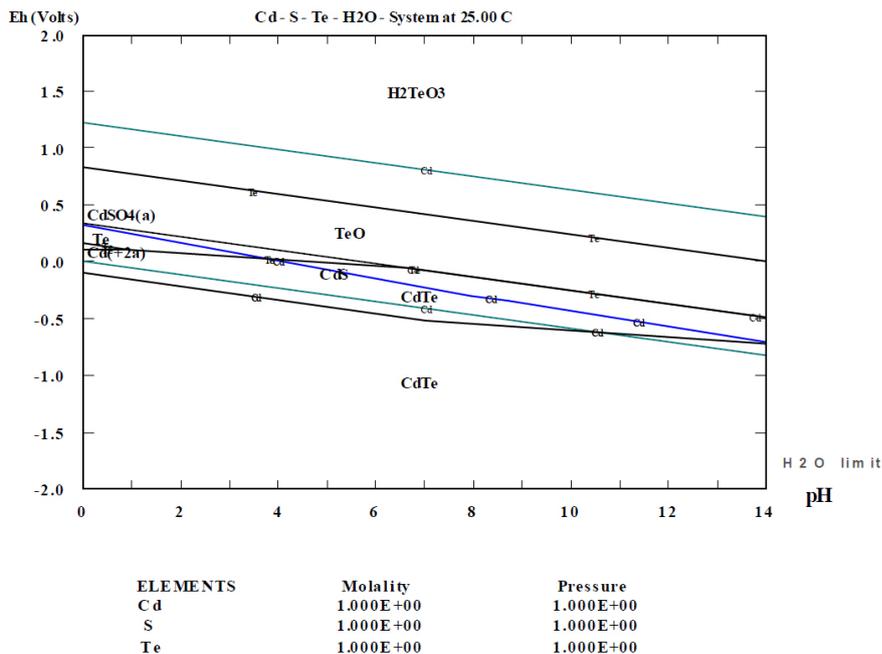


Figure 1 Tellurium vs. Cadmium reduction simplified eH-pH diagram

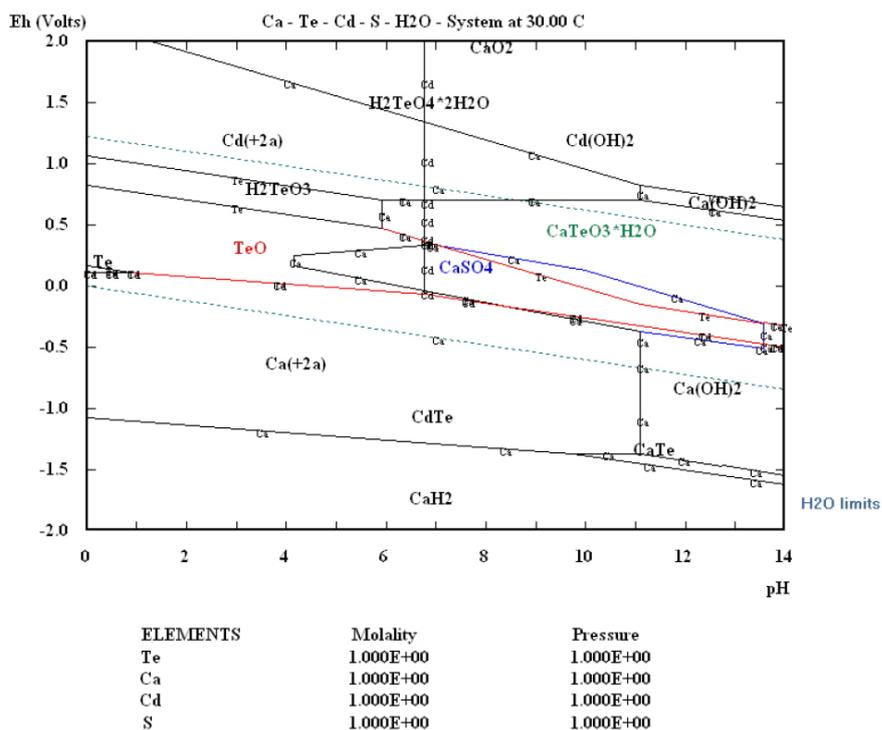


Figure 2 Tellurium vs. Cadmium lime-precipitation simplified eH-pH diagram

The results indicated that:

- Caustic soda precipitation occurred almost stoichiometrically, with an overall reagent excess about 4%;
- Soda ash precipitation was less effective for tellurium and the excess of reagent required was significant due to the buffering tendency of the reagent;
- It was decided to select caustic soda for the bulk precipitation test.

Bulk Precipitation Test Results

The bulk precipitation test was carried out using NaOH (the selected reagent) and 6 L of blend PLS. The addition was carried out by adding the reagent in one increment. The amount of 50% wt. NaOH solution required was determined during the equilibrium

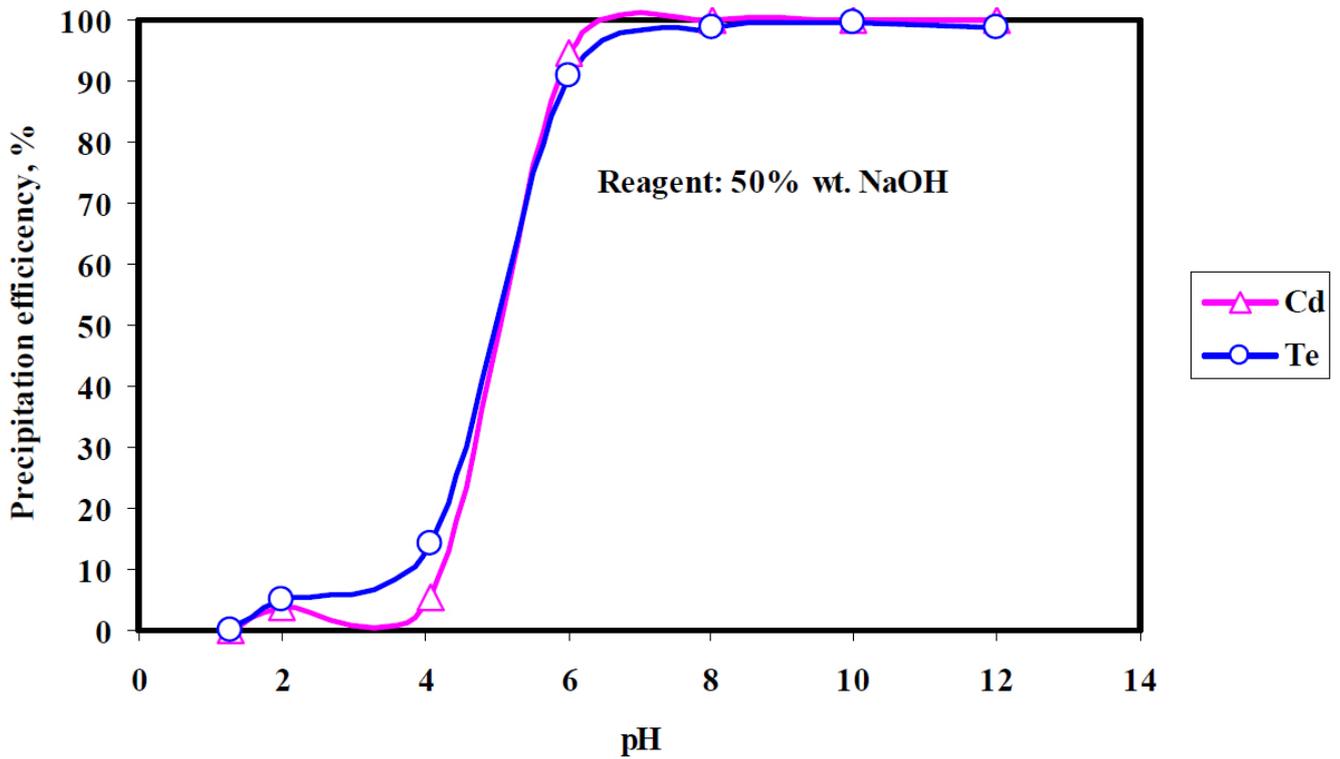


Figure 3 Precipitation Equilibrium Test – Recoveries – NaOH

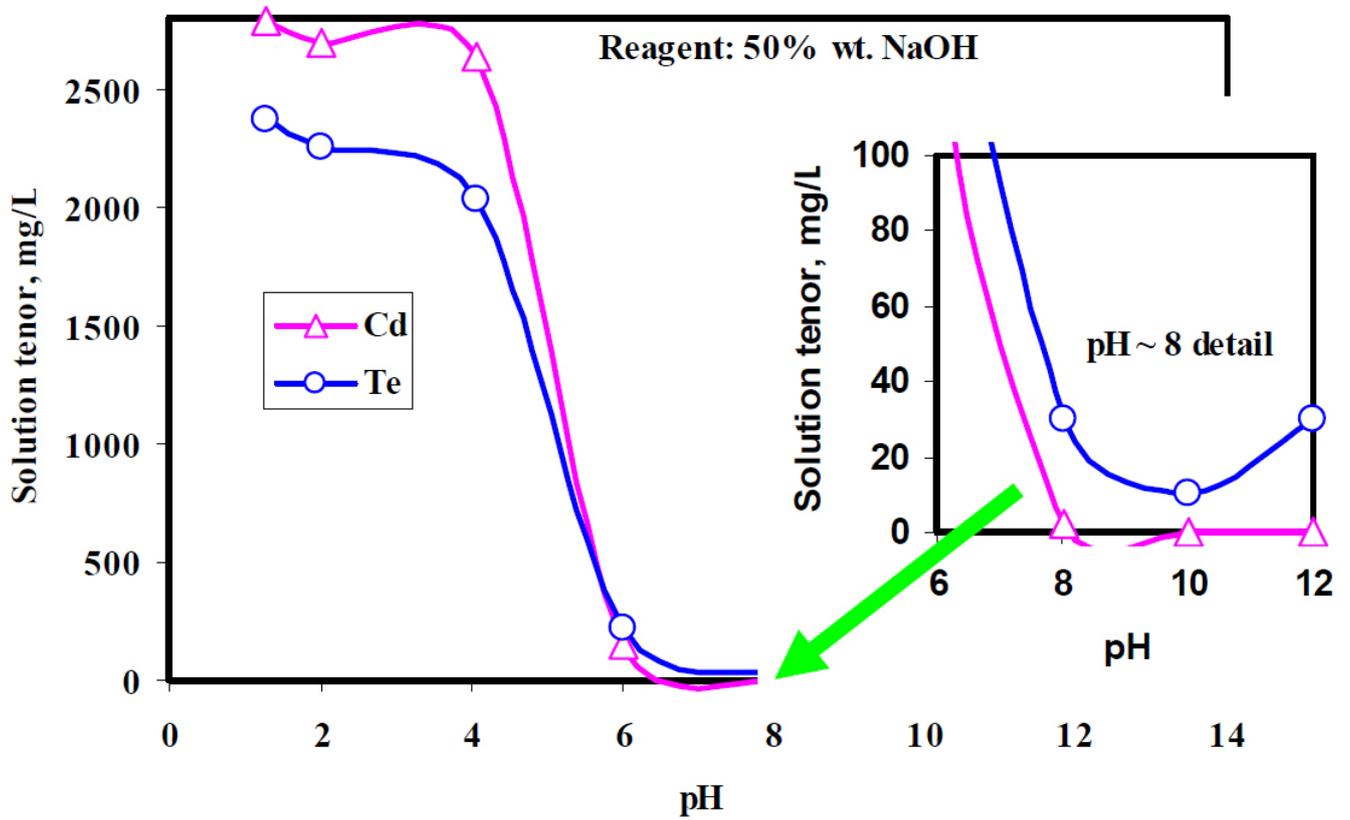


Figure 4 Precipitation Equilibrium Test – Tenor Profiles – NaOH

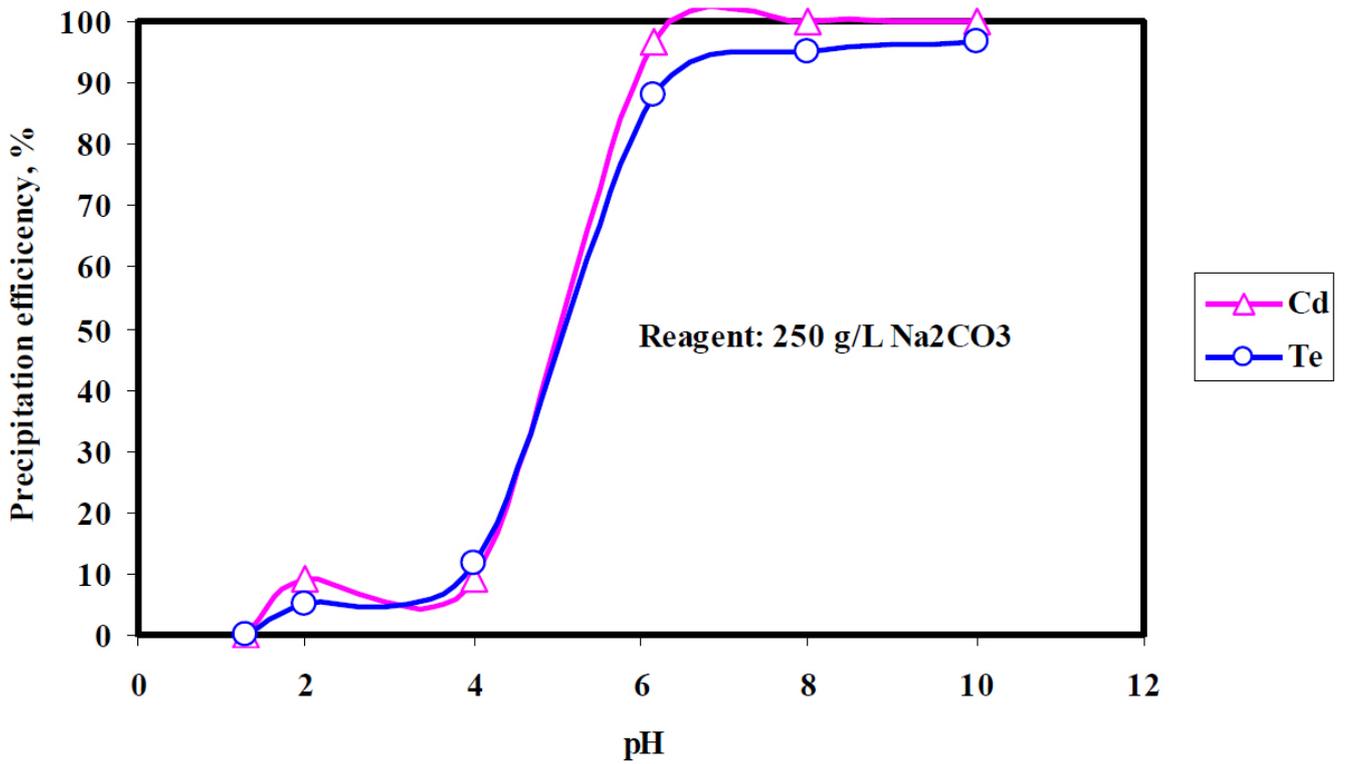


Figure 5 Precipitation Equilibrium Test – Recoveries – Na₂CO₃

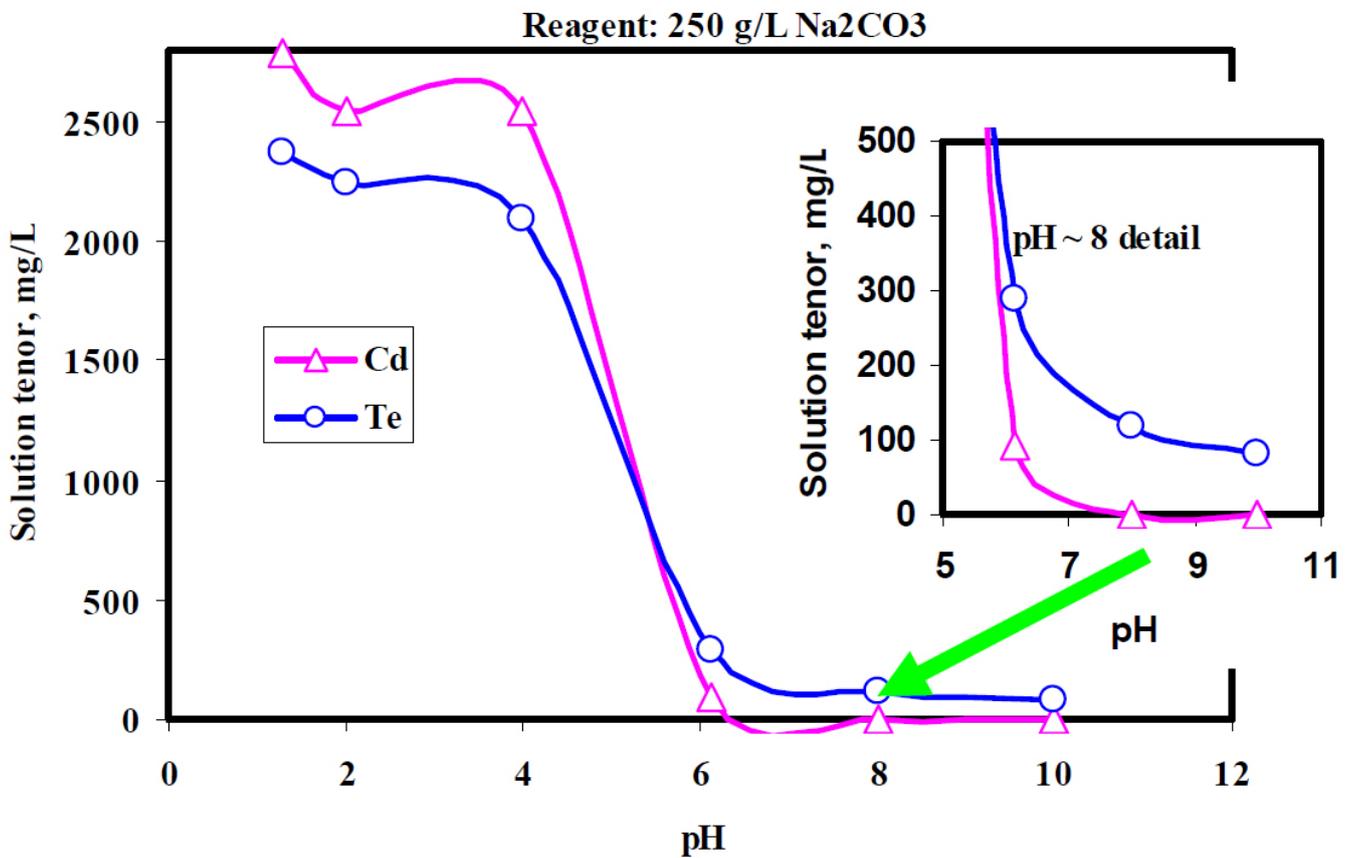


Figure 6 Precipitation Equilibrium Test – Tenor Profiles – Na₂CO₃

test. The reaction product was filtered and sampled. The results were interpreted as metal recovery values.

The results of the bulk precipitation test are summarized in Table 1. Accordingly:

- Cd and Te precipitation efficiencies were in excess of 99.6% for both metals;
- The required NaOH stoichiometry excess was about 5%;
- The precipitation discharge slurry contained about 0.8% solids assaying about 30% Cd and 27% Te;
- This product was subjected to settling, thickening and rheology testwork.

Base-line LSR (Liquid-Solid Separation and Rheology) testworks on Precipitate Slurry Discharge

Commercially available flocculation reagents were tested ("screened") by carrying out small scale settling tests. Base line static settling tests - standard Kynch tests (with rakes) were carried out, at variable reagent additions, as selected based on the reagent screening results. Thickener sizing was carried out using the Talmadge and Fitch method. The thickener unit area and hydraulic capacity were calculated.

The flocculant screening test results indicated that the precipitation slurry sample displayed settling characteristics that could be improved in the presence of Zetag 7623, a low charge density cationic flocculant.

The results predicted a relatively high specific thickener unit area yet subject to improvement by increasing the flocculant additions as well as through underflow recycling during the operation. Practically, the data called for a specific thickener unit area ranging from about 13 to 20 m²/t/day for flocculant additions ranging from 316 to 160 g/t dry precipitate feed to thickener, respectively. The solids density of the underflows produced under these conditions ranged from 2.5 to 2.7% wt. and it was raised to about 10% by underflow recycling during the operation.

The thickened precipitate sample subjected to rotational concentric cylinder rheology measurements displayed a Bingham plastic behavior

Table 1 Bulk Precipitation Summary

Eq'm pH	NaOH solution, grams		*Excess %	Filtrate Tenor, mg/L		Precipitation efficiency, %	
	*Stoic	*Actual		Cd	Te	Cd	Te
1.46	0	0	n/a	2790	2370	0	0
10.1	103.3	108	4.6	0.2	< 10.0	99.99	99.58

Initial free acid: 6.3 g/L H₂SO₄.

The NaOH solution was added to the PLS solution during a 120 second time period, increasing the PLS temperature by 3.2°C.

Reagent used: 50% wt. NaOH, solution density: 1460 g/L.

*Stoic, Actual - stoichiometry (calculated) and actual (added) amounts, respectively.

Excess - stoichiometry excess calculated as: 100(Actual-Stoi)/Stoi.

characterized by a yield stress of 9 Pa at 3% wt. solids. Although the testwork was relatively limited due to schedule pressure, it was expected that in practice, the ultimate density of the thickener underflow would be dually determined by settling behavior and flowability. This was entirely confirmed by the commercial operation which consistently produced thickener underflows containing in excess of 12% wt. solids.

BASE LINE METAL RECOVERY TESTWORK SUMMARY

Cadmium solvent extraction (CdSX)

Cadmium solvent extraction and electrowinning (CdSXEW) testwork was carried out on a solution mimicking a typical PV scrap/ CS combined PLS combined in a proportion consistent to their ratio in actual plant recycle streams.

An ambient temperature extraction isotherm was generated for a feed containing 10 g/L Cd, 6.7 g/L Te, 0.8 g/L Fe, 0.55 g/L Cu and ~50 mg/L Al. Cadmium was extracted with an organic phase containing 10% D2EHPA in Isopar M aliphatic diluent.

The equilibrium data were produced at ambient temperature, pH range from 1 to 2.6 and O/A ratio of 1:1. The subsequent ambient temperature isotherm curve was produced at pH ~ 2.6 and O/A ratios ranging from 10/1 to 1/1 at 10% vol. DEHPA concentration.

Results summary:

- Satisfactory loading of the organic phase with cadmium was obtained, with maximum loading approaching 3 g/L in the organic phase (Figure 7). At the lower concentration end, the extraction isotherm was predicting the possibility of attaining low raffinate Cd

concentrations, provided that there is sufficient extractant present to load all the iron plus cadmium;

- Accordingly, it was concluded that it should be possible to attain a low raffinate concentration (<50 mg/L Cd) from a feed of 10 g/L Cd in four countercurrent contacting stages, at an O/A ratio of 4/1;
- Equilibrium data (Figure 8) indicated that iron was co-extracted by the organic along with the cadmium, and in preference to cadmium. Therefore, at the highest A/O ratios tested, Fe was loaded preferentially to Cd, and the Cd loading dropped off. Copper was also co-extracted by the D2EHPA;
- The behavior of copper was very similar to that of cadmium as it was displaced by iron at high loadings. Therefore, under conditions where Cd is fully extracted, it can be expected that Cu will also be fully extracted. There was no evidence that any tellurium is extracted;
- Physically, the system appeared to behave well. Phase separations were rapid and complete.

The above results were fine-tuned through a simulated continuous countercurrent extraction-stripping process on a laboratory scale using batch contacts in order to produce bench scale cadmium electrowinning feed.

Furthermore, the results were applied to design and operate a small scale continuous (micropilot) CdSX exercise which produced the scale-up criteria for a mid-scale commercial plant.

Strip liquor produced from the loaded organic became the electrolyte from which cadmium was electrowon in a small test cell.

Cadmium electrowinning (CdEW)

The feed electrolyte for electrowinning was produced by combining the strip liquor of each cycle of solvent extraction cycle. The concentration of the rich electrolyte feed was 31.4 g/L cadmium, 154 g/L sulphuric acid, 3.1 mg/L iron and 0.7 mg/L copper. Bench scale electrowinning was carried out in two cells of inert plastic construction with working volumes of 600 and 800 mL, using lead alloy (Pb/Ca/Sn) anodes and stainless steel (316 SS) cathode blanks for the first two cycles (each of 24 h). Aluminum alloy (HS1A)

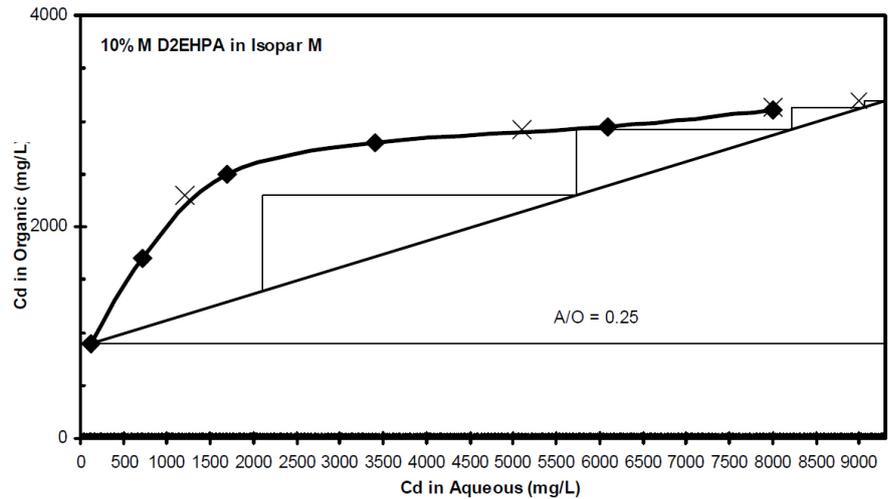


Figure 7 Cadmium SX Isotherm Curve

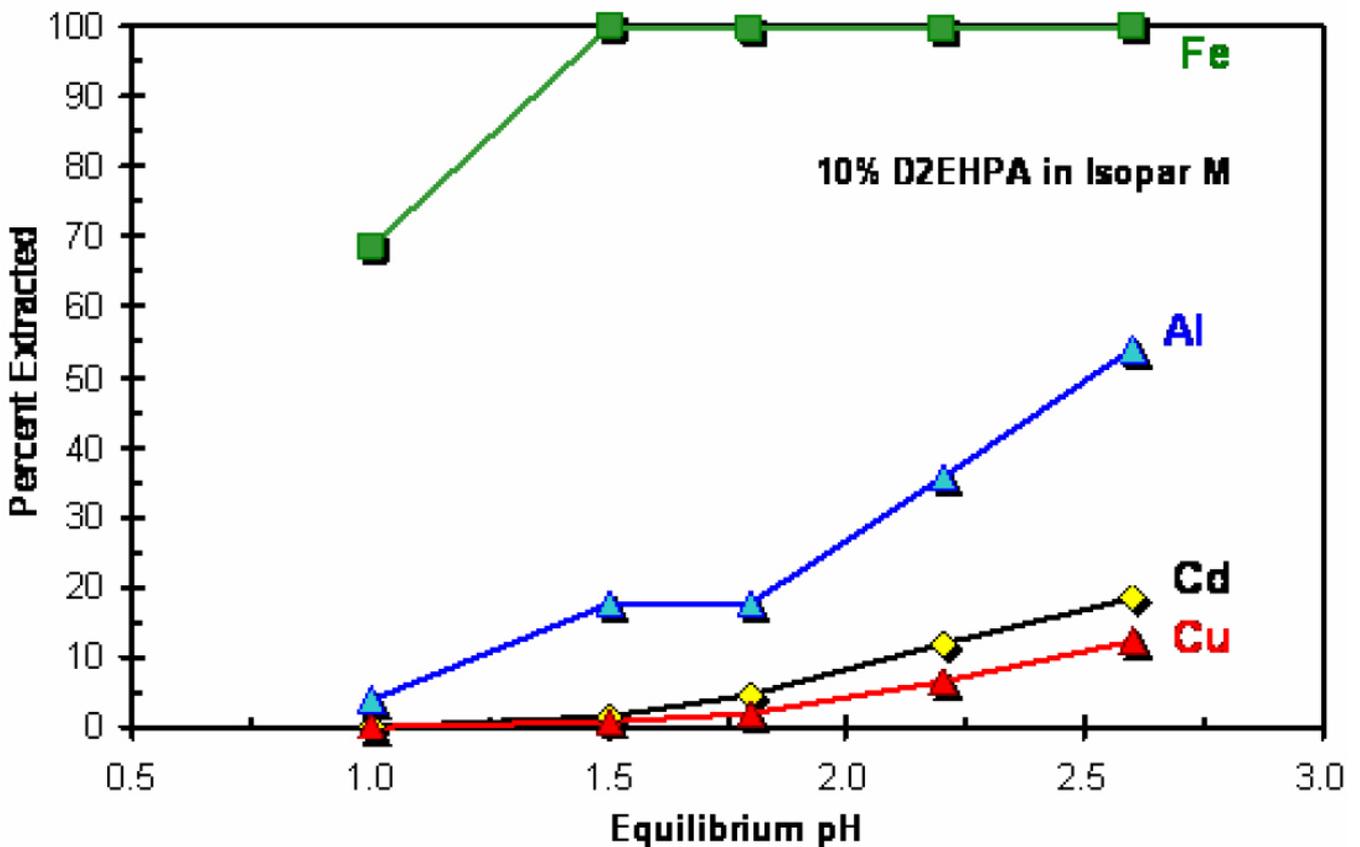


Figure 8 Cadmium SX pH equilibrium Curves

was used for the cathode in the subsequent cycles. The cathodic current density (c.d.) was 50 A/m². Operating current was calculated assuming a current efficiency of 80%. Cell voltage was approximately 2.4 V in all tests. The temperature during the tests ranged from 22 to 24°C.

Power to the cell was provided by a constant current DC rectifier supply. A total of five electrowinning cycles were

carried out. In the first one, the cell was filled with rich electrolyte and the cell was operated in batch mode to reduce the cadmium concentration to the target operating level, while raising the acid concentration. In subsequent cycles, electrolyte was fed continuous into the cells, and allowed to overflow to maintain a set cathode immersion level. During the electrolysis of aqueous solutions of cadmium sulphate, metals more electropositive than cadmium will

plate at the cathode in addition to cadmium. In order to remove some of these more electropositive ions from the cell solution, the first step taken was the removal of copper from the electrolyte, using the same test cell under particular conditions. Five batch cycles of approximately 20 second each were performed to plate as much of the copper as possible from the solution. These cycles were operated at current density of 100 A/m².

The cell was filled with the feed electrolyte containing 0.5 g/L of gelatine and operated for 24 h in batch mode to bring the cell contents to the spent electrolyte conditions for continuous electrowinning.

At the end of that time the cathode was removed, weighed and cleaned. The plated cadmium was dried to determine the weight and the actual current efficiency and with that information, the flow of electrolyte for the continuous cycle was corrected.

Preliminary conclusions from the first Cd EW exercise (in conjunction with data from Table 2 and Table 3):

- Smooth cathodic deposits of cadmium were difficult to produce. This was attributed to the nature of the electrolyte.
- Progressive improvements were

Table 2 Cadmium Electrowinning Conditions and Results

	BATCH	CYCLE 1	CYCLE 2	CYCLE 3	CYCLE 4
Cathodic Current Density (A/m²)	50	50	50	50	50
Average voltage, V	2.4	2.4	2.4	2.4	2.4
Cathode Material	SS (316SS)	SS (316SS)	HS1A, A1 alloy	HS1A, A1 alloy	HS1A, A1 alloy
Gelatin, g/L	0.5	1.5	1.5	1.5	1.5
Plating time, h	24	24	24	24	24
Initial H₂SO₄, g/L	154	154	154	70	50
Final H₂SO₄, g/L	161	181	181	94	64
Total Metal plated, g.	5.92	5.68	6.06	7.81	9.24
Metal plated (sheets), g.	1.1	0	0	1.9	2.3
Current Efficiency	51.6%	50.6%	54.7%	70.5%	82.7%

Table 3 ICP Scan of the plated metal in selected cycles

SAMPLE ID	Al	Ca	Cu	Fe	Mg	Mn	Na	Pb	Zn	Cd
Batch Powder	0.001	0.007	0.049	0.011	0.0011	0.0002	0.017	0.26	0.002	99.65
Batch Sheets	0.001	0.001	0.076	0.002	0.0001	0.0001	0.002	0.14	0.001	99.78
Cycle 3 Powder	0.011	0.002	0.013	0.005	0.0004	0.0001	0.11	0.027	0.001	99.83
Cycle 3 Sheets	0.009	0.001	0.005	0.01	0.0001	0.0001	0.055	0.021	0.001	99.9
Cycle 4 Powder	0.01	0.001	0.016	0.003	0.0002	0.0001	0.01	0.046	0.001	99.91
Cycle 4 Sheets	0.02	0.001	0.011	0.008	0.0001	0.0001	0.012	0.044	0.001	99.9
70 g/L Cd-Day 1	0.011	0.001	0.001	0.008	0.0002	0.0001	0.002	0.15	0.003	99.82
70 g/L Cd-Day 2	0.002	0.001	0.016	0.003	0	0	0.002	0.12	0.001	99.86

however achieved and a better deposit was obtained at higher current efficiency as changes were progressively made to the electrolyte acidity;

- It was determined that working with a solution in the feed of more than 30 g/L of cadmium and between 20 to 50 g/L of sulphuric acid, it was possible to obtain plated cadmium without dendritic deposition, and with a current

efficiency higher than 80 %;

- Since cadmium is very prone to dendritic deposition, the industry practice is to plate thin sheets (0.2 mm) so that they can be stripped before significant dendrite formation takes place;
- Current efficiency for Cd plating above 80% is considered to be satisfactory.

Tellurium electrowinning (TeEW)

One tellurium electrowinning bench scale test was performed using the small cell apparatus that had been previously used for cadmium recovery. The test was carried out for 24 hours.

The feed electrolyte was obtained by alkaline-leaching of the residue resulting from the acid leaching of the Coater Overspray composite sample using ~120 g/L sodium hydroxide, for 2 hours at

100°C. The resulting solution contained 57 g/L Te and 101 g/L of NaOH.

Electrowinning was carried out in a cell with a working volume of 950 mL. Stainless steel (316 SS) cathodes and anodes were used. The cathodic current density was controlled at 250 A/m². Operating current was calculated assuming a current efficiency of 85%. The temperature during the cycle ranged from 22 to 25°C (Table 4).

After 26 hours about 30.34 g of metal assaying 99.8% Te was deposited at the cathode forming a perfect smooth deposit. No dendritic or powder-like deposit was found in the cathode or the cell. This amount of tellurium equates to a current efficiency of 96 % which is similar to the efficiencies reported in the literature and in practice. The concentration of NaOH in the spent electrolyte was 115 g/L.

FINAL CONSIDERATIONS, IMPLEMENTATION STATUS AND GOING FORWARD

PROCESS CONSIDERATIONS

There are two basic versions of the First Solar's recycling flowsheet:

- Version 1.0 (Figure 9) – the very first implemented – it treats PV modules and produces a + 6 mm EVA fraction, a -6 mm washed cullet product and a Cd/Te precipitate;

Table 4 Tellurium Electrowinning Conditions and Results

Cathodic Current Density (A/m²)	250
Average Voltage, V	1.7
Plating time, h	26
Initial NaOH, g/L	101
Final NaOH, g/L	115
total Metal plated, g.	30.34
Metal plated (sheets), g.	30.34
Current Efficiency	96.10%

Table 5 ICP Scan¹ of the plated Te cathode after 26 h

Sample ID	Al	Ca	Cu	Fe	Mg	Mn	Na	Pb	Zn	Te
Te sheets	0.0002	0.003	0.0001	0.003	0.0001	0.0001	0.19	0.002	0.001	99.801

¹All other chemical elements normally included in an ICP Scan were below detection limits.

- Version 2.0 (Figure 10) – being developed – it treats PV modules and produces a + 1.5 mm EVA fraction, a - 1.5 mm washed cullet product and a Cd/Te precipitate.

The main difference between V1.0 and V2.0 flowsheets versions consists of the size fraction of the leach feed, which in turns dictates how that unit operation can be performed:

- V1.0 feed is too coarse (~ 6 mm) to allow for conventional agitated leach thus it requires a rotary reactor (drum). This leads to material handling complications which in turns requires excessive capital and operating expenditures (capex/opex), as well as significant real estate availability.
- V2.0 leach feed consists of a relatively finer material (~ 1.5 mm) that can be pumped and mixed, hence suitable for agitated leach, EVA elutriation, easy washing and subsequent filtration. It can be applied to all recycle feeds and using the same equipment. It allows for significant capex/opex savings, ease of operation and constant discharge specifications, and at lower residual Cd level.

Each of the above versions is suitable to incorporate refined downstream recovery versions by implementing of CdSXEW and TeEW technologies.

In case of V2 for example, the process models would be therefore Versions 2.1, 2.2 and 2.3 (Figure 11) as applied to the PV, CS and WW cake recycle feeds. These flowsheets are being developed at the time of writing this paper.

IMPLEMENTATION STATUS

The project is being managed on a fast track basis. Therefore, two recycling plants have been designed, built and commissioned, while the technology is being improved and completed. In summary:

- V 1.0 one leach (rotary reactor) – separation – bulk precipitation: installed and commissioned in Perrysburg and

Frankfurt-Oder plants in 2006 and 2007, being installed in Kulim plants KLM1 and KLM 2 - 2008;

- Version 2.0 leach (agitated mix) with downstream process option to be selected - work in progress, with its implementation pending third party's acceptance of the fine glass cullet;
- Cd and Te SXEW and integrated pilots – work in progress.

GOING FORWARD

- A commercially applied process was established for the recycling of CdTe PV modules based on hydrometallurgy as enabling technology;
- The currently applied PV recycling process version V1.0 is capable to produce glass cullet assaying below 5 ppm Cd, comparable to the 0.5 ppm level of Cd level in the Earth's crust. It is envisaged that the agitated leach version V2.0 will bring the said level to that order of magnitude;
- Base line recycled-metal recovery testwork from a composite of various recycling leach solutions consisting of CdSXEW produced cathodes assaying up to 99.9% Cd;
- Base line recycled-metal recovery testwork consisting of Te alkaline leach of Cd-free recycle intermediate products followed by electrowinning produced cathodes assaying 99.8% Te;
- Above results allowed for the bench scale development of a robust downstream flowsheet V 2.3 aimed towards recycling and subsequent recovery of the Cd and Te contained in 89% of the recyclable materials consisting of PV panels, coater overspray and waste water cake.

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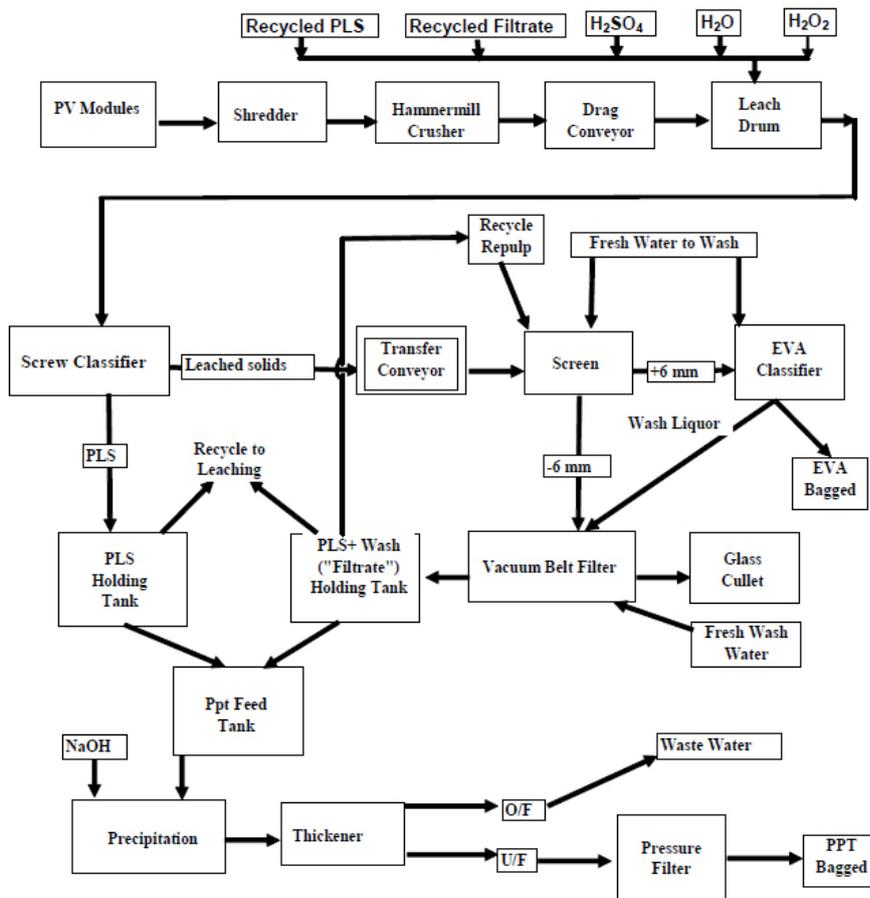


Figure 9 Flowsheet version V 1.0 – drum leach, transfer conveying

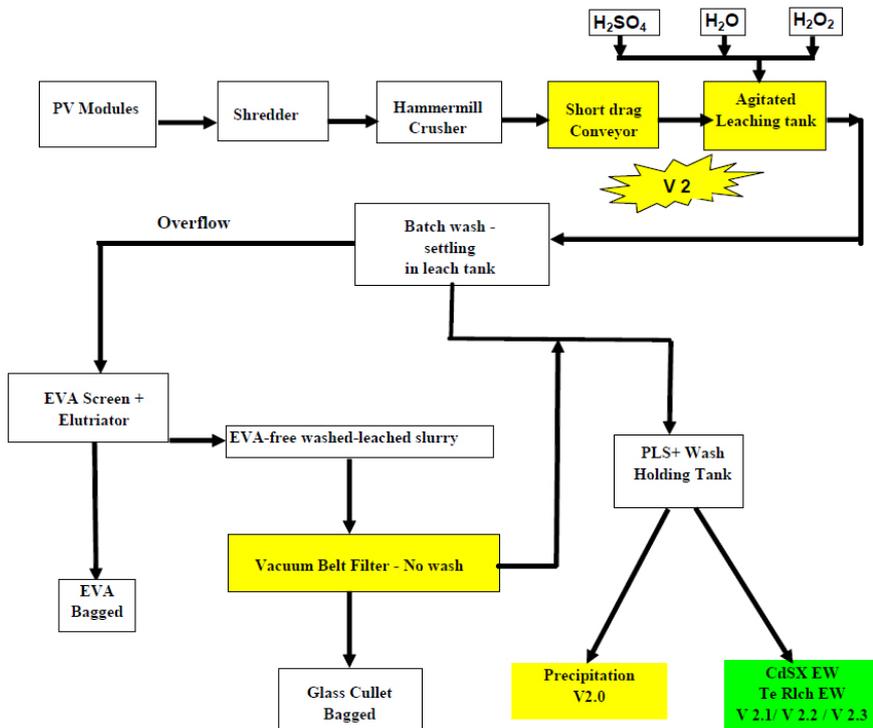


Figure 10 Flowsheet version V 2.0 – agitated mixing leach, pumping

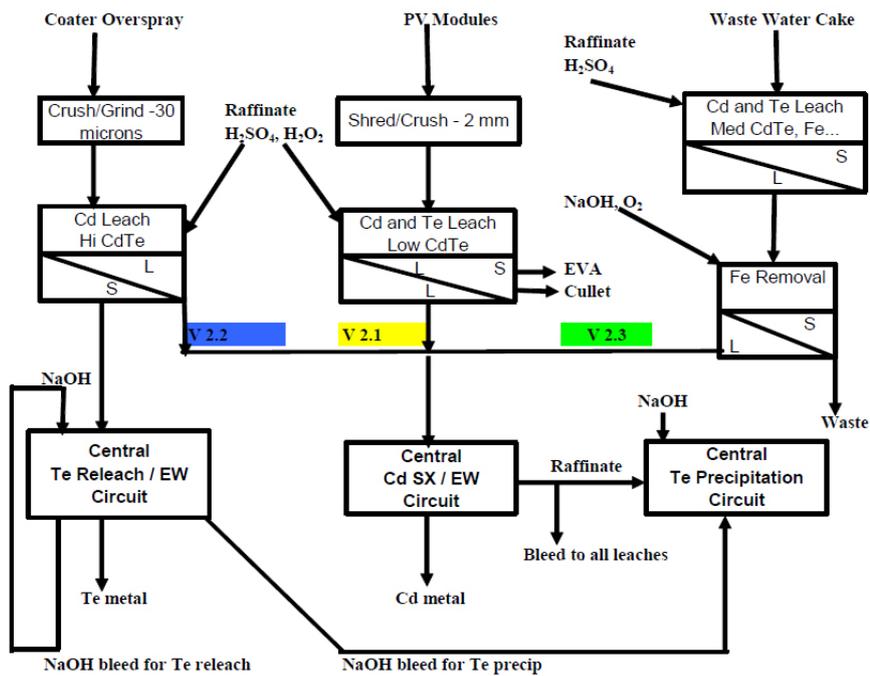


Figure 11 Flowsheet version V 2.3 treating PV, CS and WW cake

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