

HYDROMETALLURGICAL RECYCLING OF THE SEMICONDUCTOR MATERIAL FROM PHOTOVOLTAIC MATERIALS – PART ONE: LEACHING

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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. This paper (part 1) describes the results of the leaching testwork, whereas the metal recovery testwork results are described in the following paper (part 2).

INTRODUCTION

A new generation of low-cost solar modules based on thin films of photoactive materials such as copper indium diselenide (CuInSe_2 or "CIS"), cadmium telluride (CdTe), gallium arsenide (GaAs), etc. deposited on inexpensive substrates has increased the potential of rapid acceptance and commercialization of solar energy. First Solar, a recognized leader in the area of cadmium telluride thin films based photovoltaic ("PV") modules has adopted a proactive and long-term strategy based on the concepts of product life cycle management. First Solar's goals include minimizing the environmental impacts of its technology over all product life cycle stages from raw material sourcing through end-of-life collection and recycling. A key element of First Solar's goal is to implement recycling processes for semiconductor materials that provide a high recovery rate, produce materials that can be used in new solar modules, and minimize life cycle impacts. Recycling of tellurium also leads to the reintegration of a valuable material into the material cycle.

Recycling of PV wastes can be realized using pyrometallurgical methods. However, the high energy use would be expected to have a negative impact on a life cycle assessment. Hydrometallurgical processes appear more feasible for small decentralized operations. Such is the case projected for First Solar who is in the advanced stage of implementing a process to recycle its entire PV manufacturing waste in all of its manufacturing facilities and collected end-of-life modules using hydrometallurgy as enabling technology. SGS Minerals Services was commissioned to carry out metallurgical testwork, process design, construction of certain circuits as well as overall plant start-up and commissioning services in support of this project. Two recycling plants of sufficient scale to support all manufacturing waste, warranty returns and premature end-of-life modules have been commissioned since 2006, the start of the project, and two plants are being built at the time of writing this paper.

OBJECTIVES

The priorities of the project work were defined by communication with the client, First Solar and its advisors. Accordingly, emphasis was placed on the development of recycling processes to allow the reintegration of cadmium and tellurium from manufacturing waste and end-of-life modules into new solar modules and to ensure a high level of glass recovery suitable for use in the production of float glass, which can ultimately be used in First Solar modules.

With no previous example of commercially applied Cd/Te recycling technology, it was decided to produce the necessary data by the means of conventional hydrometallurgical testwork, involving several steps including:

1. Recycle feed characterization;
2. Base line and pre-optimization leaching tests;
3. Purification tests;
4. Cadmium and Tellurium recovery tests;
5. Elaboration of conceptual flowsheet and design criteria.

Part One presents data on items (1) and (2) from above and Part Two presents items 3 through 5.

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

TESTWORK RESULTS OUTLINE

RECYCLE FEED

Of the cadmium entering into solar module manufacturing process, the following is a list of the plant outputs to which it reports:

- final product, i.e. photovoltaic ("PV") modules and in the form of cadmium telluride;
- an intermediate product called "coater overspray" in the form of a cadmium telluride of varying purity;
- the plant waste water treatment filter cake in the form of cadmium and tellurium precipitates, along with significant amount of impurities;
- the photovoltaic ("PV") scrap consisting of end of life modules and manufacturing scrap in the form of cadmium telluride containing trace amounts of metallic impurities,
- Non-recoverable waste.

Photovoltaic panels (PV) recycle-head samples

The test samples were prepared by First Solar using its dry comminution circuit part of the existing Perrysburg process.

The recycle feed consisting of manufacturing scrap and reclaimed end-of-life photovoltaic module test-samples were subjected to shredding and subsequent hammermilling (i.e. crushing)

to reduce nominally 100% minus 12 mm (½ inch).

Two types of crushed PV module samples were tested: laminated and unlaminated.

The laminated modules contained a coating consisting of Ethyl Vinyl Acetate ("EVA") layer.

Particle size distribution ("PSD") determinations results indicated that:

- About 87% of the crushed laminated module sample passed the ¼" screen;
- The ¼" laminated module sample screen reject contained over 99% of the ethyl-vinyl-acetate (EVA) contained in that sample;
- The EVA adhered to the surface of the crushed + ¼" glass as such that the cumulative weight of the resulting "plastic-glass" + ¼" fraction represented about 12% of the total sample weight;
- About 88% of the crushed sub-module (unlaminated) sample passed the ¼" screen. This sample did not contain EVA film;
- The specific gravity of both samples was about 2.5.

Atomic adsorption determinations (Table 1) indicated that the crushed submodules contained more Cd and more Te compared to the crushed (laminated) modules, i.e. 0.098% Cd vs. 0.038% Cd and 0.11% Te vs. 0.041% Te, respectively. This is, of course, due to the additional glass contained in a module.

Detailed ICP (inductively coupled plasma emission) scan results are also provided in Table 1. The results were found to be consistent with the atomic adsorption results.

Table 1 Head Assays - PV panels

ICP MS SCAN	Ag g/t	Al g/t	As g/t	Ba g/t	Be g/t	Bi g/t
CRUSHED SUBMODULES	<2	420	<30	4.4	<0.03	<20
CRUSHED MODULES	<2	1700	<30	21	0.22	<20
	Ca g/t	Cd g/t	Co g/t	Cr g/t	Cu g/t	Fe g/t
CRUSHED SUBMODULES	70000	970	<4	7	1.2	990
CRUSHED MODULES	66000	360	<4	12	2.1	1000
	K g/t	Li g/t	Mg g/t	Mn g/t	Mo g/t	Na g/t
CRUSHED SUBMODULES	140	<5	26000	11	<8	130000
CRUSHED MODULES	550	<5	25000	78	<8	110000
	Ni g/t	P g/t	Pb g.t	Sb g/t	Se g/t	Sn g/t
CRUSHED SUBMODULES	<20	<30	<30	<10	<30	110
CRUSHED MODULES	<20	<30	<30	<10	<30	58
	Sr g/t	Ti g/t	Tl g/t	V g/t	Y g/t	Zn g/t
CRUSHED SUBMODULES	62	65	<30	<4	3.1	<10
CRUSHED MODULES	47	160	<30	<4	3.2	<10
AA	Cd%	Te%	Cu			
CRUSHED SUBMODULES	0.098	0.110	<0.002			
CRUSHED MODULES	0.038	0.041	<0.002			

Table 2 Head Assays – Typical recycle-waste streams

	Cd%	Te%	Cu%	Al%	Fe%	S%	S=%
COATER OVERSPRAY ("CS")	48.6	46.8	<0.001	<0.02	0.034	4.01	0.32
CLEAN CS ("CCS")	46.9	51.9	0.00057	0.02	0.042	0.53	0.02
WW FILTER CAKE	10.9	7.79	0.014	0.24	20	0.12	nd
SHREDDER DUST	0.84	0.83	<0.001	0.16	0.31	0.11	nd
SANDBLAST MEDIA	4.18	4.6	0.006	33.3	0.215	0.11	nd
	Na g/t	Ca g/t	Mg g/t	Sn g/t	Ti g/t	Ag g/t	As g/t
COATER OVERSPRAY ("CS")	<20	47	21	<20	1.1	<6	<30
CLEAN CS ("CCS")	31	36	17	<20	0.9	<2	<30
WW FILTER CAKE	11000	46000	6600	130	340	38	<30
SHREDDER DUST	84000	67000	25000	950	140	<6	<30
SANDBLAST MEDIA	20500	16000	5700	7850	12000	<6	<30
	Ba g/t	Be g/t	Bi g/t	Co g/t	Cr g/t	Cu g/t	Li g/t
COATER OVERSPRAY ("CS")	<0.2	<0.03	<60	<50	<4	1.1	<5
CLEAN CS ("CCS")	7.6	<0.03	<40	<20	7	5.7	<5
WW FILTER CAKE	26	<0.03	<60	<50	95	140	<5
SHREDDER DUST	12	0.08	<60	<50	310	11	<5
SANDBLAST MEDIA	68	3.05	<60	<50	605	56	42
	K g/t	Mg g/t	Mo g/t	Ni g/t	P g/t	Pb g/t	Sb g/t
COATER OVERSPRAY ("CS")	<20	1.4	<10	<20	<100	<60	<10
CLEAN CS ("CCS")	50	0.9	<5	<20	<30	<20	<60
WW FILTER CAKE	170	530	<10	48	910	<60	<10
SHREDDER DUST	170	66	17	<20	<100	<60	<10
SANDBLAST MEDIA	650	125	190	<20	<100	93.5	<10
	Se g/t	Sr g/t	Tl g/t	V g/t	Y g/t	Zn g/t	Moist., %
COATER OVERSPRAY ("CS")	<30	1.6	<30	<4	<0.2	8	1.84
CLEAN CS ("CCS")	<30	0.19	<30	<4	<0.2	6	<0.5
WW FILTER CAKE	<30	72	<30	<4	1.1	310	78.8
SHREDDER DUST	<30	42	<30	<4	2.4	68	0
SANDBLAST MEDIA	<30	275	<30	13	60	65	0

Manufacturing waste recycling-head samples

The manufacturing waste recycling-head samples consisted of two varieties of "coater overspray" samples, a plant waste water treatment filter cake sample, a shredder dust sample and one sandblast media sample.

These samples were subjected to chemical analyses and subsequent testwork on an "as received" basis.

Typical head assays are summarized in Table 2.

To be noted the variety of Cd and Te grades, as well as impurities in the various samples, predictive of a possibly complex hydrometallurgical flowsheet in order to achieve the project objectives.

The sulphur in the coater overspray samples (CS) tested was present as cadmium sulphide (CdS), as minor component along with cadmium telluride (CdTe) as major species according to the XRD pattern.

BASE LINE LEACHING PROCESS CHEMISTRY CONSIDERATIONS

The driving force of the leaching process is oxidative in case of both the CdS (major component) and CdTe (minor component) contained in the PV panels

as well as at least one variety of coater overspray.

Relevant thermodynamics data are shown below (Table 3).

Therefore the focus of the leaching testwork was to optimize the sulphuric acid and hydrogen peroxide additions. Because the initial process was carried out under excessive acidity (250 g/L H₂SO₄), a primary objective of the testwork was to significantly reduce it as to allow for large scale processing including subsequent metal recovery.

LEACHING TESTWORK SUMMARY

Given the relatively coarse size of the crushed PV panels recycle leach feed; the only practical agitated leach option available commercially consisted of a rotating reactor similar to a cement mixer. Thus the bench scale preoptimization and optimization and leaching tests were carried out under the following common conditions:

- Bottle-roll operation (~ 1 kg feed) to simulate conservatively the tumbling action of the cement mixer;
- Ambient temperature (21°C);
- Residence time - 6 hours;
- Solution kinetic sampling was carried out at pre-determined time periods;
- Vacuum filtration and washing were carried out at the end of each test.

The differentiating factor between the test conditions consisted of the reagent scheme, aiming to minimizing the overall reagent cost per (metric) ton of feed processed.

The optimum conditions were confirmed by several bulk leach tests (25 kg each) carried out in locked-cycle.

Each leach test was accompanied by comprehensive data logging, chemical analyses and metallurgical balancing. The leach discharge slurry produced under the optimum conditions was subjected to engineering data generation consisting of liquid-solid separation testwork.

Conventional agitated leach was applied in the case of all other test-samples.

Table 3 Leaching thermodynamics data

CdTe + 4H ₂ O ₂ (l) + H ₂ SO ₄ = CdSO ₄ + H ₂ TeO ₄ + 4H ₂ O					
T	deltaH	deltaS	deltaG	K	Log(K)
C	kcal	cal/K	kcal		
0	-267	-51	-253	2.124E+202	202
100	-273	-71	-247	4.058E+144	145
CdTe + 3H ₂ O ₂ (l) + H ₂ SO ₄ = CdSO ₄ + H ₂ TeO ₃ + 3H ₂ O					
T	deltaH	deltaS	deltaG	K	Log(K)
Cd	kcal	cal/K	kcal		
0.000	-220	-16	-216	8.671E+172	173
100.000	-222	-19	-215	6.708E+125	126
H ₂ TeO ₄ + 2H ₂ O + 3SO ₂ (g) = Te + 3H ₂ SO ₄ (ia)					
T	deltaH	deltaS	deltaG	K	Log(K)
Cd	kcal	cal/K	kcal		
0	-29	-186	-78	3.53E+62	63
100	-145	-236	-57	2.60E+33	33

Photovoltaic panels (PV) leach results

Extractions

The extractions were calculated based on the metallurgical balance and were expressed both versus the direct and calculated heads (Table 4). As expected, certain differences occurred due to accountability problems caused by analytical limitations at the very low concentrations/grades, shown especially in case of the tellurium.

Given the excellent recoveries under the pre-optimized conditions for Tests 6 and 11 (laminated and unlaminated samples respectively), it could be concluded that the Te and Cd extraction efficiencies were in the high nineties. To illustrate this in case of Tests 6 and 11, if the true <50 ppm Te residue grades could be determined to be say 5 ppm and 11 ppm, respectively, then the Te extractions would be 99% for both tests. It was included in the objectives of further testwork to investigate the possibility of lowering the analytical detection limit for Te in residues.

Reagent consumptions

The actual sulphuric acid consumption was determined based on free acid titrations. Accordingly, the actual consumption was about 19% from the initial addition under the pre-optimized conditions (Table 5).

Most of the acid (>96%) was not consumed under the high addition non-optimized scenarios (>43 kg/t). The unconsumed acid would need to be neutralized in a downstream process. The hydrogen peroxide added (13 kg/ton feed) was either consumed or decomposed during the process. No surfactant was used during the tests and based on the results with the test-samples provided it appeared that there was no need for it.

An important consequence of the low acid requirement was the possibility of recycling the PLS (pregnant leach solution) into the leaching circuit resulting in an increase in the Te and Cd tenors.

The number of recycles could be limited by physical criteria, such as filterability and washability, as well as metallurgical criteria caused by limitations as to the solubility of leached metals.

The implications of lower acidity in the leaching stage were:

- Good leach discharge liquid-solid separation, excellent washing/dewatering, vacuum filtration possible;
- Lower capital and operating expenditures compared to the original process;
- Lower caustic consumption during the

subsequent processing (precipitation or SX) stage;

- Lower ionic strength overall leading to good precipitate discharge liquid-solid separation;
- Higher purity precipitated Cd/Te product.

As an overall consequence, the test results opened the possibility of reducing the reagent cost to approximately US\$ 30/ton, or even lower when operating at increased solids densities. The reagent cost prior to this work, calculated based on 250 g/L H₂SO₄ and without adding the cost of surfactant was US \$235. All calculations include the cost of sodium hydroxide required to neutralize the excess acid and subsequently recover the Te and Cd as a precipitate. It was also demonstrated that surfactant was not required during the leaching. Hence the savings realized in reagent cost due to optimization were of about one order of magnitude.

Bulk leach confirmations

The confirmatory locked cycle bulk leach tests produced the following results (Table 6):

- The laminated feed produced about 99% Te extraction, leaving residues assaying from 4 to 7 ppm Te, displaying a slight increase with the number of cycles;
- The laminated feed consistently produced Cd extraction in excess of 99%, leaving residues assaying below the 5 ppm detection limit throughout the three leaching cycles;
- The unlaminated feed produced 96% Te extraction with fresh lixiviant, corresponding to 50 ppm residual Te. The tellurium extraction efficiency decreased to about 88% after two cycles, corresponding to 134 ppm residual Te, probably due to the relatively higher metal grade in this feed, requiring additional hydrogen peroxide and reaction time;
- The unlaminated sample Cd leaching efficiency decreased from 99.8% to 98.3% throughout the three cycles, leaving residues assaying from 5 to 18 ppm Cd, displaying a slight increase with the number cycles;

- The actual acid consumption was about 1.4 kg/t dry feed in case of both samples, corresponding to about 22% utilization efficiency.

Additional testwork on various CdTe samples, as well as in conjunction with the commercial operation revealed that tellurium extractions could be improved by further lowering the acidity. This is because it was learned at a later time (during the overspray leaching testwork presented in a subsequent section of this paper) that excessive acidity tends to promote rather selective Cd leaching while forcing the Te into the residue. In case of the PV panels tested, the subsequent optimization leaching work

consistently produced 99% Te recovery on both samples when the actual acid consumption was limited to less than 1.5 kg/t feed. These results were confirmed at commercial scale.

Table 4 Pre-optimization tests results summary - Extractions

TEST NUMBER	REAGENT DATA				EXTRACTIONS IN PLS AND WASH. %			
	H ₂ SO ₄		H ₂ O ₂	COST	VS. DIRECT HEAD		VS. CALC'D HEAD	
	g/L	kg/t FEED	kg/t FEED	US\$/t	Te	Cd	Te	Cd
LAMINATED MODULE								
1	250	190	2.6	\$235	101	93	>90	>99
2	50	43	2.6	\$55	114	102	>91	97
6	10	9	12.8	\$30	122	108	>91	>99
7	10	9	7.7	\$22	107	111	>90	>99
8	10	9	2.6	\$14	100	104	>90	94
9	5	4	12.8	\$25	115	104	>91	99
TEST FEED HEAD ASSAYS					0.042	0.039	0.053	0.042
UNLAMINATED MODULE								
10	5	4	12.8	\$24	92	89	74	95
11	10	9	12.8	\$29	111	88	>96	99
12	50	43	2.6	\$55	73	60	56	56
13ABC	5	4	4.3	\$11	109	86	79	81
TEST FEED HEAD ASSAYS					0.098	0.110	0.126	0.109

Direct head based extraction values - average of the PLS only, PLS and Wash and Feed vs. Residue values.

Calculated heads - based on all reaction products, i.e. washed/dried residue, PLS and wash.

Common conditions: bottle roll, 21°C, 6 hours residence time, solution kinetic sampling, vacuum filtration and washing.

Pre-optimized conditions: as above plus four hours residence time.

Reagent cost calculated on the basis of NaOH required for neutralization and Cd precipitation

No surfactant was used for the tests.

Reagents unit cost - First Solar supply basis on technical grades, as detailed below:

Sulfuric acid 93% H₂SO₄ at US\$ 295/t, Sodium hydroxide 50% wt. NaOH at US\$ 550/t

Hydrogen peroxide 35% H₂O₂ at US\$ 0.25/lb.

Power consumption and related cost not included.

Test 13ABC did not involve advanced washing - not part of the optimization - it produced PLS for further testwork.

Test 13ABC was of two hours duration, hence the lower amount of hydrogen peroxide added.

Table 5 Pre-optimization tests results summary - Acid consumptions

TEST NUMBER #	VOLUMES		FREE ACID		EQUIVALENT H ₂ SO ₄		K FACTOR %
	In	Fin	In	Fin	ADDITION	CONSUMPTION	
	mL		g/L H ₂ SO ₄		kg/t FEED		
LAMINATED MODULE SAMPLE							
1	761	763	262	259	190.2	1.72	0.9
2	856	858	48	46	42.8	1.61	3.8
6	877	888	10	8	8.8	1.67	19
7	877	884	10	8	8.8	1.70	19.4
8	877	879	10	8	8.8	1.74	19.8
9	878	889	5	4	4.4	0.83	19
UNLAMINATED SUBMODULE SAMPLE							
10	878	889	5	4	4.4	0.83	19
11	877	888	10	8	8.8	1.67	19
12	856	858	48	46	42.8	1.61	3.8

Reagent data as pure equivalent units
 K - consumption factor = 100*Consumption/Addition
 Consumption and Addition values are specific, i.e. expressed per ton of feed processed

Table 6 Bulk PV leach tests results summary - Metallurgical balances

TEST NUMBER	PLS		WASHED RESIDUE				
	WEIGHTS, mg		dry wt.	Grades, %		Weights, mg	
	Te	Cd	G	Te	Cd	Te	Cd
Laminated module							
Closed loop tests feed total IN			75000	0.046	0.038	34500	28800
Individual test products OUT							
1	15287	12834		<0.00040	<0.0005	<100	<125
2	24785	20127	24924	0.0008	<0.0005	199	<125
3	35990	30849		0.0007	<0.0005	174	<125
Total test products OUT and calculated heads							
1+2+3	35990	30849	74771	<0.049	<0.042	<474	<374
Unlaminated submodule							
Closed loop tests feed total IN			75000	0.110	0.092	82500	68700
Individual test products OUT							
4	25742	22734		0.005	0.0005	1246	125
5	37796	40127	24925	0.008	0.0010	1944	249
6	46018	60253		0.013	0.0018	3340	449
Total test products OUT and calculated heads							
4+5+6	46018	60253	74775	0.070	0.081	6530	823

Each test was carried out using 25 kg feed.
 Leach residue final weight was estimated based on the weight-loss values determined by the pre-optimization tests.
 They were 0.305% and 0.3% for the laminated and unlaminated sample, respectively.

Additional process design data

The following data was produced and applied for the design of the commercial recycling plant:

- The ethyl-vinyl acetate content (EVA) of the crushed laminated sample ranged from about 1% to 3% in the bulk residue and its distribution was about 20% in the +3 mesh size fraction and

about 0.1% in the 3 mesh size fraction;

- The crushed laminated sample generated leach residue screened at 3 mesh produced a size fraction distribution of 25% reject and 75% passing;
- The crushed unlaminated sample generated leach residue screened at 3 mesh produced a size fraction

distribution of 20% reject and 85% passing;

- Vacuum filtration testwork was carried out on laminated modules and unlaminated sub-modules bulk leach discharge slurries resembling 73-75% solids content -3" screen discharge;
- According to the belt filter design example of the data produced, the

laminated module leach residue throughput was about 870 kg/m²/h for 5% residual moisture; the unlaminated sub-module leach residue throughput was about 1725 kg/m²/h for 5% residual moisture. The cake thickness did not influence the throughput, whereas the target moisture did. One percent increase of the target moisture lead to a dramatic increase of the filter output, practically doubling it.

Manufacturing waste recycling leach results

Waste water filter cake leaching
The acid leach tests from the waste water filter cake were carried out as follows:

- Equilibrium tests – dissolution vs. pH by varying the sulphuric acid addition;
- Confirmation of the equilibrium test results by a bulk test at a selected pH value, based on the equilibrium test results;
- A series of three counter current tests aimed to investigate selectivity trends and to producing solution and residue samples for downstream testwork, particularly iron removal from solutions and tellurium re-leach from the residues.

All tests were carried out on the ‘as received’ sample, with conventional agitated mixing and ambient temperature (25°C). The rate of sulphuric acid addition was very low during the equilibrium test (several hours duration) in order to allow for establishing the equilibrium conditions of each relevant pH value.

Counter current tests were carried out in order to confirm whether the equilibrium test results could be applicable in a real process conditions, whereby the high acidic PLS could be neutralized using fresh WW cake feed, whilst selectively leaching the cadmium during the process. Accordingly, the high acid (pH~1) PLS was contacted with fresh feed (WW cake) at two equilibrium pH values. The goal of these tests was to ascertain leaching efficiencies, iron deportment and most importantly, to assess potential cadmium and tellurium entrapment into the residue due to iron reprecipitation.

Iron re-precipitation was expected to occur due to its instant oxidation in the filter cake contacted with air.

In summary, the results indicated that:

- The equilibrium test (Figure 1) produced cadmium and tellurium re-leach extraction efficiencies in excess of 99% and 90%, respectively. Relative selectivity (Cd versus Te) was observed within pH values ranging approximately from 2 to 3. Accordingly, the Cd extraction at pH~3 was 83% compared to 6% Te extraction at the same pH value; the Cd extraction at pH ~2 was 99% compared to 32% Te extraction at the same pH value.

- These results were only partly confirmed by the counter-current tests (Table 7) meaning that their practical applicability would be limited. In addition, the liquid-solid separation of the filter cake leach products was problematic;
- Finally, WW cake PLS processing would require more aggressive iron control compared to the PV PLS.

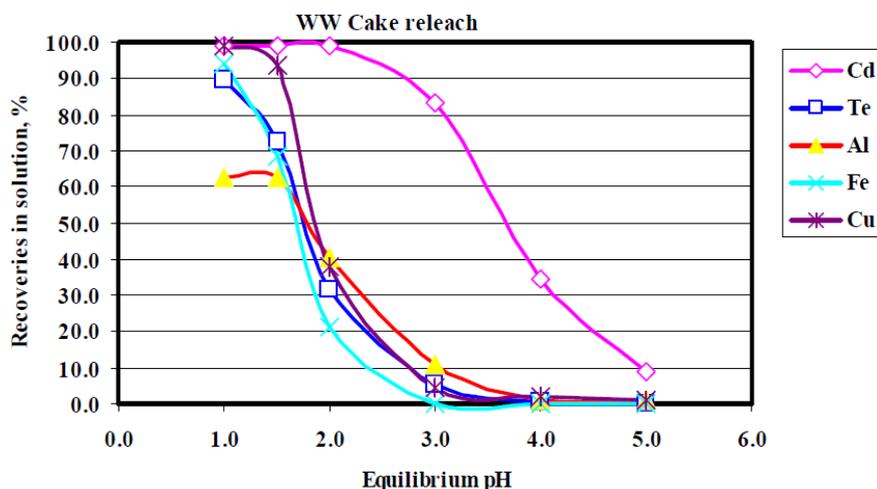


Figure 1 Waste Water Cake re-leach sample pH Equilibrium Curve

Table 7 Counter-current Re-leach Test Summary – WW Cake Sample

PRODUCTS	ASSAYS, % IN SOLIDS, ppm IN PLS				
	Cd	Te	Al	Fe	Cu
Solids					
WW Cake Feed	11.4	8.63	0.24	20	0.01
Leach discharge solids pH ~ 1	0.35	3.71	0.17	5.36	0.01
Leach discharge solids pH ~ 2	6.94	7.10	0.16	18	0.01
Leach discharge solids pH ~ 3	7.40	8.20	0.16	18.88	0.01
Solutions					
Leach discharge solutions pH ~ 1	15000	9920	174	24000	18
Leach discharge solutions pH ~ 2	25086	15753	194	32000	11
Leach discharge solutions pH ~ 3	20600	282	140	380	0.6
Leach efficiencies					
Leach efficiency pH ~ 1	99	90	77	94	89
Leach efficiency pH ~ 2	68	55	19	41	-213
Leach efficiency pH ~ 3	practically zero				

Note: pH 2 and pH 3 leaches were carried out using PLS from the pH ~ 1 leach.

Coater Overspray leaching

The acid leach tests from the coater overspray samples were carried out as follows:

- Base line tests aimed to investigate selective impurity removal versus both Cd and Te;
- Base line tests aimed to investigate selective Cd versus Te leaching;
- One series of three counter current leaching tests aimed to confirm Cd selective leaching, estimate reagent consumption and to produce solution and residue samples for downstream testwork particularly Cd solvent extraction / electrowinning and tellurium re-leach / electrowinning from the residues.

The base line coater overspray leaches ("CLN" series) were carried out on impure and clean coater overspray samples, coded as CS and CCS, respectively. The feed test-samples were fine-ground using laboratory mills. The K_{80} of the resulting leach-feed ground slurry samples (measured using a Malvern Mastersizer 2000 laser sizer) ranged from 16 to 45 microns throughout the various tests that were performed.

Oxidative agitated leaching tests were carried out at ambient temperature (25°C) and without cooling to allow for the exothermicity of the reactions to increase the temperature and subsequently the rate. The initial leach solids density was about 9% wt. Pre-determined amounts of hydrogen peroxide were added continuously during the tests, with concomitant monitoring of the pH and redox potential. Residence times ranging from one to four hours were tested.

The results of the base line oxidative agitated leaching tests (Table 8) indicated that:

- Cd vs. Te leach selectivity - four hours residence time, 218 g/L initial free acid (as H_2SO_4) and 581 kg/t H_2O_2 (equivalent pure) produced nearly 100% Cd extraction versus and 9% Te extraction from the purer sample CCS (Test CLN1) and 97% cadmium extraction versus 8% Te extraction in case of the impure sample CS (Test CLN2);
- Non-selectivity vs. impurities - one hour

residence time, 7 g/L initial free acid (as H_2SO_4) and > 560 kg/t H_2O_2 (equivalent pure) extracted 22% Cd and ~ 19% Te from both samples (Tests CLN3 and CLN4). The expectation was that under these conditions the Cd and Tellurium would be left in the leach residue whilst the sulphur would be extracted. Since this did not happen, the benefit of the oxidative acid leach for the coater overspray remained the possibility for selectively leaching the cadmium;

- Test CLN5 and CLN6 - two hours residence time investigated the effect of increased hydrogen peroxide addition and two extreme sulphuric acid additions. The results indicated that increasing the oxidative power did not translate into selective sulphur removal, nor did it affect the Cd/Te selectivity;
- Test CLN7 investigated the effect of lower initial acidity present in the recycled PLS from test CLN1 and CLN2, hence simulating a counter-current contacting);
- The results indicated that the tellurium co-extraction was lowered to 6% (from 9% in Test CLN 1) whilst the cadmium extraction remained practically 100%.

Counter current oxidative agitated leaching tests series CS-CCS C/C T1 through CS-CCS C/C T3 were carried out in order to simulate the second and third contacting stages of a commercial circuit, whereby the pregnant leach solution was contacted with fresh feed. This allowed investigating the effect of initial acidity and solution ionic strength on the cadmium selective leach efficiency.

The counter current coater overspray leaches were carried out on equal weight proportion blend of the impure and pure clean coater overspray samples, ground to K_{80} ~ 33 microns. Each of the stages was accompanied by liquid-solid separation (mainly filtration), followed by samples removal and analyses. The data allowed for the calculation of the metallurgical balances around each individual counter-current contacting stage.

Counter-current simulation tests results (Table 9) indicated that:

- Cd vs. Te leach selectivity was confirmed – at lower residence time

(two hours), lower initial acidity (159 g/L H_2SO_4) and 580 kg/t H_2O_2 (equivalent pure) addition produced 99.9% Cd extraction and 3.3 % Te co-extraction (Test CS-CCS C/C T2).

- As interim kinetic results indicated (test CS-CCS C/C T2 kin), reducing the oxidizing agent addition by 50% resulted in 86.1% cadmium extraction with virtually no tellurium co-extraction;
- Reducing the initial acidity to 47 g/L H_2SO_4 still produced high cadmium extraction (99.3%) however the tellurium co-extraction increased to 19.3% (Test CS-CCS C/C T3).

Overall, the results suggested that a two-stage stage leach should be sufficient under the pre-optimized conditions for the selective leaching of the cadmium from the coater overspray defined as follows:

- Fresh feed leach feed solids density: 10% weight;
- Initial acidity: 150 g/L;
- Hydrogen peroxide addition – 580 kg/t H_2O_2 (equivalent pure) added in two equal portions (i.e. 50% of the above total for each stage);
- Residence time: one hour per stage;
- Temperature: ambient – no cooling – spiking to 70-80°C allowed;
- Reactor free board ~ 30% to allow for frothing.

Tellurium re-leach from the coater overspray acid re-leach residue

The acid leach residues from various tests consisted primarily of paratellurite. A base line alkaline leaching test on a selective acid leach residue extracted practically 100% of the tellurium contained. The test conditions (100°C, 120 g/L NaOH, 2 hours) and results are summarized in Table 10. The resulting pregnant leach solution was subjected to a Te electrowinning test.

Table 8 Base line coater overspray leaches summary

Test ID	CLN1	CLN2	CLN3	CLN4	CLN5	CLN6	CLN7
Leach feed ID	¹ CCS	² CS	CCS	CS	CCS		
Feed grams dry equiv.	86		88.9	88.2	88.9		149.4
Grind target	45 mics	16 mics	26 mics	29 mics	26 mics		
Grind conditions	A	B	C	C	C		
Addition, H ₂ O _s @ 50% wt., g	100				200		[†] 173.7
³ Initial H ₂ SO ₄ g/L	218		7	241	50	[†] 123.3	
Final H ₂ SO ₄ g/L	121	125	0	113	12	41	
Temperature	20°C						
Residence time	4h		1h	2h			
⁴ Spec. Consumption H ₂ SO ₄	678	491	79	615	375	446	
⁴ Spec. Consumption H ₂ O ₂	581		562	567	1125		581
Weight loss, %	39	36	9	8	40	49	35
Extractions, Cd, %	100%	97%	20%	22%	100%	94%	100%
Extractions, Te, %	9%	8%	<1%	1%	<9%	<26%	<6%

¹ CdTe Cleaner Coater Scrap Feed

² CdTe Impure Coater Scrap Feed

³ Equivalent pure

⁴ kg per ton of dry feed -Equivalent pure

[†] 1:1 g H₂O₂ : g CCS (wet) as on CLN1

[‡] Free acid from the combination of CLN 1 and CLN 2 PLS (50:50 v/v)

Grinding conditions legend:

"A": 50% wt./25' in ball mill (2000g charge, Mill #2)

"B": 50% wt./60' in pebble mill (500g charge)

"C": 50% wt./60' in ball mill (2000g charge, Mill #1)

Table 9 Counter-current coater overspray leaches tests results

Test ID	CS-CCS C/C T1	CS-CCS C/C T2	1CS-CCS C/C T2 (kin)	CS-CCS C/C T3
	Common conditions			
Leach feed ID	² CCS + CS			
Grind conditions	50% wt./70' pre 2.25 kg in ball mill #1			
Grind target	33 microns			
	Specific conditions			
Feed grams dry equiv.	2000			2200
³ H ₂ O ₂ @ 50% wt., g	2320	2320	1160	2250
⁴ Initial H ₂ SO ₄ g/L	193	159		110
Final H ₂ SO ₄ g/L	159	110	n/a	47
Initial Temperature	35°C	39°C		16.1
Final Temperature	70°C	63°C	73°C	68°C
Residence time	120 min.		45 min.	120 min.
⁵ Spec. Consumption H ₂ SO ₄	338	415	n/a	504
⁵ Spec. Consumption H ₂ O ₂	580		290	580
Extractions, Cd, %	99.90%	99.90%	86.10%	99.30%
Extractions, Te, %	9.70%	3.30%	0.00%	19.30%
Weight loss, %	36.80%	36.50%	nd	48.10%
Residue grade, Cd, %	0.09%	0.07%	10.90%	1.06%
Residue grade, Te, %	79.80%	81.60%	71.70%	74.30%

¹ Kinetic sample @ 50% addition of H₂O₂
² CdTe Cleaner Coater Scrap + impure Coater Scrap Feed 1:1

³ 1:1 g H₂O₂ : g CCS + CS (wet) as on CLN1, except for the kinetic sample

⁴ Equivalent pure

⁵ kg per ton of dry feed -Equivalent pure

CONCLUSIONS – PART 1 - LEACHING

- Oxidative leaching of laminated photovoltaic scrap recycle feed produced extractions of about 99% for Te and Cd leaving residues assaying as low as 4 ppm and 5 ppm, respectively;
- The actual acid consumption was about 1.4 kg/t dry feed in case of both samples, corresponding to about 22% utilization efficiency while the hydrogen peroxide consumption was 13 kg/ton feed;
- 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 bulks leaches and subjected to metal recovery testwork – the results are described in the following paper (part 2).

Table 10 Tellurium re-leach from the coater scrap acid re-leach residue

Test ID	CS-AIKLT
Leach Feed ID	1 CLN1 + CLN2 (CS/CCS) Leaches Residue
Feed weight, grams	80
Temperature	95-100°C
Final pH	10.2
NaOH, g/L	120
2 Spec. Consumption NaOH	256
Residence time	2 h
Extractions, Te, %	~100%

1 40 grams each
 † specific consumption, kg 100% NaOH per ton dry feed. - NOT FOR DESIGN

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