TECHNICAL FEASABILITY ASPECTS RELATED TO THE HYDROMETALLURGICAL RECYCLING OF PAY METALS FROM THIN FILM PHOTOVOLTAICS

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ABSTRACT: The paper is addressed primarily for non-metallurgists interested in gaining an inside view into the factors affecting the effectiveness of the recycling process. Whilst the metallurgical content covers most of the relevant basics, it is delivered in a simple and direct form. A brief overview of the metallurgical project structure is provided within the specific context of photovoltaics recycling aiming primarily for metals recovery. Essentials of technical and economical feasibility of sustainable recycled-pay-metal production are presented. Emphasis is placed on novel process flowsheet development from low-grade, low-to-medium throughput, highly variable feedstock – all these being characteristics of the "recycling feed", defined as such. Moreover, a quick review of the criteria for selection of commercially proven unit operations enabling the said novel flowsheet is provided. A summary of key factors influencing the performance of recycling plants from design through ramp-up and full commissioning is provided. Technical process risk mitigation strategies are reviewed and exemplified, with focus on the recycling of metals from thin-film photovoltaics. Critical "big picture" success (or failure) factors discussed include process chemistry cost implications, effect of separation and handling on plant operability, water usage and facility requirements.

Keywords: CdTe, economic analyses, recycling.

1 OBJECTIVES DEFINITION

The objectives of the recycling activity need to be defined as such to allow for a realistic approach to project execution. In case of thin-film photovoltaics (TFPV), the main discernable objectives are:

- Ensuring environmental compliance;
- Recovering pay metal values;
- Meeting third-party specifications.

The environmentally related objective is broader as it tends to be politically driven by large. It is commonly justifiable despite of its generally prohibitive cost.

The pay metal recovery related objective is economically driven, meaning that its affordability is generally market-limited. However, it could present increased importance when targeting strategic supply as well as to creating short-term momentary price-momentum leverage in tight markets when the opportunities arise.

1.1 Discharge limits versus economical recycling

Current corporate sustainability policies within the solar sector place prioritize on consistently meeting the environmental objectives whereas the other objectives tend to be subordinated. On the other hand, the main thrust of a recycling project should be to recover the pay metals during the projected lifetime of the operation. Defining the battery limits in the proposed case of a TFPV recycling project is consistent with these considerations.

The environmentally related objectives are required to define a regulation-compliant residual metal discharge target-limit in the liquid effluent(s). This reality defines a fixed set of parameters which in turn will decisively influence the reagent consumption, washing and liquid-solid separation capital and operating costs, including reagent and water consumptions. Regarding the solid-discharge streams however, it is necessary to determine an acceptable value primarily based on the stability of the chemical form under which the metal is present in these streams. As opposed to a liquid effluent, a stable solid residue can be disposed safely for centuries, even millennia. It is important within this context to point out that metal recovery values will be largely unaffected above the 95% extraction. For example, based on previously published data [1], a 10 ppm residual Cd could be produced at a reagent cost of about US$ 17 per ton of recycle plant scrap-feed leached with 20 g/L H_2SO_4 (i.e. ~ 17 kg/t at 65% wt. solids) for 6 hours, followed by washing. In comparison, that cost doubled for producing a 1 ppm Cd clean-cullet discharge, at which the recovery was already in excess of 99%. TCLP leachability data indicated that the 5-10 ppm Cd discharge-residue, i.e. glass cullet was stable. (Note: Cd occurrence in the Earth crust ranges from 0.5 to 5 ppm). According to these data there was no practical advantage in pursuing costly lower level discharge. By contrary, it would induce undue financial strain onto the recycling project economics. Secondly, advanced extraction of residual metals involves increased emissions thus negatively affecting the carbon footprint of the main production plant, i.e. defeating the scope of solar power itself.

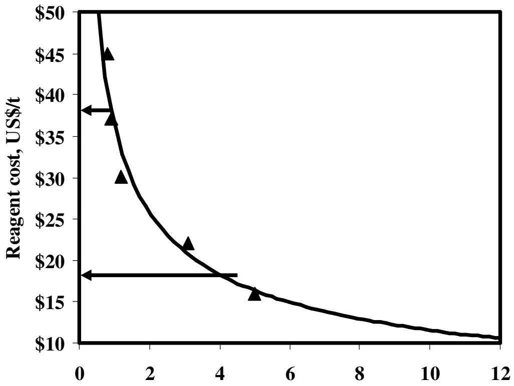

Figure 1 Reagent cost versus discharge grade

1.2 Defining recycle plant feed

Recycle feed definition and classification should be included within the context of the project objectives because of the fact that under a certain set of operating parameters, the reagent cost varies inversely proportional to recycle scrap-feed head grade at a certain reagent utilization value, as it will be detailed further below. In addition, it is necessary to include the impact of high-grade low-tonnage streams commonly generated as process waste. Integration of these streams can make a significant difference on the process flowsheet, water management and overall process economics.

1.3 Secondary objectives

Third-party related objectives assume the reintroduction into the economical circuit of secondary recycled values, for example glass in the case of TFPV recycling. These objectives should be treated with minimum priority unless economically justified. As an example in the case of the glass cullet, the cost of recycled glass should be competitive on the same specification basis. Also, the chemical specifications should be defined relative to the size fraction of the cullet. On the same basis, recycling glass for the "sake of recycling" should be avoided as this could severely impact the process economics.

2 METALLURGICAL PROJECT STRUCTURE

The recycling-metallurgical project structure proposed is based on its similarities with the mining-metallurgical project. The analogy between the mining- and recycling-metallurgical projects relies on several factors including but not limited to underlying process technology, testwork matrix, operation life-time, environmental impact, process economics, etc. The main dissimilarities include plant throughput and feed grade. Currently, TFPV scrap-recycling plants throughput is generally low compared to mining operations. For comparison a 10 or even 100 t/day recycling plant feed rate pales in comparison to a tailings-reprocessing gold plant leaching at a throughput of several orders of magnitude higher, i.e.10,000 t/day, which in turn is well below of a typical oil sands plant federate of about 10,000 t/hour. Whilst these nameplate examples are for reference only, their significance is that throughput can markedly determine process economics within a certain domain of well-defined matrix of process variables (i.e. grade, liberation, separation, etc.) and for a given flowsheet. In addition, lower throughputs generally are more suitable for batch processing, a modus operandi carrying inherently decreased capital costs ("capex") and increased operating costs ("opex"). Regarding the feed grade, the mining projects involve almost exclusively high grade feed stocks, i.e. very economical, and as such, even their tailings contain significantly more metal than the bulk of the TFPV scrap modules.

Pursuant to above considerations, the recycling-metallurgical project structure should be phased-out in our opinion as follows:

- Process selection, testwork matrix and conceptual flowsheet development;
- Pre-feasibility stage – initial Real Data Model Process model ("RDM") based on test data;
- Pilot confirmation of the bench-data including engineering design and scale-up criteria generation;
- Feasibility stage in conjunction with updated – validated process RDM, process economics and sensibility study;
- Purchasing, construction, start-up and commissioning;
- Ramp-up to nameplate throughput.

Base line considerations on selected topics from the above list are discussed briefly further below.

2.1 Process selection

Hydrometallurgy (i.e. extraction of metals using aqueous solutions) is suitable for metal recycling since the TFPV scrap recycle "feed" can be characterized as:

- Low but markedly variable grade;
- Complex;
- Relatively low throughput;

Hydrometallurgical flowsheets meet stringent process, environmental and economical criteria such as:

- Robust – proven integrated process flowsheets based on technically feasible unit-ops;
- Low and controllable emissions, facile water management;
- Commercially applicable in relatively short time frame.

2.2 Process design and deliverables

As a primarily hydrometallurgical process, a well-designed TFPV scrap recycle process should ensure:

- Advanced extraction and recovery of metal pay-values whilst producing stable and containable discharge streams – i.e. "process chemistry ";
- Effective handling and separation of process feed, discharge and intermediate process streams including coarse bulk solids, fine-slurries, etc. – i.e. "process physics";
- Adequate unit operations and equipment selection with a view to wear, tear and corrosion and within the context of required suitability for multiple feed thus allowing for a certain degree of flexible operation.

Process design focus should be placed on:

- Testwork data and subsequent modeling, including sensitivity scenarios;
- Integration of all unit operations, closing the mass, energy and metallurgical balances, optimizing the water management scheme (consumption, recycling and discharge limits);
- Assessing batch vs. continuous operations, inclusion of the capital and operating expenditures into a project-specific economic model;
- Overall footprint, including discharge streams staging areas and surge volumes tankage or tailings pond(s);
- Note: if "plant around the building" design is required, particularly in urban environments, with limitations due to pre-existing production facilities – the equipment selection option should be revisited as to ensure meeting building clearance requirements.

Since each topic listed herein is relatively broad, this paper will address relevant examples from two key areas, namely process chemistry implications and basic process physics aspects as key defining criteria for unit operation selection. A process economics example is included.

3 PROCESS CHEMISTRY IMPLICATIONS

3.1 Reaction mechanism

The first commercial cadmium-telluride (CdTe) scrap recycling operation was commissioned by First Solar in 2006 at their Perrysburg, Ohio facility. The original Perrysburg recycle plant was replicated in various First Solar operations worldwide. A summary of the underlying metallurgical testwork data were published commonly by Fist Solar and SGS [1]. SGS was retained initially for the metallurgical process testwork and flowsheet development. This mandate was further broadened by inclusion of plant design and assembly contributions, as well as final inspection and commissioning. This paper provides in-depth metallurgical interpretation of the referenced published data in light of SGS' own metallurgical expertise, also backed by a certain amount of its proprietary data and specific metallurgical expertise. The results could be considered an operational breakthrough in that they allowed for the reduction of the reagents cost associated to leaching and metal-precipitation with sodium hydroxide by over one order of magnitude compared to the previous data, as illustrated in Figure 2 (showing the relationship between reagent costs versus initial acidity, and also highlighting the 2006 SGS-First Solar milestone). Those data were produced based on the leaching a scrap-feed grading about 100 ppm CdTe for six hours at about 65% wt. solids, at average hydrogen peroxide addition of about 2.6 kg/t equivalent H_2O_2 producing a clean washed-cullet assaying from about 5 to 10 ppm residual cadmium. This performance was possible based on the application in practice of the common knowledge that the leaching of the CdTe film is an oxidative process.

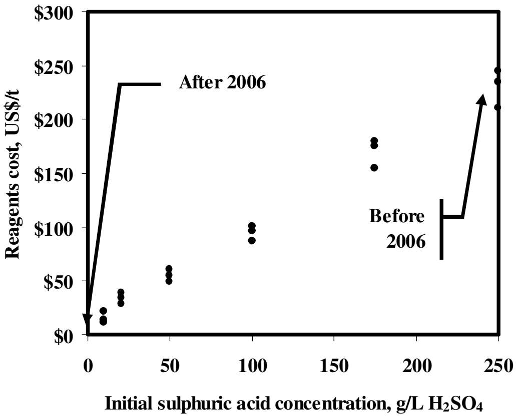

Figure 2 Reagent cost versus initial acidity

3.2 Reagent utilization

Furthermore, it was learned that conducting the leaching on the basis of one rigid-well-defined hydrogen peroxide addition regardless of the feed grade lead to a rather large variation of its utilization coefficient, as shown in Figure 2. However, these results, produced at a constant initial free acidity of 20 g/L H_2SO_4 confirmed the oxidative nature of the CdTe leaching, whereby the acidity was needed for kinetic purposes.

Hydrogen peroxide utilization coefficients of 30-50% (direct proportional to the feed-grade) are practically achievable resulting in about 40% reduction of the reagents costs (Figure 4). This is possible by applying a strict Emf (i.e. oxidative potential) control. Increasing acid utilization in conjunction with Emf controlled hydrogen peroxide addition allows for further reduction of the reagents cost as shown in Figure 5. Reagent cost reduction is possible because acid recycling increases the tenors of leached metals in solution whilst reducing the amount of neutralizing agent (NaOH). The practical modality of increasing the acid utilization is by multiple-contacting including counter-current leaching. Counter-current washing is the most effective unit operation that allows for maximizing the PLS tenor whilst optimizing the water consumption, as depicted in Figure 6 for the case of a typical blend of leach discharge.

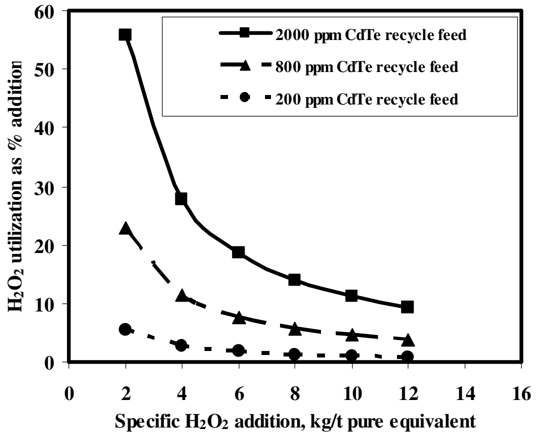

Figure 3 Peroxide utilization vs. addition and feed grade

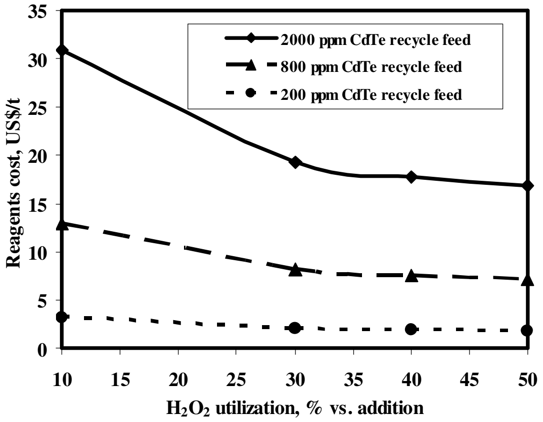

Figure 4 Reagents cost vs. peroxide utilization

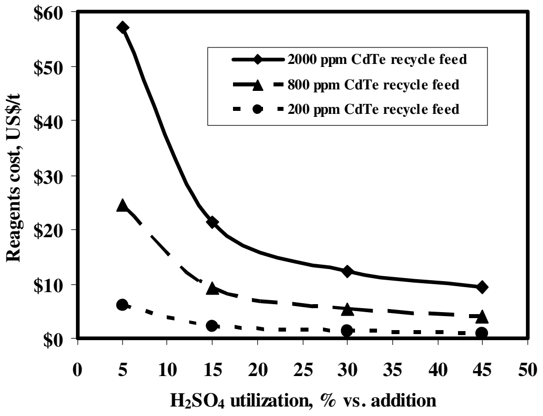

Figure 5 Reagents cost vs. acid utilization

3.3 Real Data Process Model (RDM)

Test data such as discussed herein allow for conceptual flowsheet development of practically any

TFPV recycling operation. In order to become pilotable, the process mass and energy balances need to be established. The target operating throughput and parameters of the pilot plant need to be defined based on the requirements of the planned commercial recycling operation. This can be done in a process-safely approach by establishing the process model initial parameters using the test data. This proprietary SGS approach is referred to as Real data Modeling (RDM). In addition to the process-chemistry input, the RDM receives critical process-physics inputs, reflective of the handling and separation behavior of the process streams, particularly solids, slurries, pulps, as well as gaseous components, when applicable. These data are referred to as "engineering data", and they are the most important component of the RDM.

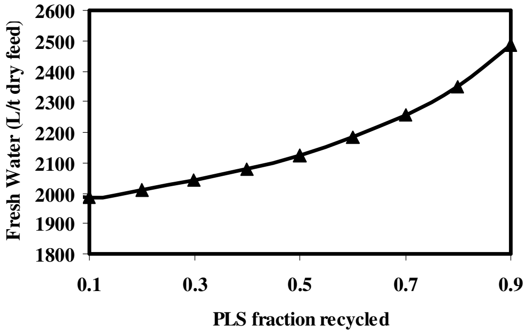

Figure 6 Water usage vs**.** PLS recycle fraction

4 UNIT OPERATION CONSIDERATIONS

The selection of key unit operations in conjunction with the handling, separation and transport equipment is practically the most critical process development stage. This is because generally, process chemistry can be validated by relatively low-cost, commonly available testing. Also, the sample requirements are relatively modest. Physical behavior testing on the other hand requires larger amounts of sample for it tends to be markedly equipment-dependent in certain instances and scale-up is not always straightforward. For example, the comminiton (i.e. size reduction) of the glass panels involves not only the shredding and crushing, for which the conditions can be readily determined for a particular type of equipment, along with generation of scale-up data. In fact, it is the less obvious issues that need more testing and expert-attention, such as abrasion, dust control, screening and especially transport. For example, dry-screening, is generally attractive due to its apparent simplicity. Yet safe handling of the dust with elevated Cd levels both inside and outside the hammer-mill (i.e. screen, conveyor, hopper, etc.) could impact severe operating complications and subsequent cost escalations. Comparatively, wet-screening is safer, and it can be combined with effective size-fractioning, which in turn can produce customized leaching sequences with "built-in" optimized washing and dewatering. Handling and transportation of the oversized material requires a different design approach compared to the finer passing fractions. Shredded-crushed glass panels could display unusual flow behavior during screening, pumping and filtration, quite different in fact compared to a similar feedstock of mineral origin. This is partly due to the presence of the polymer film (i.e. ethyl-vinyl-acetate, known as EVA), and partly due to the relative abundance of fines within a relative coarse matrix. This configuration could render coarse slurry pumping heavily dependent on the solids content (% weight), whereas the pumping of the finer fractions occurs according to relatively well-known rheology. These two markedly opposite flow behaviors are reflected downstream, i.e. in the separation properties of the coarse and fine size leached fractions. As expected, a 6 mm nominal screen-reject leach-feed would settle-out instantly at every turn of a rotary reactor, or under insufficient agitated mixing. For that very reason, however, the leach discharge would wash and dewater instantly without the need for a filter. In fact, a filter would be difficult to operate with such a coarse feed due to the resulting excessively high air-flow levels (i.e. loss of vacuum). These considerations could lead to the conclusion that non-agitated leaching would be ideally suited for the coarser size-fractions. On the other hand, a finer size fraction, even nominal 1 mm is commonly amenable for agitated mixing and the discharge is pumpable and filterable. Both scenarios need to be confirmed by metallurgical testwork, with emphasis on engineering data generation.

The engineering data produced for handling and separation consist of settling-thickening, washing, rheology, vacuum and pressure filtrations and drying. The metallurgical response data and the engineering design criteria are fed into a real data model built using algorithms derived from generally accepted mass transfer calculations. The net RDM deliverables consist of process scale-up and equipment design criteria packages (complete mass and energy balances, physical sizing of the key equipment, flowrates, concentrations, operation targets, etc.). From this point on, the RDM can be used for various technical simulations, such as feed grade and composition variability within the hard-data validated metallurgical performance targets. Pilot data are used to update the RDM in preparation of the commercial plant commissioning and ramp-up.

5 BASE-LINE PROCESS ECONOMICS

The RDM output can be used for base-line economic sensitivity analysis for scoping level at a +/- 35% range of accuracy for capital and operating expenditures. The example provided illustrates the case for a recycling facility operated in a developed country (i.e. Western) jurisdiction for 25 years lifetime. The feed is assumed size-reduced to about half-inch (~ 6 mm) nominal crushed-size. The reagent utilizations were 30% for both acid and peroxide, amounting to about 10% or less from the total operating expenditures. Real estate and infrastructure were included in opex as rent. Equipment cost estimation was based on 2006 USD prices. Specific operating expenditure example for 800 ppm CdTe PV scrap-recycle feed is provided in Table I. Corresponding capital expenditure example covering the case for a 200-2000 ppm range CdTe PV scrap-recycle feeds is provided in Table II.

The resulting correlations illustrated in Figure 7 indicated that both the capital and operating costs were insensitive to the feed grade within the set limits. The main determining economic factor was the plant throughput, as the data indicated that the costs started leveling-out at plant capacity in excess of 42,000 tons per year. This capacity resembles a low tonnage-low grade mining-metallurgical operation. Strategically, this would justify a stand-alone “green-field” development project as opposed to an existing (i.e. “brown-field”) extension. Such a project would require careful consideration of the overall layout, building clearances, utilities, etc. And most likely, a tailings pond would be required to allow for reasonable permitting as well as comfortable operation.

Table I Opex sensitivity example, USD$/t scrap feed

Throughput, t/year	1314	10512	42048
Reagents	7.11		
Labour	113	21	9
Energy	6.5	1.9	1.3
Water	0.13	0.04	0.03
Maintenance	13.01	3.83	2.56
Rent	2.6	1.9	1.8
Environmental	6.5	1.9	1.3
Overhead	19.5	4.6	2.6
USD$ / ton feed	168.6	42.8	25.3

Table II Capex sensitivity example

Throughput, t/year	1314	10512	42048
Capex, USD$, millions			
Development	$1.2		
Engineering	$0.36	$0.54	$0.66
Equipment	$3.00	$6.59	$11.14
ECPM	$0.90	$1.98	$3.34
Contingencies	$1.09	$2.06	$3.27
Total capex	$6.55	$12.37	$19.61
Specific capex USD$/t scrap			
Per year	$4,986	$1,177	$466
Per 25 years	$199	$47	$19

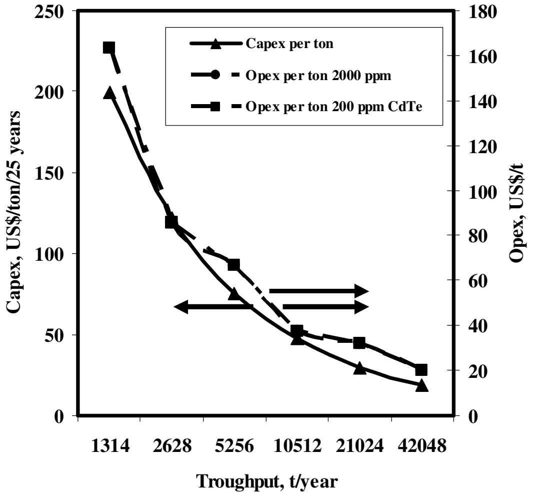

Figure 7 Capex and opex sensitivity curves

Inclusion of high grade recycle-feedstocks (various dusts, coater overspray, rollers, etc.) would positively impact the economics, whilst requiring additional capital and operating expenditures. This is because this strategy would provide significantly increased recycled metal output. Naturally, such a facility would include a small refinery, thus the saleable product would consist of metals instead of intermediates.

Some of the underlying metallurgical data that can be used for modeling these scenarios were published previously [2]. The same paper provides metal recovery information that can be used for the initial modeling of the complete recycling operation by including additional leaching, separation and purification circuits, as well as one solvent extraction and two electrowinning circuits targeting cathode deposits assaying 99.8% Te and 99.9% Cd.

6 CONLUSIONS

- The recycling and environmental compliance requirements need to be defined in synergy and within one integrated, sustainable and economically viable stand-alone operation;
- Leaching of the CdTe thin film photovoltaic modules is an oxidative process that can be optimized with respect to the main two reagents utilization efficiency (~ 30%) thus limiting the reagent costs to 10% or less versus the total operating expenses;
- The selection of key unit operations in conjunction with the handling, separation and transport equipment is practically the most critical process development stage in case of novel processes involving hydrometallurgical unit operations within a typical recycling flowsheet;
- Process chemistry and engineering data produced by testwork was input into a proprietary SGS recycling process real data model. The process output consisted of a pre-feasibility level engineering process package;
- A subsequent base-line economic sensitivity analysis for scoping level +/- 35% range of accuracy capital and operating expenditures indicated that the main determining economic factor was the plant throughput. Accordingly, the capital and operating costs started leveling-out at plant capacity in excess of 42,000 tons per year;
- Such a plant capacity resembles a low tonnage-low grade mining-metallurgical operation;
- Similar test-data-backed process models can be established for various recycled feeds, and preferably, with the inclusion of high-grade / low tonnage streams.

7 REFERENCES

[1] A. Mezei, M. Ashbury, M. Canizares, R. Molnar, H. Given, Hydrometallurgical recycling of the semiconductor material from photovoltaic materials – Part one: Leaching”, paper presented at Hydrometallurgy 2008 - 6th International Symposium, Phoenix, Arizona, 2008.

[2] A. Mezei, M. Ashbury, M. Canizares, R. Molnar, H. Given, Hydrometallurgical recycling of the semiconductor material from photovoltaic materials – Part two: Metal recovery”, paper presented at Hydrometallurgy 2008 - 6th International Symposium, Phoenix, Arizona, 2008.