

SENSE

Recycling of Production Waste



Project Coordinator University of Stuttgart

Project Partners Wuerth Solar GmbH & Co.KG.

Free Energy Europe SA

Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung

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EXECUTIVE SUMMARY

The project “Sustainability Evaluation of Solar Energy Systems (SENSE)” (CONTRACT N°: ENK5-CT-2002-00639) was co-funded by EC during 2001 to 2006. Within the project two objectives were achieved: the identification of possible **recycling strategy** for thin film Photovoltaic (PV) modules (CIGS, CdTe and a-Si) and the analysis of **environmental performance** of these PV modules. A consortium of manufactures, recyclers and scientists developed a practical applicable recycling system and assessed the environmental impact of production and utilization of thin film PV modules as well as of the developed recycling system.

This paper reports on the project regarding the **recycling of production waste**, examined by the partner Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung (ZSW).

1 RECYCLING STRATEGY CIGS

The work of ZSW in this work-package was concentrated on the development of processes to extract rare and precious metals from the various types of scraps which are created in the manufacturing plants for CIS-modules and which come up when CIS modules have finished their useful life and have to be recycled.

Figure 1 shows the typical composition of CIS thin-film solar modules. The biggest amount of material is glass (84%), followed by the aluminium frame (12%) and the polymer encapsulant (3%, e.g. EVA). The most essential materials forming the photovoltaic layers (Mo, Cu, In, Ga, Se, Cd, Zn, S) are only a very small fraction of about 23 grams in a 15 kg square meter sized module. Nevertheless it is necessary from several reasons (material prizes, material availability, legal and political reasons) to establish closed loops of materials.

The wastes produced in a real CIS manufacturing plant with a production yield less than 100% can roughly be classified as:

Mixtures of materials produced during manufacturing, such as

- CIGS particles from evaporation plants
- Used targets (ZnO, ZnO:Al, Mo, In, Ga, Cu)
- Chemicals from the chemical bad deposition process
- Blasting sands and grinding debris
- Mixed contaminated materials

and more or less complete modules like

- Malfunctioning raw modules
- Complete, but off-spec modules
- Modules damaged during transport and mounting

There is a limited material yield in both sputter deposition and thermal evaporation, producing waste with high metal content. Material yields are usually kept strictly confidential by the industry, but they are normally clearly below 75%, and often in the range between 30% and 70%, depending on the process, substrate size, material, and skills of the operators. Independent of this uncertainty it is possible to estimate the quantities of metals in the wastes which from time to time have to be removed from the evaporation plants, sputtering machines, laser patterning machines, etc. and which may be collected with vacuum cleaners or by other appropriate means. If, for instance, 30 tons of indium are incorporated in modules with together 1 GWp (a probable annual production in a few years), the producers used between 50 tons and 100 tons indium as input material. The difference, i.e. at least 20 tons of indium, is not consumed but stays somewhere in the machinery and must be removed.

Materials in standard CIS modules

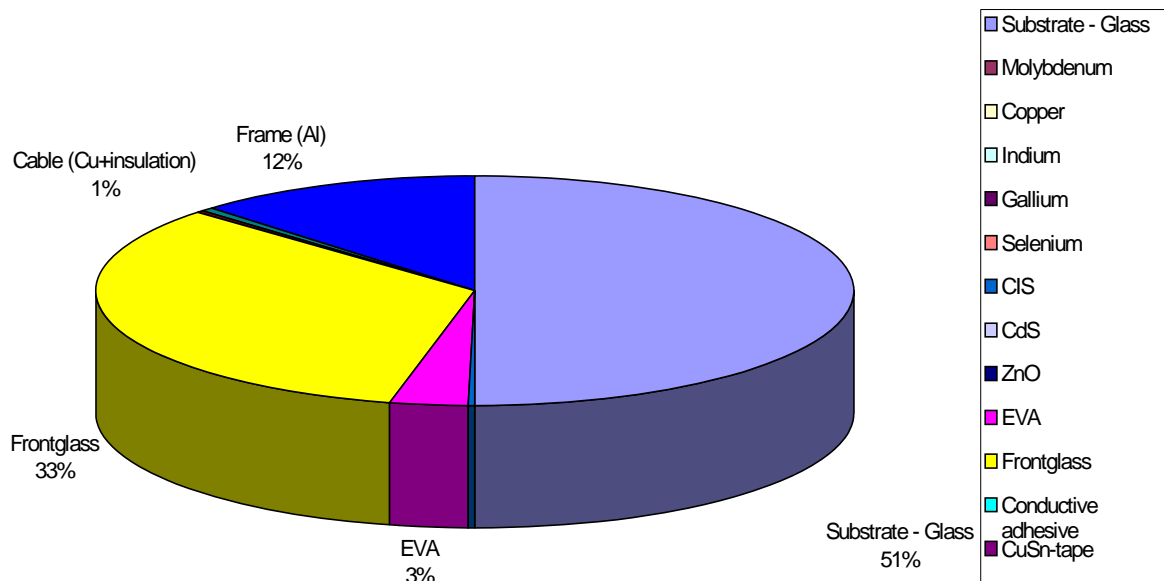


Figure 1: The composition of typical CIS thin-film solar modules as they are fabricated by companies like Wuerth Solar, Avancis, Sulfurcell etc.

Figure 2 summarizes the various types of wastes which have to be considered when a closed-loop recycling of CIS modules should be established an all steps of the product life-cycle.

Many of these wastes, e.g. clean glass and contaminated water can be treated with established methods. Other materials are more specific and special methods of recycling have to be developed. Some of the factions of wastes can be treated together. Contaminated glass, broken modules, semi-finished modules and end-of-life modules could for instance be collected and subjected to a common treatment. This treatment should be done in a way that it results in fractions of clean glass and metal-rich fractions, which afterwards could be combined with similar metal-rich materials coming from the vacuum machinery. From the viewpoint of precious metals content these are the most attractive materials. In a long-term aspect the complete modules are also very important since there volume will increase tremendously in the future with increasing production capacity of the CIS manufacturing companies.

In the SENSE project we treated the metallic wastes from the machinery as well as complete modules. It is possible to establish a process flow in which both types of waste can be treated, at least in the final steps of the separation and cleaning of the precious materials.

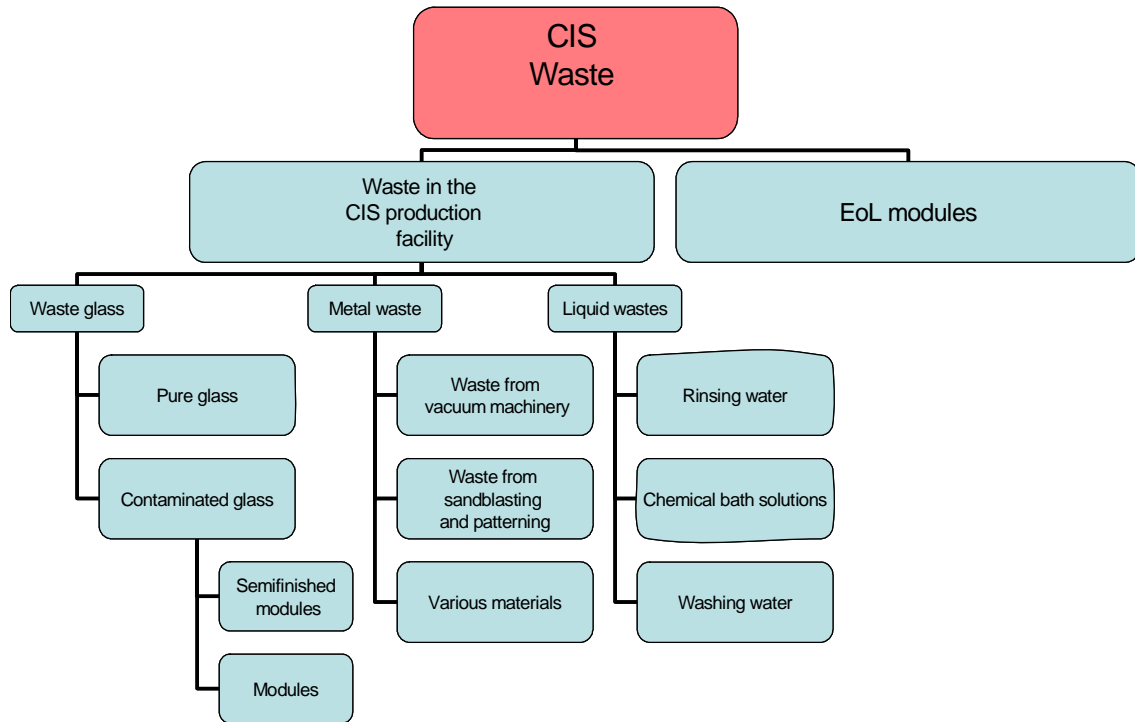


Figure 2: Schematic overview of the types of CIS wastes

2 WINNING OF METALS

There are two principal paths for winning of metals from mixtures: Pyrometallurgy and hydrometallurgy. These can also be combined in various ways. After a study of the existing literature we decided that for the purpose of winning of the precious metals out of the CIS-wastes the hydrometallurgical processes are more suitable. They are characterised by wet-chemical process steps like dissolution, precipitation, separation, electroplating, cementation etc.

Figure 3 outlines a process flow which was developed in the project and which suited for the extraction of the elements indium, gallium and selenium from the metal-rich manufacturing wastes and from metal-containing fractions from module recycling. A solid waste as it can be gathered for instance in an evaporation plant or a sputtering machine is first homogenized and brought to a suitable grain size by milling and screening. Then the material is dissolved in an oxidizing acid. The solution is filtered and insoluble fractions are removed. In a first liquid-liquid extraction step the indium from the solution is transferred into an organic solution while the other metals remain in the inorganic solution, which can be treated further to win the gallium and the selenium. In the stripping step (re-extraction) the indium is transferred again into an inorganic, acid solution. From this it can either be precipitated as a fairly pure indium hydroxide or it can directly be deposited as metal by electroplating. Both materials can be purified further in-house or be sold to a metal refining company.

From the inorganic solution from the first extraction step the elemental selenium can be simply precipitated by addition of sodium sulphite or sulphur dioxide. For the winning of the gallium a further extraction step (liquid-liquid extraction or ion-exchange) can be added. It is necessary to establish as closed as possible material loops for the process chemicals (acids, ion exchanger, extractants, water).

3 PROCESS CHEMICALS

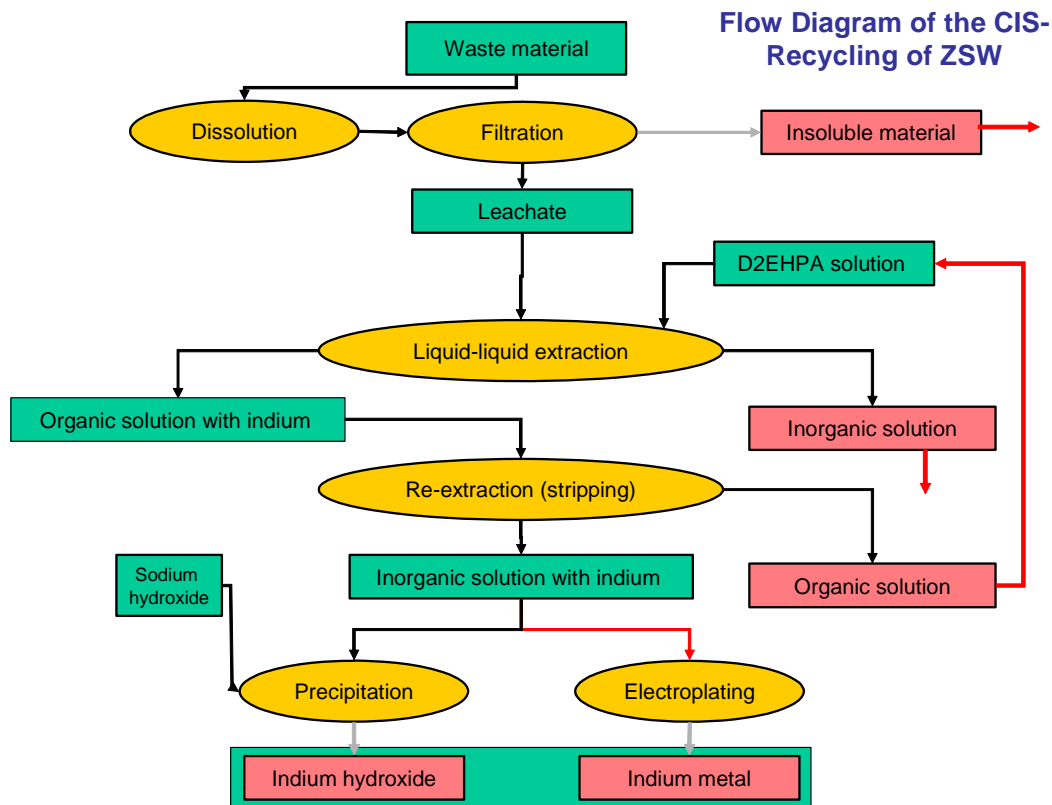


Figure 3: Process flow for treatment of waste materials from CIS factories

The following describes the experimental procedures more in detail:

The experiments were made with CIS coated glass plates and with a grinding dust coming from the edge grinding of the CIS modules in the Würth Solar plant

Possible other materials are crushed modules, blasting sand, residual material from the evaporation plants.

The dust consists mainly of wear debris of the polymer bonded grinding wheels (polymer and abrasive) and below 10% of the materials of the CIGS layers (Mo, CIGS, CdS, ZnO).

The wear debris and the CIGS could be separated by chemical dissolution with an acid mixture which had to be optimised in terms of dissolution efficiency and rate.

Tested reagents:

- a) Nitric acid
- b) Sulphuric acid and hydrogen peroxide
- c) Sulphuric acid, phosphoric acid and hydrogen peroxide

Dissolution of layers on glass with nitric acid

A series of concentrations (1 to 6n) at room temperature was tested. The results are as following:

- a) Only with 6n HNO₃ dissolution after 1 hour, delamination and disintegration of the CIGS, dissolution of the Mo.
- b) With concentrated HNO₃: delamination within seconds, formation of nitric gases.

Experiments with 1 to 6 n H₂SO₄ together with H₂O₂ (30%)

Delamination time depending on concentration from 10 to 35 minutes.

Complete dissolution was reached after 1 hour with 6n H₂SO₄, after 3 hours with 4n H₂SO₄. In detail:

- At first delamination under development of gas bubbles (oxygen): dissolution of the Mo base layer
- formation of CIGS flakes
- slow dissolution of the flakes

Influence of temperature (Figure 4):

Experiment were carried out with 6n H₂SO₄ + H₂O₂.

- a) 28°C: delamination time 15'
 dissolution time 45'
- b) 80°C: delamination time <1'
 dissolution time 15'
- c) above 85°C: decomposition of H₂O₂

Resulting receipt after a series of experiments (depending on the amount of material to be dissolved):

100g 2n H₂SO₄ + 11g 30% H₂O₂ solution

Reaction products:

According to the acid and oxidizing environment the reaction products in the aqueous solution are:

- Mo^{6+} ions
- Cu^{2+} ions
- In^{3+} and Ga^{3+} ions
- Se^{4+} ions
- Sulphate ions

No precipitation was observed even after a longer time.

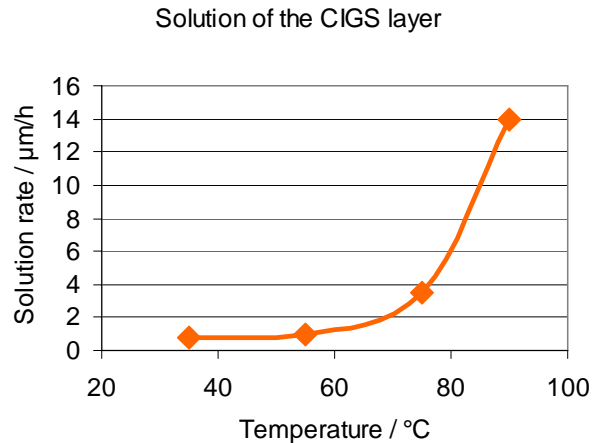


Figure 4: Temperature dependence of the dissolution of CIS+Mo layers on glass with $6n \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$

Removal of selenium

Precipitation with reducing SO_2 (prepared by reaction of concentrated sulphuric acid with sodium sulphite): Formation of tomato coloured precipitate (amorphous selenium) which can easily be removed by filtration. It is also possible to add sodium sulphite to the solution to produce the precipitate (the disadvantage is the additional introduction of sodium, the advantage is the easier handling).

Removal of cadmium (this step was not performed during the experiments)

Ion exchange with cation exchanger resin TP 207 (Bayer)

Remaining water can be used for processes (rinsing)

Removal of indium and gallium**Indium:**

a) Liquid-liquid extraction with D2EHPA)

- Solvent petrolether (aliphatic hydrocarbon with boiling point around 100°C) – (a wide range of other aliphatic hydrocarbons as kerosene, petroleum, Shellsol can also be used)
- Extractant: D2EHPA – Di(2-ethylhexyl)phosphoric acid - trade name **Baysolvex® D2EHPA** (D2EHPA is used for separation and winning of rare earth metals and for extraction of zink, vanadium, beryllium etc.)

b) Stripping with HCl

c) Precipitation as hydroxide or electro-deposition as metal.

The indium received after electroplating is very pure. Main impurity is molybdenum.

Gallium: Liquid-liquid extraction or ion exchange with resin

Figure 5 illustrates these process steps.

First dissolution experiments with the sulfuric acid/hydrogen peroxide mixture were dissatisfactory, because the strong evolution of foam slowed down the process too much. Nitric acid was thus chosen for the subsequent experiments. The disadvantage of nitric acid is that nitric gasses evolve which must be treated in an industrial environment. Dissolution was fast and nearly complete. The abrasives and other impurities remained insoluble and could be filtered off. 1 kg of waste could be dissolved within three hours at 80°C with 20% HNO₃. The resulting solution mainly contains Mo, Se, In, Ga, Zn, and Fe.

A one-step liquid-liquid extraction with D2EHPA essentially transfers all of the indium and some of the molybdenum into the organic phase. From there the indium can be brought back into an inorganic phase by stripping with 8 M hydrochloric acid.

The addition of NaOH causes the precipitation of In(OH)₃, which can be separated by filtering. 178 g In(OH)₃ could be gained from 1 kg of raw material.

The inorganic fraction of the liquid-liquid extraction contains all the elements besides indium. In a next step, selenium can be extracted by precipitation with Na₂SO₃ (alternatively with SO₂ gas). A fine, red, well filterable precipitate is produced. In the experiment, 435g of red Se could be gained from 1 kg of raw material.

In a further treatment of this solution, the gallium can be removed by adding sodium hydroxide to a pH of 2. The filtered hydroxide is not very pure, but can be further purified by electrolytic processes, crystallisation, or zone melting. In the experiment, 69 g of Ga(OH)₃ could be gained from 1 kg of raw material.

Some pictures from CIS recycling

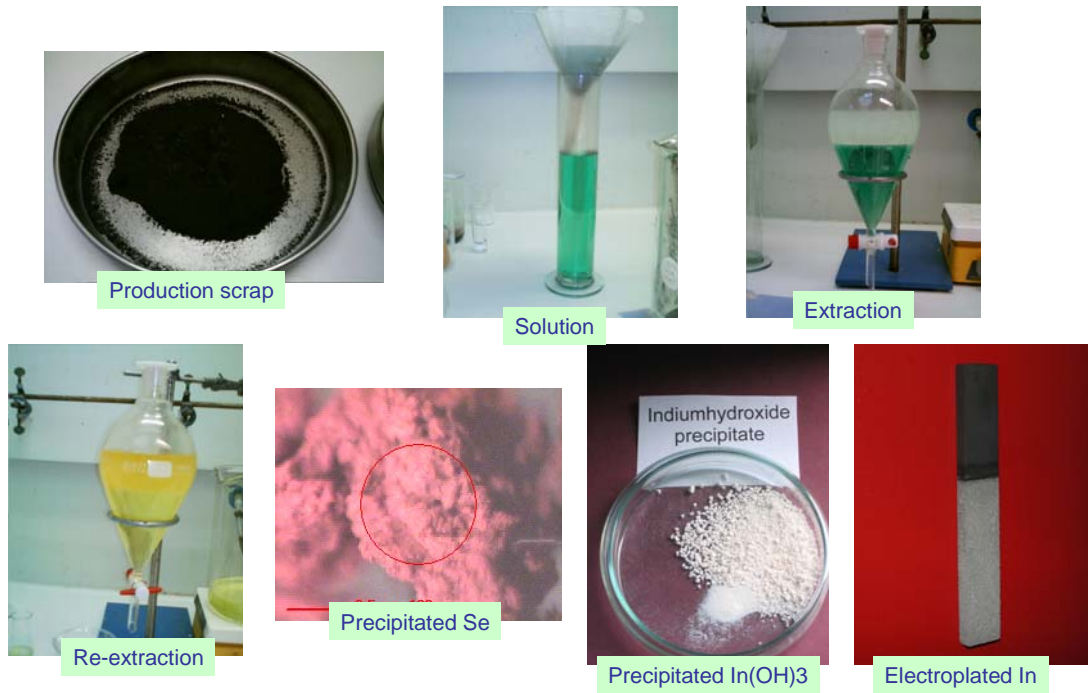


Figure 5: Some pictures from the experiments for the extraction of indium from the manufacturing waste

Table 1: Quantitative results of the recycling experiments: Mass and Energy Flows for 1 kg of raw material (manufacturing waste)

Solutionprocess	
HNO ₃ 65 % [l]	5
Deionised Water	15
Heat [kWh]	2.44
Residuals(Si-C etc.) [g]	295
Extraction	
D2EHPA [l]	6
Toluol [l]	14
Back-extraction	
8 M HCl [l]	20
Precipitation of In(OH)₃ (HCl)	
NaOH 32% [l]	14.40
Output In(OH)₃ (Indium content) [g]	178.2
Precipitation of Selenium from etching liquor (HNO₃)	
Natriumsulfite [g] Na ₂ SO ₃	696
Output red Selenium [g]	435.6
Precipitation Ga(OH)₃ from etching liquor (HNO₃)	
NaOH 32% [l]	6
Output Ga(OH)₃ (Galliumcontent) [g]	69.3

4 CONCLUSIONS

The above described experiments show the following conclusions:

- A recycling path for mixed CIS wastes could be shown
- The process is suited for manufacturing scrap as well as for EoL-modules
- Standard hydrometallurgical processes and chemicals have been used
- Recycling use of the chemicals (acids, solvents, extractants) necessary and possible
- Re-winning of pure indium is feasible
- Further process refinement to be done by respective industries

There are also pyrometallurgical methods available for the recycling of this type of materials (UMICORE). It depends on the specific circumstances at the metal refining company which path will be preferred.

The dramatic increase of CIS production facilities at the end of the SENSE project will hopefully increase the interest of companies such as UMICORE (project partner at the beginning of SENSE) to deal with these materials, at least with the manufacturing wastes, but also with the end-of-life modules.

Recommendations:

- Concentrate on recycling of scraps from manufacturing
- Establish at least re-winning of glass, indium and gallium (selenium)
- Establish co-operation of the growing number of a-Si, CIS and CdTe module manufacturers for recycling of manufacturing scrap
- Look for synergy with LCD recycling
- For EoL modules and take-back solutions establish co-operation of the complete PV-industry (Thin-film and silicon)

CONTACT

Michael Held
Maiya Shibasaki

University of Stuttgart
Chair of Building Physics (LBP)
Department Life Cycle Engineering



University of Stuttgart

Chair of Building Physics (LBP)
Life Cycle Engineering (GaBi)



Hauptstrasse 113
70771 Leinfelden-Echterdingen
Germany

Phone + 49 (0) 711 48 9999-29
Fax + 49 (0) 711 48 9999-11

E-mail michael.held@lbp.uni-stuttgart.de

Internet www.lbpqabi.uni-stuttgart.de