Recovery of Solar Valuable Materials, Enrichment and Decontamination

RESOLVED

LIFE04 ENV/D/000047
Introduction

Photovoltaics (PV) is one of the most promising technologies of the renewable energy sources. In recent years the annual production of PV modules has been growing steadily reaching a total capacity of 3400 MWp installed within the EU in 2006. The thin film technology (CdTe, CIS) gains in importance due to its low production costs and the low energy and materials demands during production. Additionally, the prices for the rare materials indium and tellurium will continue to increase. With the expected strong rise of the demand for thin film PV modules, recycling of indium and tellurium becomes more important in the future.

![Annual average prices for the pure resources Tellurium (99.95 %) and Indium (99.97 %)]

RESOLVED – Project Background

When renewable energy technologies such as photovoltaic systems are compared to fossil fuels there is an even greater expectation, especially among critics, for them to use state-of-the-art technologies in order to achieve environmental compatibility. It is therefore necessary to investigate how further progress can be made in achieving environmental compatibility in manufacture, operation and end-of-life-cycle.

Within the RESOLVED (Recovery of Solar Valuable Materials, Enrichment and Decontamination) project the feasibility of sustainable photovoltaic thin film module recycling by means of wet-mechanical processes is demonstrated. Today recycling of thin film modules – if they are recycled at all – is done by using chemical processes. The wet-mechanical treatment demonstrated in the RESOLVED project can be seen as an alternative and a new approach to the PV recycling with a minimum use of chemicals.

RESOLVED had a budget of 1,147,877 €, of which 563,288 € were contributed by the European Union.

The execution of the works within the project was conducted by:

BAM Federal Institute for Materials Research and Testing

in cooperation with the following partners:

First Solar Inc.

Deutsche Solar AG

Utrecht University

University of Miskolc

The Problem with Recycling of Thin Film PV Modules

The semiconductor layers of important thin film cell types are based on cadmium telluride (CdTe) or copper indium diselenide/disulfide (CIS). These very thin films < 3 µm are encapsulated between two glass plates.

To recover the valuable films the module has to be dismantled. The released semiconductor can be removed afterwards. The last steps are the enrichment of the valuables and the purification of the metals.
Technical Solution

To consider both possibilities – modules with and without glass breakage – a “two-way” closed loop recycling strategy was developed. According to the left hand loop the recycling strategy for modules without glass breakage and production rejects (mostly not laminated coated front glass, which is referred to as sub-modules) was demonstrated. In the first step the end-of-life panel is dismantled thermally to release the semiconductor layers on the front glass. The thermal dismantling step can also be skipped in case of incorrectly coated sub-modules. The valuable semiconductor films can be vacuum-blasted from the glass matrix in the second step. The blasted front glass and the back glass are decontaminated and will be given to the conventional glass recycling. The blasting fines, containing the semiconductor, as well as the blasting abrasive and glass fines, will be later treated by wet-mechanical processes, such as flotation to enrich the valuable materials (CdTe or CIS) in a pre-concentrate.

The right hand loop considers all types of module waste, including broken glass pieces. The treatment of small pieces of broken modules would be nearly impossible using the left hand cycle. This technology includes crushing of all (damaged and undamaged) PV-material in a mill, wet-mechanical treatment of the crushed material by attrition and separation of the semiconductor fines by wet-mechanical processes. Crushing in the mill does not only produce small particles but also leads to the additional destruction of the module compound. In the crushed material, large pieces of the EVA-foil are present besides glass particles of different size with the semiconductor films on the surface. The enrichment follows the left hand loop along the lines by wet-mechanical treatment.
Recycling of Entire Modules or Sub-modules

- **Pre-treatment by Thermal Dismantling:**
  The encapsulant ethylene vinyl acetate (EVA) is destructed at temperatures of 450 – 500 °C. The thermal treatment leads to two single glass plates with the semiconductor on the front glass (CdTe) or back glass (CIS) for the blasting treatment and a clean glass plate.
  Pre-treatment does not apply for sub-modules as they are not encapsulated.

- **Recovery of the Valuables by Vacuum Blasting:**
  Vacuum blasting is a special blasting technique using vacuum instead of air pressure, which is gentler to the glass surface than sand blasting, which is typically used for edge treatment during module production. In this process, a vacuum is created on a limited part of the surface, and as result, the blasting medium hits the surface with high energy. Together with the thin-film material the blast medium is directly evacuated by suction with an industrial vacuum cleaner. With this procedure, dust emissions are prevented and a closed loop of the blast material can be a wide range of conventional materials (e.g., corundum, glass beads, etc).

- **Recovery of the Valuables by Wet Mechanical Treatment Attrition:**
  The technological aim of the attrition is the wet exposure, the release of the semiconductor and the separation of the semiconductor from the glass components. The separation requires the application of energy, which generates a fluid flow and a motion (shear and friction forces) between the particles. Initially, investigations were done with a gyro-wheel mixer. For the demonstration of the wet-mechanical process mixing devices with rotating agitator of the company Maschinenfabrik Gustav Eirich were used. These mixers are typically used during soil washing to separate toxic substances from soil particles. A similar effect is desired in the thin film separation from the glass within the module recycling. A major point is that there is no use of chemicals during that process, as only water addition is necessary.

Recycling of all Modules inclusive Glass Breakage

- **Pre-treatment by Crushing:**
  Crushing of the modules in the mill produces small particles and leads to the destruction of the module compound that the semiconductor film is released from in the wet-mechanical treatment. In the crushed material, large pieces of the EVA-foil are present, as well as glass particles of different sizes, all of which have a semiconductor layer on the surface.
Flotation, Purification and Process Analysis

The products from both recycling pathways (i.e. thermal dismantling followed by blasting and crushing followed by attrition) are then handled by flotation to separate the semiconductor material from the glass. Flotation is a wet-mechanical processing technology widely used in mining industry to concentrate ores or separate minerals from coal.

- **Enrichment of the Valuables by Flotation:**
  The flotation process is a method for the separation of particles from a mixture that consists of the collection of particles on the surface by bubbles. Flotation was chosen to separate the semiconductor material from the rest of the particle mixture and to get a pre-concentrate for the final purification. This is done by making the surface of the semiconductor hydrophobic, so that it can be adsorbed by the bubbles and will ascent to the surface were foam with the flotation product emerges. The glass particles have to be depressed to remain in the water. The flotation product containing the valuables is then removed with the froth. The glass residues remain in the tailings at the bottom of the flotation cell.

- **Purification by Hydrometallurgy**
  The production of semiconductors for PV applications requires extreme high purities of the input materials, i.e. 99.999%, usually called 5N. Waste treatment processes do not yield raw materials of 5N quality, and neither do natural resources, which means that they have to be processed in order to obtain pure materials. The product from flotation is leached with acids to recover the semiconductor materials. The relevant elements Cadmium and Tellurium are then precipitated from solution and fed into the normal production processes for PV module semiconductors. This closes the recycling loop.

- **Process Analysis**
  Processes with high output flows of non-homogeneous materials require a fast and reliable process analysis in order monitor the efficiency of the separation. Classic wet-chemical analysis subsequent to a batch-type sampling procedure cannot provide the necessary data. Within the project, a non-invasive method was developed for application in waste treatment processes with large material flows. Online X-ray fluorescence analysis, which can be used to characterise chemical elements, was used. The analysis is performed in an enclosed space, so that no hazardous matter is emitted to the environment.

The result data flow compares the input flow with the flow of valuables in flotation or attrition, in the flow of tailing and in the carrier medium where the concentration is zero in ideal case.

**Results**

- **Pre-treatment of the Modules**
  Thermal destruction of the EVA-layer had been successfully demonstrated at a temperature of 500°C. The module was divided into two glass plates – one glass with the semiconductor films on its surface and one clean glass. Thermally opened modules were further treated in the blasting process. With the demonstrated crushing methods, the modules were adequately treated for the following wet mechanical separation process.
• Separation of the Semiconductor from the Glass Substrate
Vacuum blasting brought excellent results in semiconductor removal with minimal glass abrasion. The most effective abrasives were glass beads, zirconium oxide, aluminum oxide and iron. The possibility of using various blasting abrasives was proved. The used abrasives were analyzed by Environmental Scanning Electron Microscope (ESEM) and compared to the unused ones. Used abrasives do not show any significant alterations in the surface.

Used blasting abrasive (glass beads), ESEM picture

Wet-mechanical separation was most effective when using the Eirich intensive mixer. The total recovery of CdTe after the attrition process was 78.7 %. While the glass fraction was cleaned, the largest portion of CdTe was transferred into the fraction < 150 µm with a content from initially 643 mg/kg to 2260 mg/kg that could be further enriched by flotation.

CdTe-Material (white) among glass (dark grey) < 150 µm from the attrition process in a 25 L Eirich intensive mixer (ESEM picture, 1000x enlarged)

For the attrition with CIS material, similar results were achieved. Approximately 54 % of the CIS content in the input material was recovered after attrition. 40 % of the recovered semiconductor material was shifted into the fraction 150 µm. The input material for flotation contained 340 mg/kg indium (CIS).

• Enrichment of the Valuables
The feasibility to flotate semiconductor materials (CdTe and CIS) - which is a novel approach - was demonstrated. Several flotation reagents and consumptions for CdTe and CIS material were tested and optimised. The best results for semiconductor enrichment were achieved using the collector group of xanthates. The glass was depressed by sodium silicate (soluble glass).

In the first flotation stage a recovery of CdTe of 70 % was achieved, and the pre-concentrate contained 4 % CdTe.

For CIS material all together 3 % of the entire material was yielded, however, 11 % of the total indium content was accumulated.

Environmental Compatibility of the Recycling Process
Material use is always accompanied by environmental impact. Recycling processes have to be assessed in order to determine whether their impact to the environment is lower compared to other scenarios. Ideally, recycling processes cause no negative impacts to the environment and are beneficial. In order to assess the impacts of the RESOLVED project, a Life Cycle Assessment (LCA) has been performed.

The LCA showed that the recycling pathway with crushing and wet-mechanical treatment is beneficial in all considered categories. The thermal route has disadvantages in the categories global warming, ozone depletion potential and consumption of non-renewable energy. This was due to the fact that this process requires more energy than mechanical steps. However, the module production is not included in the LCA. Tellurium and Indium represent a concern, since these two elements are particularly scarce, and future demand could exceed the amount of known reserves. This fact makes recycling processes even more attractive.


Results from LCA of different recycling options

Conclusions

The most important results of the RESOLVED project are listed as follows:

- A twin-strategy (two coalescing recycling loops) for the thin film PV recycling was developed for the first time.
- The feasibility of the wet mechanical processing of end-of-life modules was demonstrated by using both methods attrition and flotation as well as by the application of the combined thermal, dry mechanical (vacuum blasting) and wet mechanical methods.
- The feasibility of all process steps was demonstrated in the semi technical scale as well as in the laboratory scale.
- A new enclosed and environment-friendly online analysis for treatment of high output flows of non-homogeneous materials was applied and demonstrated.
- It was shown that pre-concentrated valuable materials could be purified via wet mechanical processing. The quality of the purified metals Cd and Te is sufficient for the production of new CdTe modules.
- The Life-Cycle-Analysis (LCA) proved that the recycling strategy, which includes module crushing and wet mechanical separation and enrichment, has clear environmental advantages in comparison with the land-filling and incineration options, as well as in comparison with the thermal treatment, which has detrimental effects because of fuel consumption in the thermal process.
- With the demonstrated recycling the RESOLVED project can make a contribution to the prevention of photovoltaic waste streams and to preserve natural resources.

Future Prospects

Potential for commercialization of the RESOLVED recycling strategy is given. Based on this, a series of research and development activities concerning the improvement of the washing process after attrition, as well as increasing the selectivity of flotation within the recycling procedures will be necessary. Following steps should include the optimisation of the demonstrated single processes and their implementation into a large-scale application. For this purpose the cooperation with appropriate companies would be necessary. Due to the predicted increase in the waste amounts from 2.333 t to 132.750 t in 2030 (Okopol study 2007) and furthermore, the market price constant increase in the last few years of the key materials tellurium and indium used in thin film PV modules, it is predicted that the technology of thin film recycling will be economically feasible in the upcoming years.