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**Light Cycle: Recycling PV Materials**

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The extraordinary development of the photovoltaic market over recent years has emphasized the need for a sustainable method for disposal of PV modules once they reach the end of their life. Recognizing this, the industry has been busy developing strategies and techniques that make the most of the valuable materials contained in their products and simultaneously improve their positive environmental impact. David Appleyard reports

Sleek, modern and high-tech, with a lifespan of 25 years or more, it is sometimes difficult to imagine a photovoltaic module being disposed of. Indeed, with the first significant volumes of PV installations only really beginning in the early 1990s, the appearance of large numbers of end-of-life modules are still another 10 or 15 years away. 

The issue of life-cycle assessment and ultimate disposal of retired modules and materials has nonetheless long been a significant one for the industry. In the face of rapid growth over recent years, and projections of continued growth despite the economic downturn, this issue has gathered momentum. At around 3800 tonnes, the total PV waste expected in Europe for 2008 is still relatively small. However, this figure is expected to double every two to four years, and is forecast to reach 35,000 tonnes in 2020.

The majority of Europe’s photovoltaic producers are German and the country is currently home to the world’s largest PV market. Furthermore, given its early lead in Europe, it is no surprise that Germany will be the first European country to see large volumes of PV modules reaching the end of their operational lives and becoming a disposal issue. PV waste generated in the country accounted for about 80% by mass in 2008 and it is forecast to still be producing around half of all European PV waste in 2020. Logic suggests that it will also be one of the first countries to develop dedicated facilities for PV materials recovery processes.

However, in Europe, second place in terms of installed solar PV is held by Spain, followed by the Netherlands, Italy, France, Austria, Luxembourg and the UK. Such nations would also be expected to progressively develop appropriate infrastructure as their requirements grow, which itself depends to a certain extent on future PV market development.

What format such infrastructure would take would further depend on how the individual national markets develop. For instance, in Germany there is a broad mix of both utility-scale installations and much smaller domestic units. This compares with Spain, which is dominated by larger grid-connected applications or, say France, where BIPV holds a significant share. Beyond Europe, there are the large US and Asian markets, particularly Japan, to consider.

**Technologies and treatments**

The market share, materials prices, availability, and consumption during production, are all factors that determine the economic threshold for materials recovery, but PV modules contain various high value materials which in many cases can be economically recovered. Indeed, materials shortages – a notable example coming from silicon – can limit growth in the industry and increase prices. Recycling is therefore one option that can ease materials supply constraints. Research into module recycling started at an international level at the beginning of the 1990s, with companies like AEG and successors, Pilkington Solar International GmbH, BP Solar, Siemens Solar, Soltech, Solar Cells Inc. – a precursor to FirstSolar – and institutes such as AIST, Japan and BNL, USA, all getting involved.

The range of technologies representing the current PV product market is sufficiently broad to require a variety of approaches to recycling and materials recovery. Currently, there are two major groups; crystalline and thin-film. For modules with crystalline solar cells the recovery of silicon, metals and especially silver are particularly important. For thin-film technology the key high value materials are metals, including tellurium and indium.

Although many companies are actively considering the issues involved, First Solar, the US-based thin-film manufacturer, and Deutsche Solar AG – whose systems cover crystalline silicon modules – are the only two companies to have implemented active module recycling schemes to date.

**Squeezing value from waste**

Crystalline PV technologies still have a market share of more than 90% in Europe and even as this decreases, the total recycling load will remain proportionately dominated by crystalline modules over the coming decades.

Karsten Wambach, head of SolarMaterial, a business unit of Deutsche Solar AG, oversees the pioneering work at the company in materials recovery and Life Cycle Analysis (LCA). By developing a benchmarking system with core research, the company aims to quantify the avoided carbon dioxide emissions and energy payback time that result from the recycling process, for instance considering factors such as the energy saved during primary silicon production. He says the company was conceived with an environmental policy along the whole value chain, and is fundamentally concerned with optimizing the entire process on an economic and environmental basis.

In the past, the main focus of the recycling efforts had been the recovery of complete cells, which were separated from the module by means of thermal decomposition of the plastic encapsulation. Recovered wafers were then reprocessed in an etching line and used for new module assemblies with no apparent loss in performance.

The technique proved that old silicon wafers maintain quality and display good long-term stability, with the energy balance calculation in one trial recycling operation showing that the original modules had an Energy-Pay-Back time (EPBT) of seven years, a figure which fell to two years with modules using recovered cells.

However, as the thickness of wafers decreases it is expected to become more difficult to recover intact cells and, today, the main focus is to recover the silicon as a raw material, recovering separate pure fractions of different metals, glass and silicon. A primary requirement of such a strategy is that any recovered silicon must be pure enough for reuse in wafer manufacturing and have low costs.

In the current recycling process, In the current recycling process, despite any damage to the returned products, all the modules – complete or crushed – are thermally decomposed. Next, the different materials are separated from each other, for example by density and sieving. Silicon cell materials are then etched in a similar series of processes to remove metallization layers, anti-reflective coatings and so on. During the removal of the metallization layer the silver typically found in older modules is dissolved in acids and then precipitated before finally being recovered by electrolysis. With more modern aluminium backside metallization silver content is lower, but research suggests that the silver can still be economically recovered.

After crushing and etching, the silicon material is melted and directionally solidified. In general, the edges, tops and bottoms of the ingots are cut off and recycled as well. The bricks are cut to solar wafers which can be sold to cell manufacturers.



Table 1, above, shows the composition of crystalline modules and the quantities typically recovered through the recycling process.

Having launched a pilot recycling plant in 2003, the company has now developed a proprietary technique to recycle solar PV materials, with a particular focus on technology relating to broken cells. Solar silicon by-products like cut-offs of crystals, ingots or bricks, broken wafers and process failures, have became an important material source. Indeed, recycled materials always had a long tradition in crystalline solar silicon technology and make a significant contribution to the company’s feedstocks, supplying up to 40% including scrap from the semiconductor industry in the 1990s, around 20% of the increased global total demand today. Silicon to be reclaimed is sourced from pot scrap, the sides, tops or bottoms of multicrystalline ingots and wafer breakageand even by-products of poly silicon manufacturing. However, depending on the production process, in each case the material is contaminated to varying degrees and the recovery process must be adapted to reflect this.

With recycling of silicon developed to such a point that it allows assurance of feedstock supply while maintaining the high purity required by PV applications, recycling under current market conditions appears cost effective for many kinds of material. Further improvements to the processes are expected to maintain cost effectiveness even if the market conditions change and, market aside, efficient silicon recycling always carries an environmental benefit when compared to the primary production of silicon, the company says.

**Thin-film turns up the volume**

Though the market share of thin-film technologies remains relatively small, led by CdTe and CIS type modules, it is expected to grow dramatically over the coming years (see *Renewable Energy World*, Jan/Feb 2008, pages 32–40). The proportion of thin-film technologies in newly installed systems is expected to increase to at least 20%–30% by 2020. Even newer technologies, such as pigment-based cells, are also forecast to grow to form a significant share by 2020.

While the major constituents of the active medium of most thin-film products, indium and tellurium, are not particularly rare elements – both are obtained as by-products of metals production, copper and zinc respectively – supply and demand may still critically affect potential growth. The semiconductor layer is normally less than 1% of the module composition for thin-film technologies.

In one recycling process, initially a thermal treatment removes the EVA bonding layer allowing the module to be separated into the various components. The front glass can then be removed and collected for glass recycling while the pane with the semiconductor material can be treated chemically.

The environmental impact of thin-film recycling processes is negligibly small in comparison with the production processes and it is reasonable to conclude that recycling such modules will result in a lower environmental impact. Recycling CIGS and CdTe modules also secures valuable resources (indium, tellurium, selenium).

For polycrystalline thin-film CdTe modules, a mixture of mineral acids and hydrogen peroxide solution may be used to remove the semiconductor layer. Afterwards the solution is passed through a chelating resin column, for the removal of copper and iron, and a cation-exchange resin to remove cadmium and iron. In a subsequent treatment cadmium (Cd) is recovered by electrolytic deposition and tellurium (Te) by reactive precipitation. An alternative treatment involves treating crushed modules in an attrition process. Due to the shear and friction forces on the surface of the particles the semiconductor material is separated from the glass particles.

The take-back and recycle strategy launched by FirstSolar, which supplies CdTe modules, is also based on a crushing process. The modules are shredded and crushed in a hammer-mill into approximately 4–5 mm pieces – small enough to ensure the lamination bond is broken. The semiconductor films are removed by the addition of acid in a slowly rotating, stainless steel drum. The drum is emptied into a classifier where glass materials are separated from the metal-rich liquids, which move on to the precipitation unit. The metal compounds are precipitated in three stages at increasing pH and are concentrated in a thickening tank. A resulting filter cake or ‘cullet’ is further processed by a third party to separate the various component materials for use in new modules. Using the process, 95% of the semiconductor material is recycled for use in new modules, together with 90% of the glass.

The company, which is unique in offering a pre-funded collection and recycling scheme, says its module recycling process enables substantially all components of its frameless modules to be recovered, sourcing valuable materials, and reducing the life cycle energy consumption. Industrial-scale recycling facilities are located at each of its plants.

FirstSolar says the programme is designed to provide collection and recycling of waste modules at no additional cost to customers, reducing the number of PV modules that are disposed of as waste at end-of-life. Their initiative sets aside the estimated future cost of collecting and recycling the modules at the time of sale.

Lisa Krueger, who heads up FirstSolar’s sustainable development group, says that the company’s policy of ‘Product Life Cycle Management’ or extended producer responsibility formed part of its earliest foundations.

As with Deutsche Solar, FirstSolar’s strategy included a product life cycle analysis to determine the full impacts of the product from the sourcing of raw materials, through manufacturing, transportation to project site and the module collection and recycling components. The company says that the results of this analysis indicate that CdTe PV technology has the lowest carbon footprint of all current PV technologies, primarily due to its lower energy use during module production, and achieves the lowest energy payback time.

**Sowing the seeds of change**

Individual company initiatives aside, in response to the growing demand for a robust approach to dealing with the entire product life cycle, in May 2007, Germany’s renewable energy agency the BSW and the European Photovoltaic Industry Association (EPIA), commissioned a study on the development of a take-back and recovery system for photovoltaic products. Completed in March 2008, this study on the relevant technical, ecological, economic, legal and political parameters is the basis for the work of the European ‘PV Cycle Association’, which was founded in Brussels in July 2007.

An open association, with 37 members, currently representing some 75% of the European photovoltaic market, this voluntary industry body was created in order to provide a focused approach to realizing an adequate recovery system for end-of-life PV modules, together with any intermediate products or those damaged during their transport, assembly or operational phases.

By taking responsibility for PV modules throughout their entire value chain and clearly addressing future recycling needs now, the industry hopes to offer true sustainability, very much in line with its consumer perception of a ‘clean’ energy option.

Given that the PV industry is still relatively young, it is perhaps not surprising that it is already taking into consideration the environmental impacts of all stages of the product lifecycle. Taking early action may also possibly head off potential legislative interdicts, the like of which have been imposed on other related manufacturing sectors such as consumer microelectronics, for instance under the EU’s WEEE Directive.

Certainly EU policy shows a clear trend towards waste avoidance, recycling and eco-design requirements. FirstSolar’s Krueger notes that similar factors are driving the US market, particularly in California. Achieving recycling goals without legislation keeps the full organizational and cost control within the PV industry, an obvious advantage. But even so, Jan Clyncke, managing director of PV Cycle, points out that the PV industry is the only manufacturing sector to have devised, developed and implemented its own recycling programme. It is through PV Cycle that the photovoltaic industry plans to install an overall waste management and recycling policy across the EU, the wider European Economic Area (EEA), which includes nations such as Norway and one separate EFTA country, Switzerland.

In December 2008, members signed a joint declaration committing them to set up a scheme to collect a minimum of 65% of all modules installed in Europe since 1990 and to recycle 85% of the waste. The alliance adds that minimum collection, as well as the recycling rates of the voluntary system, will be significantly above those of any waste Directive, even if future review processes establish higher minimum rates.

Already covering 31 countries, the PV Cycle initiative as envisaged hopes to demonstrate that it is both possible and profitable to implement region-wide take-back and recycle structure for PV products that will have at its heart high value recycling, with no materials being disposed of either through landfill or incineration.

Succeeding will undoubtedly encourage other markets such as the US and Japan to adopt similar policies. And by counting companies such as GE, Sanyo and Sharp among its membership, PV Cycle could already be judged a global-scale PV initiative. ‘Co-operation is excellent, including with those companies outside of Europe,’ observes Wambach. Nonetheless, its immediate focus is clearly Europe and inevitably considerable obstacles remain to be overcome.

Acknowledging that the targets are ambitious, Clyncke comments: ‘We are not aiming for 27 solutions, it is not required with an appropriate structure.’ Besides which, he adds, the EU provides a tool with a Communication on voluntary agreements. This sets out seven criteria such as targets, consideration for civil society, and so forth, which acts as the basis for the first draft on the PV Cycle voluntary initiative. The group hopes to commence negotiations with the European Commission in April this year (2009) and once these discussions are finalized it is likely that the document will be sent to both the EU Council and Parliament for further feedback and comment.

Clyncke is optimistic that a completed agreement will be ready in the next six to nine months and expects that with an EC stamp of approval, the acceptance and implementation of the strategy by the various national authorities will become that much easier. The association has a logistics model close to completion, together with its associated costing estimates.

**The goal of the closed loop industry**

It is already clear from the development of the PV market and the range of products available, that any recycling system must be able, not least for economic reasons, to treat a wide range of different products. This range of products is also expected to expand over time as new technologies reach commercial volumes.

Certainly processes for other technologies are under development, although some doubt remains over how rapidly commercial technologies will emerge. SolarMaterial has already developed a new process which is capable of managing most types of solar modules, including those from different manufacturers. Although still at pilot stage, in due course the company is looking to commercialize the process and is currently looking for investment partners. Even so, while they have made an early start, Wambach notes that there is ‘a lot of activity, with many companies looking at recycling.’

A key future development is likely to see recycling built into new PV products. Krueger points out that module designs are already changing from both a cost and an environmental perspective, in a process of continuous improvement. An example comes from the use of frameless modules, which have dispensed with the requirement for an aluminium frame found in earlier types.

‘There are still many questions to answer’, says Clyncke, ‘but we are making some important decisions. ‘Ultimately’, he adds, ‘it is the market which will give us the right direction.’

Observing that as the first industry to implement such a scheme, it will have to learn by experience without the benefit of comparison with other waste flows, Clyncke says: ‘We cannot look to benchmark from other industries, this is the challenge.’

But, with two different operational processes already able to successfully and economically treat modules of both major types, it seems that perhaps, as young as it is, the PV industry is leading the way.

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