Cycling critical absorber materials of CdTe- and CIGS-photovoltaics

Material efficiency along the life-cycle

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Abstract

Chalcogenide (CdTe) and chalcopyrite (CIGS, CIS) photovoltaic (PV) production increased on average over a 100 % per year during the last decade. The used semiconducting compounds (II-VI, I-III-VI_2 compounds and their quaternary and pentenary alloys) are especially suitable for solar cells due to their high absorption coefficient, their long-term stable performance and their fast processability. Due to their high absorption coefficient, very thin-layers (< 2 µm) are sufficient to absorb most of the useful spectrum of the light. However, used absorber materials such as indium (In) and tellurium (Te) are regarded as critical and their limited availability and their high costs can, to a certain extent, impede the deployment of those PV technologies. Therefore, this work analyses how efficiency measures along the life-cycle of CdTe- and CIGS-PV modules can reduce the net-demand for these materials. Efficiency measures include the decrease of the specific material content of the solar cell (i.e. amount of material per power), the decrease of the material input in production, the recycling of production waste, and the end-of-life recycling of PV modules. Several recycling technologies for CIGS- and CdTe-PV modules have been developed in the last years which recycle the thin-film materials. This work describes possible recycling paths based on proven recycling concepts. Afterwards it is estimated how much tellurium can potentially be recovered from CdTe-PV production and end-of-life waste to substitute for “primary” tellurium. Then there is an assessment of how material efficiency measures along the module’s life-cycle can reduce the net material demand for CIGS and CdTe solar modules and thus the material costs. The results show that recycling technologies are sufficiently explored and commercially available, although they are not yet economically viable (costs exceed revenues). Should Te be recycled from end-of-life modules, the CdTe-PV industry has the potential to fully rely on recycled Te as of 2038. This is possible because demand begins to decline after 2020 despite market growth due to efficiency measures during production and at product level. If end-of-life modules were to provide 20% of the production feedstock, and 60-85 % of the material feedstock is used, then the costs for the technical grade Te could increase by 260 % and indium 430 %, respectively, and both technologies would still be competitive against crystalline silicon photovoltaics. However, in the long term the photovoltaic future might not rely on current critical materials but instead on low cost and more abundant materials such as iron pyrite or organics. Until then both CIGS- and CdTe-PV can support a high share of the photovoltaic market if the materials are used efficiently.

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List of abbreviations

AGR	Annual growth rate
Cd	Cadmium
CdTe	Cadmium telluride
CIGS	Stands for the compounds $CuInSe_2$, $Cu(In,Ga)Se_2$, $Cu(In,Ga)S_2$, and $Cu(In,Ga)(Se,S)_2$
Cu	Copper
E_g	Band gap
EPIA	European Photovoltaics Industry Association
EPR	Extended producer responsibility
Ga	Gallium
GW	Giga watt
IC	Integrated Circuit
In	Indium
MFA	Material flow analysis
MW	Mega watt
OLED	Organic light emitting diode
PV	Photovoltaics
RFID	Radio frequency identification
S	Sulphur
Se	Selenium
Te	Tellurium
US DoE	U.S. Department of Energy
W_p	Watt peak

1 Introduction

1.1 Motivation and aim

Photovoltaic (PV) energy generation is one of the most advanced renewable energy technologies. Solar modules having a capacity of more than 51 GW generated 4 % of the European energy demand in 2011 (EPIA, 2012). A variety of PV technologies are available or under development. The first generation, silicon technologies, still dominates the market with a market share of 92 % in 2011(Hering, 2012). However, the second generation, based on inorganic compound semiconductors, experienced high growth rates of over a 100 % annually in the last decade (Figure 1-1). The most prominent technologies within the second generation are cadmium telluride (CdTe), copper-indium-gallium-diselenide (CIGS) or copper-indium-selenide (CIS) solar cells. The rapid market growth led to a surge of the demand for the employed materials such as indium, gallium and tellurium, which are regarded as critical (section 2.2). Their availability and costs might, to a certain extent, restrict the market development of those technologies (section 2.4). Therefore, this work assesses how resource efficiency measures along the life-cycle of those “thin-film” PV modules reduce the material demand, as well as when and to which extent recycled material from end-of-life modules can substitute for “primary” material.

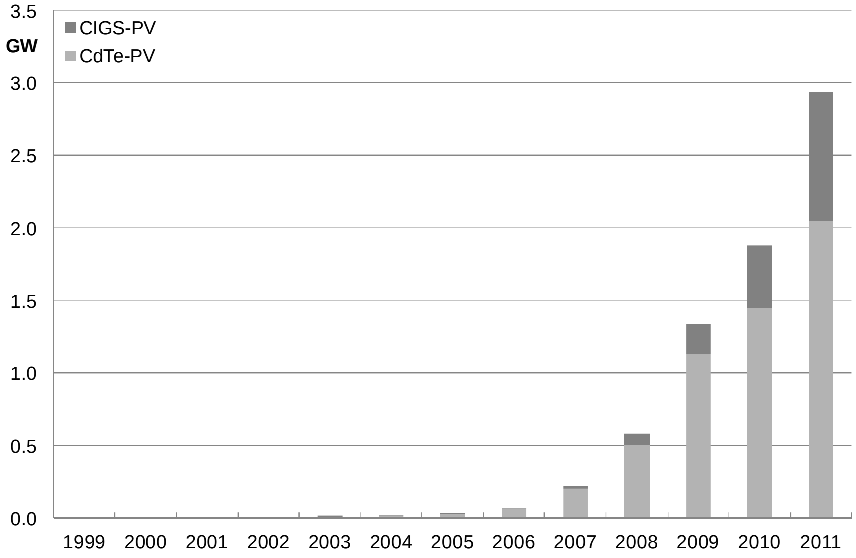

Figure 1-1: CdTe- and CIGS-PV production in giga watt peak (GWp) (Hering, 2012)

1.2 Research approach and thesis structure

The following steps were taken during this research based on the general procedure for material flow studies (Brunner and Rechberger, 2004; van der Voet, 2001). The steps were not necessarily taken subsequently (Figure 1-2)

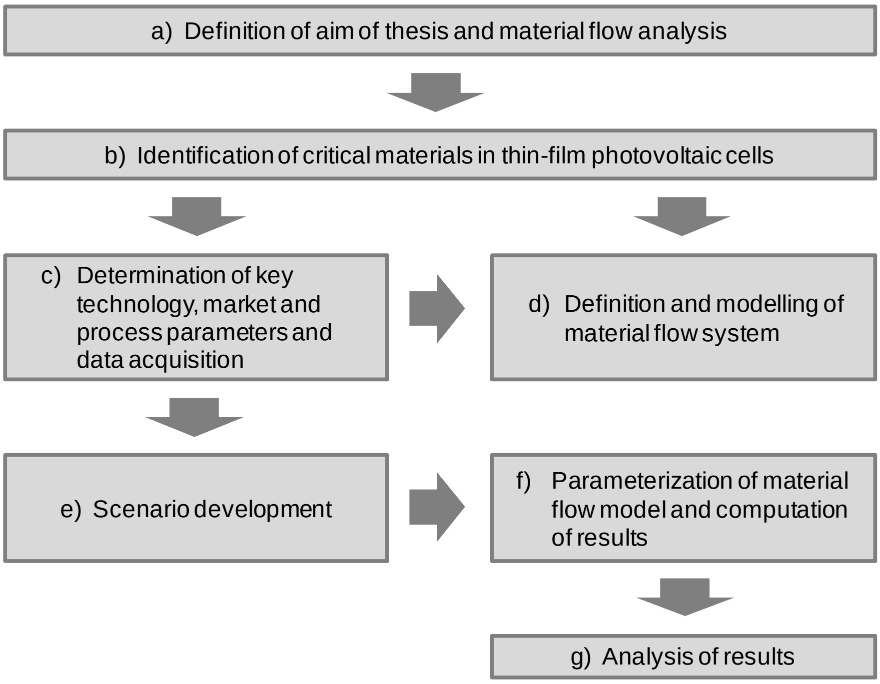

Figure 1-2: Approach

a) The aim of this thesis is to estimate the influence of resource efficiency measures along the life-cycle of CIGS- and CdTe-PV modules on the flows of critical absorber materials. The appropriate method for this task is to conduct a “Material Flow Analysis (MFA)”. A short introduction to the method is given in chapter 1.3 and further described in sections 4.2 and 5.2.
b) In chapter 2 the criticality of materials used for CdTe and CIGS solar cells are analyzed. First the composition of CIGS and CdTe solar cells is described (section 2.1). Then those materials regarded as critical are identified by a meta-analysis of criticality studies (section 2.2). Key data about the availability of the identified critical materials are presented in section 2.3. Studies that estimate possible restrictions to the development of CdTe- and CIGS-PV through the availability of the critical materials are reviewed in section 2.4. A résumé explaining the need of a detailed MFA is given in section 2.5.
c) In order to define the material flow model in time and space, to set the system boundaries, to identify relevant materials, processes, flows and stocks, key parameters influencing the material use along the life-cycle of CdTe- and CIGS-PV modules need to be determined. The required data was collected via expert interviews and desktop research. The interviews were partly carried out during the research project „Material efficiency and resource conservation (MaRess)“[1] and a study commissioned on *NanoSolar’s* behalf assessing recycling concepts for CIGS solar modules[2]. Further

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[1] Materialeffizienz- und Ressourcenschonung, Bundesumweltministerium, 2007-2010

[2] Basisstudie im Auftrag der Firma. Nanosolar, “Recyclingkonzepte für CIGS-Solarmodule“, TU Berlin, Institut Technischer Umweltschutz, Fachgebiet Abfallwirtschaft, 2010

information was collected during the first and second “Conference on PV Module Recycling” and the “28th European PV Solar Energy Conference and Exhibition“. Part of the information gained was used to describe feasible recycling paths for CdTe- and CIGS-PV (chapter 3), published in (Marwede et al., 2013).

d) Based on the collected information, the life-cycle of PV modules was modeled using the freeware STAN developed at TU Vienna.
e) Scenarios were developed based on the collected information. A set of parameters for the material flow system was determined for each scenario and the scenarios were described in a storyline.
f) Based on the model and the scenarios two MFAs were conducted and published, submitted for publication respectively:
    1. An estimation of future tellurium recycling flows from CdTe-PV for different technology pathways and market developments (chapter 4, Marwede and Reller (2012)).
    2. A comparison of life-cycle material costs for CdTe- and CIGS-PV modules on the basis of life-cycle material flows under different material efficiency scenarios (chapter 5, Marwede and Reller[3]).
g) In chapter 6 the results are summarized and discussed in order conclude with future prospects.

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[3] Marwede M, Reller A. Estimation of life-cycle material costs of CdTe- and CIGS-PV absorber materials based on life-cycle material flows: Manuscript submitted for publication.

1.3 Methodology “life-cycle flows of critical materials”

Figure 1-3 shows the used methods within this thesis. Information was collected via several sources in order to develop scenarios used to compute the life cycle flows of CdTe- and CIGS-PV with the help of (dynamic) material flow analyses.

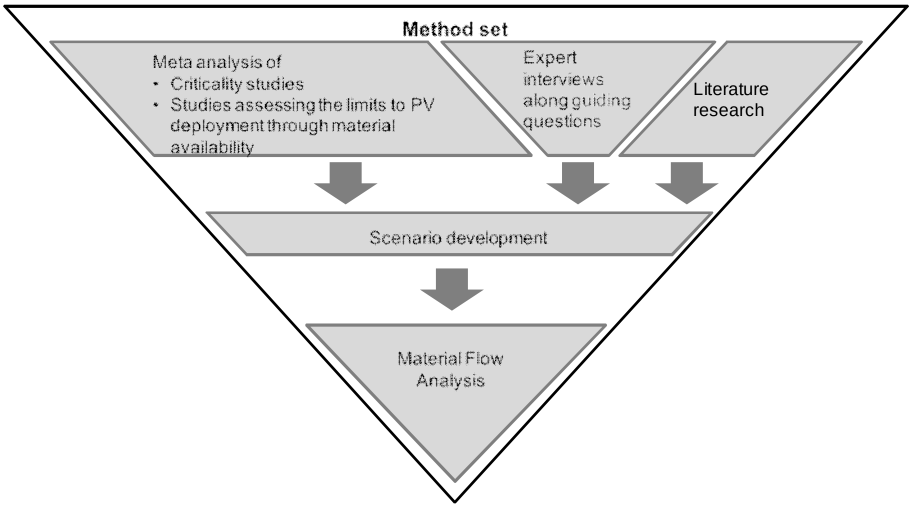

Figure 1-3: Method set

A meta-analysis of criticality[4] studies is conducted to identify the most critical materials used for CIGS- and CdTe-PV. Also reviewed are studies that estimate possible restrictions to the development of CdTe- and CIGS-PV through the availability of the critical materials in order to identify the most limiting materials. To obtain the information required to design the material flow model and develop scenarios, existing literature was reviewed and experts were interviewed. The literature review included scientific research articles, technology reviews, conference articles and technology roadmaps in order to gain information about the status quo of processing technologies and product characteristics as well as their future development. To complement the picture, 43 experts from various points in the value creation chain (equipment manufacturing, PV module production, recycling, metal refining and research) were interviewed to obtain data a) which is not publicly available and b) is based on the current state of the art. Part of the information gathered has not been published before because it is sensible information or derived from work in the research and development stage. Guiding questions (appendix A.2) were developed for the interviews which were then journalized and evaluated together.

The information gained in the expert interviews, during the meta-analyses and literature research was used to write an overview about current recycling technologies for CdTe- and CIGS-PV modules (chapter 3). Another part of the information was used to design the material flow model and develop scenarios. For each scenario a set of parameters (and flows) was determined, which reflect current, and future technological and market

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[4] There is no clear definition of the term “critical” with respect to materials. In general the criticality of a material is based on the assessment of its availability, the vulnerability of the consumers to supply restrictions and ecological risks. The criticality is expressed qualitatively or quantitatively by using various indicators such as depletion time, concentration of production, recyclability, substitutability, price volatility, future demand and many more. In academia the assessment of criticality is a relatively new research field. Materials are assessed on a national, global or regional level or for single technologies or industry sectors. Moreover ecological, political, social and technical aspects are connected to criticality (Achzet, 2012).

developments in each life-cycle phase and its uncertainties by using lower end, realistic and optimistic values. Market scenarios and technology trajectories were developed for the dynamic material flow analysis.

Scenarios should not be seen as “real” future developments, but as hints on how to make decisions in light of possible or preferable “futures”. A scenario constructs a possible future which is bound to conditions or incidents, which will have been fulfilled or happened between now and a future point in time. *Explorative* scenarios deal with past and present trends and develop probable futures. “What happens, if …?“ is the right question. On the other hand, *normative* scenarios describe a path to a desired future; normally the steps are developed backwards from a desired situation in the future. The questions to be asked are: “Is it possible to reach this future, and which measures have to be taken?”. (Durance and Godet, 2010; Shell, 2008; Wehnert and Jörß, 2009)

In practice, both approaches meld as is the case in this work. On the one hand, future material flows will be estimated based on market and technology developments. On the other hand, different technology pathways are compared in order to analyze their effect on material use. The flows are estimated using a material flow analysis (MFA). A general description of the method is given in the following paragraph. Further details on the model itself can be found in the sections 4.2 and 5.2.

A MFA regards physical material flows of the economy as an industrial metabolism (Ayres, 1989). Material flows include the transfer, storage and transformation of materials within a material flow system and the exchange of materials with the system environment (Brunner and Rechberger, 2004). A MFA can be used to estimate the material throughput or intensity of an economy, but also on a smaller scale to assess recycling systems. A MFA helps to identify key influencing factors, opportunities for optimization as well as unexpected or hidden material flows and inventories in an economy or in the environment (Bouman et al., 2000; Brunner and Ma, 2009). To estimate future material flows, the formerly static MFA was modified to dynamic models (Elshkaki et al., 2005; Kleijn et al., 2000; Melo, 1999). The main difference between the static and dynamic models is the consideration of stocks (van der Voet, 2001).

Within a material flow system, material is exchanged between processes (production and recycling), the inventory and sinks (e.g. land filling of end-of-life modules). A process is defined by its transfer coefficients. A transfer coefficient ($0 < a_{jk} < 1$) determines, which part of an input F_{ij} to process P_j is transferred to the subsequent process P_k (with m number of processes and sinks).

$$F_{jk}^{out}(t) = a_{jk} F_{ij}^{in}(t) \;\; for\; i \neq j \; and \;\; j \neq k; \forall\; i, j, k \in [1,...,m] \tag{1-1}$$

With side conditions

Mass balance:

$$\sum_{k=1}^{n} a_{jk} = 1 \text{ for } \mathrm{j} = 1,.., \mathrm{n} \text{ (n : number of processes)} \tag{1-2}$$

Sinks have no outflow:

$$a_{jk} = 0 \text{ for } \mathrm{j} = \mathrm{n}+1,...,\mathrm{m} \text{ (m - n : numberof sinks)} \tag{1-3}$$

Material flows and stock influence each other. A stock grows when the inflow is higher than the outflow. Due to the mass balance the change of a stock S in time equals:

$$\frac{dS}{dt} = F^{in}(t) - F^{out}(t) \qquad \text{1-4}$$

Stocks are important to predict future waste streams of products with long lifetimes, e.g. PV modules (Kleijn et al., 2000). The outflow of a stock is determined by the average lifetime of a product. Some of the products will reach their end-of-life earlier than the average, others later. Unfortunately, empirical data on the lifetime of products is often not available. However, the lifetime of a product can be modeled using a probability density function *f(t)*, in order to predict recycling flows and achieve a reasonable picture of the change in material stocks. The probability p_t that a product has a lifetime of *t* years equals with *T* as continuous random variable:

$$p_t = P(t \le T \le t+1) = \int_t^{t+1} f(\tau)d\tau \qquad \text{1-5}$$

The outflow of a stock $F^{out}(a)$ in year *a* equals the sum of the inflows from previous years multiplied by the probability p_t of a product being discarded after *t* years.

$$F^{out}(a) = \sum_{t=o}^{a} p_t \bullet F^{in}(a-t) \qquad \text{1-6}$$

Using formula (1-4) the stock at the time a+1 results in

$$S(a+1) = S(a) + F^{in}(a) - \sum_{t=0}^{a} p_t F^{in}(a-t) \qquad \text{1-7}$$

In order to determine today's flows from the past, historical flows and life expectancies have to be known. Uncertainties are covered by scenarios inter alia because statistics for the future do not exist.

2 Composition of hetero-junction solar cells and criticality of applied materials

This chapter deals with the criticality of absorber materials and the impact of their limited availability on the deployment of CdTe- and CIGS-PV. Section 2.1 describes the composition of hetero-junction solar cells and modules. The constituents regarded as critical are identified (section 2.2) by screening various criticality studies. For each critical material the most important facts are summed up and an explanation is given as to why they are regarded as critical (section 2.3). Section 2.4 summarizes the results of studies assessing to which extent the availability of some materials can restrict the development of CdTe and CIGS-PV. A short résumé is given in section 2.5.

2.1 Composition of the absorber of hetero-junction solar cells

The principle of the photovoltaic effect is based on the transfer of light quanta on the electronic subsystem of a semiconductor and the “collection” of their energy before it’s transferred into heat. An internal field of a semiconductor junction is needed for this energy collection. The most important type of semiconductor junction is the pn-junction. There are two different types of pn-junctions: the homo-junction and the hetero-junction. The homo-junctions joins p- and n-type layers of the same material and band-gap, for example p-Si/n-Si. Hetero-junctions are composed of semiconducting compounds with different band-gaps – for example a p-type CdTe in contact with an n-type CdS. Typical semiconductor compounds are chalcogenides (II-VI compounds) or chalcopyrites (I-III-VI_2- compounds and their quaternary and pentenary alloys). In principle III-V compound solar cells such as InP and GaAs also show excellent photovoltaic properties. However, material and processing costs of those are so high that they are only used for space applications and potentially for terrestrial concentrating PV-systems. (Pfisterer, 2003; Scheer and Schock, 2011)

These compounds are generally not amphoteric which means they show either p- or n-conductivity. Compounds which differ significantly in their band-gap E_g are joined together to form the pn-junction of the solar cell. The semiconductor with the lower band-gap determines the voltage of the solar cell. This is the decisive part of the hetero-junction and is called the “absorber”. Its optimal band-gap is the same as of homo-junction solar cells, i.e. in between 1.3 and 1.6 eV.. The other part is called the “collector”. It should have a wide-band gap to absorb just a small part of the solar spectrum, but its conductivity should still be sufficient. Both parts have to match with regards to their lattice constant, thermal expansion coefficient, and electron affinity. Incongruences of these parameters results in the formation of so-called interface states which increase the recombination losses. So called “buffer” might be necessary to compensate the mismatch. The choice of the appropriate buffer layer has a high influence on the conversion efficiency. (Pfisterer, 2003; Reiß, 2003)

Three different structures of hetero-junction solar cells exist (Pfisterer, 2003):

1. The absorber sits on top in a *front-wall* solar cell – facing the sun. The photon-generated carrier density is the highest at the surface of the absorber. Thus charge carriers have to cross the whole absorber to be collected at the junction. The spectral sensitivity equals $h\nu > E_g(absorber)$.

2. The collector is placed in front of a *back-wall* solar cell. Depending on its thickness and its optical and electronic characteristics it might contribute to the photo-current. If not, the spectral sensitivity covers the range
$E_g(\mathit{absorber}) < h\nu < E_g(\mathit{collector})$.
3. The *window-absorber* structure is a special case of the *back-wall* structure. It is the optimal structure for a hetero-junction. It works as a “window” in case the band-gap of the collector is sufficiently wide. The incidental light is mainly absorbed near the immediate neighborhood of the pn-junction so that charge separation and collection work under ideal conditions.

Figure 2-1 shows a substrate (a) and superstrate (b) layout of a window-absorber hetero-junction. A typical CdTe solar module consists of n-ITO/n-CdS/p-CdTe (ITO = Indium-Tin-Oxide) with very thin CdS-layers acting solely as buffer layers plus a back contact. The photovoltaic module is called CI(G)S if the absorber is based on $CuInSe_2$ or the compounds $Cu(In,Ga)Se_2$, $Cu(In,Ga)S_2$ and $Cu(In,Ga)(Se,S)_2$ (chalcopyrites). More details about the material composition of CdTe- and CIGS-PV modules can be found in sections 3.2 and 5.3.1.

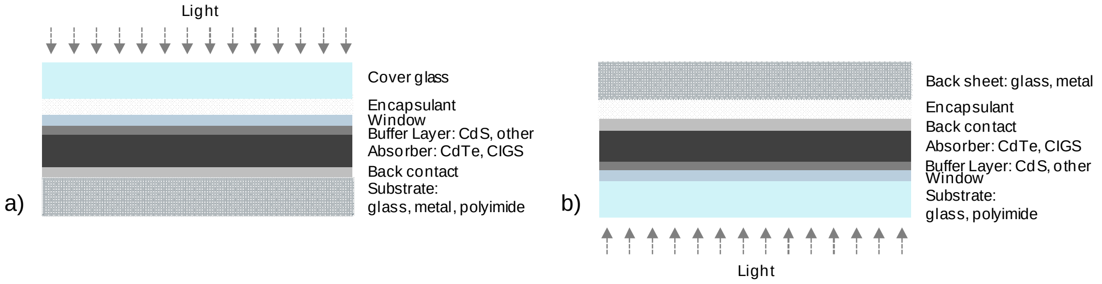

Figure 2-1: Substrate (a) and superstrate (b) structure of a window-absorber hetero-junction solar module

2.2 Criticality of absorber materials

A meta-analysis of 11 different criticality studies was conducted to see which absorber materials are regarded as critical. The results can be seen in Table 2-1. The studies address different geographical and technological levels. They concentrate either on national economies or the world economy. Nassar et al. (2012) estimate the criticality of materials from the copper family for a putative CIGS- and CdTe-PV manufacturer. Five of the studies restrict the perspective to certain technologies, for example energy or green technologies, which often include CIGS- and CdTe-PV. Some studies assess just a few elements of the periodic table while others include a wide range of elements. Sulphur is addressed in none of the studies.

In general, Cu is regarded as non-critical. In and Ga are rated as critical from nearly all studies apart from US Department of Energy (2011) which regards only In as near-critical in the short term for clean energy technologies in the US. Se is generally valuated as less critical than In and Ga. Te is regarded as highly critical for green technologies, i.e. CdTe-PV. Details about the critical absorber materials In, Ga, and Te are presented in the following section. Additionally, the current state of the research about Cd emissions during the life-cycle of CdTe-PV modules and the toxicity of the compound cadmium telluride are summed up.

Study	Scope	Cu	In	Ga	Se	Cd	Te
(Achzet et al., 2011)[a)]	World, energy technologies	Trade: M	Reserves: M Trade: H Ecological impact: L Processing: L Substitutability: L Recyclability: M	Reserves: M Trade: H Ecological impact: L Processing: L Substitutability: M Recyclability: H		Ecologic impact: H Others: L	Reserves: M Trade: H Ecological impact: M Processing: L Substitutability: L Recyclability: M
(Angerer et al., 2009)	World, demand of emerging technologies in 2030	Low demand	High demand	High demand	Low demand		
(APS, 2012)	USA, emerging energy technologies		Critical	Critical	Critical		Critical
(Buchert et al., 2009)	World, sustainable technologies		Short-term: Serious supply restrictions Rapid demand growth	Short-term: Serious supply restrictions Rapid demand growth			Short-term: Serious supply restrictions Rapid demand growth
(ECN, 2010a)	EU	Not critical	Critical	Critical			Not Critical (High economic importance)
(Erdmann et al., 2011)	GE	Middle criticality	High criticality	High criticality	Middle criticality		Middle criticality
(Morley and Eatherley, 2008)[b)]	UK	Rank 49 of 61	Rank 47 of 61	Rank 46 of 61	Rank 53 of 61		Rank 42 of 61
(Moss et al., 2011)	EU, supply chain risk for low carbon technologies		High risk	High risk	Medium risk	Low risk	High risk
(Nassar et al., 2012)[c)]	Putative CdTe- and CIGS-PV manufacturer	32 (100)			52 (100)		58 (100)

Study	Scope	Cu	In	Ga	Se	Cd	Te
(Nassar et al., 2012)	USA	44 (100)			45(100)		40(100)
(Nassar et al., 2012) c)	Global	32(100)			47(100)		33 (100)
(NRC, 2008)	USA	Not critical	Critical	Not critical			
(US DoE, 2011)	USA, clean energy technologies		Near-critical (short-term) Not critical (medium term)	Not critical (short term) Not critical (medium term)			Near critical (short-term) Near critical (medium-term)

Table 2-1: Assessment of criticality of absorber materials by various studies

blank: not available
a) H: risks from known constraints; M: risks from potential constraints; L: no known constraints
b) Materials are ranked in order of a decreasing “Material Insecurity Index” based on an analysis of nine criteria affecting material security, i.e. rank 1 is the most insecure.
c) Criticality vector magnitude: highest score is 100

2.3 Fact sheets

2.3.1 Indium (In)

Annual production[a)]	670
Reserves[b)]	n/a
Price[c)]	685 $/kg
Crustal abundance	0.05 ppm

a) Excludes US production
b) Not available
c) Price (2011) is based on 99.99%-minimum-purity indium at warehouse (Rotterdam) (USGS, 2013)

Properties

Indium is a crystal-line, silvery-white metal – element of main group III (boron group). Some indium compounds are semiconductors (Achzet et al., 2011). Indium is not regarded as toxic (Noël, 2003).

Origin, production and reserves

The abundance of indium is higher than that of silver, i.e. 0.05 ppm at the Earth's crust (Noël, 2003; Phipps et al., 2008). However, indium does not occur in native states. It is found as trace element in base metal sulphides – particularly chalcopyrite, sphalerite, and stannite (USGS, 2013). Thus indium is only produced in conjunction with zinc, copper and lead (Achzet et al., 2011). As a result, exact numbers for reserves are unavailable. However, there are considerable reserves of zinc, and metal producers report increasing extraction rates from metal sulphides – other than zinc – containing as little as 100 ppm indium (Achzet et al., 2011; Phipps et al., 2008). Moreover, recent improvements of recovery process technologies make the treatment of tailings and slags economically viable when the price is high (Phipps et al., 2008; USGS, 2013). In 2012 the world refinery production of indium equaled 670 tons. China currently controls nearly 60 % of the world's refined indium production and the Chinese government restricts indium exports with a combination of export quotas and export tax (Achzet et al., 2011; ECN, 2010b; USGS, 2013). Global consumption of primary and secondary In in 2011 was estimated to be more than 1,800 tons. Secondary In is reclaimed mainly from ITO production scrap (Green, 2012; Phipps et al., 2008; USGS, 2012b).

Green (2012) estimates a maximum of 600 t/year of In available for PV in the distant future with a nearly zero growth rate potential, apart from recycling. This is roughly in line with calculations from Fthenakis (2009), who estimates that the amount of In extractable from Zn production, which is available for CIGS-PV, peaks around 2055 at 700 t. End-of-life module recycling would add another 250 t at this time.

Uses

Indium is mainly used as Indium-Tin-Oxide (ITO) for transparent contacts in flat panel displays. ITO manufacturers are the fiercest competitors to manufacturers of CIGS-PV because they have the ability to pay much more for the element on per area basis than the CIGS-PV industry can (Woodhouse et al., 2012). Besides In is used for used for semiconducting compounds for example in light emitting diodes or CIGS solar cells. (Fthenakis, 2009) estimates that 5 % of the primary In production is used for CIGS PV, which is higher than the numbers stated by (Achzet et al., 2011) in Figure 2-2. Other uses are alloys and surface coatings.

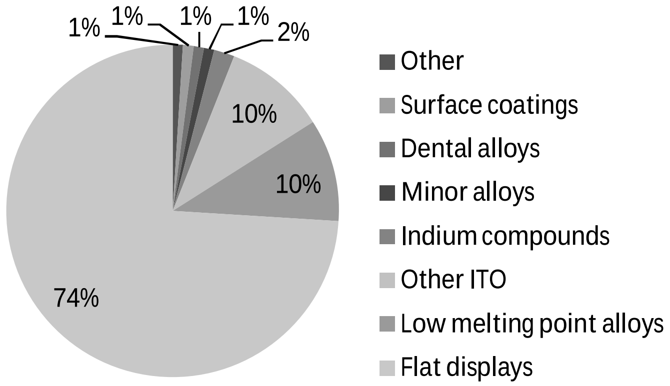

Figure 2-2: Uses of indium (Achzet et al., 2011)

Price

After the French zinc producer Metaleurope closed its Pb/Zn/In smelter in France in 2003, the Japanese ITO manufacturers that served the LCD industry had to seek new sources primarily in China. However, Chinese suppliers could not make up for the drop in supply. This led to a dramatic price increase between 2002 and 2005 because the LCD industry was massively growing during this time (Figure 2-5). As part of the supply response to the rapid growth in demand, global secondary production of indium and recycled indium increased significantly from 2005 through 2007 (in conjunction with a price drop), when it accounted for a greater share of total indium production than primary production. Global ITO demand continued to rise until 2011, leading to some price spikes caused by supply deficits (US DoE, 2011). In 2012 the average indium price was 10-25 % lower than in 2011 due to slow and uncertain world economy in 2012 (Metal Pages, 2012; USGS, 2013).

Substitutability

A possible substitute for ITO is Antimony-Tin-Oxide (ATO). However, antimony is also regarded as rare and is hazardous to human health. Possible non-rare alternatives for ITO which have already been developed are carbon nanotube coatings, poly-ethylene dioxythiophene (PEDOT) and graphene quantum dots. GaAs can substitute for In compounds in solar cells and other semiconductor applications. (Achzet et al., 2011; USGS, 2013)

Recyclability

Indium is mostly recovered from production scrap from ITO and indium sputtering, which includes the spent targets and chamber scrapings. An estimated 60-70% of the indium on spent targets is recycled (Hsieh et al., 2009; Mikolajczak, 2009; Speirs et al., 2011). ITO recycling is mainly done in China, Japan, and the Republic of Korea – the countries where ITO production and sputtering take place. Several processes have been developed to recover In from CIGS productions scrap and CIGS modules (chapter 3). Fthenakis (2009) estimates that about 60 t of In will be set free in 2040 through end-of-life recycling of CIGS-PV modules. It is also possible to reclaim indium from scrapped flat panel displays

(Jalalpoor et al., in press). However, making recycling of In from CIGS-PV modules and flat-panels economically viable remains a challenge (Achzet et al., 2011; USGS, 2013).

Criticality aspects

The criticality of In originates mainly from its concentration of supply (countries and refineries) and the limitation to expand production (co-product) in combination with an expected growth in demand due to its importance for key high technologies. Although substitutes have been developed, they are yet to be used in commercial products. Also, post-consumer recycling of displays and solar cells has to proof prove its economic viability, even though it is technically possible. (Achzet et al., 2011; Buchert et al., 2009; ECN, 2010b; Erdmann et al., 2011; Morley and Eatherley, 2008; Moss et al., 2011; US DoE, 2011)

2.3.2 Gallium (Ga)

Annual production[a)]	273 t
Reserves	n.A.
Price[a)]	688 $/kg
Crustal abundance	16 ppm

a) Estimated based on the average values of U.S. imports for 99.9999%- and 99.99999%-pure gallium in 2011. (USGS, 2013)

Properties

Gallium is a silvery, white metal. Compounds of Ga with elements of main group V show semiconducting properties. Gallium is only slightly toxic. (Greber, 2003; Green, 2012)

Origin, production and reserves

With an average concentration of 16 ppm in the Earth's crust, Ga is one of the rarer elements; about as abundant as Pb. Minerals containing Ga are not considered of economic importance due to their extreme rarity. Ga is mainly produced as a by-product of aluminum-oxide. Gallium concentration in bauxite ranges between 0.003 % and 0.008 %, depending on the location. Data on the reserves and production of Ga is difficult to obtain and unreliable, because the actual recoverable amount of Ga is not disclosed. However, the United States Geological Survey (USGS) estimates the world resources of Ga to exceed 1 billion kilograms, however, only a small part of Ga bound in bauxite and zinc ores is actually economically recoverable (USGS, 2013). Ga primary production was estimated to be 273 t worldwide in 2012, whereas production capacity was estimated to be 468 t: 270 t refinery capacity, and 198 t recycling capacity (USGS, 2013). Dittrich et al. (2011) estimate 800 t per year to be potentially available from bauxite with the use of present technology (as reported in Green, 2012). (Achzet et al., 2011; Greber, 2003; Green, 2012; USGS, 2013)

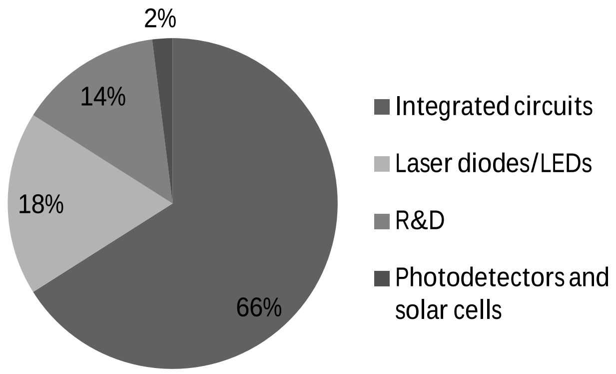

Figure 2-3: Uses of gallium (Achzet et al., 2011)

Uses

Ga combined with elements of the main group V (GaAs, GaN …) is used in semiconductor components. About 2/3 of annual Ga production is used for integrated circuits (ICs) for high-frequency applications, and 1/3 for opto-electronics (light-emitting diodes, laser-diodes, photo-detectors, solar cells) (Graedel and Erdmann, 2012). A small portion of annual production is used for special alloys and for research. A rise in demand is especially expected from LEDs and photovoltaics as well as GaAs/GaN based electronic components, e.g. in smart-phones, optical communication, and power electronics. (Buchert et al., 2009; USGS, 2013)

Price

In Figure 2-5 the historical Ga prices between 2002 and 2012 are plotted. The price of gallium dropped from greater than 2,300 $/kg peak in 2001 to the 200–300 $/kg range in 2002 due to the bursting of the tech bubble (exaggerated expectations of the cell phone market), the 2001 economic recession and the accumulation of stocks. The price spiked temporarily at 850 $/kg during 2007. Since 2010 a number of factors were driving up demand for Ga such as the growing demand for smart-phones, for CIGS solar cells, and for high-brightness LEDs. In mid 2011 the average price had increased to 985 $/kg. However, prices fell again because the expectations in the LED market growth were overrated. The average price in 2012 was 556 $/kg. (US DoE, 2011; USGS, 2012b, 2013).

Substitutability

LEDs based on organic compounds (so called OLEDs) can potentially replace conventional LEDs. They are already used as displays in small electronic devices replacing liquid crystal displays (LCDs) with LED backlights (Deubzer et al., 2012). For some applications SiGe is a possible alternative for GaAs based hetero-junction bipolar transistors, but there are no substitutes for GaAs or GaN based ICs in certain applications owing to their unique properties (USGS, 2013). All other non-gallium containing solar cell technologies can replace CIGS and GaAs solar cells.

Recyclability

Current end-of-life recycling rates for Ga are below 1 % (Graedel et al., 2011), but substantial quantities of post-industrial scrap generated in the manufacture of GaAs-base devices are reprocessed (USGS, 2013). Also Ga from CIGS manufacturing scrap is recycled (Olivier Bracher, personal communication, 25.09.2012). In principal it is possible to recycle Ga from CIGS modules. However, an economic recycling of the small amounts of gallium found in semiconductor components such as solar cells or ICs is probably difficult to achieve (Achzet et al., 2011).

Criticality aspects

The main factors influencing the availability of Ga are a high expected demand growth for economic important emerging technologies coupled with the limited possibility to expand production (Erdmann et al., 2011; Moss et al., 2011; US DoE, 2011). Furthermore substitutability is difficult, at least in some application, due to the good performance of the Ga compound semiconductors (Morley and Eatherley, 2008). Moreover a future recycling of Ga from (opto-)electronic devices will probably be difficult because of the tiny content distributed over many products(Achzet et al., 2011).

2.3.3 Tellurium (Te)

Annual production	500-550 t
Reserves[a)]	24,000 t
Price[b)]	350 $/kg
Crustal abundance	0.01 ppm

a) Estimates include tellurium contained in copper resources only
b) Average price in 2011 published by Metal-Pages for 99.95% tellurium. (USGS, 2012b, 2013)

Properties

Tellurium is a crystalline, bright silver-white metal, which is rather brittle and easily crushed. Tellurium is a p-type semiconductor which demonstrates the phenomenon of piezoelectricity and becomes superconductive at 3.3 K. Some Te compounds have very good thermoelectric properties (see uses). Elemental Te is generally considered to be less toxic than Se, but organic compounds and reactive tellurides (e.g. H_2Te) can be a health hazard. Indications of carcinogenic, teratogenic, or mutagenic effects of tellurium or its compounds are not known. (Knockaert, 2003)

Origin and production

The abundance of tellurium in the earth's crust is comparable to that of platinum, 0.01 ppm (Knockaert, 2003). However, the Te concentration in minerals is insufficient to allow an economic recovery as a principal mining product; therefore, it depends on the concentration in the processing of other non-ferrous metals like copper, zinc, gold, and lead. Copper ores are the primary source of commercial Te, with more than 90 % of the Te coming from anode slimes collected from electrolytic copper refining (USGS, 2013). Te reserves contained in copper resources are estimated to 24,000 t (USGS, 2013). Te found in anode slimes from copper electro-refining were an estimated 1,300 t in 2005 (Green, 2006) and 1,200 t in 2006 (Ojebuoboh, 2008); 30 % to 45 % of the Te content in the slime is recovered as metal product (ECN, 2010b; Ojebuoboh, 2008). Hence in 2005/2006 360 to 585 t Te were produced. For 2010, the United States Geological survey estimates the annual Te production to be between 500 and 550 t (George, 2012). In case of a growing Te demand, Te production can be increased through higher recovery rates of Te from anode slimes as well as through increased copper production driven by the global economy. Scenarios predict an annual Te production of 1,400 t in 2020 (Fthenakis, 2009) and 1,850 t in 2030 from copper electro-refining. On the other hand the copper industry is moving to cheaper extraction methods – solvent extraction, electro-winning versus electrolytic recovery – which means that Te output may be lower pro rata of copper output in the future (ECN, 2010b). However, there are also known Te-rich mineral deposits in China and Mexico from which direct mining of Te is economically sustainable, containing in total about 2,500 t of Te (Green, 2012; USGS, 2011). In 2010 the Chinese company *Apollo Solar Energy* started mining Te from the two Chinese mines, the Dashuigou and Majiagou projects, containing 765 t of Te (USGS, 2011). The company expects to obtain approximately 50% to 60% of the Te needed for their products by the end of 2011 from those mines (Apollo Solar Energy, Inc, 2011). A five year purchase contract between Apollo Solar and an unknown CdTe-PV manufacturer has been signed to provide 5N Te with projected sales of about 110 Mio US-$ (Apollo Solar Energy, Inc, 2010).

Uses

Te is used for metallurgy, in the chemical industry, and for electronic devices like PV, flash memory, CDs, DVDs, infrared and thermoelectric devices. The highest demand growth is foreseen for electronic devices and CdTe-PV. (ECN, 2010b; Green, 2006; Morley and Eatherley, 2008; Ojebuoboh, 2008).

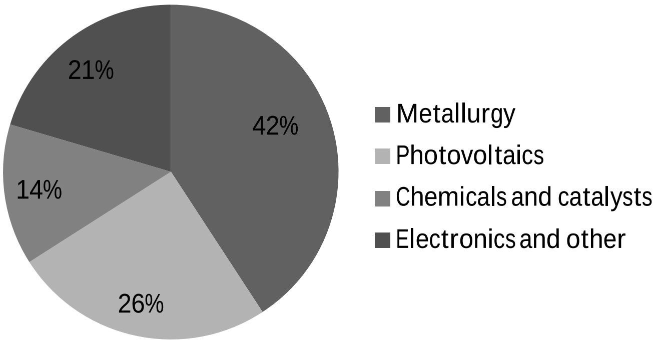

Figure 2-4: Uses of tellurium (Achzet et al., 2011)

Price

The price of Te increased dramatically in 2010 until it peaked in mid-2011 at 430 $/kg before decreasing to 118 $/kg by the end of 2012 (Figure 2-5). Some of the price increase was attributed to speculative buying based on belief that supplies would not meet the growing demand for Te in solar cells (US DoE, 2011). The price of Te significantly decreased in 2012 because the solar cell market oversupply caused several CdTe-PV manufacturers to file for bankruptcy or curtail production (First Solar, 2012a; pv-magazine, 2012a, 2012b; USGS, 2013).

Substitutability

Several materials can replace Te for most uses – usually combined with losses in production efficiency or product characteristics. Bismuth, calcium, lead, phosphorus, selenium, and sulphur can be used in place of tellurium as an alloying additive in steel. Several of the chemical process reactions catalyzed by tellurium can be carried out with other catalysts or by means of non-catalyzed processes. The selenium-tellurium photoreceptors used in some xerographic copiers and laser printers have been replaced by organic photoreceptors in newer machines. A direct substitution of Te in CdTe solar cells is not possible. Technologies such as GIGS solar cells or amorphous silicon solar cells are the two direct competitors. (ECN, 2010b; USGS, 2013)

Recyclability

Recovery of industrial scrap from the deposition process in the PV industry provides a growing stream of secondary tellurium. However, this will decrease through time as the deposition processes become more efficient and the sector growth levels off (ECN, 2010b; Marwede and Reller, 2012). Tellurium cannot be recycled from ferrous scrap due to its dilution as an alloying element (Moss et al., 2011). The metal refineries *Umicore*, Belgium and *Dowa*, Japan can recycle Te from electronic scrap (flash memory), but actual production levels from recycling feed are currently low (Moss et al., 2011). End-of-life streams of CdTe-PV modules are expected to arise from 2030 onwards (Fthenakis, 2009; Zuser and Rechberger, 2011). Zuser and Rechberger (2011) estimate that in 2040 900 t of Te will be available from PV module recycling. According to Fthenakis (2009) the annual Te availability will be increased by 240-250 t in 2040 through end-of-life recycling.

Criticality aspects

A high supply risk is seen for Te because of its high reliance on imports (Nassar et al., 2012) and its high economic importance (ECN, 2010b; US DoE, 2011) combined with the lack of substitutability and the limitations to expand production capacity (co-product) (Morley and Eatherley, 2008; Moss et al., 2011). However, a short-term supply shortage which was foreseen by Moss et al. (2011) and Buchert et al. (2009) seems unlikely owing to the current consolidation of the PV industry as one of the main demand sectors.

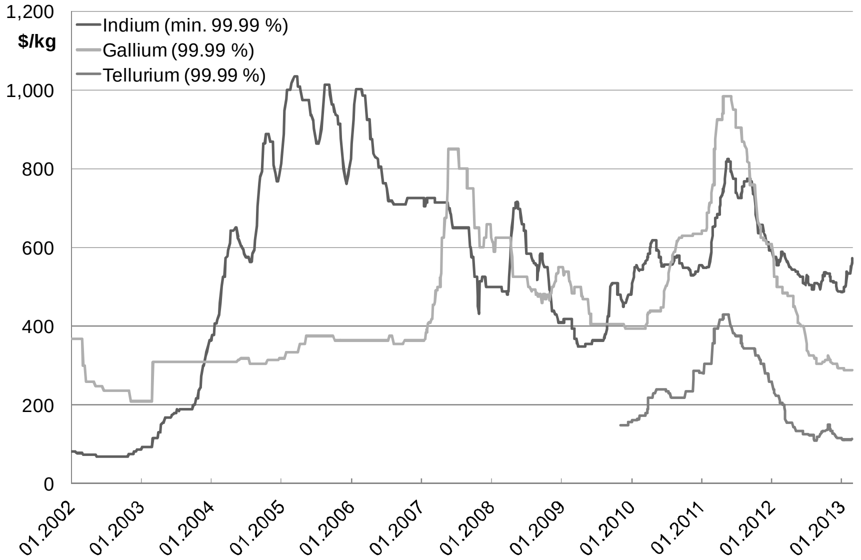

Figure 2-5: Historical indium, gallium, and tellurium prices in the EU (Metal Pages, 2013)

2.3.4 Cadmium (Cd) and environmental and health risks of cadmium telluride in PV modules

Annual production	23,000 t
Reserves	500,000 t
Price[a)]	1.98 $/kg
Crustal abundance	0.08-0.5 ppm

a) Average New York dealer price for 99.95% purity in 5-short-ton lots (USGS, 2013)

Cadmium is a soft, ductile, silver-white metal. Its occurrence is estimated to be between 0.08 and 0.5 ppm at the earth's crust. Cadmium is only economically recovered from zinc minerals (Schulte-Schrepping and Piscator, 2003).

Cadmium is classified as toxic. As a result of the environmental and health concerns, the use if the metal is decreasing and its use legally banned (Achzet 2011) – apart from some exemptions – for example in Europe for the use in photovoltaic panels (European Parliament, 2011). However, the legal ban of Cd use for PV was already controversially discussed before the last final draft of the corresponding directive (pv magazine, 2010). The toxicity of the compound cadmium telluride has been explored to a much lesser extent. Some studies suggest that CdTe is carcinogenic and that it harms the environment (Sollmann and Podewils, 2009). Some studies conclude that the compound CdTe is less toxic than Cd alone (Fthenakis and Zweibel, 2003; NGI, 2010; Sollmann and Podewils, 2009; Zayed and Philippe, 2009). However, no documentation on the environmental long-term behavior of CdTe is available (NGI, 2010).

Cadmium bound in CdTe-PV modules could be released during production of the modules, the use phase and at end-of-life. The emissions during module production depend primarily on the processes employed (section 4.3.3). Fthenakis (2004a) estimates that in case of electro-deposition of CdTe combined with chemical surface deposition of CdS, not more than 1 % of the Cd and Te used would be lost in the forms of very dilute liquid and waste streams – after recycling of the residuals. In vapor transport deposition, a process used by the largest manufacturer *First Solar*, 10-30 % of the feedstock materials (CdTe, CdS, $CdCl_2$) may eventually be disposed of as cadmium-contaminated solid waste. In both cases, the Cd is collected and safely disposed or recycled (Fthenakis, 2004a).

During the use-phase, emissions of Cd are very unlikely, because Cd in CdTe-PV modules is present as a chemically stable compound, which is enclosed and sealed in between two glass sheets. One argument in favor of the Cd use for PV is that sequestering Cd in PV modules is more environmental friendly than leaving the Cd in the waste stream of zinc mining – provided that there is a sound recycling of the end-of-life modules (Raugei and Fthenakis, 2010). During use Cd can potentially be released in the event of fire. However, experiments demonstrated that in this case, most of the CdTe is encapsulated in the molten glass matrix (Fthenakis et al., 2005). Even in the unlikely event that all Cd is released during fire, the concentration of Cd in the air stays well below critical levels according to model calculations by LFU Bayern (2011).

At the end-of-life, Cd could leak from modules in abandoned landfills or from uncontrolled dumping of modules. The risk of uncontrolled spreading of Te and Cd connected to deposited CdTe modules in approved landfills is considered to be low, but uncontrolled dumping will result in substantially greater environmental risks (NGI, 2010). In hydrometallurgical module recycling processes run by *First Solar,* 95-97 % of the thin-film layers were recovered and end up in a filter cake (Krueger, 2010; Lisa Krueger, personal communication, 07.09.2009). The CdTe producer *5N* recycles up to 95 % of the Cd from recycling residues and production scrap (Huot, 2011). This means that in the best case 8 % of the Cd contained in the modules will be wasted and presumably safely disposed at end-of-life. Despite established recycling programs and legal requirements it is impossible to ensure that all end-of-life CdTe-modules will enter the correct recycling chain. For example, if modules are treated (accidently) in glass recycling plants, staff can be exposed to dust containing Cd originating from the shredding and crushing processes (Roland Pohl, personal communication, 23.06.2010; Pohl and Kummer, 2010).

All in all, appropriate treatment reduces waste containing Cd to a minimum. However, improper treatment of waste containing CdTe, or uncontrolled dumping of the modules can result in environmental and health risks.

2.4 Possible restrictions to the development of the CdTe and CIGS-PV market due to the availability of critical absorber materials

Several studies assessed if the availability and costs of absorber materials (Te, Ga and In) limit the market development of CI(G)S- and CdTe-PV (Andersson, 2000; Feltrin and Freundlich, 2008; Fthenakis, 2009; Green, 2012; Wadia et al., 2009; Zuser and Rechberger, 2011; Zweibel, 2010)[5]. The studies deal with limitations by resource availability estimating:

1. the maximum annual PV production with annually refined absorber material,
2. the maximal cumulative capacity or maximal electricity generation with available reserves, or
3. the material demand as a result of market scenarios (Zuser and Rechberger, 2011).

Table A-1 (Appendix A.3) shows the results of Andersson (2000), Feltrin and Freundlich (2008), Fthenakis (2009), and Zweibel (2010), who estimated the maximum producible PV capacity either based on yearly production or on reserves. It is difficult to compare the results because of differing assumptions about available reserves, (future) material production, photovoltaic market developments and the specific material demand per watt peak (W_p). Additionally these values change over time due to economic and technological developments. Despite those factors, indium and tellurium are generally identified as the limiting materials for the deployment of CIGS- and CdTe-PV, therefore the following discussion is limited to these two materials.

The cumulative CdTe- and CIGS-PV production predicted by Feltrin and Freundlich (2008) and Andersson (2000) would be reached in between 2015 and 2017 – if one believes that their assumptions about the specific material demand are right and the annual market growth rates of both technologies equal the average of the last decade (over 100 %). However, these assumptions are unrealistic for several reasons:

a) Available reserves change over time and Te reserves associated with copper mines are currently estimated to be higher than in 2000 and 2004, respectively. Furthermore, new possible sources can be tapped if prices are high enough.

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[5] Wadia et al. (2009) will not be discussed further in the following paragraphs, because they base their calculations on theoretical maximum conversion efficiencies and absorber layer thicknesses and thus reaching far higher production capacities.

b) Growth rates over a 100 % in the coming years seem implausible due to the current poor market situation. Furthermore, rapid growth cannot possibly be maintained due to the limitations through annual Te production (see below).
c) The specific material demand cannot be assumed to be static due to changes of production processes, module composition, and conversion efficiencies.

Nevertheless, both studies indicate that the cumulative CIGS-PV production achievable is lower than that of CdTe-PV. Also Zuser and Rechberger (2011) show that in a very optimistic market scenario the cumulative material need will be several times higher than the reserves[6].

Figure 2-6 shows the annual CIGS- and CdTe-PV production possible through annual Te and In availability compared to total annual PV production of the accelerated PV market scenario developed by the European Photovoltaic Industry Association (EPIA, 2011). Both technologies together could support around 40-100 % of total PV production in 2020 and 2030 according to estimations by Fthenakis (2009). CIGS- and CdTe-PV can even surpass predicted annual production according to the estimations by Andersson (2000) and Zweibel (2010). However, both Andersson (2000) and Zweibel (2010) neglect material losses during production and their assumptions for the specific material demand (t/GW_p) are quite optimistic. Therefore, Fthenakis' (2009) estimations can be judged as more realistic. However, even in Fthenakis' (2009) optimistic scenarios, average annual growth rates (AGR) until 2030 would equal 13 % for CdTe-PV and 23 % for CIGS-PV – much less than the average AGR between 2001 and 2011 of over a 100 % for each technology (Figure 1-1). Green (2012) estimates that the Te supply available for PV in 2020 would just cover the demand in case CdTe-PV production grows less than 26 % annually. Zuser and Rechberger (2011) predicts that annual In and Te demand at peak times between 2010 and 2040 will be several times higher than current production. All these estimations clearly show that the market growth of both technologies will be restricted to a certain extent by the availability of material.

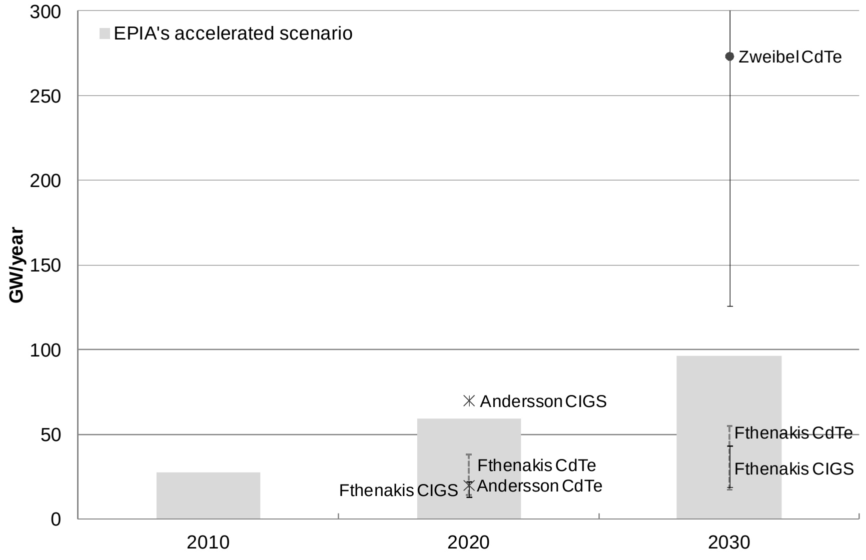

Figure 2-6: Annual CdTe- and CIGS-PV production range constrained by annual material availability against annual PV production in EPIA's accelerated scenario (Andersson, 2000; EPIA, 2011; Fthenakis, 2009; Zweibel, 2010)

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[6] Zuser and Rechberger (2011) states indium reserves as 5,600 t.

Apart from the material amount available, the material price plays a role for the competitiveness of the PV industry. The authors Green (2012), Woodhouse et al. (2012), and Woodhouse et al. (in press) look at the maximal allowable price for the absorber materials. In 2011 the semiconductor grade CdTe compound price contribution to the total module price of 0.74 \$/W_p was around 0.06-0.08 \$/W_p (Woodhouse et al., in press). Green (2012) assumes that thin-film modules would have to be able to be sold profitably at well under 50 US-¢/W_p by 2020 due to the expected price reductions in mainstream silicon products. Technical grade Te would have to cost less than 3.33 ¢/W_p in case semiconductor grade tellurium required for the solar cell costs three times as much, corresponding to an allowable technical grade Te price of 470-510 \$/kg in 2020 (65-71 t Te per GW_p). This would be 35-45 % higher than the Te price in 2011. Woodhouse et al. (in press) computes that by 2030 CdTe-PV modules could be produced at 47 US-¢/W_p (21 t Te per GW_p). The CdTe-compound price, consisting of the costs for the technical grade materials and a tolling charge, could then increase 100 \$/(kg·year) to about 2,400 \$/kg in 2030 with material costs being still below 10.5 ¢/W_p during the whole period (Woodhouse et al., in press).

Green (2012) calculates In costs of 6 ¢/W_p at an average indium price of 674 \$/kg (83 t In per GW_p). He concludes that even without extra tolling costs for converting In to a suitable purity, this would still be too high to be competitive in the present market. Woodhouse et al. (2012) estimate In and Ga material costs to be lower: 2.3 ¢/W_p for CIGS solar cells (23 t In and 7.5 t Ga per GW_p). Through intensive recycling of production scrap, 20 % module efficiency and an absorber layer thickness of 1 µm, the In material intensity could be reduced to around 6.3 t/GW_p. This would enable the absorption of material price increase of 2.6 times the prices in 2012 (Woodhouse et al., 2012). However, these are long term goals.

The price analyses show that both technologies can potentially absorb a price increase. How high depends on the possible reduction of the material demand per giga-watt peak – which is achieved by material efficiency measures in manufacturing and technological developments at product level (conversion efficiencies, absorber layer thickness) – as well as the price of competing photovoltaic technologies.

2.5 Résumé

Some conclusions can be drawn from this chapter. Criticality studies indicate that of all absorber materials in CdTe and CIGS solar cells, Ga, In and Te are especially regarded as critical. Furthermore, Te and In are the limiting materials for the expansion of CdTe- and CIGS-PV. However, the estimations of potential PV production on the basis of current annual production and reserves are unsatisfactory because both values depend on many factors and are therefore changing. Andersson (2000), Fthenakis (2009), Green (2012), and Zweibel (2010) circumvent this static approach by estimating future annual material production. Results based on theses estimations indicate that market growth for both technologies cannot keep up with the pace of the last decade. However, even with low annual growth both technologies together can probably support up to 100 % of annual photovoltaic installation in 2020 and 2030. All existing and emerging PV technologies together (compound, silicon, organic and concentrating solar cells …) can therefore support a much higher market development in the future. However, high material prices due to supply and demand imbalances can have an increasingly negative influence on cost reduction amongst others because display producers as the main competitors to CIGS-PV producers can absorb a higher price increase. Furthermore, a substitution of In or Te in the compound is not possible. The capability to absorb a price increase depends on the technological developments of the modules and the production processes. Material efficiency measures both on module and process level are part of the solution to handle possible constraints. Future recycling potentials – both from end-of-life products and within the value chain – are not yet fully understood and warrant future study (Candelise et al., 2011). Therefore, the following chapters deal with:

1) a review of module recycling processes and their costs (chapter 3),
2) future recycling flows of tellurium from CdTe-PV (chapter 4), and
3) a comparison of life-cycle material flows and costs of CdTe- and CIGS-PV (chapter 5).

3 Recycling paths for thin-film chalcogenide photovoltaic waste

3.1 Introduction

Photovoltaic (PV) energy production is one of the most promising and technological mature technologies for renewable energy production. At the end of 2010 the cumulative photovoltaic capacity around the world reached more than 40 GW (EPIA, 2012). During 2010 alone PV modules with a capacity of 27 GW were produced, of which 1.9 GW were chalcogenide solar cells (Hering, 2011). Chalcogenide solar cells consist of II-VI and I-III-VI_2 semiconductors such as $CdS/CuInSe_2$ (CIS), $Cu(In,Ga)Se_2$ (CIGS) and CdTe. These compounds are suitable for terrestrial photovoltaic energy generation because of their high efficiency, long-term stable performance and low cost production (Romeo et al., 2004). Their high optical absorption makes them an ideal material for the conversion of sunlight into electricity (Razykov et al., 2011; Romeo et al., 2004). Consequently a thin layer (≤ 2 µm) is sufficient to absorb most of the useful parts of the light spectrum (Razykov et al., 2011; Romeo et al., 2004), therefore these technologies count among thin-film photovoltaics.

However, employed materials such as In, Ga and Te are regarded as critical (APS, 2012; ECN, 2010a; Moss et al., 2011; US DoE, 2011) and hazardous materials, which, as with Cd, may harm the environment if they are not recovered or disposed of properly. Moreover, several studies show that the availability of In and Te can, under certain conditions, limit the market growth of chalcogenide PV technologies (Andersson, 2000; Feltrin and Freundlich, 2008; Fthenakis, 2009; Green, 2009; Wadia et al., 2009; Zuser and Rechberger, 2011; Zweibel, 2010).

A proper recycling of photovoltaic waste will therefore become increasingly important considering the growing number of installations and expansion of production. Several recycling technologies for chalcogenide solar modules have already been developed by PV manufacturers, research institutions and small and medium enterprises. Some of them are even in operation (pre-commercially). This paper will present feasible recycling paths for chalcogenide photovoltaic modules. The paths are derived from a review of proven recycling processes analyzing available literature and interviewing key experts in this field.

In section 3.2 the composition and design of chalcogenide PV modules are described. Possible recycling paths for the recovery of thin-film materials as well as advantages and disadvantages of the processes are presented in section 3.3. Environmental impacts, costs, and research and development needs are discussed in section 3.4. Concluding remarks are given in section 3.5.

3.2 Composition of chalcogenide photovoltaic modules

A chalcogenide is a chemical compound consisting of at least one chalcogen (oxygen, sulphur, selenium, and tellurium) and at least one more electropositive element (Merriam-Webster Dictionary). Chalcogenide solar cells include CdTe (II-VI semiconductor) and the chalcopyrite family (I-III-VI_2 semiconductors) $CuInSe_2$ and the alloys $Cu(In,Ga)Se_2$, $Cu(In,Ga)S_2$ and $Cu(In,Ga)(Se,S)_2$. For simplification, all are hereafter called “CIGS solar cells”. A schematic cross-section of the superstrate and substrate layout of CdTe and CIGS solar module is shown in Figure 3-1.

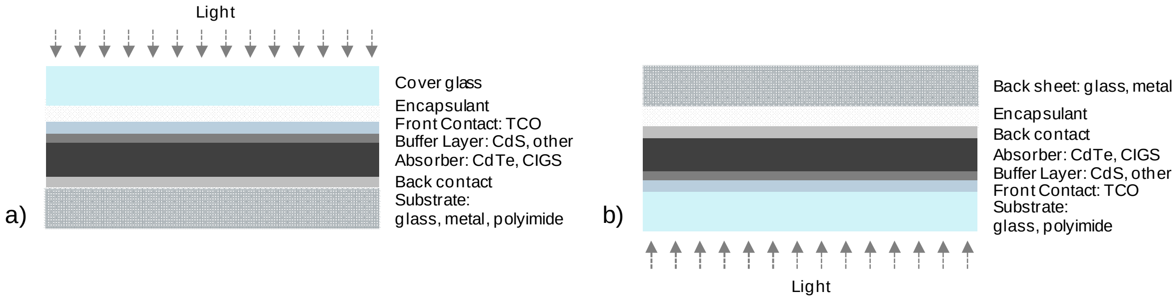

Figure 3-1: Schematic cross-section of (a) substrate and (b) superstrate layout for chalcogenide solar modules

For both technologies low-iron float glass is used as cover glass; in some cases fitted with overprints and anti-reflex coatings (Sander et al., 2007). The cover glass – or in the superstrate layout the back sheet – is glued by means of a plastic adhesive (ethylene/vinyl-acetate (EVA), polyvinyl butyral (PVB), and others). In most cases EVA is used as an encapsulation foil, which mainly consists of a thermoplastic. After the lamination process the thermoplastic becomes an elastomer which cannot be further melted (Krauter et al., 2011). Thin-film PV modules are sometimes framed for mechanical stability and protection. Depending on the size and design of the module, the frame – often made of aluminum – accounts for 12-15 % (Sander et al., 2007). The frame, as well as the junction box and connecting cables, can usually be removed without difficulty. Frameless modules are also very common and are often, but not exclusively, used for structurally integrated roof and facade modules.

CIGS cells are usually manufactured in the substrate configuration, which requires an additional encapsulation layer and/or glass to protect the cell surface. Cells are typically grown on soda-lime glass, but also on metal (steel, titan) or polymer foils. Molybdenum is the most employed back contact. Because of a high absorption coefficient, a very thin CIGS absorption layer (0.1-0.3 μm) is sufficient for absorbing the incident radiation (Razykov et al., 2011), but for compositional uniformity over large areas the absorption layer should be at least 1 μm thick (Singh and Patra, 2010). CdS is commonly used as a buffer layer to form a hetero-junction, however, “Cd-free” buffer layers such as ZnS, ZnSe, ZnInSe and In_2S_3 are also explored. A transparent conductive oxide (TCO) such as Indium-Tin-Oxide (ITO) or Al doped ZnO is employed as a front contact. (Kazmerski, 2006; Razykov et al., 2011; Romeo et al., 2004; Sander et al., 2007)

Flexible CIGS modules – for example produced by the US-American companies Solo-Power and Ascent Solar – are completely encapsulated by polymers and have a clearly different material composition, where polymers and steel, instead of glass, dominate the types of material. Because of the use of fluoropolymers, these modules will be a new challenge for recycling (Sander et al., 2007).

CdTe solar cells can be grown both in substrate and superstrate configuration. However, the highest efficiencies are achieved in the superstrate configuration in which layers of TCO, CdS, CdTe, and the metal back contact are sequentially grown on glass substrates. The glass substrate can be inexpensive soda-lime glass, or for higher processing temperatures, alkali-free glass (generally borosilicate). The most commonly used TCO is SnO_x:F, but also by using ITO, ZnO:Al, and $CdSnO_4$ as TCO high efficiency solar cells can be made. The CdS buffer layer forms a hetero-junction with the CdTe layer. The thickness of the CdTe layer depends on the deposition methods and is typically in the range of 2-6 μm, whereas just 2 μm are required to absorb most of the useful spectrum of the light. In research, thickness is reduced below 1 μm (Amin et al., 2007; Jones et al., 2009). A quasi-ohmic back contact is formed by a combination of a buffer layer and metallization – commonly Cu/Au, Cu/graphite, or graphite pastes doped with Hg and Cu (Kazmerski, 2006; Razykov et al., 2011; Romeo et al., 2004).

Typical indicative material compositions are shown in Figure 3-2. The exact composition depends on the module design and the thin-film layer configuration. Therefore, in case the material input in the recycling process in not known, the composition and material content have to be analyzed beforehand.

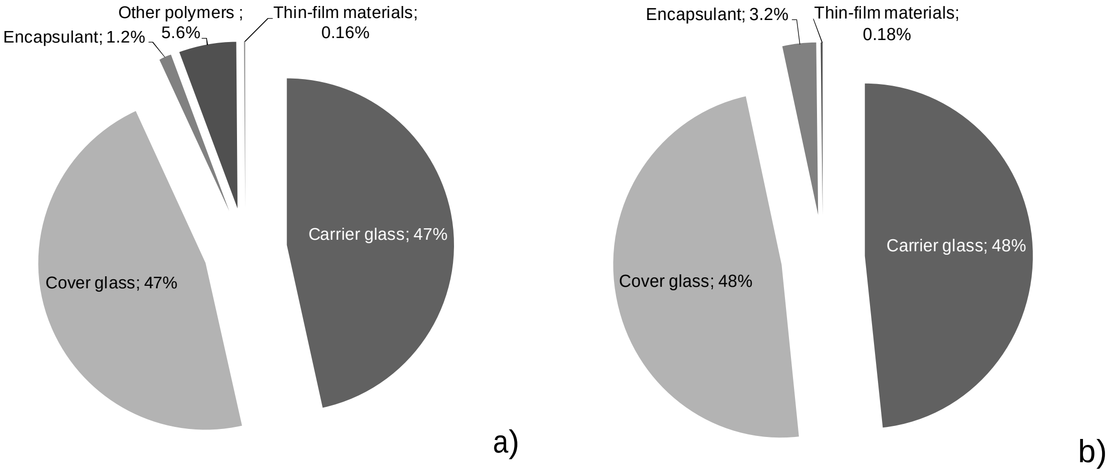

Figure 3-2 Material composition of glass-glass CIGS (a) and CdTe (b) PV modules (exemplary numbers, without junction box, cable and Al frame) (Sander et al., 2007)

3.3 Recycling paths

There are different types of photovoltaic waste arising:

- photovoltaic modules turning up as warranty returns, end-of-life-waste or as production rejects (laminates modules or submodules (coated substrates))
- production residues from the deposition processes (chamber scraping, filter load, edge grindings etc.) - normally a mix of thin-film materials at times contaminated with sandblasting abrasives and surface materials of equipment components
- not fully utilized pure raw material input (e.g. sputter targets)

The following chapter describes possible recycling processes to recover thin-film materials from thin-film chalcogenide (sub)modules and production residues. Several companies and research institutes developed recycling processes for thin-film chalcogenide photovoltaics. The US-American CdTe-PV producer *First Solar* (formerly *Solar Cells*) operates recycling facilities located at their production plants. The facilities mainly treat production waste (submodules, deposition overspray), in addition to recycling end-of-life modules or warranty returns. Also the German CdTe-PV producer *ANTEC Solar* has a pilot-scale facility suitable for small samples (Stefan Oelting, personal communication, 24.05.2012), which is based on a recycling process patented by Campo (Campo, 2002, 2003). The Canadian metal refinery *5N Plus* has developed processes to recycle residues, non-laminated and laminated modules of CdTe- and CIGS-PV (Dattilo, 2011; Huot, 2011;

Nicholas Audet, personal communication, 04.06.2012). *Umicore*, a Belgian refinery and precious metal recycler, has developed a hydrometallurgical process to recover Cu, In, Ga and Se from CIGS (production) scrap with a refining capacity of 50t/yr (Oosterhof, 2011). The company also recycles spent indium-tin-oxide targets in their pyrometallurgical recycling line (Meskers et al., 2010). The German company *Loser Chemie* developed a universal physical-chemical process for the recovery of non-silicon thin-film materials from photovoltaic waste (Palitzsch and Loser, 2011, 2012). The current capacity of the pilot line is 10 tons per week. The concentrated metals can then be further processed in a metal refinery and the glass can be reused for float glass or container glass production (Palitzsch, 2010; Palitzsch and Loser, 2011, 2012). The German company *Saperatec* operates a pilot plant for the separation of bondings and coatings. The focus of the operations is currently on the recycling of thin-film photovoltaic modules, i.e. delamination and removal of the thin-film materials from the substrate – especially from production wastes (saperatec, 2012a). Another German waste management company – *Lobbe Industrie Service* – plans to build a recycling facility for thin-film and crystalline PV modules as well as LCDs with a capacity of several thousand tons a year (EUWID, 2012). The *Colorado School of Mines* developed a recycling process for *PrimeStar Solar's* CdTe PV modules (DeFilippo, 2011; Pat Taylor, personal communication, 17.05.2012). Besides those processes designed for commercialization, thin-film photovoltaic recycling was investigated in several research and demonstration projects in the United States of America, Japan and Europe.

Figure 3-3 shows possible recycling steps that can be divided into different stages:

- (partial) delamination of PV-modules by physical disintegration (shredding, milling), by chemical or thermal decomposition of the encapsulation foil or by cryogenic embrittlement
- de-coating of substrate (cullet or intact substrate) and separation of non-metallic fraction (encapsulation foil, glass) from metallic fraction (semiconductors, metals)
- extraction and refining of elements.

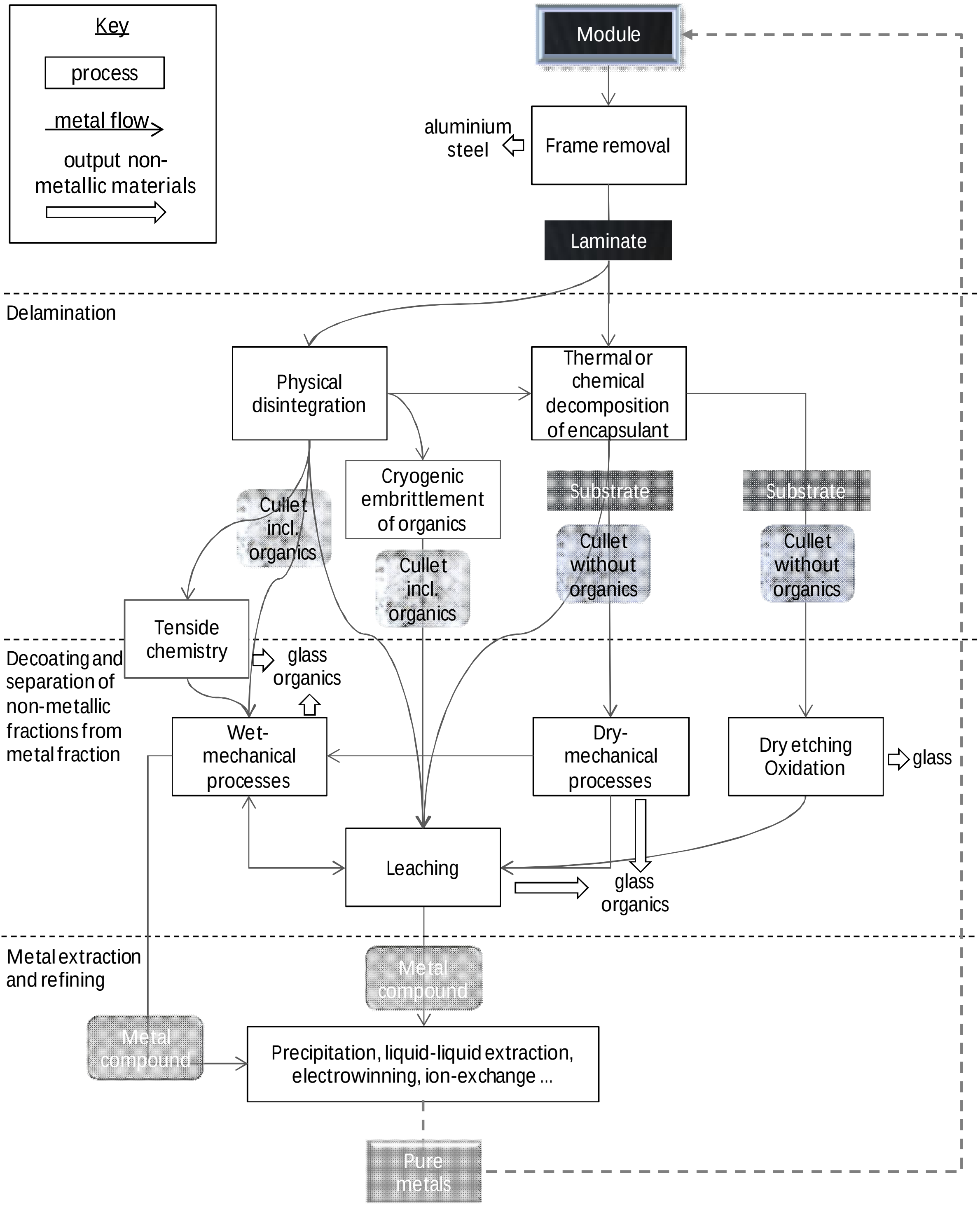

Figure 3-3: Metal flows along feasible recycling paths

3.3.1 Delamination

The first obstacle is to break open laminated modules, which are laminated to withstand mechanical loads and moisture ingress for over 25 years. New technologies like adhesives instead of encapsulation foils are in development to prolong the operational lifetimes which will make it even more complicated to delaminate the modules. There is a clear trade-off between design for long lifetime and easy disassembly of modules. Currently the focus of the producers is on extending the lifetime in order to produce more energy

(Marwede et al., 2012). Only a life cycle analysis can assess how much a possible higher recycling effort lessens the environmental benefits of the additional energy produced.

One way of delamination is the physical disintegration of the modules by shredding and milling - which has been proven technical feasible (Berger et al., 2010; Resolved, 2007; Sander et al., 2007) and is, for example, employed in the recycling line of *First Solar* (First Solar, 2012c). During those processes the modules are crushed and milled into small particles. However, it is not possible to fully liberate the semiconductor layer from the glass substrate, and the lamination foil only partially peels off the glass (Figure 3-4), therefore other separation processes have to follow.

Figure 3-4: Breakage of CIS module (Bundesanstalt für Materialforschung und -prüfung, 2007)

The German company *Saperatec* uses a micro-emulsion to fully remove the lamination foil and the semiconductor coatings from the glass. The emulsion contains tensides which decrease the interfacial tension between two phases of different materials leading to a detachment. With this process all physically joined compounds (adhesion, encapsulation, sealing, and coatings) can be detached. The EVA foil stays intact after delamination and floats on the emulsion (Horst Seibt, personal communication, 30.06.2010, Sebastian Kernbaum, personal communication, 16.10.2010; saperatec, 2012b).

Kushiya et al. (2003) heated the module up to 250°C to be able to push the coated substrate horizontally over and away from the cover glass. The polymer coated substrate was immersed into an acetic acid solution for 24 h at room temperature resulting in a bloated EVA, which allowed the ZnO based window layer and the buffer layers to dissolve in the acetic acid. The CIGS absorption layer remained on the glass.

It's also possible to decompose the organic components (encapsulation foil, insulating material) at 300-600 °C pyrolitically, heating up either crushed or intact modules (Campo, 2002; Campo, 2003; Guarde, 2006; Müller et al., 2006; Sander et al., 2007). Gaseous composition products that generate during the pyrolysis process are discharged and have to be scrubbed. In the closed down pilot recycling process for crystalline silicon modules, the company *Sunicon* pyrolysed the polymers for an easy removal of the cover glass and crystalline solar cells. Pyrolysis was chosen, because the lamination foil was considered as non-reusable and the method was economically feasible (Karsten Wambach, personal communication, 09.09.2009; Müller et al., 2006).

Lobbe filed a patent application for their process: the organic components of the crushed modules are embrittled at minus 196°C using nitrogen to break up the laminate. Glass cullet and lamination foil are transferred to an acid wash to solubilise the metals (EUWID, 2012; Friege and Kummer, 2012).

Another approach is to dissolve the encapsulant in a solvent. The *Fraunhofer Institute for Process Engineering and Packaging IVV* developed a solvent process to dissolve thermoplastics, including Polyethylene and other non-styrenic polymers, separating them from insoluble polymers and non-polymers such as dust, metals and glass splinters through sieving (Mäurer and Schlummer, 2004; Mäurer and Schlummer, 2008). The solution is precipitated after the cleaning step. The resulting damp polymer powder is pressed and dried for reuse. The approach was tested in laboratory scale trials with EVA coated glass panels. These were treated with PE selective solvents, leading to swollen EVA liners which easily delaminated from the glass surface. Even if swelling the polymer decreases process efforts for circulation of the solvents (drying from EVA), a complete dissolution would be favorable. Less cross-linked EVA substrates on the one hand, or more EVA specific solvents on the other may help to resolve this challenge but will require further research.

The European project "Sustainability Evaluation of Solar Energy Systems (SENSE)" proved water jet cutting as one feasible option to delaminate the modules, whereas experiments with microwave delamination, supercritical water oxidation and hot wire cutting were discontinued (Guarde, 2006; Shibasaki et al., 2006). *5N Plus* also tested irradiation to decompose EVA through the glass (localized heat treatment) (Dattilo, 2011; Huot, 2011).

3.3.2 Decoating and separation of non-metallic fractions from metal compound

The thin-film materials can be removed from the substrate after separating the module laminate. Two consecutive projects, one funded by the EU-LIFE Program (Berger et al., 2010; Resolved, 2007) and the other supported by German Federation of Industrial Research Associations (AiF) (Wolf et al., 2010), demonstrated two (wet-)mechanical recycling processes. One process-chain targets intact thin-film PV modules and the other broken modules (Figure 3-5). The main focus was the use of no or small amounts of chemicals during the process.

Broken modules are crushed and then treated (wet-mechanically) in an intensive batch mixer for the complete attrition of the semiconductor materials from the carrier glass. The material is further crushed due to the strong forces during the mixing process. Following the attrition process, the mixture of semiconductors, glass and EVA is rinsed and sieved into different fractions. The glass fractions >150 µm and EVA foil remain in the screen. The fraction < 150 µm, containing a pre-concentrate of semiconductor materials and glass dust, can be used for the subsequent flotation process. A flotation product was sent to *5N Plus* for the leaching of the flotation products by adding acids (H_2SO_4 or HCl) and hydrogen peroxide thus leaving an inert material with levels of Cd and Te below legislated limits (Resolved, 2007).

For complete modules, a vacuum blasting pilot line was developed to remove the active layer from the intact carrier glass. With this process it's possible to skim the semiconductor layer from the substrate with minimal glass abrasion so that high value recycling of the decontaminated glass panel becomes possible. In a second step the abrasives are separated from the valuable materials through an air separator and a cyclone separator. A significant pre-concentration of the valuables could be reached in this one-step separation, which equals a recovery rate of 25 %. It is estimated that higher concentrations and recovery rates can be achieved by multi-step mechanical-pneumatic separation. Fluidization is another not yet tested approach, which is regarded as feasible in order to separate abrasives from metals. Flotation can be used to enrich the valuables and to separate them from abrasives and glass particles. During flotation tellurium and indium were enriched by the factor three (valuables yield of the flotation of Te 12.2 % and of In 35.3 %) (Berger et al., 2010; Jürgen Wolf, personal communication, 13.04.2010; Resolved, 2007; Wolf et al., 2010).

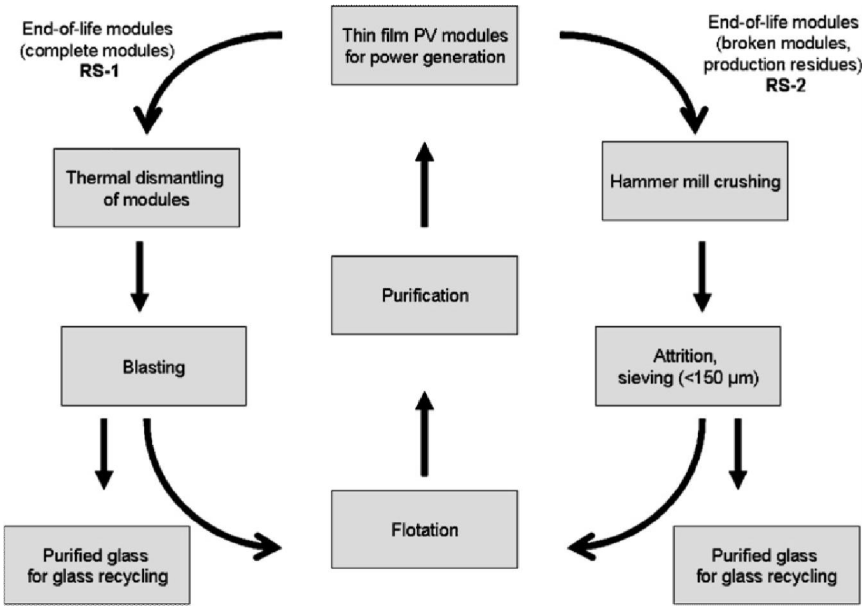

Figure 3-5: Two recycling strategies for thin-film PV modules (Berger et al., 2010)

Kushiya et al. (2003) also used a dry-mechanical method to remove the CIGS absorber layer: the absorber was mechanically scraped off using a metal blade. The CIGS dust was removed and collected by a vacuum. The Mo electrode remained on the substrate and worked as a solid “lubricant” for the metal blade. A diluted nitric acid was used to remove the Mo back contact from the soda-lime glass. The solution was neutralized and filtered which resulted in a Mo rich sludge.

It's also possible to remove the thin semiconductor layer from the carrier glass using tenside based micro-emulsions: physical capillary active forces remove the inorganic or organic binder together with the semiconductor layer from the substrate, whereby the semiconductors and metals are not chemically dissolved and can then be separated from the solution and handed over to a metal refinery. The solution is reusable and is circulated in a closed loop (Kernbaum, 2011; Horst Seibt, personal communication, 30.06.2010; saperatec, 2012b).

A dry etching process for recycling PV scrap was used by *Antec Solar* (Campo, 2002, 2003). After mechanical disintegration and pyrolysis of the adhesive, the module fragments are exposed to a chlorine-containing and preferably also nitrogenous gas atmosphere at a temperature of more than 400° C. resulting in an etching process. Gaseous $CdCl_2$ and $TeCl_4$ that are generated in the etching process are made to condense (separately) as precipitate on cold surfaces (cooling traps). Resulting $CdCl_2$ and $TeCl_4$ are sent to a metal refinery where semiconductor grade Tellurium is extracted (Antec Solar, 2012).

The *Colorado School of Mines* filed a patent application for their recently developed recycling process (DeFilippo, 2011; Pat Taylor, personal communication, 17.05.2012). In this process CdTe is oxidized during a thermal delamination process under an inert atmosphere and can then be removed (Pat Taylor, personal communication, 17.05.2012).

Delaminated modules, cullet, residues or production scrap can be leached in diluted acids. During these processes the metals are solubilised and converted into other chemical types of bonds. Further steps are necessary to convert the compounds back to metals. Within the framework of chemical beneficiation several acids (in combination with oxidizing agents) have been tested for the leaching and reclaiming of thin-film materials from the glass of module scrap and production waste:

- nitric acid (Drinkard et al., 1998, 1999, 1999; SENSE, 2007),
- sulphuric acid (Bohland et al., 2000, 2002; Fthenakis and Wang, 2006; Wang and Fthenakis, 2005),
- hydrochloric acid (Palitzsch W, 2010),
- sodium hydroxide (Pat Taylor, personal communication, 17.05.2012), and
- a solution of ferric chloride/hydrochloric acid (Tolley and Palmer G.R., 1995). This was found to be unsatisfactory because it failed to separate Cd from Fe and Te. Furthermore the process is capital intensive (Fthenakis VM, Wang W, 2010).

Drinkard Metalox leached the metals of shredded modules with nitric acid in their pilot recycling line (Drinkard et al., 1998, 1999, 1999). During the European project SENSE (Sustainability Evolution of Solar Energy Systems) metal-rich CIGS production waste was leached in nitric acid and hydrogen peroxide (SENSE, 2007).

Bohland et al. (2000, 2002) and Fthenakis and Wang (Fthenakis and Wang, 2006; Wang and Fthenakis, 2005) used sulphuric acid for leaching. Based on their research, *SGS Mineral Services* has developed a recycling line (Mezei et al., 2008), which *First Solar* runs at their module production plants in order to treat production and end-of-life waste. In this line, shredded and milled modules (fractions < 5 mm) are filled in a slow rotating leach drum, to resolve the semiconductor films using sulphuric acid and hydrogen peroxide (Sander et al., 2007).

According to a patent by Palitzsch (2010), *Loser Chemie* uses hydrochloric acid and hydrogen peroxide to remove thin-film metals (CIGS, CdTe) from the glass, after the modules were crushed and the plastic fraction was separated from the grist. Meanwhile the solution was enhanced in order to make it reusable for several extraction cycles. In the case of CdTe modules, the resulting leachate contains high concentrations of thin-film metals (> 800 mg/l Cd, Mo, Te) (Palitzsch and Loser, 2011, 2012). Te can be extracted during a de-metalizing step, whereas Cadmium is found in the filtrate. In the process of the *Colorado School of Mines,* CdTeO3 is subjected to sodium hydroxide to selectively dissolve Te (Pat Taylor, personal communication, 17.05.2012).

The solids (glass, lamination foil) can be removed after leaching or attrition by mechanical or gravitational solid-liquid separation methods such as screening, skimming, decantation, sedimentation, filtering, flotation, fluidization etc. (Berger et al., 2010; Drinkard et al., 1998, 1999, 1999; Palitzsch, 2010; Resolved, 2007; Sander et al., 2007; SENSE, 2007).

3.3.3 Metal extraction and refining

Up to 99.999 % purity of the metals and semiconductors is required for the production of thin-film photovoltaic modules, whereby the pre-processed metals have to be enriched, separated and purified. Several chemical methods were investigated, which can be used to rewin the metals from acidic or other solutions: precipitation, liquid-liquid extraction, electro-winning, ion-exchange and oxidation/reduction. The concentration of the target metals in the feed, their chemical form and other constituents are important parameters for optimizing the yield (Suys, 2010).

In the process of *First Solar*, the metal compounds are precipitated using three stages at increasing pH value, adding sodium hydroxide (Mezei et al., 2008; Sander et al., 2007). The precipitated metals are concentrated in a thickening tank and then frame filtered for dewatering. The resulting filter cake is packaged for metals recovery by *5N Plus*. *First Solar* claims to recover 95 % to 97 % CdTe (Krueger, 2010; Lisa Krueger, personal communication, 07.09.2009). The refinery *5N Plus* extracts up to 95 % Cd and Te from recycling residues and production scrap (Suys, 2010). They recover both Cd and Te, which are purified for reuse in 5N CdTe synthesis (Nicholas Audet, personal communication, 04.06.2012; Resolved, 2007; Suys, 2010).

According to Bohland et. al. (2002) sodium carbonate is the preferred agent to precipitate Cd and Te from the sulphuric acidic etchant effluent, because it is cheap, readily available and non-toxic. Goozner et al. (1999) neutralize the nitric acidic leachate by a calcium containing base until all solubilised materials precipitate. The precipitate can then be roasted at temperatures between 400°C and 450°C to convert Cd and Te to metal oxides, whereby Ca remains unconverted in the nitrate form. After washing out the Ca, the insoluble CdO and TeO can be filtered out. The CdO and TeO mixture can be converted back to metals by reducing means.

After leaching, the *Colorado School of Mines* applied solid-liquid separation to remove the Te rich solution from the solid residue. Te is recovered from the resulting sodium telluride through electro-winning of the leached solution. The slurry, which contains Cd and other impurities, is sent to a Cd Recycler (Pat Taylor, personal communication, 17.05.2012).

Wang and Fthenakis proved ion-exchange to be effective for separating Cd from Te in sulphuric acid media (Fthenakis and Wang, 2006; Fthenakis and Wang, 2010; Wang and Fthenakis, 2005). Cd is retained in the cation exchange resin, while Te stays in the solution (Fthenakis and Wang, 2010). Subsequently, Cd can be eluted from the ion-exchange resin by acid and subsequently recovered through “electro-winning”. The remaining Te in the solution can be precipitated using sodium carbonate and sodium sulfide (Fthenakis and Wang, 2006).

Drinkard et al. (1998, 1999) electrolyze the leachate to recover Te, while the Cd is left in the solution. Evaporation of the effluent solution yields a CdO product suitable for recycling (Goozner et al., 1999).

In the project SENSE, a one-step liquid-liquid extraction with D2EHPA (Di-2-ethylhexyl phosphoric acid - Baysolvex®, Lanxess) was used to transfer In and some of the Mo into an organic phase (Sander et al., 2007; SENSE, 2007). During a second step In was brought back into an inorganic phase through stripping with hydrochloric acid. Thereafter In was chemically precipitated and separated by filtering. Se was extracted from the inorganic solution by reduction and precipitation with $Na2SO3$. Ga was removed from the inorganic solution by adding sodium hydroxide. Because the resulting hydroxide is not very pure, it can be further purified by electrolytic processes, crystallization or zone melting. Dattilo (2011) presents another order to extract the metals from CIGS compounds wet-chemically. First the compound is deselenized, then Cu is removed and finally In and Ga are separated.

Directly electrolyzing a solution containing CIGS materials showed that first Cu and Se is deposited or plated on the cathode (Drinkard et al., 1998). The electrode can then be replaced to deposit Cd onto the new electrode. Se can be separated from the copper by oxidization and distillation. Evaporation of the remaining liquor yields a mixture of ZnO and InO.

3.4 Discussion

3.4.1 Processes

Table 3-1 lists advantages and disadvantages of processes along the recycling process chain. Some general remarks and suggestions for improvements can be made.

Delamination: The encapsulation can be removed using surface chemistry (tensides), solvent processes, cryogenic processes, leaching and mechanical separation or thermal processes. The advantage of mechanical disintegration processes is that feedstock of different size and condition (e.g. broken modules, coated substrates, intact laminated modules) can be “homogenized” for the following process steps. However, the mix of different material fractions (Glass, EVA and thin-film materials) has to be separated again in the later process steps. Thermal and cryogenic processes have a comparatively high energy demand. In case of the thermal process recovering the heat or using waste heat from other processes can improve the energy balance. Solvent based delamination enables an effective separation of EVA and glass. If separated EVA may be reused or recycled to EVA grade still needs to be tested. Especially for highly cross-linked PE a material recycling is considered rather challenging. However, thermal use of separated EVA is an option, too.

Decoating and separation of non-metallic fraction: Different waste streams such as crushed materials, abraded materials, production residues or intact substrates can be treated by leaching. The waste flows along the chain can be reduced significantly if the mass materials (cover-glass, EVA) can be removed before the wet-chemical treatment. This results in the use of fewer chemicals, in smaller dimensioning of the equipment, but also in additional process steps (i.e. costs). A combination of pyrolysis and vacuum blasting for intact modules and chemical treatment of the material mix (metals and abrasives) is imaginable (Jürgen Wolf, personal communication, 13.04.2010). Another option is to treat the crushed fraction wet-mechanically (attrition) and screen out the fraction below 200 µm (the cleaned glass remains in the screen) for further wet-chemical treatment. In that case just one fifth of the original material input would have to be wet-chemically (Wolfgang Berger, personal communication, 16.09.2009).

The experiments showed that the selectivity of flotation and pneumatic separation processes is not entirely satisfactory. A multi-step flotation would improve the valuable yield and related enrichment of the semiconductors (Berger et al., 2010). Fluidization might be more effective for the separation of abrasives from the abraded metals than pneumatic processes because it’s easier to break the electrostatic forces between the particles in an aerosol (Wolfgang Berger, personal communication, 16.09.2009). Alternatively, it’s possible to leach the mix of abrasion and abrasives to extract the metals.

Metal extraction and purification: Hydrometallurgical processes are robust and technically mature and suitable for the recycling of low-grade feed and a relatively low throughput (Mezei, 2008), so, many processing steps are necessary until separation of the target metals is achieved. Furthermore, processing steps have to be adapted to target materials. Material loops for process chemicals should be established for environmental reasons (SENSE, 2007). Although pyrometallurgical processes are mature, a smelter needs large amounts of feed and feed requirements are very strict (e.g. concentration of target metals, content of heavy metals or content of contraries, which disturb the process). Pyrometallurgical processes are therefore not used for recovering metals from PV modules since a high amount of glass would have to be processed as well.

Process step	Process	Status	Advantage	Disadvantage
Delamination	Physical disintegration	Commercial	• Treatment of different types of waste (submodules, laminated modules, broken modules) possible	• Different material fractions are mixed up, which decreases value of each material fraction • EVA still partly attached to glass • Not sufficient to remove cell materials from glass substrate • High share of fine fractions (e.g. glass) • Formation of dusts containing heavy metals (health and safety measures) • Equipment wear / tear / corrosion
	Solvent (organic chemistry)	Research	• Deliberates glass from organic coating • Reusable solution • Organic components can be recovered for reuse or energy recovery	• Necessary time for delamination depends on area • Highly cross-linked lamination foils swells, because it cannot be fully dissolved, and still adheres to the glass surface
	Water jet cutting	Research	• No purification of waste gases necessary • Chemical treatment (normally) possible without further steps	• Expensive and complicated procedure • EVA layer is not completely removed • Recovery of metals difficult because of different solving behavior of the polymer in the chemical treatment • Just suitable for small modules • Cd can be found in the waste water
	Pyrolysis	Pilot	• Organics (EVA) burn with practically no residues (to easy disassembly of modules)	• Elaborate gas scrubbing process • High energy demand • Thermal stress leads to glass breakage • Slow process
	Irradiation	Research	• Easy access to the EVA	• Slow process • Very expensive equipment
Decoating and separation of non-metallic fractions from semiconductors / metals	Attrition (wet mechanical)	Pilot	• No usage of chemicals • Clean glass	• Obtained semiconductor materials have to be further enriched by chemical or mechanical methods before hydrometallurgical processing to 5N purity
	Vacuum blasting	Pilot	• Abrasives and stripped material stay in a closed system (important because of heavy metals) • Removal targeted specifically at semiconductor layer (no glass abrasion) • Clean glass	• Process works just with delaminated modules or submodules (carrier glass has to be intact) • Relatively long processing time • “Contamination” of metallic fraction with abrasives • Obtained semiconductor materials has to be further enriched by chemical or mechanical methods before hydrometallurgical processing to 5N purity
	Tenside chemistry	Pilot	• Tensides are reusable (circulation) • Complete removal of metals from glass • Delamination without mechanical or thermal input. • The organic components remain intact	• Emulsions have to be adapted to different cell technologies • Delamination time depending on area

Process step	Process	Status	Advantage	Disadvantage
	Leaching	Research/pilot/commercial	• Complete removal of metals from glass • Further extraction of metals from solution possible	• Possible encapsulation of organic materials in glass during leaching • High use of chemicals • Control of chemical reactions complicated • Possible generation of acidic fumes
	Etching in chlorine containing gas atmosphere	Pilot	• Few process steps	• High energy demand because of high temperature processes • Mixture of semiconductor materials result in high effort in purification
	Flotation (wet mechanical)	Pilot	• Relatively simple procedure • Few process chemicals	• Considerable losses of valuables during rinsing and sieving of fine fractions for input into flotation • Selectivity not high enough in one-stage flotation process • Obtained semiconductor materials has to be further processes wet-chemically to achieve adequate purities for cell production
	Dry & wet mechanical processes	Commercial	• No process chemicals • Simple processes • Equipment widely available • Low energy requirements	• No removal of dissolved solids
Metal extraction & purification	Hydrometallurgical	Commercial	• Commercially applicable in short time • Low and controllable emissions • Facile water management • Robust and proven process flow sheets based on technical feasible process options	• Many separation and concentration steps • Chemical process steps have to be adapted to respective technology
	Pyrometallurgical	Commercial	• Established industrial process • Feedstock can contain different materials	• High throughput necessary • Some materials are “lost” in slag • Heavy metals or process contraries unwanted • Pre-treatment for high concentrations of target metals necessary

Table 3-1: Advantages and disadvantages of selected processes (Berger et al., 2010; Goozner et al., 1999; Guarde, 2006; Huot, 2011; Resolved, 2007; Sander et al., 2007; SENSE, 2007) and personal communications

3.4.2 Economics

The economics of several processes were assessed. Again a comparison is difficult as scale, scope and technical specifications of assessed processes differ, however we present some indicative numbers.

- In 2010 First Solar put 40.152 Mio $ aside as liability for their module collection and recycling program (First Solar, 2011a). Divided by the annual production of 1.411 MW in 2010, around 0.03 $/W are set aside. Taking a rather conservative inflation of 1.5 % into account, 0.03 $ today will have a value of around 0.02 $ after a minimum service life of 25 years (output warranty time).
- Choi and Fthenakis (2010b) modeled different scenarios for estimating recycling costs varying costs and revenues, based on First Solar's recycling process. The resulting revenue of the base scenario is –0.02 $/W. Scenarios with low profit range result in revenues of around –0.04 $/W; the highest revenues are around 0.04 $/W.
- In the "Study on the Development of a Take-Back and Recovery System for Photovoltaic Modules" (Sander et al., 2007) cost scenarios for different take-back and recycling systems were developed. Treatment costs for chalcogenide thin-film modules are estimated to be around 120 €/t (around 0.02 €/W).
- Fthenakis and Wang (2006) estimated the costs of leaching and ion-exchange to be about 0.02 $/W (105 $/t). This cost estimation includes material and capital costs, but doesn't include labor.
- The costs for abrasion using a prototype vacuum-blasting collector including abrasives, energy and operation (without personal and allowance for depreciation) amounts to 180-210 €/t (around 0.012 €/W), depending on the used abrasives (Wolf et al., 2010).

Apparently the costs of recycling thin-film modules are higher than the value of the recovered materials (thin-film materials, glass). A high quantity of glass with low economic value has to be treated to recover the thin-film materials of low weight percentage. Heavy metals are cost drivers because precautionary safe and health measures have to be observed and disposal costs of hazardous materials are high. Moreover, current waste volumes are low so that economies of scale cannot be fully capitalized.

3.4.3 Environmental impact

A direct comparison of the results of the life-cycle analysis made for different recycling processes is not possible as they differ in scope, system boundaries, scale (lab or pilot), functional unit, et cetera. Nevertheless, some key results can be presented:

- The assessment of lab-scale processes has shown that the environmental contribution of the recycling to the life cycle impact of production and recycling is marginal (below 4.5 %) (SENSE, 2008; Shibasaki et al., 2006). The relevance of recycling is even less significant when considering that the life-cycle impact for producing photovoltaic energy is significantly lower than energy generated by fossil fuels or than the general energy mix (Fthenakis and Kim, 2011; Kim et al., 2012; Raugei et al., 2007; SENSE, 2008). Also the life-cycle Cd emissions from CdTe-PV are one to three orders of magnitude below the Cd emissions of other forms of electricity generation (Fthenakis, 2004a; Fthenakis et al., 2008).

- The potential environmental benefits due to the recycled materials nearly compensates the technical efforts (operating materials and energy use) for recycling (Raugei, 2009; Sander et al., 2007; SENSE, 2008; Shibasaki et al., 2006).
- Compared to other end-of-life treatment methods such as land filling or incineration, recycling processes are less environmental harmful (Resolved, 2007).
- Thermal delamination (pyrolysis) of modules increases the impacts of “global warming” and “ozone depletion potential” more than mechanical separation processes because this process is more energy intensive (Berger et al., 2010; Resolved, 2007).
- It is expected, that the industrialization of lab-scale process will finally lead to a net-environmental credit (SENSE, 2008).

3.5 Conclusion

The paper has shown that recycling technologies for chalcogenide photovoltaic modules to recover thin-film materials are sufficiently explored and commercially available. Nevertheless several challenges exist:

- Waste streams are not high enough to profit from economy of scale. Early installations of thin-film PV modules of the 1990s are just about to reach end-of-life. According to various predictions, significant end-of-life waste flows will first turn up in 15 to 20 years (Fthenakis, 2009; Haig et al., 2011; Marwede and Reller, 2012; Sander et al., 2007; Zuser and Rechberger, 2011).
- The fluctuating price of valuable materials leads to high uncertainties and influences the financial viability of recycling processes.
- Toxic materials increase treatment and disposal costs.
- Recyclers have to deal with various technologies and materials (absorption layers, polymers, substrates) and the technological differences between production waste (submodules, off-spec modules).
- Recycling of materials might not outweigh the environmental burden of the recycling processes.
- Lamination methods employed hamper the disassembly.
- Recyclers have to fulfill strict specification of metal containing residues as feed for metal refineries.

One prerequisite for using existing recycling facilities to capacity is an effective collection system – not only for end-of-life waste but also for warranty returns and production rejects. Before large end-of-life waste streams are expected, it may suffice to set up small integrated collection and recycling centers near the leading manufacturers located in a region. Choi and Fthenakis (2010a) developed a mathematical model for a reverse logistics and recycling infrastructure. Using the example of East-Germany, they showed that recycling facilities with small capacity in decentralized locations offer better economical and environmental benefit throughout the network system because the travel distance and logistics costs are lower. Low logistic costs are especially important considering the high mass and volume which has to be shipped to recover the valuable thin-film materials. Recycling facilities and collection systems have to be planned for variety and scale to adapt to growing waste streams.

Recyclers have to balance costs, technical efforts, quality and quantity of recyclate and the environmental impact. That means costs have to be optimized under sometimes changing boundary conditions (e.g. legislative limits for residual heavy metals, costs for auxiliaries and energy, value of recyclates, specifications for recyclate). Recyclers currently have to charge gate-fees and producers have to set aside funds for future recycling and logistics costs because they cannot be covered by the value of the recyclates (glass, thin-film materials etc.). In the future – in addition to other factors such as material prices, logistic costs, energy prices, and economy of scale – the declining content of thin-film materials due to thinner absorber layers will influence the economics. Recycling costs and environmental impacts can be driven down by minimizing the use of chemicals and energy, the re-use of process auxiliaries (chemical agents, abrasives, water) as well as energy (e.g. waste heat). Synergetic treatment of other composite materials such as security glass or other substrates with thin-film coatings may support the up scaling and economic sustainability of recycling processes. Furthermore, design for recycling of PV modules can ease their disassembly (Marwede et al., 2012; Marwede et al., 2011).

New business models for recyclers and manufacturers may also support recycling: the recycler can for example offer a “resource account”. Incoming materials are booked onto that account and are supplied back to the PV manufacturer. Module manufacturers only have to pay the treatment costs and are less dependent on market prices of materials. This could also increase customer loyalty and incentivize collection. Also manufacturers could secure the access to valuable resources accruing in installed modules by selling energy instead of PV modules or offering leasing models for PV plants.

Appropriate policies (e.g. material specific recycling targets) need to accompany the set-up of a recycling system to avoid environmental harm and secure the long-term supply of the industry with critical metals. However, PV manufacturers should take over responsibility through individual or industry wide collection and recycling systems. Besides, an ordered interplay of all stakeholders (customers, manufacturers, recyclers) combined with supportive policies is essential to recycle chalcogenide photovoltaic modules.

4 Future recycling flows of tellurium from cadmium-telluride photovoltaic waste

4.1 Introduction

According to the European Photovoltaic Industry Association (EPIA), photovoltaic energy has the potential to contribute up to 12.6 % to the global electricity supply by 2040 (EPIA, 2011). Previously, crystalline silicon photovoltaic (c-Si PV) technologies have been the dominant technology with market share of 86% in 2010. The remaining 14% was allocated to other PV technologies, including inorganic thin-film technologies. Of these emerging technologies, thin-film cadmium telluride photovoltaics (CdTe-PV) make up approximately 40 % (Hering, 2011), with very low production costs of 0.75 US-Dollar per watt peak (First Solar, 2011a). The market leader *First Solar* accounts for almost all sales of this technology by supporting a production capacity of 1.5 GW in 2010 (First Solar, 2011a). However, there are two major concerns about this PV technology: On the one hand, the potential negative environmental impacts of Cd contamination from CdTe-PV, and on the other hand, a possible shortage of the metal Tellurium (Te).

The fear of Cd emissions from CdTe-PV modules during their life cycle could be largely invalidated; previous research shows that the life-cycle Cd emissions from CdTe-PV are one to three orders of magnitude below the Cd emissions of other forms of electricity generation (Fthenakis, 2004b; Fthenakis et al., 2008). Based on these facts, Raugei and Fthenakis (2010) predicted various scenarios of worldwide Cd emissions in 2050 caused by CdTe-PV and compared them to current Cd flows in Europe. The study indicates that an expanding CdTe-PV sector will reduce, rather than increase, the amount of cadmium-related environmental pollution globally[7], provided that CdTe-PV modules are recycled (Raugei and Fthenakis, 2010).

Recycling of PV waste is essential, not only to avoid Cd emissions but also to conserve Te; various studies show that accessible Te reserves and annual Te production can, to a certain extent, limit the market growth of CdTe-PV (Andersson, 2000; Feltrin and Freundlich, 2008; Fthenakis, 2009; Green, 2009; Wadia et al., 2009; Zuser and Rechberger, 2011; Zweibel, 2010). In general, three research methods have been used to reveal limitations. These deal primarily in the estimation of:

1. the maximum annual PV production with refined Te,
2. the maximal cumulative capacity or maximal electricity generation with available Te reserves, and
3. the Te demand as a result of market scenarios.

It is difficult to compare the results because of differing assumptions about available reserves, (future) Te production, market developments and material demand per watt peak (W_p). Of course, it is to be expected that these values change over time due to economic and technological developments. Recent studies (Candelise et al., 2011; Fthenakis, 2009; Green, 2009; Wadia et al., 2009; Zuser and Rechberger, 2011; Zweibel, 2010) conclude that an absolute shortage of Te is unlikely, but temporary bottlenecks in supply and high prices will be an issue for the CdTe-PV industry. Thus extensive recycling and material efficiency is part of the solution to ease possible constraints.

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[7] Because of those arguments PV is still excluded from the European directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS).

This paper analyzes the extent to which recycling and efforts to increase material efficiency can lower the demand for primary Te. A dynamic material flow analysis was used to examine how much Te can be recovered in the future from CdTe-PV production and end-of-life scrap, as a substitute for primary material, and how much Te has to be disposed of. Worldwide scenarios projected until 2040 show how material efficiency measures – higher material utilization in production, decrease of material content in PV modules, and recycling of production scrap and end-of-life modules – will affect demand, waste flows, and recycling flows of semiconductor grade Te.

4.2 Research process and methods

Figure 4-1 depicts the research process undertaken in this study. Key parameters and main processes, which represent the life cycle of a PV module and influence the PV waste flows, were determined via desktop research and personal questionnaire-based interviews with photovoltaic manufacturers, recycling companies, and research institutes. Based on this information, a dynamic material flow system corresponding to the life cycle of a CdTe-PV module was modeled using the material flow analysis software STAN as well as further computation of market developments and lifetime probabilities.

Furthermore, we used the information collected to develop scenarios, which represent different technological trajectories at the product and processing level. These trajectories are described in storylines. The parameters and necessary flows were implemented in the material flow model. The results were analyzed and indicators developed, which describe the efficiency of the system.

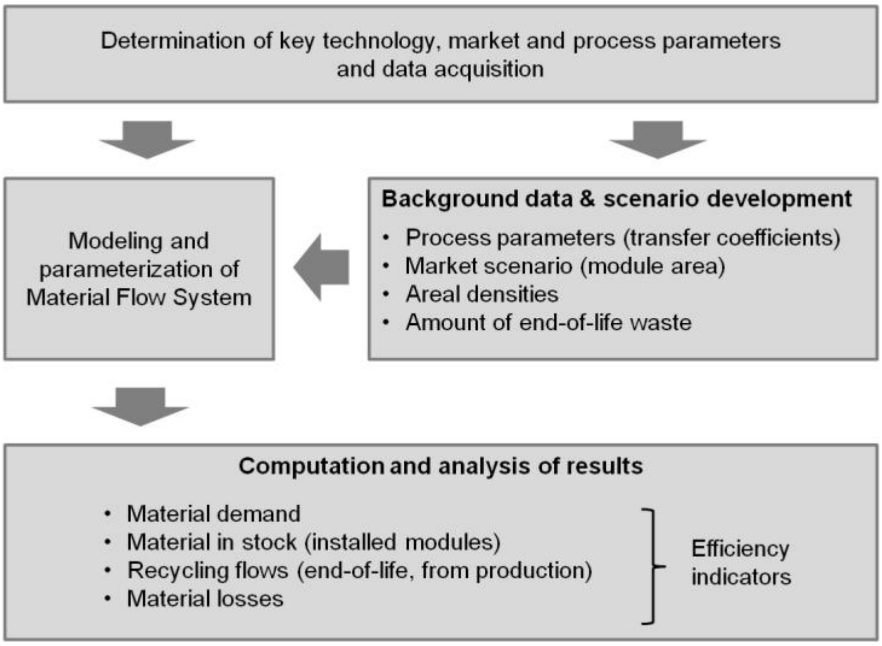

Figure 4-1: Research process

A material flow analysis (MFA) regards physical material flows of the economy as an industrial metabolism (Ayres, 1989). The most important element of a MFA is the mass balance; it helps to identify unexpected or hidden material flows and inventory in an economy or in the environment (Bouman et al., 2000). A MFA can be used to estimate the material intensity of an economy, but also on a smaller scale to assess recycling systems. It helps to identify influencing factors in recycling flows and opportunities for optimization

(Brunner and Ma, 2009). To estimate future material flows the formerly static MFA was modified to a dynamic model (Elshkaki et al., 2005; Kleijn et al., 2000; Melo, 1999).

Within a material flow system, material flows between processes, stocks, and sinks (sinks have no outflow). A process is defined by its transfer coefficients. A transfer coefficient determines which part of an input to a process is transferred to the subsequent process. The mass balance principle demands that the sum of the transfer coefficients for a specific input equals 1 (Brunner and Rechberger, 2004)

The material flow system for CdTe-PV was modeled using the graphical interface of the software STAN (Figure 4-2 and Figure 4-3). STAN calculates flows, sinks, and stocks based on formulas found in Cencic and Rechberger (2008). Table 4-1 shows the key flows and process parameters necessary to determine the remaining flows, the stock "installed modules", and the sink "discarded material". The necessary data for the scenario assumptions can be found in section 4.3.

		Parameters	Section
Flows	Produced modules	Yearly production of CdTe-PV in square meter Areal density of Te in CdTe-PV cells	4.3.1 4.3.2
	End-of-life modules	Lifetime probability Percentage of early returns	4.3.5
Processes	CdTe-Deposition	Material utilization Recovery overspray	4.3.3
	Process line	Overall equipment efficiencies Percentage of production rejects collected for recycling	0
	Recycling & Refining	Recycling rates Refining rates	4.3.6
	Collection	Collection quota	4.3.7

Table 4-1: Flows, processes and key parameters to determine waste streams

The following paragraphs describe the processes and formulas used to calculate the key flows of the system. Figure 4-2 shows the subsystem "production" of the material flow system (Figure 4-3). A box represents a process and an arrow a flow. Flows are either imported (I) from the system or exported to the system (E), which is shown in Figure 4-3. Recycled material (flows "recycled material production" and "recycled material EoL") is credited to the feedstock to determine, how much can be substituted by recycled material. The feedstock is therefore composed of recovered material from production scrap (off-spec modules and overspray), recovered material from end-of-life modules, and additional material imported from external sources (flow "demand").

In the subsystem, material utilization rates of the CdTe-deposition process and overall equipment efficiencies are the key parameters in determining waste streams. The transfer coefficients of the process "CdTe deposition" define how much of the raw material deposited ends up on the substrate. The remains (overspray) coats the equipment and deposition chamber and has to be removed regularly. The process "recovery" defines how much of this overspray can be transferred to a refinery. The process "module production" represents the overall equipment efficiency of the production line. It determines how many modules, i.e. module area, are rejected during production (off-spec modules). The process "collection" specifies how much of the "off-spec modules" are directed to recycling or are discarded, respectively. Besides overspray and rejected modules, material waste also occurs during edge grinding and scribing of cells and contacts. This amount, however, is neglected in this material flow analysis.

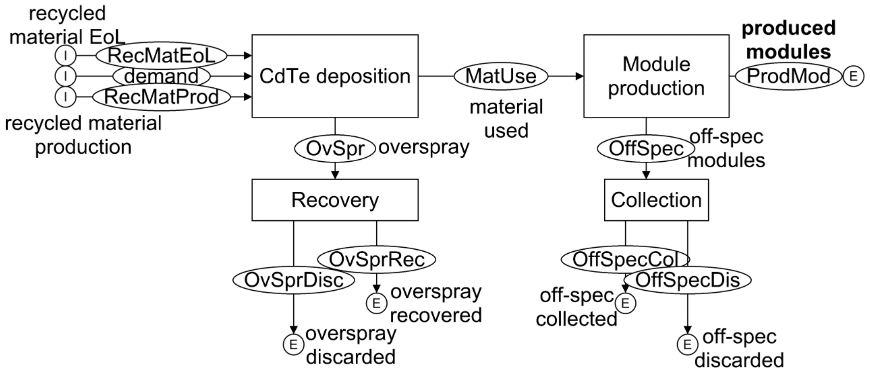

Figure 4-2: Subsystem production of the material flow system (Figure 4-3)

To assess the efficiency of the production system, three indicators are used. The indicator “material utilization” specifies how much of the raw material ends up in the final module, i.e. the material bound in produced modules divided by the feedstock. The “material recovery rate” indicates how much of the production scrap (material in rejected modules and excess material from deposition) can be reprocessed into high quality material (semiconductor grade)[8]. Finally, the “scrap rate” can be calculated, which equals the share of discarded material at feedstock.

Subsequent to the parameterization of the processes in the subsystem, the remaining flows in the subsystem can be calculated by STAN after inputting the flow “produced modules” $F^{pm}(a)$, i.e. the amount of material r bound in the produced modules in the year of production a. The flow $F^{pm}(a)$ into the stock “installed material” (Figure 4-3) is calculated by inputting the module area A_a in year a and assigning an areal density μ_{ra} to the flow. Note that the area produced is set equal to the area installed in a given year.

$$F^{pm}(a) = \mu_{ra} \cdot A_a \tag{4-1}$$

The size of the stock “installed material” is dependent on its inflow $F^{pm}(a)$ and outflow $F^{EoL}(a)$. The material outflow “end-of-life (EoL) modules” of the stock “installed material” is determined by the lifetime of the modules. Some of the modules will be scrapped earlier than average, others later. As statistics on the lifetime of CdTe-PV modules are hard to come by, the lifetime of the modules is computed by using a statistical distribution function $f(t)$. The probability p_t of scraping a product with a service life to t years is:

$$p_t = \int_t^{t+1} f(\tau) d\tau \tag{4-2}$$

The outflow of the stock $F^{EoL}(a)$ in year a (flow “EoL modules” in Figure 4-3) equals the sum of the inflows from previous years multiplied by the probability p_t of a product being discarded after *t* years:

$$F^{EoL}(a) = \sum_{t=o}^{a} p_t \bullet F^{pm}(a-t) \tag{4-3}$$

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[8] Even if cadmium is not recovered for reprocessing to high purity material, it is recovered for environmental and safety reasons and afterwards deposited safely.

The process “module recycling” determines how much material is recovered during the treatment of off-spec modules and end-of-life modules. In the model, recovered material and production waste from deposition is further purified in a refinery to semiconductor grade material, which is then fed back into the production. The processes “module recycling” and “refinement” appear twice to be able to differentiate the recycling flows. The indicator “end-of-life recycling rate” describes the efficiency of the end-of-life recycling chain, and shows how much of the material bound in end-of-life modules is reprocessed to semiconductor grade material.

The sink “discarded material” gathers all the material that cannot be recovered and purified to semiconductor grade material. The boundary of the system is depicted in Figure 4-3 as a dotted line, which represents that the mining and processing of primary or recycled material coming from sources other than CdTe-PV has not been accounted for.

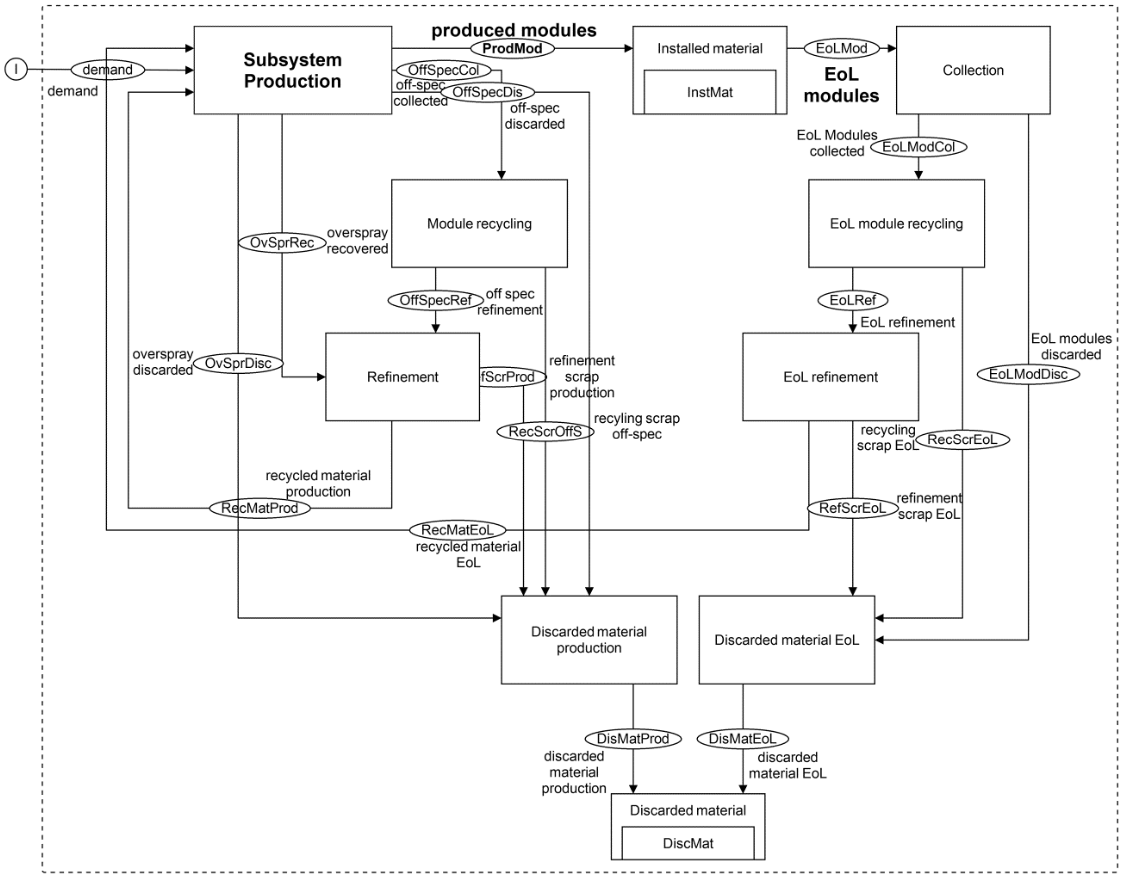

Figure 4-3: Material flow system for CdTe-PV along the life-cycle

4.3 Background data and scenario development

The following paragraphs present the data necessary to determine the transfer coefficients of the processes in the material flow model described above, and the required data for the formulas. The information is derived from desktop research and personal questionnaire-based interviews with photovoltaic manufacturers, recycling companies, and research institutes. Using this data, three scenarios were developed; hereafter labeled as “breakthrough”, “steady advance”, and “slow progress” scenario. These scenarios represent different market developments and technological trajectories, more specifically; lifetime expectancies, material efficiency in the production processes and material content of the solar cell, as well as collection quotas and recycling efficiencies. All assumptions are listed in Table 4-3. The base year of the scenarios is 2010 and global Te flows within the life-cycle of CdTe-PV modules are predicted thirty years into the future.

4.3.1 Produced area

The material bound in produced modules is calculated by multiplying the areal density of Te in the CdTe-cell by the annual area produced (Formula 1). The area produced A in year a is identical to the yearly installed photovoltaic power C_a in watt peak (W_p) divided by the required area per W_p, which is dependent on the efficiency of the module η_a[9]:

$$A_a = C_a / (I \cdot \eta_a) \qquad \text{4-4}$$

C_a can be taken from a market scenario. Here market scenarios are computed with the use of annual growth rates (AGR):

$$C_{a+1} = C_a \cdot (1 + AGR) \qquad \text{4-5}$$

The annual growth rates are taken from the sigmoid function $S(x)=1/(1+exp(-x))$ as:

$$AGR = S(x)/(S(x-1)-1) \qquad \text{4-6}$$

to model a typical S-formed market growth of a new technology.

In 2010 the market share of CdTe-PV was about 5 % (Hering, 2011). It is typically difficult to make robust assumptions about market shares for the future. Currently, several manufacturers have delayed or abandoned their expansion plans or even close down factories due to the precarious market situation (First Solar, 2012b; pv-magazine, 2012a, 2012b). The scenarios introduced follow the prospective production capacities of the main producers in the near future. We also consider EPIA's prediction that CdTe-PV will have a market share of over 10 % by 2020 (EPIA, 2011). Furthermore it's assumed that the CdTe-PV market share shrinks from 2020 onwards, i.e., the CdTe-PV market will grow slower than the overall market (sigmoid growths), as emerging technologies will enter the market. Considering these criterions, annual growth rates (AGR) are calculated to reach an annual CdTe-PV production capacity of 4 GW_p in the "slow progress" scenario (market share: 2.5 %), 8.1 GW_p in the "steady advance" scenario (market share: 5 %), and 12.2 GW_p in the "breakthrough" scenario (market share: 7.5 %).

The conversion efficiency of the modules determines the area produced each year. First Solar (2011a) reported in 2010 a 0.5 % annual improvement of PV module conversion efficiency, ultimately amounting to 11.6% by the end of 2010. Wadia et al. (2008) calculated a maximal theoretical conversion efficiency of 33 % for CdTe-PV cells, whereas the generally considered maximum efficiency for CdTe-PV modules is 18 % (Raugei, 2012). Until now, the highest CdTe-PV module efficiency has been confirmed at 14.4 % (First Solar, 2012d), while the highest research-cell efficiency has been confirmed at 16.7 % (Kazmerski, 2011). The technology roadmap of the International Energy Association (IEA) has set a goal for conversion efficiency of 15 % by the year 2030 for commercial CdTe-PV modules (IEA, 2010). Zuser and Rechberger (2011) predict in their scenarios that module conversion efficiencies will reach 15 %, 16.7 % respectively, by 2040.

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[9] Measured at standard test conditions (light intensity I=1,000 W/m² at 25°C)

Here it is presumed that conversion efficiencies in 2010 are equal to the average of *First Solar's* modules (11.3 %) in the same year (First Solar, 2011a). In 2040 module conversion efficiencies are assumed to reach 18 % (breakthrough), 16.5 % (steady advance), and 15 % (slow progress). The required area per watt peak from 2011 to 2039 is interpolated.

4.3.2 Areal density

The areal density μ_{ra} depends on the thickness of the semiconductor compound layer in year a, its density ϱ, and the weight percentage ω_r of material r in the semiconductor compound layer.

$$\mu_{ra}=d_a\cdot\varrho\cdot\omega_r \qquad 4\text{-}7$$

In a CdTe solar cell, a cadmium telluride and cadmium-sulphide layer of commonly 2-5 μm form the p-n junction (Razykov et al., 2011). The Norwegian Geotechnical Institute (NGI) reports that in 2009 the CdTe-layer thickness of First Solar's module was 2.2 μm (NGI, 2010). This value approximates the results of the leaching test conducted by the NGI, yielding a layer thickness of 2.1 μm (Green, 2011). Taking into account that not all production in the year 2010 can be attributed to *First Solar*, layer thicknesses between 2 and 3 μm are set in the scenarios. Assuming that the CdTe-layer with a density of 6,200 kg/m³ is stochiometric, 53 % of its weight is Te.

One possible way to decrease material demand in the future is a thinner active layer. Just 2 μm are required to absorb most of the useful part of the solar spectrum (Razykov et al., 2011), 0.44 μm to absorb 85 % of available energy equal or larger than the material band gap (Wadia et al., 2008). In research thickness is reduced below 1 μm (Amin et al., 2007; Jones et al., 2009). To avoid the loss of the spectrum while reducing the thickness, the light can be trapped in the cell by either reflecting the light with a mirror on the backside or bending it when it enters the cell to make the path of the incident light longer (or a combination of both methods). Amorphous silicon cells with about the same absorption coefficient as CdTe are already made with these optical enhancements, with layer thickness ranging between 0.1 to 0.3 μm (Zweibel, 2010).

In the "breakthrough" scenario it is assumed that using similar light trapping methods the CdTe-layer thickness can be reduced to 0.1 μm by 2040 – from 2 μm in 2010. In the "slow progress" scenario the thickness, equaling 3 μm in 2010, can't be decreased to less than 2 μm because of unacceptable efficiency losses. Finally, in the "steady advance" scenario, a thickness of at least 1 μm is required – starting with 2.5 μm in 2010.

4.3.3 Material utilization

Measures to reduce material content per watt peak include reducing layer thickness and increasing conversion efficiency. Besides these measures, which occur at module level, improving the material utilization of the deposition processes and the overall production efficiency can also reduce the raw material feedstock. Both values are necessary to be able to compute the flows in the "subsystem production" (Figure 4-2).

Based on available data, Green (2011) estimates that approximately 40 % of the raw material feedstock is used in production. Fthenakis (2009) implicitly assumes a higher utilization rate of about 60 % for 2008. According to Fthenakis, the current Te demand equals 100 t/GW$_p$ (personal communication, 05.10.2011). Assuming a material content of

0.06 g/W_p (conversion efficiency 11.7 %, layer thickness 2 μm), it can be concluded that the material utilization hasn't improved mentionable since 2008. It's not clear, whether the recycling of production waste is already included in these numbers.

How much of the raw material feedstock becomes deposited on the substrate depends on the deposition process. The two leading methods currently in use for the deposition of CdTe-films on substrates are *vapor transport deposition* of CdTe and CdS powder and *electrodeposition* of CdTe in combination with *chemical surface deposition* of CdS (Fthenakis, 2004b).

In *vapor transport deposition*, CdTe and CdS are deposited from the compounds in powder after vaporization. Typical material efficiency rates range from 50 % to 70 %; higher rates are predicted for scaled up production lines (Fthenakis, 2004b). In the *high-rate vapor transport deposition* process of *First Solar* most of the unused vapor condenses on the reactor's wall, shielding transport belts, etc. Less than 1 % of the vapor is carried out in exhaust streams (Fthenakis, 2004b). In another process, *atmospheric pressure chemical vapor deposition*, most of the non-film generating vapor is released into the exhaust stream, where it can subsequently be filtered out (Johnson et al., 2006).

Part of general maintenance to ensure proper functioning includes the removal of material built-up on the equipment components. Loose material in the chamber can be extracted with an industrial vacuum cleaner. Some components are sandblasted on site; others are treated physically and chemically by a service provider at its respective facility. Usually, physically removed materials are discarded together with the abrasives used for cleaning; less contaminated material may be further processed to recover raw materials. A recovery of the metals found in the filter slurry of the wet-chemical cleaning processes is to-date neither economical nor technical feasible (Thomas Marx, personal communication, 16.03.2011).

A pre-commercial method of production is *cathodic electro-deposition* of CdTe thin-films. According to Vasilis Fthenakis (2004b) less than 1 % of the Cd and Te are wasted during this process since deposition only occurs on surfaces held at the cathode. Zweibel (1999) states a material deposition rate of 95 % in the electro-deposition pilot line. Additionally, he estimates that productions costs per square meter (capital costs plus maintenance and material costs) can be reduced by over 50 % when using electro-deposition instead of vapor deposition. The US-company *EncoreSolar* was founded in 2010 to pursue this production technology (Basol, 2011; Encore Solar, 2012).

Due to the lack of information available and the various production processes in use, it is difficult to acquire reliable values for material utilization rates There is also a high uncertainty as to how much of the overspray can be recovered and further purified. Thus, a relatively broad range of material utilization rates and recovery rates for the overspray are assumed for 2010. For the purposes of this research, the "breakthrough" scenario utilizes the best available technology, electro-disposition, by 2040. The other two scenarios employ the currently most widespread technologies, with gradually improving efficiency until 2040.

4.3.4 Overall equipment efficiency

Another waste stream is comprised of modules that fail during production, e.g. glass substrates that break during the high temperature production processes or modules, which do not fulfill quality or power specifications (flow "off-spec modules" in Figure 4-2). In thin-film production high overall equipment efficiencies are important to drive costs down. In scaled-up production an overall equipment efficiency of more than 90 % is not uncommon; up to 98 % is aimed for in a 1 GW plant (Christian Kaufmann, personal communication, 19.03.2009, Arun Ramakrishnan, personal communication, 11.10.2010, Tom Clarius, personal communication, 02.05.2011). In pilot lines equipment efficiencies are considerably lower.

The "breakthrough" scenario uses an overall equipment efficiency rate of 95 % for scaled-up production in 2010. In pilot lines an efficiency of 85 % ("slow progress" scenario) is not unusual. In all scenarios, efficiencies are predicted to improve continuously until 2040. Due to the many process steps (up to 20) a cap of 98 % is set in the "breakthrough" scenario; meaning that in average per process step, 1 out of 1000 modules is "off-spec".

In the best case scenario, 100 % of off-spec modules are recycled. In the other scenarios not all off-spec modules can be recycled in 2010, because not every producer has its own recycling plants and the recycling capacities of the existing pilot lines are still limited; this should, however, improve with time.

4.3.5 Lifetime probability

The last waste stream included in the analysis is comprised of end-of-life modules. The amount of end-of-life modules depends on their lifetime. The lifetime is the time span between the module's production and the time a module is scrapped, either due to technical failures or for non-technical reasons. Therefore, the lifetime depends on many internal (e.g., power degradation, delamination) and external reasons (e.g., damage by hail or fire, profitability).

The lifetime is not to be mistaken with the power output warranty time, after which a module still reaches a certain performance (e.g. 80 % of original power output after 25 years). Reliability studies suggest 0.8-1 % relative power degradation per year (Enzenroth et al., 2007; Ross et al., 2007), indicating that the 80 % power warranty threshold is reached after 20 to 25 years. Due to the robust construction of the modules designed to last at least the output warranty time, it is probable that modules can be used longer than this.

Due to the fact that the first CdTe-PV modules were installed in the 1990's, returns are still low. Therefore, reliable statistics on the lifetime of CdTe-PV modules don't exist. Consequently, a probability function is used to calculate the lifetime probability of CdTe-PV modules; for this the Weibull distribution has been proven adequate (Elshkaki et al., 2005; Melo, 1999):

$$f(t) = \frac{\alpha}{\beta}\left(\frac{t}{\beta}\right)^{\alpha-1} e^{-(\frac{t}{\beta})^{\alpha}} \qquad 4\text{-}8$$

Melo (1999) describes how to calculate the shape parameter α and scale parameter β by assuming a mode and presuming that a percentage of products will reach end-of-life within a certain time-span. This method is applied in this paper.

In this analysis, the lifetime probability of photovoltaic modules $p_{t,PV}$ in their year of age t consists of two parts: probability of early returns of modules due to product defects or damages through transport and installation $p_{t,er,}$ and probability of modules first becoming deinstalled at end-of-life $p_{t,eol}$. The percentage of "early returns" (ER) quantifies how much of the yearly production is returned in early life.

$$p_{t,PV}=ER\cdot p_{t,er}+(1-ER)\cdot p_{t,eol} \qquad 4\text{-}9$$

The yearly material outflow of Te "EoL-modules" of the stock "installed material" are calculated by formulas (4-2), (4-3), (4-8), and (4-9) taking into account all since 1999 installed CdTe-PV modules. Because it is unclear which Weibull parameter represents the reality best, different modes are used (Table 4-2). In all scenarios 99.9 % of the modules will be scrapped within 40 years[10].

The percentage of overall production that is returned before the product warranty time (usually 5 years) depends on the module quality. Ross et al. (2007) report that warranty returns of *First Solar's* products have been reduced to less than 0.25 %. However the "Photovoltaik Magazin" reports that modules with a total capacity of about 30 MW_p, which were produced between June 2008 and June 2009 by *First Solar*, degraded significantly shortly after installation (photovoltaik-magazin, 2012). Those warranty cases amount to 4 % of *First Solar's* production of estimated 800 MW_p during this time span (First Solar, 2009, 2010a). According to the information gathered from expert interviews, other thin-film manufacturers report return rates between 0.25 % and 2 %. The "Study on the Development of a Take-Back-and Recovery System for Photovoltaic Products" approximates that 1.3 % of sold PV modules are returned either because of damages during installation and transport or efficiency degradation during the first year of operation (Sander et al., 2007).

In the "breakthrough" scenario an optimistic 0.25 % of warranty returns are assumed. In the "steady advance" scenario it is assumed that 2 % of the modules will come back, and in the "slow progress" scenario, respectively 4% of the modules would be returned (Table 4-2). The Weibull parameters for early returns are chosen so that early returned modules will show up in the first 5 years of use.

	ER	Weibull parameters		
		mode	α	β
Early returns	–	–	0.9	1.0
Breakthrough	0.25 %	32	12.8	32.2
Steady advance	2.00 %	30	10.0	30.3
Slow progress	4.00 %	28	8.2	28.5

Table 4-2: Parameters of Weibull distributions

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[10] A sensitivity analysis showed that the amount of end-of-life waste arising in 2040 is strongly dependent on the assumed mode of the Weibull-distribution, whereas the effect of varying the longest technical lifetime is marginal.

4.3.6 Recycling and refining

Both production rejects (off-spec modules) and end-of-life modules can be treated to recover the raw materials. Several processes to recover CdTe from CdTe-PV modules were developed on the lab- and demonstration-scale (Berger et al., 2010; Bohland et al., 2000; Campo et al., 2003; DeFilippo, 2011; Fthenakis and Wang, 2006; Goozner et al., 1999; Kernbaum, 2011; Palitzsch, 2010). The German company *saperatec* is building a pilot scale process line for the separation of thin-films from glass substrates (Kernbaum, 2011). *Loser Chemie*, a producer of chemicals for water treatment, has developed a universal process to recover thin-film metals from PV modules and production residues (Palitzsch, 2010). The materials produced from both companies have to be further processed and purified by a refinery.

Currently, the only industrial scale CdTe-PV module recycling facilities are run by *First Solar* – and are mainly involved in the treatment of production scrap. *First Solar* claims to recover 95 % to 97 % of CdTe, which then ends up in a filter cake (Krueger, 2010; Lisa Krueger, personal communication, 07.09.2009). Out of this filter cake and other residues from production, the refinery *5N Plus* extracts 80 % to 95 % Cd and Te that can be reused in 5N (99.999 %) CdTe synthesis (Andreas Wade, personal communication, 25.11.2010; Lisa Krueger, personal communication, 07.09.2009; Suys, 2010). Besides CdTe/CdS residues 5N Plus also recycles non-laminated substrates and laminated modules.

In the “breakthrough” scenario, all off-spec modules are treated; 97 % of the Te can be recovered during module recycling, and 90 % turned into 5N Te in a refinery. In the “slow progress scenario” it is assumed that 20 % of off-spec modules are discarded (e.g. deposited in landfills) as not every factory has its own attached recycling plant. Also, less thin-film material, just 90 %, is recovered during recycling and 80 % of this recycled material can be synthesized into 5N CdTe. The transfer coefficients of the “steady advance” scenario lie approximately in the middle of the other two scenarios. In all scenarios the coefficients improve over time.

4.3.7 Collection

What percentage of the modules will be collected in the future is unclear. In Europe, photovoltaic producers have founded the initiative “PV Cycle”. The aim of this organization was at creating a voluntary, industry-wide take-back and recycling program for end-of-life modules in Europe, but the environmental agreement proposed to the European Commission by PV Cycle was rejected. Thus, although currently excluded from the European e-waste directive, PV modules will, in the future, be subject to the revised e-waste directive. The legislation foresees the possibility to join a collection scheme such as PV Cycle or to fulfill the obligation by collecting and recycling modules individually. The legislation imposes collection rates for PV modules of up to 85 % and recycling rates up to 80 % (European Parliament, 2012). As glass already makes up more than 95 % of CdTe-PV module’s weight (Sander et al., 2007), this legislation doesn’t guarantee the recovery of the thin-film materials.

Currently, the collection rates of household e-waste in industrialized states are still quite low. In Europe, rates are reported at roughly 25% (medium sized appliances) to 40% (larger appliances) (Huisman et al., 2008); In the USA, 8 % of mobile devices and 38 % of computers are recycled (EPA, 2011). An assessment of various compliance schemes in

Europe concludes that it should be possible to collect around 75% of the large appliances (Huisman et al., 2008).

In addition to statutory provisions also softer instruments exist, which guarantee the take back and recycling of modules. For example, a loan from the German development bank "Kreditanstalt für Wiederaufbau (KfW)" requires the system-installer or module-producer to take back and dispose the modules at no charge in accordance with regulation (KfW, 2009). Another possibility is individual collection schemes. *First Solar* has set up an individual collection and recycling program that includes, among other measures; managing collection, setting aside funds, and requiring the owner to register their installation (First Solar, 2011b). Presumably, other CdTe-PV producers will follow a similar approach of individual producer responsibility.

In the scenarios presented, the collection rates for end-of-life PV modules can be considered quite high for two reasons; as CdTe-PV modules contain hazardous Cd, producers are required by the general public and the lawmaker to have efficient collection schemes. Furthermore, the installation of PV modules – usually within a large PV system – is less dissipative than the use of small electric appliances. In all scenarios collection rates improve over time.

Table 4-3 shows the underlying data of the material flow analysis that was presented above. Each combination represents one scenario. Values between 2010 and 2040 are interpolated.

Scenario	Breakthrough		Steady advance		Slow progress	
Year	2010	2040	2010	2040	2010	2040
Annual installation [GW_p]	1.5	12.2	1.5	8.1	1.5	4.0
Conversion efficiency η [%]	11.3	18.0	11.3	16.5	11.3	15.0
CdTe-layer thickness [μm]	2	0.1	2.5	1	3	2
Material utilization rate	75%	99%	65%	85%	55%	70%
Overspray recovery	75%	99%	50%	75%	70%	85%
Overall equipment efficiency	95%	98%	90%	95%	85%	90%
Collection off-spec modules	100%	100%	90%	100%	80%	90%
Collection EoL modules	95%	99%	80%	90%	65%	80%
Material recovery module recycling	97%	99%	95%	97%	90%	95%
Material recovery refining	90%	95%	85%	90%	80%	85%

Table 4-3: CdTe-PV production, conversion efficiencies, layer thickness, and transfer coefficients of three different scenarios

4.3.8 Storylines

In the following paragraphs, storylines are used to describe plausible future developments in each scenario, based on the set of assumptions in Table 4-3. They reflect, illustrate, and validate the quantitative assumption by setting them into the broader context, considering qualitative, technological, economic, and legislative issues.

Scenario "breakthrough"

High market growth rates and fast technological development are mutually beneficial. CdTe-modules stand out because of their high efficiencies, good performance, and high product quality. More than 94 % of the modules produce energy for more than 25 years. Due to efficient take-back and collection systems just a few end-of-life modules will find their way around the compulsory recycling laws. Strict environmental regulations have been passed stipulating high collection rates and material specific recycling quotas for critical materials. This development goes together with high enough commodity prices to cover declining recycling costs due to economy of scale. High commodity prices also lead to major efforts to reduce material use in manufacturing and to reduce the thickness of the CdTe-layer, which can be achieved thanks to efficient light trapping.

Scenario "steady advance"

The CdTe-PV output increases with reasonable growth rates. The product quality and performance is satisfying; only 16 % of the modules return within 25 years. Due to material efficiency measures and improved yields the production costs decrease further. There is no ban on using Cd in PV in Europe or USA, but environmental laws are strict. Producers have to make sure that collection and recycling is improved as current collection is dissatisfying. Due to a lack of onsite recycling capabilities by CdTe-PV producers, not all production discards are recycled.

Scenario "slow progress"

The industry experiences product quality problems that lead to a high amount of warranty returns in the first years of use. Due to a fast degradation of power output, over 30 % of all modules are already returned before they reach the output warranty time of 25 years. Industry and research are experiencing problems in increasing cell efficiency and in reducing layer thickness below 2 μm. Due to the slow technological development, the price advantage of CdTe-PV compared to other PV technologies can't be sustained. Therefore CdTe-PV looses market shares. Due to inefficient collection systems and take-back programs, the collection rate is lower than in the other two scenarios. Moreover, the time it takes to scale-up pilot recycling processes and run them efficiently will have been underestimated.

4.4 Results

In the following paragraphs the results of the material flow analysis are presented. Figure 4-4 shows the amount of Te bound in produced modules (left axis) as a function of the yearly produced capacity of CdTe-PV (right axis) for the three different market scenarios. Although the "steady advance" scenario starts off with less material bound in produced modules, it soon overtakes the slow progress scenario. In all scenarios the amount of Te installed annually drops after a peak in between 2018 and 2022 due to measures taken at module level to improve material efficiency; higher module efficiencies and thinner material layers compensate the market growth. Therefore the amount of Te installed in the "steady advance" scenario nearly equals that of the "slow progress" scenario in 2040, although double the capacity is being installed.

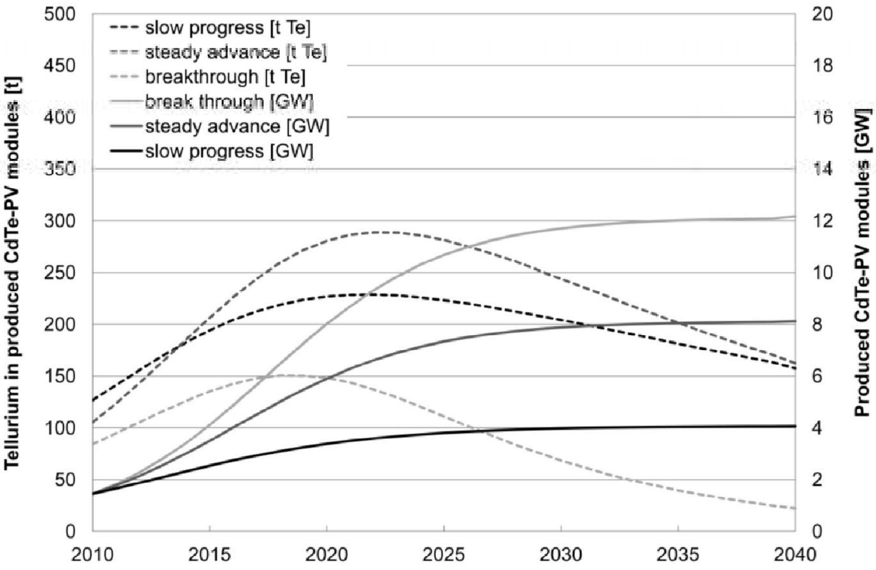

Figure 4-4: Three scenarios of yearly produced capacity (right axis) and tellurium bound in produced modules (left axes)

The peak can also be seen in Figure 4-5, which depicts the feedstock for production, i.e. the "primary" demand plus the recycled material from production scrap and end-of-life modules. In the "breakthrough" scenario, material efficiency measures can best compensate the market growth; the highest market growth goes hand in hand with the lowest Te feedstock of all scenarios. For the "slow progress" scenario the compensation doesn't work as good as for the other two scenarios; the feedstock is all the time the highest.

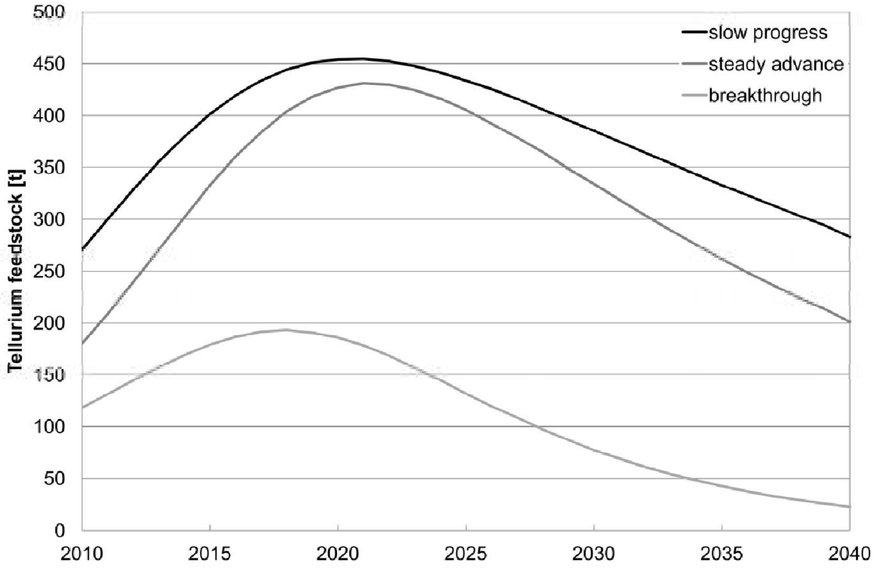

Figure 4-5: Feedstock of different scenarios

The indicator metric tons Te feedstock needed per giga watt peak produced modules (Figure 4-6) shows both the effect of material efficiency measures in production (material utilization, overall equipment efficiencies) and the material efficiency measures on module level (layer thickness, conversion efficiency). In 2010, between 82 t and 187 t of Te feedstock is needed to produce one giga watt of CdTe-PV modules. This means that in the "slow progress" scenario 152 t more Te is needed than in the "breakthrough" scenario (118 t) to produce the same capacity (1.5 GW_p in 2010). The specific feedstock demand is potentially improved in 2040 by 98 % in the "breakthrough" scenario, 80 % in the "steady advance" scenario, and 63 % in the "slow progress" scenario.

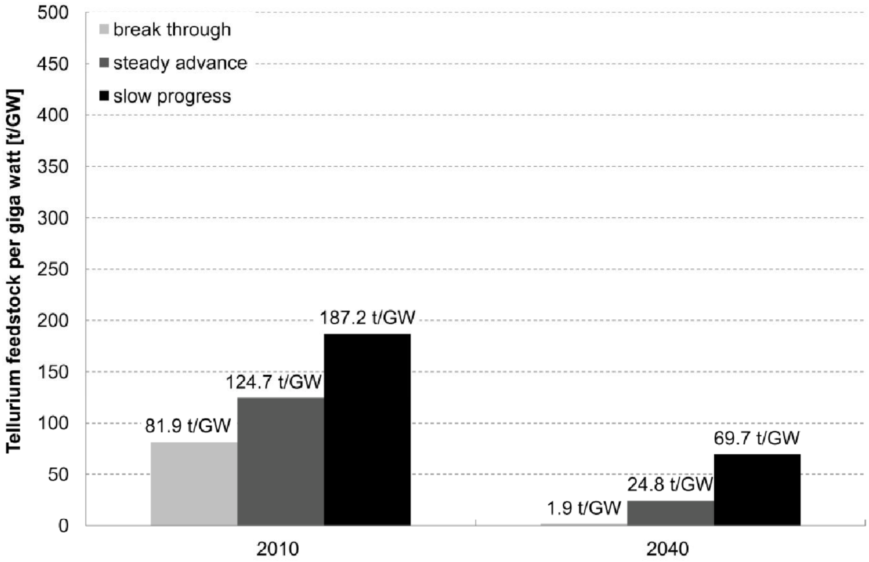

Figure 4-6: Feedstock per giga watt

Figure 4-7 shows the feedstock of the "slow progress" scenario composed of external supply (flow "demand"), recycled Te from CdTe-PV production scrap, and recycled Te from end-of-life modules. A peak value of 455 t Te will be needed in 2021 to produce 3.5 GW_p of CdTe-PV modules, or 130 t/GW_p (30 % improvement since 2010). The amount of recycled material from production scrap is predicted to decline from 2020 onwards due to efficiency measures, while the amount of Te resulting from end-of-life (EoL) recycling becomes more significant (see also Figure 4-12).

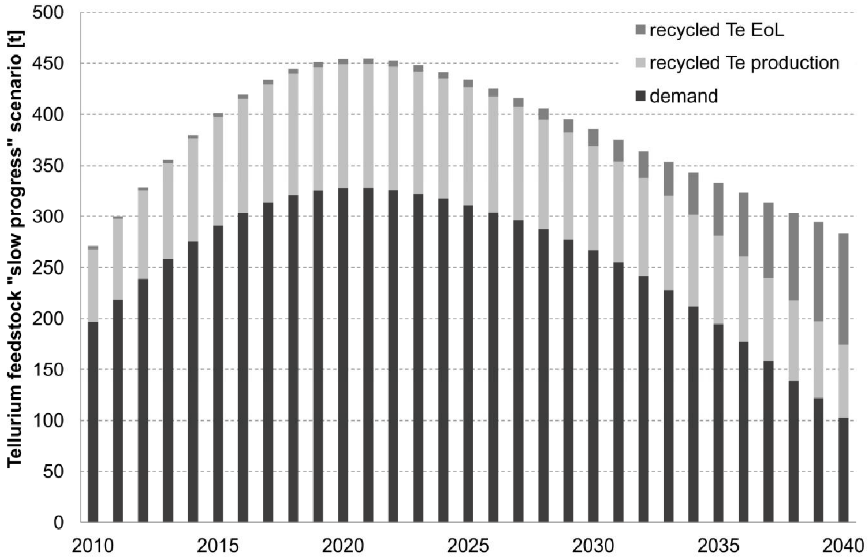

Figure 4-7: Tellurium feedstock in the "slow progress" scenario

In the “breakthrough” scenario, due to the high material utilization, production waste is predicted to play an inferior role compared to the recycled Te from EoL modules from 2034 onwards. The latter will actually surpass the feedstock by 60 % in 2040 (Figure 4-8). In this scenario, the CdTe-PV industry could be self-contained by 2038.

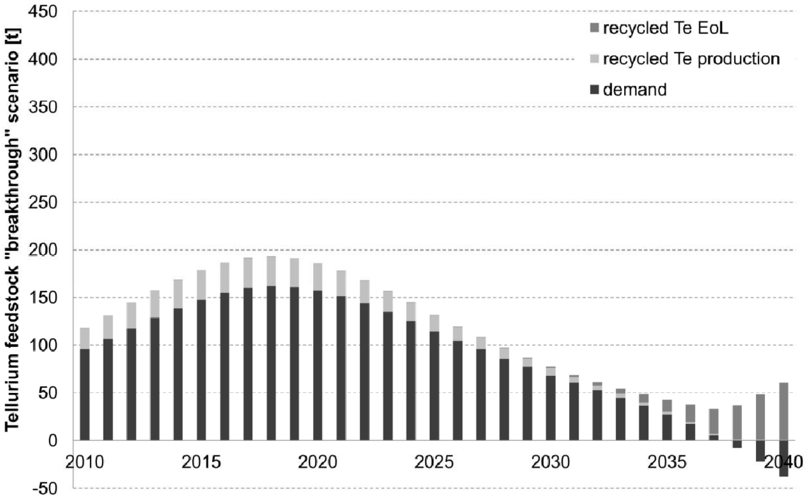

Figure 4-8: Tellurium feedstock in the “breakthrough” scenario

Even more interesting than the feedstock is the Te demand (Figure 4-9), because it indicates how much material has to come from external sources. Examples of possible sources are: primary Te from mining or recycled Te from other industries. The difference between the feedstock and demand at peak times amount to around 30 t in the “breakthrough” scenario, 90 t in the “steady advance” and 200 t in the “slow progress” scenario. In the “breakthrough” scenario the CdTe-PV industry could recycle more material from end-of-life modules than is necessary for production by 2038 (Figure 4-8).

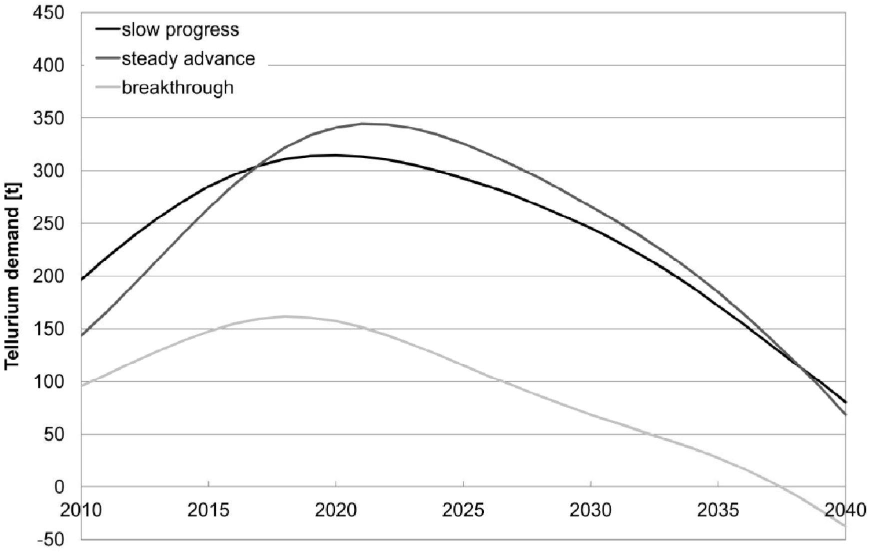

Figure 4-9: Tellurium demand

To assess the efficiency of the production system, the three indicators: “material utilization”, “recovery rate”, and “scrap rate” have been compared for each scenario below (Figure 4-10; definition of indicators in section 2). In 2010 about 50 % to 70 % of the feedstock is used in the final product and between 50 % and 70 % of Te found in production scrap (overspray and off-spec modules) is able to be recovered. Thus, 10 % to

30 % of the feedstock is scrapped. It is notable that in 2010 the recovery rate in the “slow progress” scenario is higher than in the “steady advance” scenario, primarily because more of the overspray can be recycled in the former scenario. But, because the material utilization is much lower in the “slow progress” scenario, the absolute amount of scrap is higher than in the “steady advance” scenario. In 2040 this situation reverses and the recovery rate of the “steady advance” scenario is 4 % higher than in the “slow progress” scenario; however, the recovery rate is still 20 % below that of the “breakthrough” scenario. Material utilization is predicted to increase by 16 % to 26 % by 2040. In the “breakthrough” scenario nearly 100 % of feedstock is bound in the cells or recycled in 2040, whereas in the “slow progress” scenario 12 % of the feedstock is still scrapped.

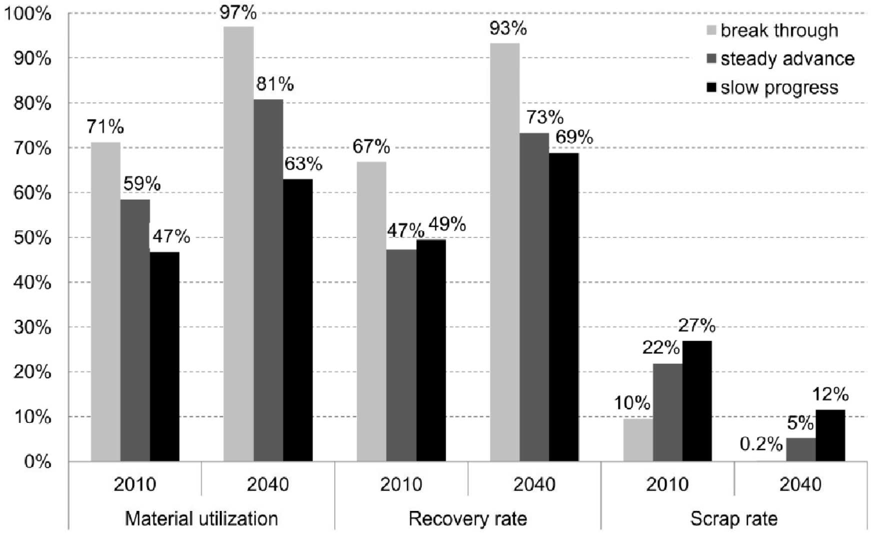

Figure 4-10: Material utilization, recovery rate, and scrap rate in production

The composition of production scrap of the “slow progress” scenario, the scenario with the highest amount of production scrap, is illustrated in Figure 4-11. In the “slow progress” and “steady advance” scenarios, the share of overspray at production scrap is above 78 % during the whole time-span. In the “breakthrough” scenario, the share falls to one third of overall production scrap in 2040 due to the high material utilization in the deposition process.

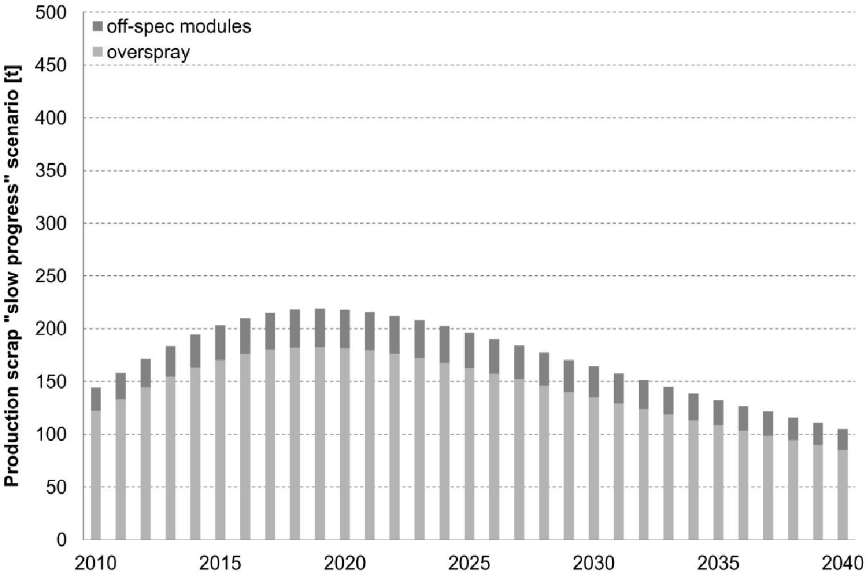

Figure 4-11: Composition of production scrap (“slow progress” scenario)

In the “breakthrough scenario the amount of Te bound in end-of-life modules (Figure 4-12) will surpass the amount of production scrap in 2033. In the “steady advance” scenario this will happen in 2036, and in the in the “slow progress” scenario in 2038. It should be noted that in the “slow progress” scenario the amount of end-of-life Te is at its highest, although more Te is found in installed modules in the “steady advance” scenario (Figure 4-4 and Figure 4-15). This is because modules will be scrapped earlier in the “slow progress” scenario than those in the other two scenarios. Depending on the scenario, the mode (the peak of the lifetime probability function, i.e. the most realistic lifetime) moves in time, such that in the other two scenarios fewer modules will be scrapped before 2040. Thereafter, it will change as indicated by the gradient of the dotted curves. In 2040, the amount of Te recycled from EoL modules in the “steady advance” scenario will actually be nearly as high as in the “slow progress” scenario. The amount of end-of-life Te, which is recycled and fed back into production, equals the amount of Te in EoL modules multiplied by the annual “end-of-life recycling rate” seen in Figure 4-13 for the years 2010 and 2040.

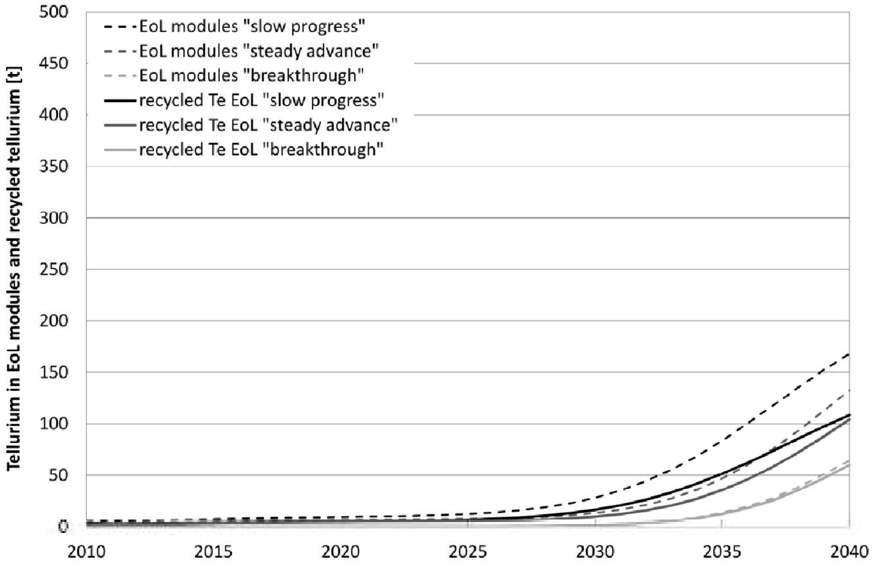

Figure 4-12: Tellurium bound in end-of-life modules and recycled tellurium from end-of-life modules

Of course the “breakthrough” scenario has the highest recycling rate, but even in 2040, 7 % of the Te is lost along the chain “collection”, “module recycling”, and “refinement”.

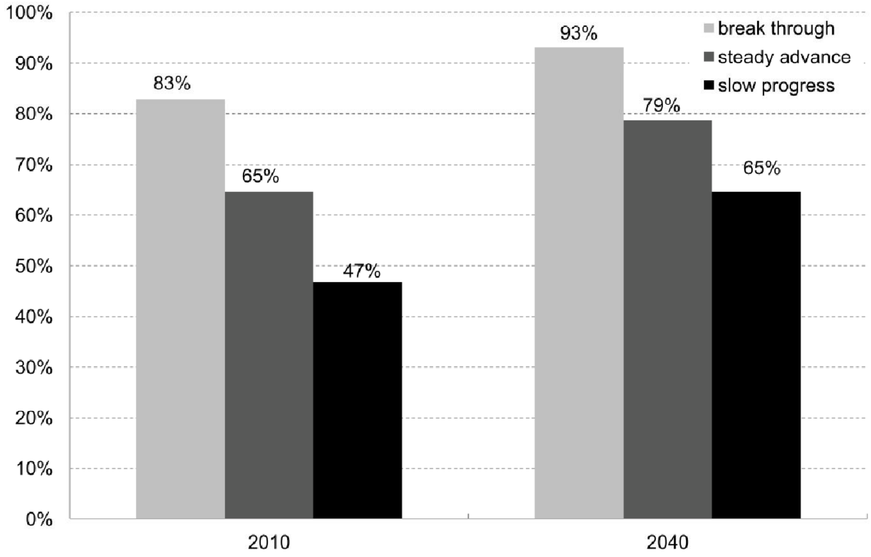

Figure 4-13: End-of-life recycling rate

The total cumulative amount of Te waste disposed of (stock “discarded material” in Figure 4-3) can be seen in Figure 4-14. The amount of Te disposed as production scrap and end-of-life waste is the highest in the “slow progress” scenario. In this scenario 2,620 t Te will leave the life cycle within 30 years. In the “breakthrough” scenario just 7 % of that amount is predicted to accumulate in waste deposits or dissipate in the environment.

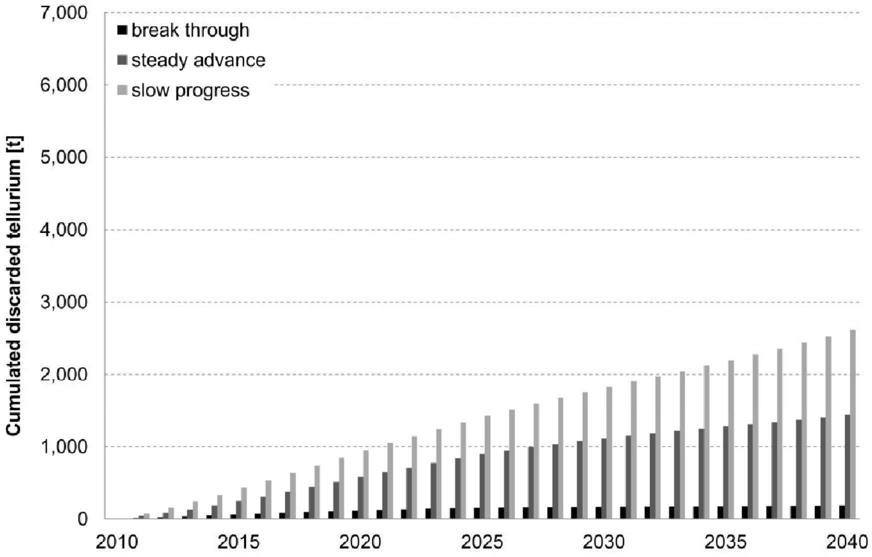

Figure 4-14: Stock of discarded tellurium

The amount of Te that is not exiting the material cycle accumulates in installed modules as a new stock (Figure 4-15). In 2040, this “urban mine” is predicted to contain from 2,780 t (“breakthrough”) to 6,300 t Te (“steady advance”) in modules installed since 1999. This stock will not start to “shrink” until the late 2030’s. I.e. more Te will then leave the stock in end-of-life modules than Te is added in newly installed modules.

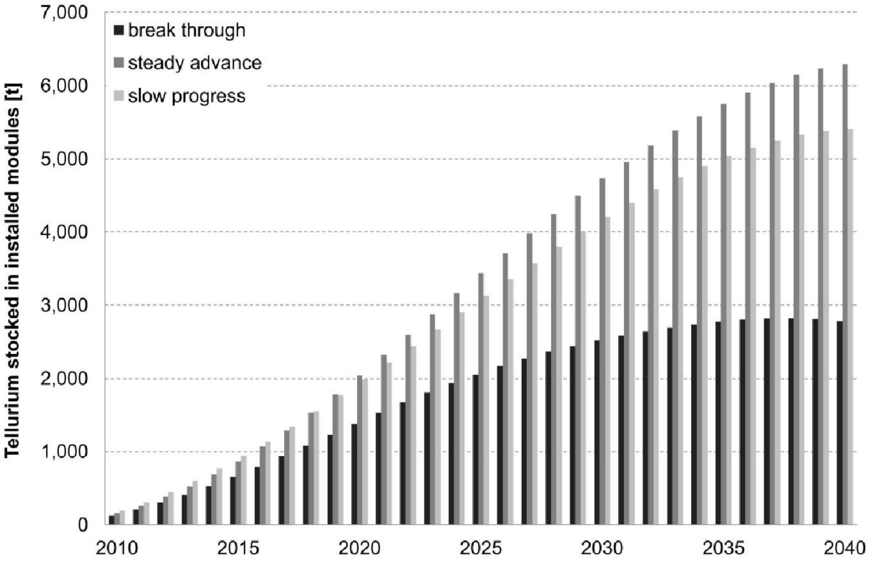

Figure 4-15: Tellurium stocked in installed modules

4.5 Discussion

According to the scenarios described, the Te demand for CdTe-PV in 2010 is estimated to equal from one to two fifths of worldwide Te production. After this the demand continues to grow until it reaches its peak between 2018 and 2021. The highest demand is reached in 2021, with a maximum of 344 t, as seen in the "steady advance" scenario. The total amount of Te produced in 2020 (1,400 t) and 2030 (1,850 t) as predicted by Fthenakis (2009) and Zweibel (2010) suggest that no temporary shortage in supply will occur, as long as the increase in demand for other applications stays below 12 % to 16 % per year. To check this conclusion we doubled the market share of CdTe-PV in the "steady advance" scenario to 10 % in 2040 (ceteris paribus). In this case, the demand peaks at 610 t in 2024. Hence even in this modified scenario a Te shortage seems implausible. However, Te production will have to adapt to the increased demand from CdTe-PV until peak times. After demand peaks, efficiency measures in production and an increase in Te from recycled end-of-life modules lead to a decline of demand despite market growth.

Figure 4-16 shows the Te feedstock per giga watt compared to the estimations from Zuser and Rechberger (2011), Andersson (2000), Fthenakis (2009), and Zweibel (2010). The error bars indicate the maximal and minimal of specific feedstock according to the scenario assumptions of the authors. A similar trend in decreasing Te feedstock from 2008 to 2040 is noticeable, with the highest changes between 2010 and 2020. Note that Andersson (2000) and Zweibel (2010) calculate the feedstock on the basis of the material content in the cell, and by doing so underestimate the real demand for production[11].

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[11] In Fthenakis (2009) analysis, the Te feedstock in 2008 is 1.75 times the module's content calculated on the basis of his assumptions on layer thickness and conversion efficiency (1.2 times the material content in 2020). Zuser and Rechberger (2011) calculate the specific feedstock based on conversion efficiencies, layer thickness, and material utilization rates.

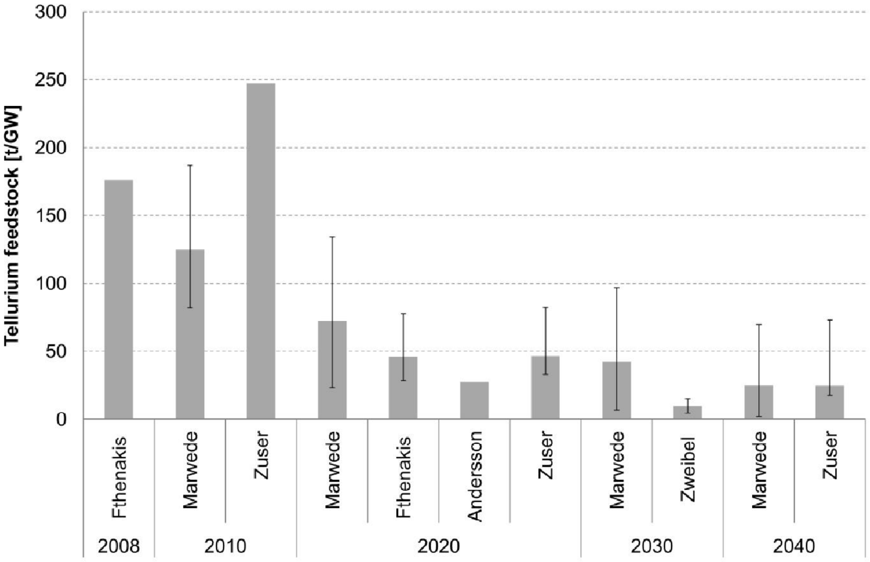

Figure 4-16: Tellurium demand per giga watt produced

Zuser and Rechberger (2011) and Fthenakis (2009) also look at the relevance of recycling of end-of life modules. Zuser and Rechberger (2011) assume that modules are replaced after 20 years of operation and that 90 % of the Te will be recovered. Fthenakis (2009) assumes a module lifetime of 30 years and an average 10 % loss in each module collection and recycling. In Fthenakis' estimations of Te availability for CdTe-PV, about 10 %-20 % comes from recycled Te in 2040. In Zuser's and Rechberger's analysis, the share of recycled Te from EoL modules at Te demand accounts for 20 % in 2040. In this MFA, recycled Te from EoL modules make up around 50 % of the feedstock in the "steady advance" scenario, and 40 % in the "slow progress" scenario respectively. In the "breakthrough" scenario the amount of recycled Te from end-of-life modules actually surpasses the feedstock needed in 2040 by 40 t. This is because the efficiency measures on process and module level has driven down the feedstock needed per GW_p produced modules by 98 %. One can conclude that although assumptions on market development, material demand, lifetime, and recycling rates differ in all studies, 10 % to 50 % of the Te needed for CdTe-PV production could realistically come from EoL modules by 2040.

While the share of recycled Te from end-of-life modules at the feedstock increases over time, the absolute amount of overall production scrap declines due to efficiency measures. Overspray makes up the biggest share of production scrap. In the "slow progress" scenario the most production scrap of all scenarios is generated due to the material inefficiency in production.

In the "breakthrough" scenario the biggest market success is accompanied by the lowest cumulated demand and the least discarded material. In all scenarios, the recycling rates in the production and end-of-life phase are increasing, but still 7 % ("breakthrough") to 33 % ("slow progress") of the cumulated demand is "lost". The amount of Te that is not leaving the material cycle is piling up as an "urban mine". The most Te accumulates in the "steady advance" scenario, although the cumulated installed power (181 GW_p) is just two thirds of the "breakthrough" scenario. Nevertheless, the most Te arises in end-of-life modules in the "slow progress" scenario because modules are scrapped at an earlier time. However, the amount of recycled Te in the "steady advance" scenario reaches that of the "slow progress" scenario in 2040 due to the higher efficiency of the recycling chain and a faster growing end-of-life stream. In general, the depletion of this “mine” is delayed until the late 2030s due to the long lifetime of the modules.

4.6 Conclusion

The material flow analysis shows that recycled Te from photovoltaic production scrap and end-of-life modules can make up a significant share of the feedstock. In the best case, these recycling flows together with material efficiency measures on module and process level can reduce the “primary” Te demand to below zero by 2038. Because material efficiency measures cannot compensate for market growth until approximately 2020, a temporary shortage may occur if Te production capacities are not scaled up fast enough. This could temporarily lead to high prices until Te production has expanded. When demand from CdTe-PV declines, overcapacities in Te production may have to be cut back.

The MFA and the interviews indicate that not all overspray can be recovered due to the dissipation in the equipment and to the contamination with Cd and equipment materials. Because of this, a high material utilization during deposition is crucial. Some of the recovered materials such as the scrapings from the shields and deposition chamber have to be disposed of as hazardous waste. Further research is also needed for examining the entire recycling chain and the total amount of waste disposed.

Off-spec modules contribute only marginally to production waste, but they can be used in combination with early returns as feedstock for the start-up recycling companies until more end-of-life modules are available. Currently, the recycling costs exceed the material value of the PV modules (including glass substrates and other materials). Producers have to set aside funds to guarantee that recycling and logistics costs can be covered. Despite high recycling costs, the use of toxic Cd should require module recycling with the additional benefit of recovering Te. In addition to other factors, such as material prices, logistics, and energy prices, two diametrically opposed aspects will influence the economics and feasibility of recovering Te in the future: Firstly, economy of scale economy caused by growing waste streams and secondly, the declining material content of the modules. It is still unclear whether recycling can become economically sustainable in the future. Until economical profitability is clear, regulatory measures, economic incentives, and producer responsibility should be used to assure the take-back and recycling of CdTe-modules to avoid Cd emissions and secure valuable Te. If producers would still own CdTe-PV modules in use (as in leasing business models), they could secure the access to the valuable resources accruing in installed modules. However, the long lifetime of the modules delays the stock’s depletion for nearly 30 years. Efficient collection and take-back programs are vital in ensuring that modules will be handled appropriately. Still, reliable data about the lifespan of modules is needed. Many other aspects in addition to technical failures have to be taken into account when modeling module waste streams. It might for example become profitable to demount PV power plants after payback time (usually less than 20 years) to make use of conversion efficiency gains of new modules (repowering). Demounted modules can then be recycled for material recovery, but they may also be refurbished for re-use prolonging their lifetime. Statistics on returns are necessary to model lifetime probability more accurately.

There are also relevant uncertainties related to the market and technological development. New material extensive technologies like concentrator cells or dye-sensitized cells for example, could act as substitutes for CdTe-PV. The scenarios in this paper try to reflect these uncertainties, but so called “wild cards”, i.e. events with low occurrence of probability but significant effects, are not considered in the assumed linear developments. For example, a legal ban of Cd use for PV, which was already controversially discussed before the last recast of the European RoHS directive (pv magazine, 2010), could mean at least for some regions the end of this PV technology. The scenarios illustrated here describe what would happen when the system develops as predicted. The purpose of the scenarios is to open up room for decisions to change the system to self-set targets. These targets include high material utilization during deposition, recycling of production scrap and end-of-life modules to preserve Te resources, close observation and avoidance of cadmium emissions further down the recycling chain, as well as precise cadastral and efficient collection systems. These measures are the key for a sustainable deployment of CdTe-PV.

5 Estimation of life-cycle material costs of CdTe- and CIGS-PV absorber materials based on life-cycle material flows

5.1 Introduction

In this chapter it's assessed how material efficiency measures along the module's life-cycle can reduce the net material demand for CIGS and CdTe solar modules and thus the material costs. In order to estimate the material flows along the life-cycle a material flow model is designed. The model is described in chapter 4, in which part of the information required for parameterizing the model is already presented. Whereas chapter 4 looks "only" at future Te flows, this work estimates the product specific flows of all absorber materials both for CdTe and Cu(In,Ga)Se_2 solar cells (static approach). In order to reflect the variety and uncertainty of the data three different efficiency scenarios, each specified by a dataset, are developed. Those datasets are used to model the material flows along the module's life-cycle and estimate the material costs along the life-cycle based on the computed flows. The results of the material flow and cost analysis are presented to be discussed in comparison with previous works before some conclusions are given.

5.2 Method

A material flow system was modeled using the material flow analysis software STAN. Figure 5-1 shows the life cycle phases "Module Production", "Collection", "Recycling and Refinement" and a sink "Discarded Materials". It's a simplified diagram of the material flow model, which is described in the section 4.2.

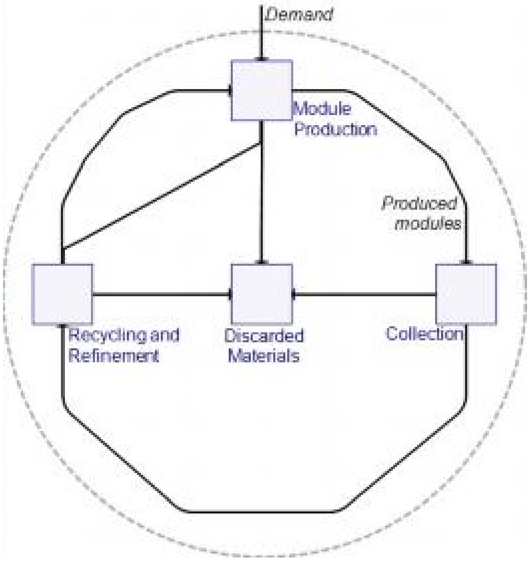

Figure 5-1: Life cycle of PV modules

In the "closed loop" model recycled material is credited to the feedstock into production in order to determine, how much of the feedstock can be substituted for recycled material. The feedstock is therefore composed of recovered material from production waste, recovered material from end-of-life modules, and additional material imported from external sources (demand). The feedstock depends on the material efficiency of the production processes, which is determined by the deposition efficiency of the deposition process and the overall equipment efficiency (yield) of the production line. The deposition efficiency determines how much of the feedstock ends up on the substrate. The remaining part consists either of not fully utilized source material (e.g. sputter targets) or of “overspray”. Both is (partially) recovered and transferred to a special metal refinery. The overall equipment efficiency of the production line determines how many modules, i.e. module area, are rejected during production (off-spec modules). The rejects are directed to “recycling and refinement” or are discarded, respectively. The process “collection” defines how many end-of-life modules are transferred to the processes “recycling and refinement”. “Recycling and refinement” includes the recovery of materials from production rejects and end-of-life modules as well as their purification. The recycled material is fed back into production. Refinement of material from sources other than PV scrap has not been accounted for.

Subsequent to the parameterization of the processes, the flows can be calculated by STAN after inputting the flow “produced modules” F^{pm}, i.e. the amount of material r bound in the produced modules. This flow is calculated by inputting the module area A in year and assigning an areal density μ_r to the flow.

$$F^{pm} = \mu_r \cdot A \qquad 6\text{-}1$$

The area produced A is identical to photovoltaic power C in watt peak (W_p) (here 1 GW_p) divided by the required area per W_p, which depends on the conversion efficiency of the module η measured at standard test conditions (light intensity I=1,000 W/m² at 25°C):

$$A = C/(I \cdot \eta) \qquad 6\text{-}2$$

How much of each material coats the substrate per square meter (areal density μ_r) depends on the thickness of the semiconductor compound layer, its density ϱ, and its material composition. All necessary information to determine the required parameters for the model (Table 5-1) is found in section 5.3.

To assess the material efficiency along the life cycle the scrap rate is calculated, which indicates how much of the feedstock is discarded during the life cycle, i.e. the discarded material divided by the feedstock. In order to calculate the material efficiency of the production system (including recycling of production waste), we calculate the material utilization rate which is the amount of material bound in produced modules divided by the demand plus the recycled material from end-of-life (EoL) modules. The end-of-life recycling rate assesses the efficiency of the end-of-life chain “collection”, “module recycling” and “refinement”. It is computed compliant with Graedel et al (2011) as the quotient of the material recycled from end-of-life modules and the material bound in end-of-life modules. Furthermore we approximate material costs within the system consisting of costs for the “raw” materials, refining costs, recycling costs and disposal costs.

		Parameters
Flow	Produced modules	Conversion efficiency Layer thickness
Processes	Deposition	Material deposition efficiency Recovery of production scrap
	Module production	Overall equipment efficiencies Percentage of production rejects collected for recycling
	Collection	Collection quota
	Module recycling	Recovery rates
	Refinement	Recycling rates
Costs	Production	Material costs
	Recycling	Recycling costs
	Disposal	Disposal costs

Table 5-1: Flows, processes and key parameters

5.3 Background data and scenario development

In this chapter the solar cell composition and the different life-cycle stages are analyzed in order to derive the necessary parameters for the material flow model.

5.3.1 Solar cell composition

CIGS cells are usually manufactured in the substrate configuration, which gives the highest efficiency but requires an additional encapsulation layer and/or glass to protect the cell surface (Romeo et al., 2004). Because of a high absorption coefficient, a very thin CIGS absorber layer (0.1-0.3 μm) is sufficient for absorbing the incident radiation (Razykov et al., 2011). Depending on the [Ga]/[In+Ga] ratio, the band gap of CIGS can be varied continuously between 1.04 and 1.68 eV. The current high-efficiency devices are prepared with a band gap in the range of 1.20-1.25 eV, which correspond to a [Ga]/[In+Ga] ratio between 25 % and 30 % (Razykov et al., 2011; Romeo et al., 2004). Commonly CdS is used as a buffer layer to form the hetero-junction. But also “Cd-free” buffer layers such as ZnS, ZnSe, ZnInSe and In_2S_3 are explored. As front contact or window, a transparent conductive oxide (TCO) such as Indium-Tin-Oxide (ITO) or Al doped ZnO is used. (Kazmerski, 2006; Razykov et al., 2011; Romeo et al., 2004; Sander et al., 2007)

CdTe solar cells can be grown both in substrate and superstrate configurations. However the highest efficiencies are achieved in the superstrate configuration, in which layers of TCO, CdS, CdTe, and the metal back contact are sequentially grown on glass substrates. The most commonly used TCO is SnO_x:F, but also ITO, ZnO:Al, and $CdSnO_4$ are applied to grow high efficiency solar cells. The CdS buffer layer forms a hetero-junction with the CdTe layer. The thickness of the CdTe layer depends on the deposition methods and is typically in the range of 2-6 μm, whereas just 2 μm are required to absorb most of the useful spectrum of the light. A quasi-ohmic back contact is formed by a combination of a buffer layer and metallization, commonly Cu/Au, Cu/graphite, or graphite pastes doped with Hg and Cu. (Kazmerski, 2006; Razykov et al., 2011; Romeo et al., 2004)

In the following section we just look at the absorber layer to simplify the comparison between the two technologies. This is reasonable because the absorber is the main constituent and the back electrode, buffer layer and front contact are typically made of similar materials and similar deposition methods are used.

5.3.2 Conversion efficiency

The conversion efficiency of the modules determines the area produced per giga watt. *First Solar* reported for 2011 an average conversion efficiency of 11.9 % for CdTe-PV modules (First Solar, 2012a). We calculated the average module conversion efficiency of nine CIGS producers as 11.8 %. The highest PV module efficiency has been confirmed at 12.8 % for CdTe and 15.7 % for CIGS modules; the highest cell efficiencies at 16.7 % (CdTe) and 19.6 % (CIGS) (Green et al., 2012). The best small-area non-vacuum CIGS solar cells demonstrated exhibit efficiencies of around 12-14 % (Hibberd et al., 2010). *Solibro* claimed to have achieved a world-record CIGS module efficiency of 17.4 % in a test module using co-evaporation (pv-magazine, 2011b). *First Solar* reported a record reaching an efficiency of 14.4 % for CdTe-PV modules (First Solar, 2012d). The generally considered maximum efficiency for CdTe-PV modules is 18 % (Raugei, 2012; Woodhouse et al., in press).

5.3.3 Layer thickness

In 2009 the CdTe-layer thickness of the main producer *First Solar* was in between 2.1 and 2.2 µm (Green, 2011; NGI, 2010). It is believed that 1 µm is an achievable target (Fthenakis, 2009; Woodhouse et al., in press; Zuser and Rechberger, 2011), although thickness is reduced already below 1 µm in research (Amin et al., 2007; Jones et al., 2009). More details can be found in section 4.3.2. CIGS absorber layers are nowadays 1.0 to 1.9 µm thick, typically 1.5-1.7 µm (Volker Sittinger, personal communication, 25.09.2012, Thomas Umschlag, personal communication, 25.09.2012). According to (Singh and Patra, 2010) the CIGS absorber layer should be at least 1 µm thick for compositional uniformity over large areas. Fthenakis (2009) and Zuser and Rechberger (2011) even assume that 0.8 µm can be realized in the long-term.

5.3.4 Material deposition efficiency

During “production”, deposition efficiency of the deposition process and overall equipment efficiencies are the key parameters in determining waste streams. The deposition efficiency depends on the applied method to deposit the absorber layer on the substrate. Different methods are described in (Dhere, 2006; Hibberd et al., 2010; Kaelin et al., 2004a; Kazmerski, 2006; Razykov et al., 2011; Romeo et al., 2004; Singh and Patra, 2010). The deposition efficiency of the absorber deposition process is defined as the ratio of the coating weight to the weight of the feedstock, i.e. which part of the feedstock ends up on the substrate. In vacuum methods deposition efficiencies are in between 20 % and 80 % (see below). In non-vacuum methods such as screen printing, electro-deposition or paste coating, which precisely direct materials to the desired location on the substrate surface, deposition efficiencies of close to 100 % are achievable (Dhere, 2006; Fthenakis, 2004a; Hibberd et al., 2010; Kaelin et al., 2004a; Kaelin et al., 2004b; Razykov et al., 2011; Zweibel, 1999).

The best methods for the formation of CIGS absorber with regards to costs, processing rates, reproducibility, and compositional uniformity are (Razykov et al., 2011; Romeo et al., 2004; Singh and Patra, 2010):

1) *Simultaneous vacuum co-evaporation* of all constituents (Cu, In, Ga, and Se) from multiple sources which are delivered to a heated substrate (400-600°C) and the

GIGS film is formed in a single growth process. The variation of the In/Ga flux ratio during the deposition allows the formation of graded band gap absorbers.

2) A *sequential process* that separates the deposition of the precursor material from the chalcogenization reaction to form a polycrystalline layer. Typically low cost and low-temperature methods such as sputtering, thermal evaporation, or electro-deposition are used to deposit the precursors (Cu, Ga, and In) followed by thermal annealing and crystallization in a Se atmosphere at 400°C to 600°C.

1) The deposition efficiency in *co-evaporation* depends on the equipment design, the substrate widths, the process and the used vaporizers. In an industrial plant for coating glass substrates of 1.2-1.4 m width 40-55 % of Cu, In and Ga is ending up on the substrate when using point sources, 50-70 % when using linear vaporizers (Frank Huber, personal communication, 26.09.2012). Most of the rest ends up in the chamber either as single layers or reacts with the other materials to form a compound (Frank Huber, personal communication, 26.09.2012).
2) In the *sequential process* Cu, In and Ga are commonly sputtered. How much of the material is sputtered depends on the form of target and its length. Of planar targets 30 % to 50 % can be ablated, of rotary targets typically 80 % with a potential of up to 90 % (Christian Hagelücken, personal communication, 15.01.2009; Ignace de Ruijter, personal communication, 11.09.2009; Christian Linke, personal communication, 06.05.2010, Axel Neisser, personal communication, 06.05.2011, Yan Wang, Li Hamlin, personal communication, 06.10.2011, Frank T. Zimone, personal communication, 25.09.2012; Willkommen and Dimer, 2007). Of the sputtered material 60 % to 90 % winds up on the substrate, depending on the geometry of the chamber and the process (roll-to-roll, single substrates); the rest coats the chamber walls, shielding, transport belt et cetera. Using the numbers above, one can estimate that 20 % to 80 % of the target material ends up on the substrate; the rest stays on the target or coats the chamber and equipment components.

The precursor films are typically reacted in either H_2Se or Se vapor at 400-500°C, sometimes combined with S or H_2S (Romeo et al., 2004; Singh and Patra, 2010). Experts state that deposition efficiencies are typically lower than for evaporating In, Ga, and Cu (Tom Clarius, personal communication, 02.05.2011, Frank Huber, personal communication, 26.09.2012). Again most of the “excess” selenium ends up in the chamber. The exhaust gas has to be wet or dry cleaned because of the high toxicity of the hydrides, for example in a dry bed absorber filled with copper granules where the harmful H_2Se is converted into non-volatile, inorganic selenium salts (Centrotherm, 2012; Dani Muse, personal communication, 25.09.2012). In this case both copper and selenium can be recovered afterwards (Dani Muse, personal communication, 25.09.2012). Another solution was developed by the company *Ebner Industrieofenbau*. It has developed an evaporator in which unused selenium is condensed and fed back into the source to have a closed loop system. A number for the material utilization is not yet available (Unknown, personal communication, 25.09.12).

Methods currently in use for the deposition of CdTe-films on substrates are described in detail in section 4.3.3. One can summarize that

1. In *vapor transport deposition*, deposition rates range from 50 % to 70 %; higher rates are predicted for scaled up production lines (Fthenakis, 2004a).

2. The deposition efficiency of *cathodic electro-deposition* of CdTe thin-films is in between 95 % and 99 % (Fthenakis, 2004b; Zweibel, 1999).
3. According to Pinheiro et al. (2006) the material deposition efficiency of *close-spaced sublimation (CSS)* can reach the value of 50 %.

One can summarize that the deposition efficiency is in between 20 % and 80 % for vacuum methods, and up to 99 % for non-vacuum methods. The following paragraph describes how much of the excess material is recovered and how many production rejects arise.

5.3.5 Production scrap

Due to the lack of information available and the various production processes in use, there is a high uncertainty as to how much of the overspray can be recovered and further purified. The in section 4.3.3 mentioned restrictions for the recovery of “overspray” from deposition for further refining indicate that recovery rates tend to be lower than assumed in the scenarios of chapter 4, probably below 25 % as stated by Woodhouse et al. (2012) and Fthenakis (2010). Besides production scrap from deposition also production rejects (broken modules or modules which do not fulfill specifications) arise as post-industrial waste. The percentage of production rejects depends on the overall equipment efficiency of the production line. In thin-film production high overall equipment efficiencies are important to drive down costs. In scaled up factories an overall equipment efficiency of more than 90 % is common, aiming at up to 98 % in a 1 GW plant (Hegedus, 2006; Christian Kaufmann, personal communication, 19.03.2009, Arun Ramakrishnan, personal communication, 11.10.2010, Tom Clarius, personal communication, 02.05.2011). In pilot lines the equipment efficiencies are considerably lower. PV modules arise also as post-consumer waste, which have to be collected for recycling.

5.3.6 Collection

Collection is the decisive factor determining in which recycling channels modules are directed. In 2011, the European collection scheme *PV Cycle* collected more than 1,400 tones of PV modules, resulting in a collection rate of approximately 70 % (Ziegler, 2012). Since 2012 PV modules are subject to the revised European electronic waste directive. The legislation foresees the possibility to join a collection scheme such as PV Cycle or to fulfill the obligation by collecting and recycling modules individually. The legislation imposes collection rates for electronic products of up to 85 % of waste generated and recycling and reuse rates up to 80 % by 2019 (European Parliament, 2012). As glass already makes up more than 95 % of thin-film PV modules’ weight (Sander et al., 2007), this legislation doesn’t guarantee the recovery of the thin-film materials. To the best knowledge of the authors there are no common collection schemes outside Europe in planning, so that collection depends on legislative requirements or individual take-back systems such as the one set-up by *First Solar* (First Solar, 2012c) or service providers such as *PV Recycling* (PV Recycling, 2013) in the Unites States. After collection modules can be transported to recycling facilities.

5.3.7 Recycling of modules

The review of recycling technologies for CdTe and CIGS photovoltaic modules to recover thin-film materials shows that they are scientifically sufficiently explored (chapter 3). However, most processes have just been proven feasible on lab scale; few have reached pilot scale. In hydrometallurgical processes, recovery rates of more than 90 % of the metal of interest are feasible (Krueger, 2010; Wiltraud Wischmann, personal communication, 12.08.2009, Nicholas Audet, personal communication, 07.09.2012; Palitzsch and Loser, 2011, 2012). Recycled residues are usually transferred to a refinery for upgrading.

5.3.8 Refining

Whether a refinery can recover single elements in semiconductor-grade purity from production scrap or recycling residues depends on the material composition, contaminations as well as concentration and value of the target elements and has to be evaluated case-by-case. The refinery *Umicore* feeds CIGS chamber scrapings to their smelter to valorize the elements In, Ga and Se, typically reaching a recovery rate of 70-80 % (Olivier Bracher, personal communication, 25.09.2012; Oosterhof, 2011). The Canadian metal refinery *5N Plus* has developed processes to recover the elements from CdTe- and CIGS-residues, targeting a typical recovery rate of 90 % or more for the metals of interest (Dattilo, 2011; Huot, 2011; Nicholas Audet, personal communication, 07.09.2012; Suys, 2010).

In case of expensive materials sputter targets are reprocessed – although some of the material may be lost due to contamination with backend tube materials (Jim Hisert, personal communication, 25.09.2012). In the case of indium an estimated 60-70% of the target material is recycled (Hsieh et al., 2009; Mikolajczak, 2009; Speirs et al., 2011). A common practice for planar targets is to fill up the “race track” with new material without wasting the material that has been left on the target (Keshner and Arya, 2004). This can be repeated up to 20 times (Tom Clarius, personal communication, 02.05.2011).

5.3.9 Life-cycle costs for the materials

Based on the material flows the life-cycle material costs of both technologies are calculated to see whether material efficiency measures can drive material costs down. We calculate the material costs for the flow demand, the recycling and disposal costs for the modules and the refining and disposal costs for the materials recycled or disposed of within the system[12].

The total material price for the demand consists of the cost for the technical grade material and a “tolling charge”, which includes the cost of converting the source materials into hyper pure material plus a margin for the refinery (Table 5-2). Woodhouse et al. Woodhouse et al. (in press) state a CdTe compound price (large volumes) of 410-560 $/kg and a purified Te price of 280- 430 $/kg. If we consider the stoichiometry of CdTe, we can calculate a tolling charge of 220 to 370 $/kg, similar to estimations from Green (2011) of 200-340 $/kg. Woodhouse et al. (2012) assume a tolling charge of 110 $/kg for the

---

[12] Transport and collection costs are neglected for two reasons: 1) Under the assumption that there is no difference in shipping costs for transporting modules to landfills or recycling facilities the difference in transport costs among the scenarios is marginal. 2) Reverse logistic costs are low compared to the other costs: for a reverse logistic system in Eastern Germany reverse logistic costs of 2.6 $/t (or 0.04 c/$W_p$) can be computed from cost estimations by Choi and Fthenakis (2010a).

manufacturing of indium sputter targets. One target manufacturer we questioned stated that they use source material of 99.99 % purity for CuGa target (75 w-% Cu, 25 w-% Ga). The materials make up the main share of the target price, the rest are processing costs and a margin (Christoph Adelhelm, personal communication, 04.12.2012). A selenium supplier charges processing costs for purifying a selenium source of typically 99.5-99.7 % purity up to 5N (99.999 %) purity (Frank Arm, personal communication, 04.12.2012).

Metal/compound (technical grade)	CdTe	Cd (99.95) [\$/kg]	Te (99.95) [\$/kg]	CuGa [\$/kg]	Cu (99.35) [\$/kg]	In (99.99) [\$/kg]	Ga (99.99) [\$/kg]	Se (99.5) [\$/kg]
Raw material costs[a)]	193	2.75	360	178	8.82	685	720	128
Tolling charge	280			44		110		31
Material price[b)]	473			222		795		159

Table 5-2: Metal costs and material prices in 2011

a) Technical grade raw material costs of Cd, Te, Cu and In taken from (USGS, 2012b); for Ga and Se average metal prices in 2011 were taken from (Metal Pages, 2013)
b) Material prices for purified and shaped materials to be used as source for production

For the life-cycle cost analysis we assume that just for the flow “demand” the full material price is charged. Through recycling, costs for the technical grade materials are saved and only the “tolling charge” accrues for the amount of recycled material. However, additional costs for recycling of modules arise. It’s reasonable to assume the costs for recycling of thin-film PV modules to be 2 ¢/W_p (Choi and Fthenakis, 2010b; Marwede et al., 2013). Additionally, we add disposal costs for the treatment and land disposal of the discarded thin-film materials and landfill costs for off-spec and non-collected EoL modules (10 \$/t Choi and Fthenakis, 2010b). All cost assumptions are listed in Table 5-3.

5.3.10 Scenarios for the material flow model

Using the information presented above we developed three different scenarios in order to compare the two PV technologies and give an outlook into the future. Each scenario is characterized through a set of indicators (Table 5-3) and described in a storyline. The scenarios “make it better” and “not bad” compare a worst case with a very efficient one assuming today’s module efficiencies and absorber layer thicknesses. The scenario “you made it” contrasts the other two with a (hypothetical) possible optimum in the future.

Make it better (Mib)!

In this scenario the absorber layer and conversion efficiencies are equal to current commercial solar cells. The deposition efficiencies are in the lower range of current commercial processes. Indium is recycled from planar sputter targets, but the material which ends up in the equipment both in CdTe and CIGS deposition is not recycled, nor are off-spec and end-of life PV modules.

Not bad (Nb)!

Here, modules reach efficiencies and absorber layer thicknesses in between current values and the possible maximum. Best available technologies are used for deposition with highest achievable deposition efficiencies. One fourth of the overspray can be recovered to be reprocessed to high purity chemical elements. The remains on the Cu, In and Ga sputter targets are also recycled. Refinery processes are adjusted to recover the valuable and toxic materials. Fortunately all off-spec modules and two fifths of end-of-life modules are treated to recover the thin-film materials.

You made it (Ymi)!

In this (more hypothetical) scenario, the maximum module efficiencies can be reached using the most efficient deposition methods in a scaled up PV factory. The absorber layer can be reduced to conceivable thicknesses. A high share of the unused materials during deposition is transferred to a refinery. All off-spec modules are treated as well as 85 % of end-of-life modules. Pre-treatment of the modules and refining of the residues are very efficient and target all absorber materials. Recycling and disposal costs per watt decrease due to the conversion efficiency gains, because the specific weight per watt decreases.

Assumptions for material flows						
Scenario	You made it!		Not bad!		Make it better!	
Technology	CdTe	CIGS[a)]	CdTe	CIGS[a)]	CdTe	CIGS[a)]
Conversion efficiency η	18.0%	20.0%	11.9%	11.8%	11.9%	11.8%
Absorber-layer thickness [μm]	1.0	0.8	2.0	1.6	2.0	1.6
Deposition efficiency	95%		75%	Cu, In, Ga: 80%; Se: 60 %	50%	Cu, In, Ga: 20%; Se: 30 %
Production scrap recovery	50%		25%	Cu, In, Ga: 62,5%; Se 25 %	0%	In 87,5%; Cu, Ga, Se: 0 %
Overall equipment efficiency	98%		90%		85%	
Collection off-spec modules	100%		100%		0%	
Collection end-of-life	85%		40%		0%	
Material recovery module recycling	97%		90%		0%	
Material recovery refining	95%		90%	In, Ga, Se: 75%; Cu: 0%	0%	In: 60%
Assumptions for life cycle material costs						
Scenario	You made it!		Not bad!		Make it better!	
Recycling costs for modules [US-¢/W_p]	1.3	1.2	2			
Landfill costs for modules[b)] [US-¢/W_p]	0.1	0.09	0.14			
Disposal cost materials[c)] [$/kg]	1.4					

Material prices				
Material price [$/kg][d)]	CdTe	CuGa	In	Se
	473	222	795	159

Table 5-3: Conversion efficiencies, layer thickness, transfer coefficients and costs

a) Stoichiometry: $Cu(In_{0.7}Ga_{0.3})Se_2$
b) Estimated by using an average module weight of 17.1 kg/m² (First Solar, 2010b; Sander et al., 2007) and a weight decrease per W_p due to conversion efficiency gains.
c) Estimated from treatment costs of 0.42-2.2 €/kg (ECN, 2002) for hazardous waste and a landfill disposal fee for hazardous waste of 50 $/t (Department of Toxic Substances Control, 2012).
d) The material price is composed of costs for technical grade material and a "tolling" charge (Table 5-2).

5.4 Results

Figure 5-2 a)-f) [Figure A–2 a)-f) in Appendix A.4] show the flows for each scenario illustrated in sankey diagrams which integrate the results of the calculations made by the software STAN. The diagrams facilitate the depiction of the losses along the life cycle. In the Mib scenario all materials are discarded either during module production or after use, while only In is recovered as production scrap for recycling. In the Nb and Ymi scenarios the loop is partially closed. In both scenarios the highest losses occur during collection. Furthermore, it's apparent that demand for the absorber materials – which is imported from outside the system – is already reduced significantly by higher material efficiencies during production and recycling while not changing the specific material content of the modules: demand is reduced by 60 % for CdTe and 70 % for CIGS comparing the Mib and the Nb scenarios. However, by introducing further measures in the Ymi scenario the demand is further decreased by more than 90 %.

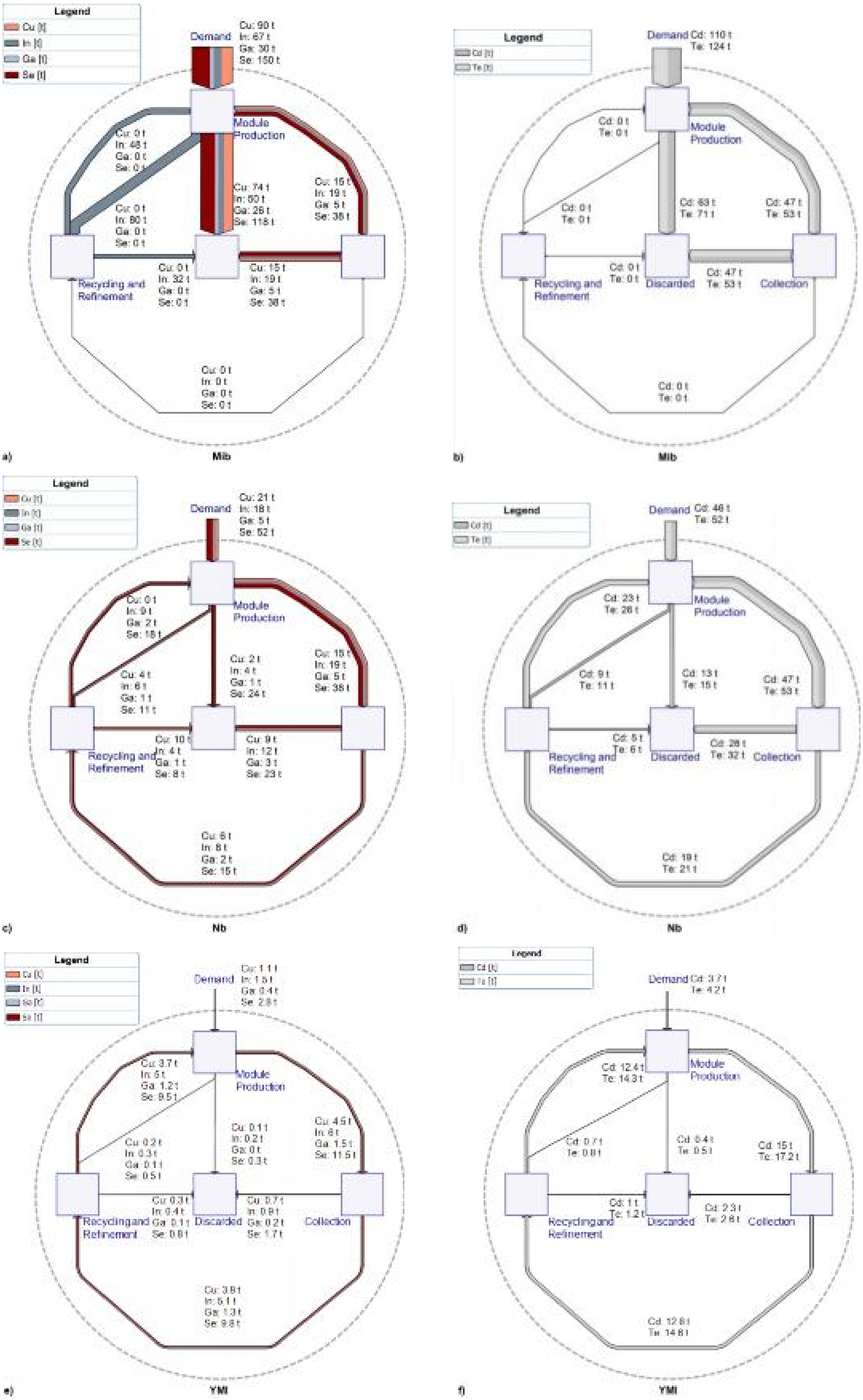

Figure 5-2: Material flows along the life-cycle of CIGS- and CdTe-PV in the “Make it better (Mib)” (a-b), “Not bad (Nb)” (c-d) and “You made it (Ymi)” scenario (e-f) in t/GW

The efficiency gains are reflected by the indicators illustrated in Figure 5-3 for CdTe- and CIGS-PV. In the Mib scenario all absorber materials are lost along the life cycle, except for In due to the recycling of sputter target. In the Nb scenario 2/3 of Cd, Te, In, and Ga, 3/4 of Se and 100 % of Cu are discarded along the life cycle. In the Ymi scenario just 1/4 of the feedstock needs to be imported to the system – in other words 3/4 stay within the system. The material utilization in CdTe-PV module production can be more than doubled comparing the Mib with the Ymi scenario. Looking at CIGS in the Mib scenario the material utilization for In is significantly higher compared to the other sputter materials Cu and Ga thanks to the recycling of the sputter target. However, material utilization can still be significantly improved by more than 50 percentage points (apart from Se) by measures taken in the Nb scenario. The improvement of material utilization from the Nb to the Ymi scenario only accounts for 13 percent points for In and Ga. A much higher gain is seen in the improvement of the EoL recycling chain from the Mib to the Ymi scenario; a recycling rate of nearly 80 % can be reached. On the other hand this means that 20 % of the material is still lost along the end-of-life chain "collection", "recycling" and "refining", although every step is very efficient in itself.

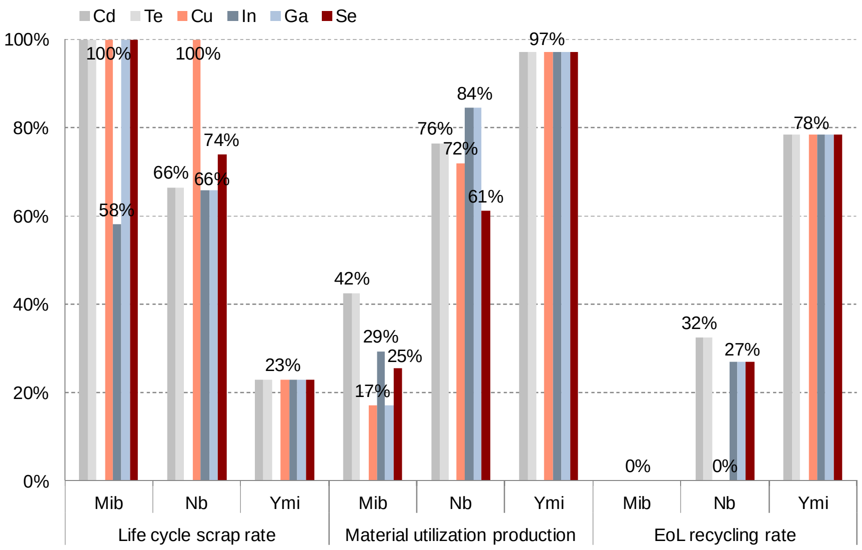

Figure 5-3: Efficiency indicators for the life-cycle of CdTe- and CIGS-PV

Figure 5-4 shows the material costs depending on the material flows estimated above. It's apparent that material costs can be saved for two reasons, although additional costs for module recycling have to be taken into account:

1) The demand, for which the total material price is charged, decreases.
2) For the recycled material just the refining costs (tolling charge) accrue.

The total costs for CIGS and CdTe are the same in the Mib scenario, but the composition is slightly different: for CIGS additional costs accrue for refining the rest of the In target. The decrease in costs between the different scenarios is higher for CIGS. Looking at CdTe, the complete costs in the Nb scenario are about 40 % lower than those in the Mib scenario due to the significant lower material demand (more than 60 % lower for CIGS), although additional recycling costs arise. In the Ymi scenario the costs can be reduced down to 20 % of the Mib scenario, down to 12 % for CIGS. The share of CdTe life-cycle material costs at CdTe-PV manufacturing costs of 75 c/W (First Solar, 2012a) is 15 % in the Mib scenario, and 9 % in the Nb scenario, respectively. The share of CIGS life-cycle material costs at

CIGS-PV manufacturing costs of 1 \$/W_p (PV Insights, 2010) is 11 % in the Mib scenario and just 4 % in the Nb scenario.

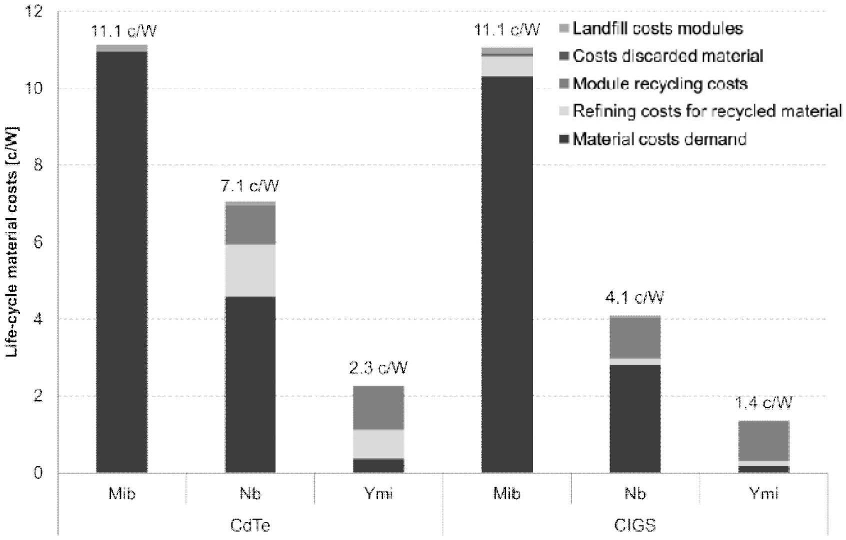

Figure 5-4: Life-cycle material costs of CdTe and CIGS photovoltaics in US-cents per watt peak

5.5 Discussion

In the long term thin-film PV production costs of 70 c/W_p need be realized to be competitive to silicon modules (Goodrich et al., accepted). Manufacturing costs below 70 c/W_p could be reached in the near-term for CdTe-PV (Woodhouse et al., 2012), and for CIGS-PV by 2020, respectively (PV Insights, 2010). If we assume a maximal material cost share of 15 % at 70 c/W_p, we can calculate how much the costs for technical grade Te and In used for production (material input: demand plus recycled material from EoL modules) can increase in order to reach this benchmark in the Nb and Ymi scenario – all other things being equal. We can do a similar estimation by calculating the possible demand costs for technical grade Te and In allowing the life-cycle costs to reach 10 c/W_p, with all other costs staying equal. Figure 5-5 shows the results of both calculations.

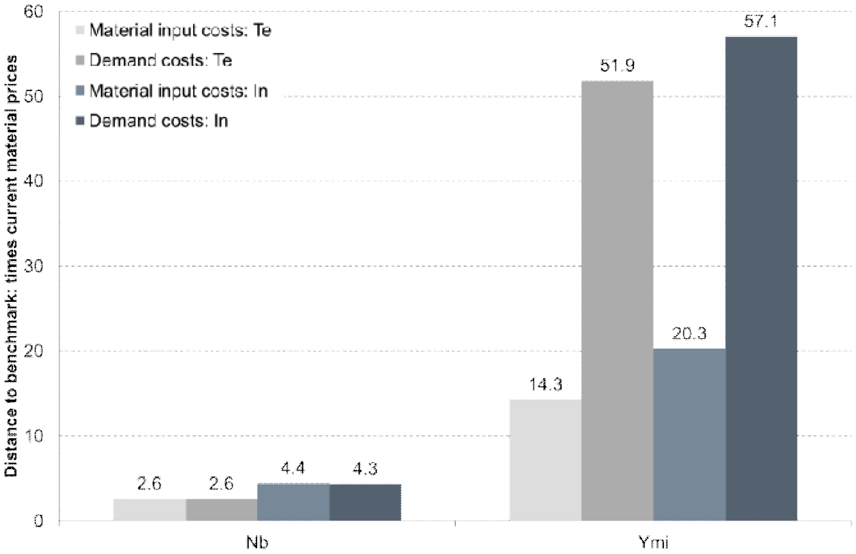

Figure 5-5: Possible multiple of today's technical grade material costs until either material costs for production or material life-cycle costs reach a benchmark of 10 c/W_p

We see that by employing material efficiency measures, costs for the technical grade material can significantly increase until the benchmark is reached. In the Nb scenario the difference in possible cost increases for the technical grade material is apparently marginal comparing both cost analysis approaches. However, in the Ymi scenario the material costs can increase a lot more when taking the life-cycle cost perspective. The reason is that recycled material from EoL modules makes up ¾ of the production demand in this scenario. This is implausible for the near future due to the long lifetime of the modules. However long term scenarios of Te flows show that in 2040 50-60 % of the Te material input in production could come from EoL modules (Marwede and Reller, 2011). In the same year 10-20 % of the In supply for CIGS-PV could come from recycled end-of-life modules (Fthenakis, 2009). Therefore not just efficiency measures on product and manufacturing level will allow higher material prices, but in the long run also the recycling of end-of-life modules.

5.6 Conclusion

The consolidation of the PV industry and the resulting fierce competition seems to direct the interests from “just” up scaling production also to other measures such as material recycling in order to save costs. The material flows and cost analysis show that material efficiency measures can significantly reduce material demand, material losses and material costs. Material utilization during production of 97 % and end-of-life recycling rates of 80 % can reduce material losses along the life-cycle down to ¼ of the required feedstock. This means that for just one quarter of the feedstock the cost for the technical grade material rises. For the other three quarters, the costs for recycling and reprocessing have to be covered, which is in total less expensive than sourcing “new” material. Although end-of-life flows will still be low in the near future, the estimations show that in the long run CIGS- and CdTe-PV could support a significant price increase of the absorber materials and still be competitive against c-Si modules. However, PV manufacturer do not directly benefit from EoL recycling flows due to the time delay, but have to the contrary put funds aside for recycling. To increase the incentive for recycling, benefits have to be evenly distributed to all life-cycle members as soon as end-of-life modules will substitute for primary material. Developing module recycling processes and setting up a collection scheme in Europe are the first promising steps to closed loop recycling of thin-film PV materials.

6 Summary, discussion, conclusion and future prospects

6.1 Summary

Chapters 3 to 5 have shown, that

a) recycling processes to recover the thin-film materials are well explored and on the edge of commercial availability;
b) in the long-term tellurium coming from CdTe-PV EoL modules can satisfy a high share of the CdTe-PV industry's demand;
c) by substituting primary material with recycled one, material costs can significantly be reduced so that thin-film PV can be competitive in the future despite possible price increase of the raw materials.

However several economical, ecological and technical challenges exist in order to realize a "closed-loop" recycling system around the CdTe- and CIGS-PV industry.

The module is designed to withstand mechanical and environmental stress for a long time (at least 25 years) in order to produce energy as long as possible. This certainly reduces the environmental impact of the module's life cycle per produced kilowatt hour on the one hand, but hampers the easy disassembly on the other hand. The current predominant design using ethylene-vinyl acetate (EVA) to laminate the modules requires plenty of energy and time to separate the module. This increases processing costs. Physical crushing and milling of the modules is fast and can treat and homogenize input streams of different size and condition (substrates, broken and intact modules). However, several steps are needed afterwards to separate the different materials (glass, metals, thin-film, and plastics) which results in lower quality recyclates due to "contaminations". The advantage of thermal (pyrolysis, cryogenics) or chemical (organic or surface chemistry) delamination processes is the complete separation or decomposition of the EVA resulting in a clean glass stream. In general, however, thermal processes are energy intensive while chemical processes are time consuming.

After delamination, the thin-film can be removed from the substrate mechanically – either dry or wet through attrition, blasting, or scraping – or they can be removed chemically. Reaching high recycling rates mechanically is more laborious than chemically. Hydrometallurgical processes are especially suitable for the recycling of low grade feed and a relatively low throughput, but require the use of strong acids. However, in both cases the recycling residues need to undergo further treatment to extract and purify the single chemical elements.

Some recommendations can be given to overcome these challenges. The recycling process should be able to be scaled up with growing waste streams. It should be multi-functional, meaning it can treat historical end-of-life modules, new products (production rejects, warranty returns), laminated modules, substrates and if possible also other products (e.g. laminated glass or displays). It should address all material fractions and avoid mixtures to increase the revenues for the recyclates. To decrease the use of chemicals, mass materials (e.g. the cover glass) should be removed before the chemical treatment and chemicals should be circulated in a closed loop. All in all, recyclers have to balance technical efforts, costs, environmental impact and quality and quantity of the recyclates. In the future – in addition to other factors such as material prices, logistics costs and energy prices – two diametrical factors will influence the economics of the processes: a) economies of scale and b) the reduction of thin-film material content.

Although currently recycling is not economically viable (costs exceed revenues), the life-cycle cost analysis has shown that through material efficiency measures including recycling of end-of-life modules costs can be saved for two reasons:

1. The demand, for which the total material price is charged, decreases.
2. Only the refining costs (tolling charge) rise for the recycled material.

In the “not bad” scenario the price for the technical grade material (for the demand) can increase by a factor of 2.6 (Te) and 4.3 (In) so that overall life-cycle material costs reach a benchmark 10 ¢/W_p at which both technologies would still be competitive against crystalline silicon photovoltaics. The pre-condition is that end-of-life recycling flows have a share of about 20 % of the feedstock, which could – in case of Te – be reached by 2036 in the “steady advance” scenario (Figure 6-1). By 2040 end-of-life modules can provide 20 % of the CIGS PV industry’s indium demand according to an optimistic scenario from Fthenakis (2009) (0.1 t/GW), and 10 % in the conservative scenario (14 t/GW), respectively.

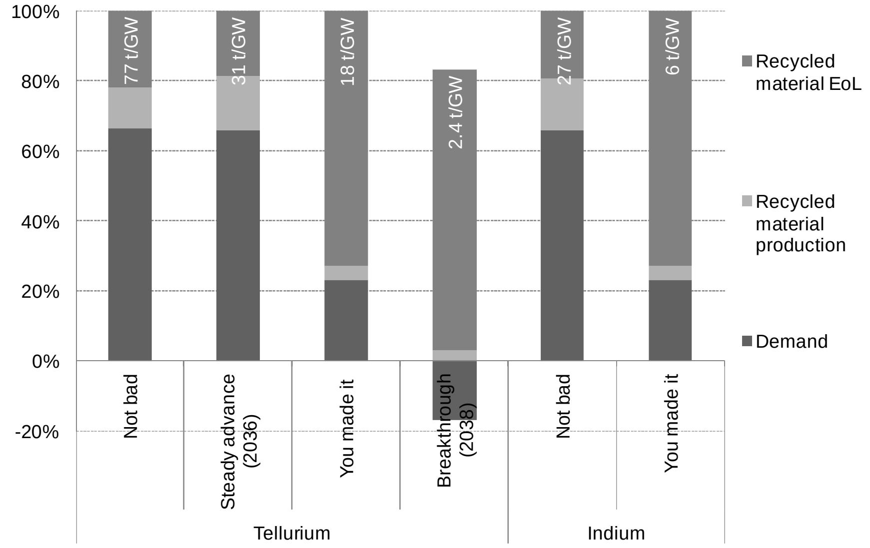

Figure 6-1: Comparison of tellurium feedstock in different scenarios

The main factor influencing the end-of-life recycling flows (Figure 6-2) is the first link in the chain: collection. Efficient collection means directing end-of-life modules (and production rejects) to appropriate recycling facilities where the thin-film materials can be recovered. Collection rates between 80 % and 90 % in the mid- to long-term lead to EoL recycling rates of between 70 % and 80 %. Combined with a low feedstock, recycled indium from end-of-life modules can support over 70 % of the feedstock (“you made it” in Figure 6-1). In the “breakthrough” scenario the recycled tellurium from end-of-life modules even surpasses the required feedstock in 2038, which means that the CdTe-PV industry could solely rely on EoL modules from this time onwards.

The decrease in the specific material feedstock (t/GW) shows the effect of the efficiency gains in production processes and the decrease of the material content in the modules. The long-term scenarios for CdTe-PV have shown that through efficiency gains (production process, material content) market growth can be absorbed from around 2020 onwards.

Therefore, even at peak times an absolute shortage of Te seems implausible. Earlier works have shown (section 2.4) that In availability restricts the deployment of CIGS-PV more than Te availability does the deployment of CdTe-PV. The decrease of the indium feedstock is therefore even more essential.

One important factor to decrease the feedstock is high material utilization rates as shown in Figure 6-2. In the long term, material utilization ≥ 97 % might be feasible through directed non-vacuum deposition methods and high overall equipment efficiencies. Using vacuum methods a material utilization rate of over 85 % is unlikely because part of the source material coats the equipment as "overspray". Within production scrap, overspray (and used targets) is the main waste flow for highly concentrated thin-film materials. A part of the overspray – though it is uncertain how much – can be recovered for recycling. The other production waste – the rejected modules – can serve as feedstock for start-up recycling companies until more end-of-life modules are available.

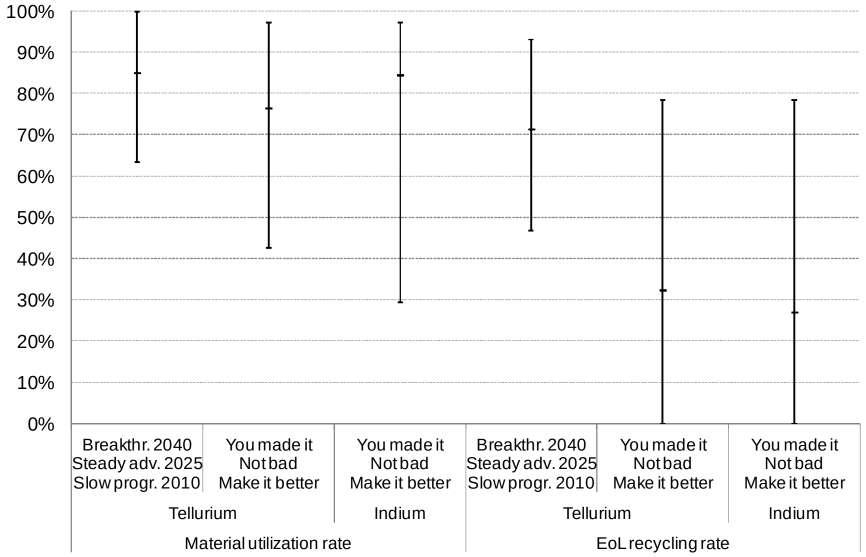

Figure 6-2: Comparison of material utilization and end-of-life recycling rates

Materials accumulate in installed PV-modules due to the long lifetime of the PV modules. In the long-term scenarios 2,800-6,300 t of Te are stocked in installed modules in 2040 – approximately 5-12 times current Te production. However, manufacturers do not directly benefit from the recycling flows due to time delays. Life-cycle ownership models such as leasing could give the manufacturer a better control over his goods along the life cycle and would allow access to the materials at end-of-life (Ayres and Peiro, 2013; Meskers et al., 2010). Manufacturers would then just pay the costs for recycling and reprocessing, which is in total less expensive than buying "new" material with fluctuating prices on the commodity market (chapter 5).

6.2 Discussion and conclusion

Results are discussed in a broader context in this chapter. The content follows the life-cycle phase “production and use”, “end-of-life flows and collection” and “recycling”.

6.2.1 Production and use

The material demand is driven by the fast growth of both PV technologies which averaged annual growth rates of over a 100 % between 2001 and 2011 (Hering, 2012). Inefficiencies in production increase the gross material demand (far) beyond the net material demand required for the solar cells. However, this research indicates that manufacturers become more and more interested in increasing material utilization for economic reasons. A recovery of production waste is especially interesting if the waste fraction is rich with valuable materials (chamber scraping, used targets) thus having a positive value. However, recycling is still not the case for CIGS-PV modules, which are stockpiled or land filled for two reasons: recycling is expensive and recycling capacities are lacking. Once recycling capacities are available, processing of stockpiled modules can lead to an additional supply of indium. This is already the case for CdTe-PV: operating recycling facilities that treat production waste, rejects and end-of-life modules, provide tellurium and cadmium.

Although absolute (geological) scarcity of Te or In is unlikely, high prices through demand-supply imbalances (relative scarcity) can be an issue for the manufacturers. How the prices of the expensive absorber materials will develop depends on many factors such as competing use, the demand for the “attractor” metals, the technical efficiency of by-product recovery, primary production and recycling flows. The inflexibility in the production of minor metals can lead to high prices until production capacities are increased. The increase of the minor metal production is usually possible where it is not fully recovered from the attractor metal. Ayres and Peiro (2013) show that the correlation between price and output for Ga, In and Te has improved since the mid-1990s, suggesting that existing sources are now being used more efficiently than in the past. There is still room to increase the recovery rate for In, Ga, Se, and Te (Ayres and Peiro, 2013; Fthenakis, 2009; Green, 2012).

Other emerging technologies compete with the CIGS-PV industry for In and Ga. Angerer et al. (2009) show that by 2030 the In demand from the display and the LED industry can increase to 0.5-2.4 times the In production of 2011, and that the Ga demand from integrated circuits (ICs) and white LEDs can increase to 1.1-4.1 times the Ga production in 2011. Yet, Angerer et al. (2009) neglect that material efficiency measures can offset the additional demand from market growth to a certain extent, as shown by the CdTe-PV example. Moreover the material content in white LEDs and displays is assumed to be higher than stated in more recent studies[13]. Therefore, Angerer et al. (2009) probably overestimate the future demand.

However, the deployment of both CdTe-PV and CIGS-PV is also dependent on what competing users are willing to pay for the materials. It is, for example, easier for LCD-TV manufacturers to absorb a higher In price, given the per square meter price for a TV-set is

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[13] A material flow analysis for white high-brightness LEDs shows that the In feedstock for production is 1/85th of that stated by Angerer et al. (2009), 1/38th for Ga, respectively (Deubzer et al. 2012). Also the In content of displays varies. Jalalpoor et al. (in press) have analyzed the In content of various LCD-TVs and found values of 641±310 mg/m² (n=9) – less than the 4000 mg/m² used in Angerer et al. (2009).

an estimated 90-110 times higher than for a CIGS module, which contain 1.5-11 times the In amount of LCD-TVs[14]. However, LCD manufacturers might start to substitute ITO with available alternatives when prices are too high, which could decrease the overall In demand. The CIGS-PV industry does not really have this option: the replacement of In with Ga depends on the required band-gap and Ga is equally expensive and critical.

The CdTe-PV industry additionally relies on the absorber material tellurium. Contrary to indium, the use of Te in other applications is declining. This can have a twofold effect: 1) the price of Te is decreasing and 2) investment in new production capacities might become less attractive (Candelise et al., 2011). The main producer, *First Solar*, looks ahead by investing in mining (pv magazine, 2011a).

In and Te cannot be directly substituted in CIGS-PV, CdTe-PV respectively, but cheaper and more abundant semiconducting compounds for thin-film PV such as CuZnSnS, CuN or FeS_2 being investigated (US DoE, 2011). Wadia et al. (2009) have analyzed material extractions costs and supply constraints of 23 promising semiconducting materials applicable for thin-film PV. They find that iron pyrite (FeS_2) is significantly more attractive both in costs and availability than all other compounds, whereas several of the leading thin-film technologies like CdTe and CIGS are not able to meet large-scale electricity meets. They conclude that “a photovoltaic future may not be dependent on either silicon technologies or currently popular thin-films” (Wadia et al., 2009). Alternative technologies also include high-efficiency (III-V semiconductor) multi-junction PV cells, concentrating solar power, advanced organic and dye-sensitized PV cells (US DoE, 2011). Organic materials will probably provide partial substitution for classical inorganic semiconductor compounds in optoelectronics in the future (organic light-emitting diodes (OLED), organics solar cells, OLED displays). However, the lifetime and performance of organic electronics still need to be improved (Photonics21, 2009).

Apart from using other compound materials (e.g. FeS_2), other technologies (e.g. organic photovoltaics) as well as other renewable technologies such as wind turbines or biogas plants can replace photovoltaic modules. The electricity generation for all three technologies depend directly or indirectly on the sun. Of these three technologies the energy yield per hectare is the highest for solar energy generation (thermal and electric), followed by wind (factor 3 lower) and biomass (factor 17 lower) (Agentur für Erneuerbare Energien, 2010). Yet wind and solar energy generation is fluctuating and needs to be balanced by biogas power plants, fossil fuelled power plants, nuclear power plants or electricity storage systems (e.g. pump storage). However, life-cycle greenhouse gas emissions from technologies powered by combustion-based natural gas and coal technologies are considerably higher than emissions from solar (both photovoltaic and concentrating solar power), wind, and nuclear technologies (Lifset, 2012), though nuclear power plants generate radioactive waste. A resource efficient and environmental friendly technology mix has to take all those aspects into account and will therefore consist of several energy generation technologies.

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[14] Indium content of LCD-TVs is 641±310 mg/m² according to Jalalpoor et al. (in press); the In content of CIGS-PV modules is calculated using following stoichiometric composition, layer thickness, and module weight: $CuIn_{0.7}Ga_{0.3}Se$, 1.0 µm, 16.5 kg/m²; CuInSe, 1.9 µm; 15.2 kg/m².

6.2.2 End-of-life flows and collection

PV modules eventually become waste after use – depending on their lifetime expectancy. Figure 6-3 shows the expected CdTe-PV EoL module flows according to the "steady advance" scenario described in chapter 4 compared to two alternative calculation methods for the same scenario (normal distribution, constant lifetime) and one estimation by Bio-IS (2011) also using a constant lifetime[15].

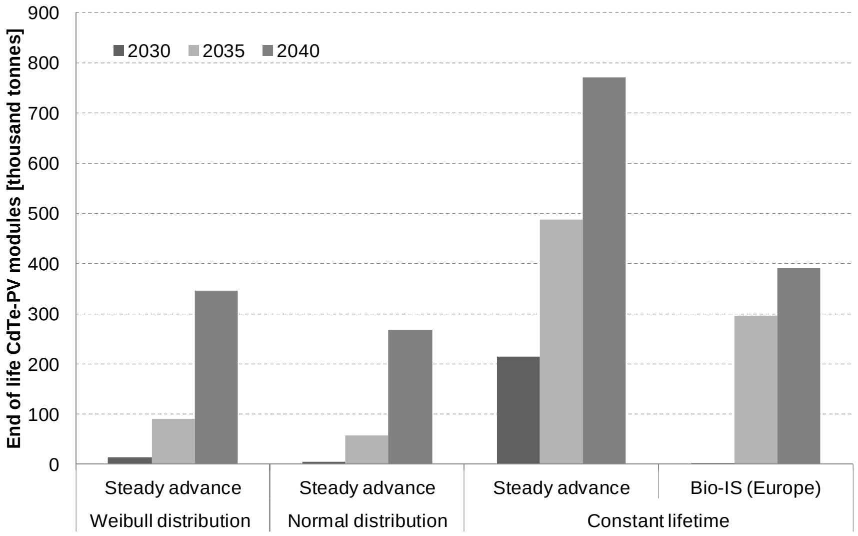

Figure 6-3: End-of-life module waste according to different estimation methods

The comparisons show that:

- the amount of end-of-life PV modules calculated using the normal distribution is lower than using the Weibull distribution, but grows faster;
- by using a distribution function, the end-of-life stream is delayed for a longer time than in the static lifetime approach leading to higher amounts in the static lifetime approach;
- in the static lifetime approach the amounts as estimated by Bio-IS (2011) in Europe are in the right relation to global flows based on the "steady advance" scenario – apart from 2030 due to the difference of 5 years in the lifetime (the share of Europe at the world PV market in 2009 was nearly 70 % but is expected to shift from developed countries to developing countries in the future (EPIA, 2011)).

One can conclude that using a distribution function is more realistic than using the static lifetime approach, however the choice of distribution and the most probable lifetime has a significant effect on the point in time when end-of-life modules arise as shown in chapter 4. Haig et al. (2011), for example, predicted photovoltaic waste to rise already in around 2022 in the UK using a Weibull distribution with a mode of about 12 years instead of 30 years.

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[15] The mode and standard deviation of the normal distribution are set equal to the ones of the Weibull distribution in the "steady advance" scenario (Figure A-2 in appendix A.5). In the constant lifetime approach the installed modules rise after their average lifetime as waste (30 years in the steady advance scenario, 25 years in Bio-IS (2011)). Bio-IS (2011) assumed a constant weight (75 t/MW), whereas the specific module's weight per watt in the steady advance scenario depends on the conversion efficiency of the module (module's weight 16.7 kg/m²).

As there has been little experience, it is uncertain how much of end-of-life PV modules can be collected in the future. In 2011 *PV-Cycle* collected 1,400 tonnes, resulting in a collection rate of approximately 70 % (Ziegler, 2012). The collection rates of large-household appliances (washing machines, refrigerators …) – the closest category to PV modules – are 76 % in the Netherlands in the official and complementary systems (Huisman et al., 2012). In Germany 80-90 % of large household appliances – share at the amount put on the market – are collected in the official and parallel systems (Sander, 2012). Similar rates for PV modules are probably achievable in developed countries for several reasons:

- legal requirement such as the European WEEE directive impose high collection rates (85 % from 2019 onwards (European Parliament, 2012)).
- modules are usually installed in a larger electronic systems (large ground-installed PV systems, roof-top PV systems) which normally requires professional deinstallation of modules,
- PV modules do not get that easily "lost" as small electronic products (they are too big to disappear in drawers or end up in household bins, for example),
- consumers' demand for "green" products and the aspiration of producers to be part of a "green" industry promotes recycling,
- the wide implementation of extended producer responsibility (EPR) in the European Union promotes recycling[16].

However, collection does not guarantee that the thin-film materials are recycled – especially in cases where PV modules are from those initially installed in developing countries or (illegally) exported to developing countries, where recycling technologies are less advanced. Hagelüken and Meskers (2010) and Ayres and Peiro (2013) also doubt that EPR provide incentives strong enough to close the material cycle. Better cooperation along the recycling chain is required in combination with a tracking of products and material streams, e.g. by radio frequency identification systems (RFID)[17] (Ayres and Peiro, 2013; Hagelüken and Meskers, 2010). Field trials on an electronic waste collection site showed that from a technical standpoint RFID can achieve the separation of brands (Hickey et al., 2012). Therefore, RFID systems can probably be used to sort PV modules by technology or brand in order to direct them to the appropriate recycling processes. The slowly growing return flows and separate collection provide the chance to implement new tracking technologies such as RFID on a smaller scale and a relatively homogeneous waste stream compared to other electronic waste. Which metals are then recycled depends mainly on their value as explained in the following section.

6.2.3 Recycling

Recycling is similar to coupled production in that it is driven by valuable materials enabling the recovery of "by-product" materials with sub-economic value or concentration (Hagelüken and Meskers, 2010). The so called Sherwood plot (Figure 6-4) – the market price as function of the dilution (1/ore concentration) – can indicate the likeliness of recycling a material from a product. Usually it's used to estimate the market price of a metal

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[16] EPR as an environmental policy approach in which a producer's responsibility for a product is extended to the post-consumer stage of a product's life cycle (OECD, 2013).

[17] Contactless identification technology which uses radio frequency signals for the querying of electronic identification tags and the subsequent reading of the information stored on these tags (Hickey et al., 2011).

required to support mining of a material from an ore with given concentration. Johnson et al., (2007) have found that most of the metals that are currently targeted for recycling have post-disassembly concentrations that lie above the Sherwood plot. In other words, if the "product ore" grade exceeds the minimum profitable grade of virgin ore, the "product ore" is commonly recovered and recycled. Green (2012) shows that the plot can also be used to estimate the market price of metals extracted from concentrates[18]. To check if the material concentration in the modules are high enough for extraction, the current metal price (technical grade) and the dilution[19] of the absorber materials in the modules are plotted in conjunction with the Sherwood plot created by Green (2012)[20] (Figure 6-4).

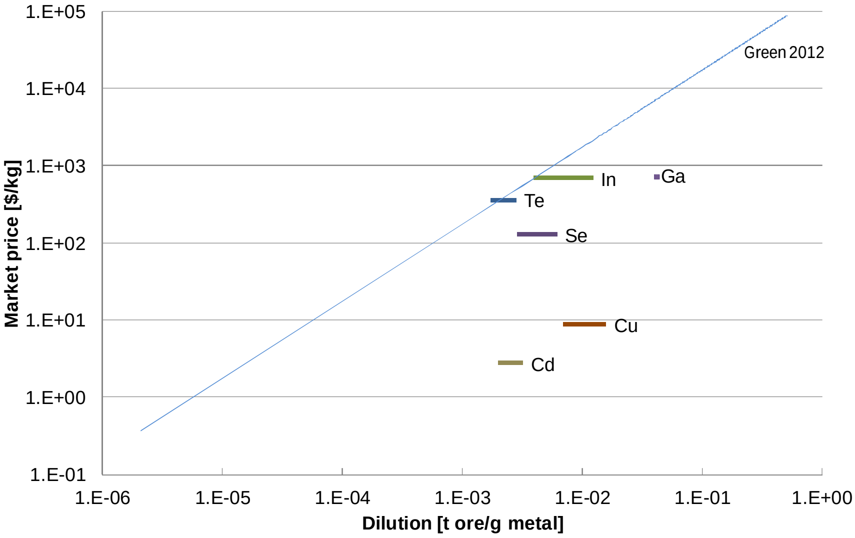

Figure 6-4: Sherwood plot (Green, 2012)

The Sherwood plot (Figure 6-4) shows

- that Ga, Se, Cu and Cd lie below the plot (i.e. material prices are not high enough to make "extraction" profitable),
- that the upper concentrations of In and Te make their extraction more likely,
- that the likelihood for recycling is decreasing when moving further downstream in production as material concentrations decrease (e.g. In target, chamber scraping, coated substrate, laminated module),
- that rising prices increase the likelihood of recycling,
- and that an expected lower concentration of the material in the modules in the future will decrease the potential for recycling.

However, a high concentration is not sufficient to guarantee recycling. Other factors influencing recycling are mass, dispersion of mass, contamination, homogeneity, logistic

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[18] For 1 % of Te in the slimes a market price of 17 $/kg can be calculated which is a not an unreasonable estimate of the Te by-product price pre 2003 (Green, 2006; 2012).

[19] The material content of CIGS-PV and CdTe-PV modules is calculated using the following stoichiometric composition, layer thickness, and module weight: CdTe; 2.0-3.0 µm; 16.7 kg/m²; $CuIn_{0.7}Ga_{0.3}Se$, 1.0 µm, 16.5 kg/m²; CuInSe, 1.9 µm; 15.2 kg/m².

[20] Green (2012) uses typical ore concentration and the average monthly price from January 2005 to November 2008 of 17 metals for the regression, not including the co-products In, Ga, Te and Se in the formation of the plot. Johnson et al. (2007) point out that the correlation is not necessarily working on the materials not included in the formation of the plot.

costs, and regulations (Johnson et al., 2007). Cd from CdTe-PV modules, for example, is recycled due to its toxicity even though it lies below the line.

Hagelüken and Meskers (2010) do not believe that waiting for the price to increase until recycling is economical feasible is an acceptable approach because too many secondary minor metals will be lost in the meantime due to the delayed reaction time of the market price. Instead Hagelüken and Meskers (2010) suggest that legislation provide ways to finance recycling of products with a negative net-value, i.e. recycling costs exceed the recyclates' value (as it is the case for thin-film PV modules). One example for legislation currently not addressing minor metals is weight-based recycling rates. For example a recycling rate of 85 % as of 2019 fixed in the European e-waste directive (European Parliament, 2012) can easily be reached by recycling the main constituent: the glass.

Liberation of minor metals from thin-film PV modules is probably easier than from complex products such as mobile phones, because fewer materials are involved, the materials can clearly be localized, and the composition and design of the modules is relatively similar across age and producers. However, unfavorable material combinations can also lead to losses of minor metals during recycling (Hagelüken and Meskers, 2010). For example: in case GIGS cells are deposited on an aluminum substrate they might end up in an aluminum smelter, where the minor metals cannot be recovered and end up in the aluminum product.

To avoid such effects an intermediary research institute can bridge the knowledge and communication gap between product designers and recyclers. Next to establishing communication channels between OEMs and recyclers, it can prove and assess possible design options scientifically (Marwede et al., 2012). Here computer based modeling/simulation of the recycling performance of products based on the realities of how products and their constituents break up during recycling processes are helpful in developing "Design for Recycling (D4R)" recommendations (van Schaik and Reuter, 2012). Marwede et al. (2012) have identified 29 different D4R measures for PV modules. These include the use of alternative encapsulation materials or the sealing of the modules (similar to thermal insulation windows) in order to facilitate disassembly. Another suggestion is to build in a "predetermined breaking point" between substrate and thin-film layers.

However, with pressing goals of cost reduction and improvement in functionality (e.g. a longer lifetime) it's difficult for product designers to alter their designs with advantageous end-of-life characteristics (Johnson et al., 2007). On the other hand it's challenging for the recyclers to develop processes which can deal with a mixture of designs and models - ranging from most recent designs to ones used 30 years ago - even though there haven't been significant changes in the design for PV modules over those 30 years. Both design and recycling can be matched by identifying manufacturing and technology trends on both sides. On one hand, one can anticipate coming designs (e.g. flexible PV modules) in order to adapt current recycling processes while on other hand design modules in such a way that they are treatable using advanced recycling methods (Marwede et al., 2012).

6.3 Future prospects

The combination of the MFA method with expert interviews in developing scenarios has proven helpful for:

- determining future global Te demand as early-warning system for a possible demand surge and supply limitations,
- estimating the net material demand along the life-cycle of CIGS- and CdTe-PV modules,
- estimating future recycling flows
    - as substitute for “primary” material,
    - as indicator whether at all and when to develop and scale up recycling systems and processes,
- estimating life-cycle material costs,
- detecting material losses along the life-cycle to derive improvement potentials along the life cycle,
- and the straight forward calculation of material efficiency indicators such as material utilization, recycling rate and scrap rate.

The challenges lie mainly in data gaps and uncertainties such as:

- future material content of the modules (technological developments),
- future efficiency of the processes (deposition, collection, recycling),
- possible substitution (material, product, system),
- and market developments.

Some, but not all, of those challenges can be circumvented by developing scenarios. The information gained from various experts helped to develop consistent assumptions and storylines. However, the approach can be further improved by including further predictive methods such as scenario workshops or wild card analysis[21].

The results of these Material Flow Analyses can be used to refine Life Cycle Assessments of CIGS- and CdTe-PV through checking used life-cycle inventories. The prediction of end-of-life flows can be used to estimate future recycling cost reduction through learning. By using a learning curve, the future recycling cost developments can be estimated as a function of the cumulated processed modules. In general, the research approach used in this work can be easily transferred to other emerging technologies in order to estimate life-cycle flows of critical materials. It has proved both robust and flexible enough to deal with insecurities and uncertainties associated with emerging high technologies.

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[21] A so called “wild card“ is a disruptive single event with low (or unpredictable) probability of occurrence but a drastic and far-reaching impact. A classical example is the attack on the World Trade Center on the 11th September 2001 (Kosow and Gassner, 2008). A “wild card” for CdTe-PV would be a ban of the use of Cd for photovoltaics in Europe which would mean the end of CdTe-PV sales in the European market.

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A Appendix

A.1 Interview partner

Surname	Name	Institution
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Arm	Frank	Retorte
Audet	Nicholas	5N
Berger	Wolfgang	Bundesanstalt für Materialforschung und -prüfung
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Cieleback	Wolfgang	Ardagh Glas
Clarius	Tom	Avancis
de Ruijter	Ignace	Umicore
Fischer	Markus	Q-Cells
Gerloff	Constantin	Solon
Hagelücken	Christian	Umicore
Hinrichs	Vollker	Heliotop
Hisert	Jim	Indium Corporation
Huber	Frank	MBE Komponenten
Jäger-Waldau	Arnulf	European Commission- Joint Research Centre
Kaufmann	Christian	HZB Berlin
Kernbaum	Sebastian	Saperatec
Krüger	Lisa	First Solar
Kux	Andreas	Q-Cells
Li	Hamlin	Sunvim
Linke	Christian	Plansee Metall GmbH
Marx	Thomas	CS Service
Mäurer	Andreas	Fraunhofer IVV
Muse	Dani	Centrotherm clean solutions
Neisser	Axel	Sulfurcell
Ölting	Stefan	Antec Solar
Ötting	Clas	Relux Entsorgung
Palitzsch	Wolfram	Loser Chemie
Peschke	Jens	5N-PV
Pohl	Roland	Reiling
Ramakrishnan	Arun	Centrotherm
Schlenker	Silke	Solarworld
Seibt	Horst	Actensa
Sittinger	Volker	Fraunhofer IST
Umschlag	Thomas	Manz
Wambach	Karsten	Solarworld
Wischmann	Wiltraud	Zentrum für Sonnenenergie- und Wasserstoffforschung
Wolf	Jürgen	GP Innovation
Woolwich	Jennifer	PV Recycling
Yan	Wang	Sunvim
Zhang	Muzi	China Renewable Energy Entrepreneurs Club (CREEC)
Zhu	Lei	Chinese Academy of Sciences
Zimon	Frank T.	Angstrom Science

A.2 Questionnaire

Material Content

- How high is the content of the material X in your module (g/m²)?
- How much can the layer thickness be reduced, i.e. how will the product specific content change?
- Which gain in conversion efficiency do you anticipate?
- Are there any substitutes for scarce, toxic or expensive materials?
- How high do you expect the market share of thin-film PV technologies to be in the future?

Material utilization and recycling rates during production

- Which deposition process do you use for material X.
- How high is the deposition efficiency, i.e. how much of the material input ends up in the cell (in per cent)?
- How much of the material losses during production is recovered for internal or external material recycling? Which part could potentially be recovered?
- Are solutions for in-line recycling of the materials available?
- Is it possible to increase the overall material utilization? If yes, how and to which extent?

Production rejects, warranty returns and lifetime

- What is the percentage of rejects at production (semi-finished products, coated substrates, off-specification modules)
- What is the percentage of returns at production (damages during transport or installation, product warranty)?
- Do you recycle production rejects and returned modules (now or in future)?
- How long do you expect the modules' lifetime, the use time to be?

End-of-life recycling

- Do you recover the coating materials?
- How much of the coating material do you recycle – now, in the near future and in 2020+?
- Which measure ensure that not just the mass materials are recovered but also the critical materials. Which challenges do you see?
- How high do you estimate the recycling costs to be (deinstalling and logistics, just the recycling process)?
- Do you see any possibilities to co-recycle other products such as displays or security glass)? Do you see those (possible) synergies as promising approach?

A.3 Maximum photovoltaic capacity

Table A-1 shows the results of those studies (Andersson, 2000; Feltrin and Freundlich, 2008; Fthenakis, 2009; Zweibel, 2010), which estimated the maximum producible capacity either based on yearly production or on reserves. The current In, Ga and Te production, reserves and CdTe- and CIGS-PV production in 2011 are also listed in Table A-1. Fthenakis (2009), Green (2012), Zweibel (2010) and Andersson (2000) estimated future material availability. They predict annual production to increase due to more mining of the main product (Cu, Zn, bauxite) and higher extraction efficiencies. Fthenakis (2009) and Zuser and Rechberger (2011) also look at secondary material available from module recycling. Feltrin and Freundlich (2008) assumes that 25 % of a reserve base[22] is available for PV production. Andersson (2000) factor all reserves into his calculations.

Material (Year)	Annual production	Annual PV Production	Reserves	
Indium (2011)	660 t	0.9 GW_p/year [CIGS]	n/a	
Gallium (2011)	273 t	0.9 GW_p/year [CIGS]	n/a	
Tellurium (2011)	500-550 t	2.0 GW_p/year [CdTe]	24,000 t	
Year (source)	Annual Te available (for PV)	Annual PV production	Te reserves (available for PV)	Max installed capacity
2000 (Andersson 2000)	290 t	5 GW_p/year	20,000 t	300 GW_p
2004 (Feltrin 2008)	–	–	11.750 t a)	82-165 GW_p
2020 (Fthenakis 2009)	1,130 t	14-38 GW_p/year	-	-
2020 (Anderson 2000)	550 t	20 GW_p/year	-	-
2030 (Fthenakis 2009)	1,200-1,600 t	17-55 GW_p/year	-	-
2030 (Zweibel 2010)	1850 t	126-421 GW_p/year	-	-
Year (source)	Annual Te available for PV	Annual PV production	Annual Te demand	
2020 (Green 2012)	400 t b)	4.7-16 GW_p/year	296-912 t	
Year (source)	Annual In available	Max annual production	In reserves (available for PV)	Max installed capacity
2000 (Anderson 2000)	290 t	7 GW_p/year	2,600 t	90 GW_p
2004 (Feltrin 2008)	-	-	1,500 t	120 GW_p
2020 (Anderson 2000)	350 t	70 GW_p/year	-	-
2020 (Fthenakis 2009)	230 t	13-22 GW_p/year	-	-
2030 (Fthenakis 2009)	290-390 t	19-43 GW_p/year	-	-
Year (source)	Annual Ga available (for PV)	Annual PV production	Ga reserves (available for PV)	Max installed capacity
2000 (Andersson 2000)	54 t	10 GW_p/year	110,000 t	20,000 GW_p
2020 (Anderson 2020)	745 t	400 GW_p/year	-	-
Zuser 2010	Cumulative demand	Maximum annual demand c)		
Indium	10,955-44,431 t	870-4,333 t		
Gallium	4,690-19,024 t	373-1,855 t		
Tellurium	51,937-244,853 t	2,843-15,690 t		

Table A-1: Maximum CdTe and CIGS-PV production enabled by material availability (partially own calculations based on: Andersson, 2000; Feltrin and Freundlich, 2008; Fthenakis, 2009; Hering, 2012; USGS, 2013; Zweibel, 2010)

a) 25 % of a reserve base of 47,000 t
b) Annual Te production of 700 t, the remaining 300 t are needed for other applications.
c) At peak times in between 2010 and 2040 as a result of market scenarios and different technological trajectories.

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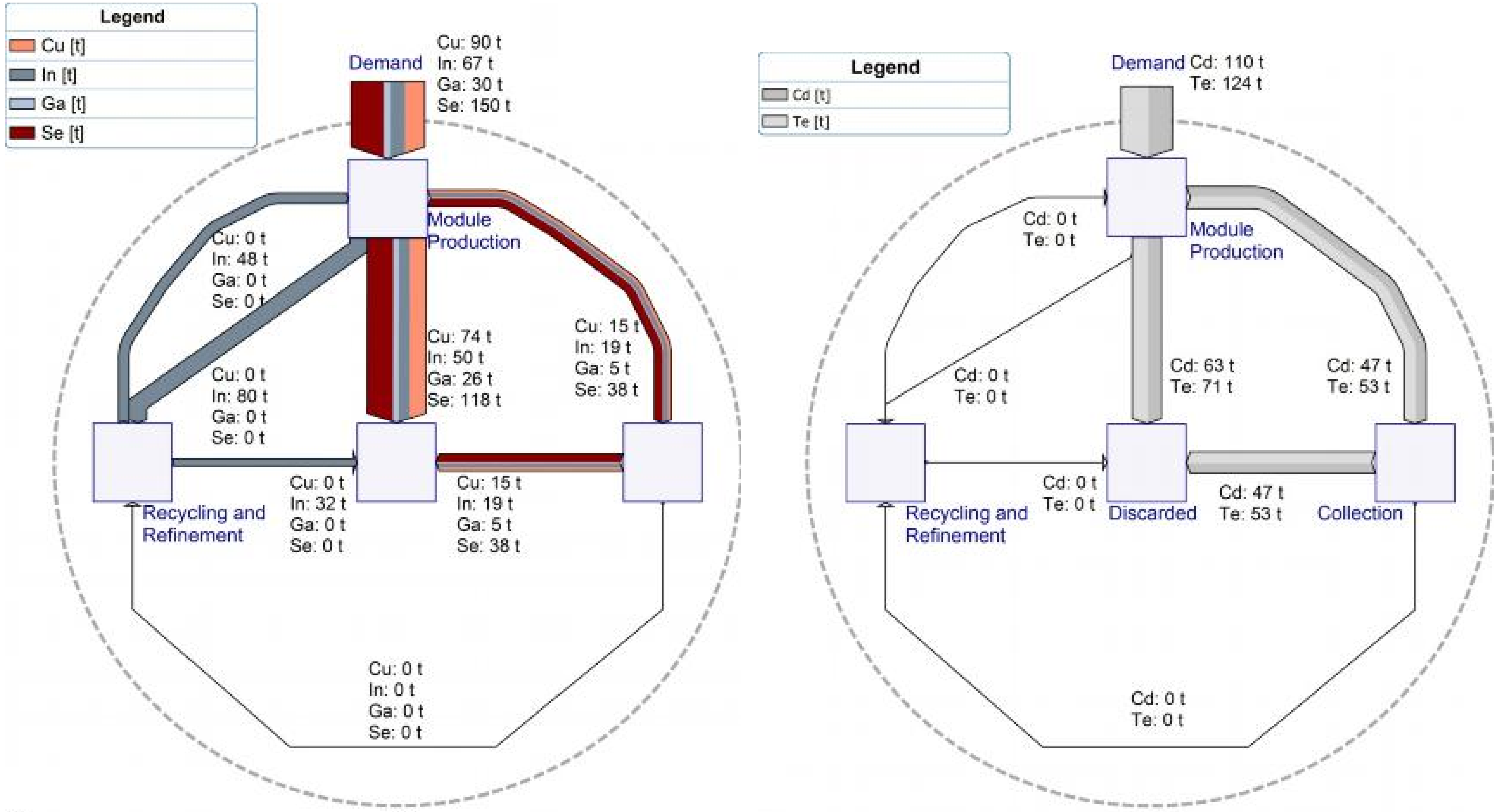
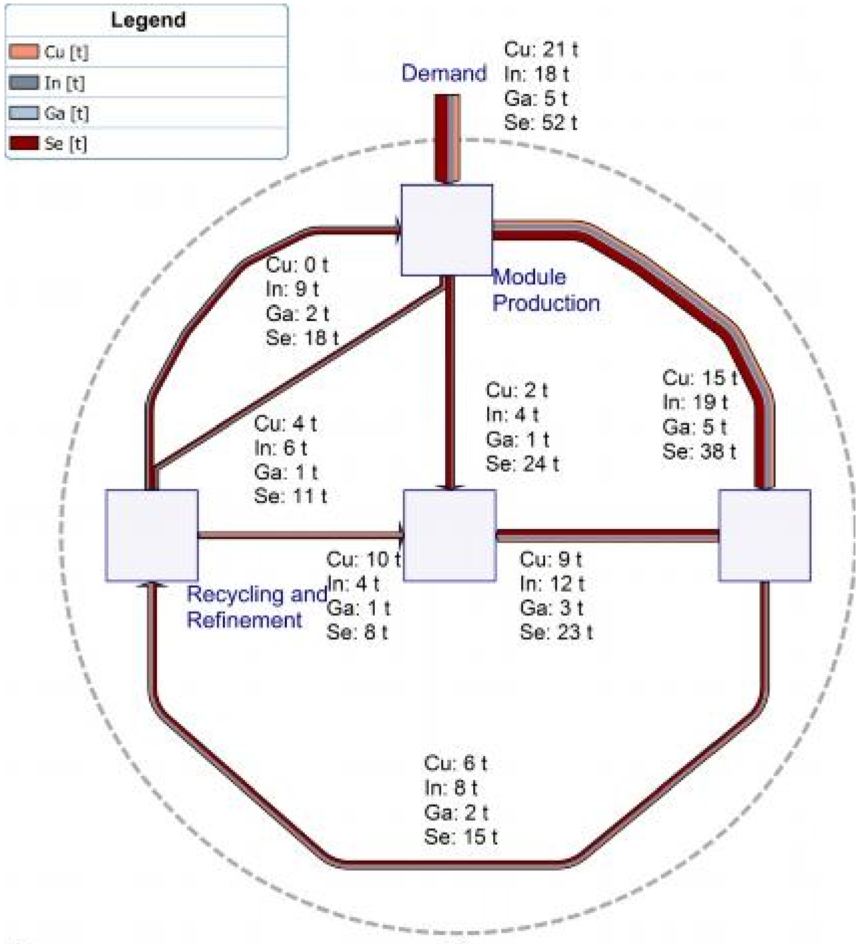
[22] For definitions of reserve and reserve base refer to USGS (2012a)

A.4 Life Cycle Material Flows (CIGS- and CdTe-PV)



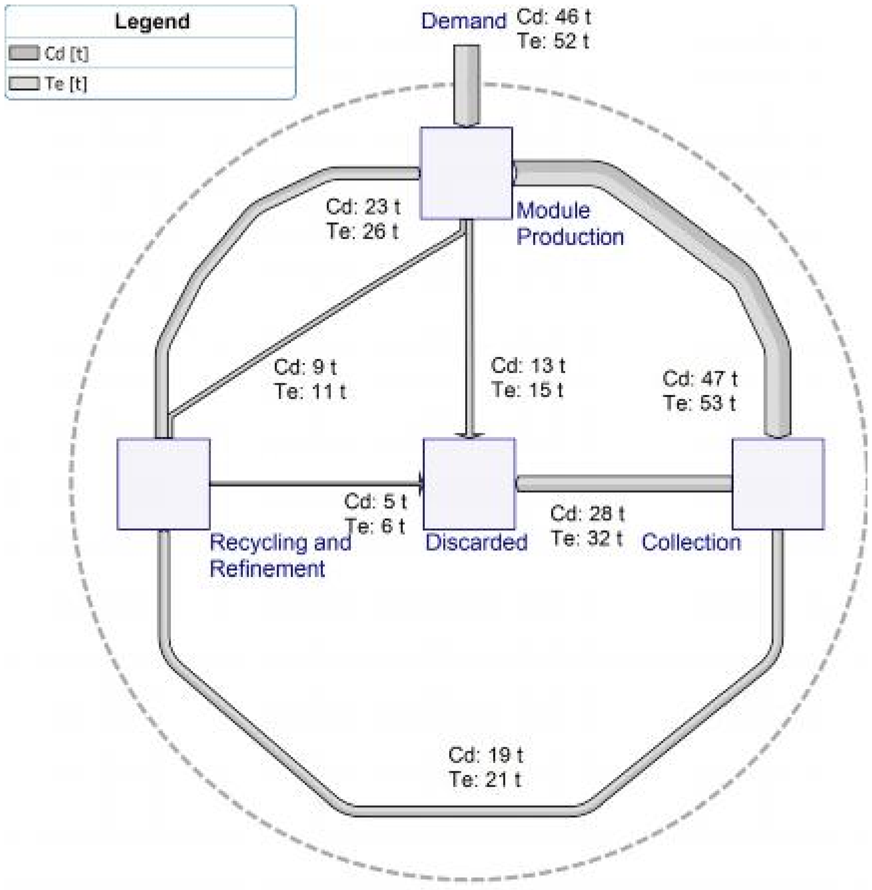
a) **Mib**

b) **Mib**


Legend
Cu [t]
In [t]
Ga [t]
Se [t]
Demand
Cu: 21 t
In: 18 t
Ga: 5 t
Se: 52 t
Module Production
Cu: 0 t
In: 9 t
Ga: 2 t
Se: 18 t
Cu: 4 t
In: 6 t
Ga: 1 t
Se: 11 t
Cu: 2 t
In: 4 t
Ga: 1 t
Se: 24 t
Cu: 15 t
In: 19 t
Ga: 5 t
Se: 38 t
Recycling and Refinement
Cu: 10 t
In: 4 t
Ga: 1 t
Se: 8 t
Cu: 9 t
In: 12 t
Ga: 3 t
Se: 23 t
Cu: 6 t
In: 8 t
Ga: 2 t
Se: 15 t

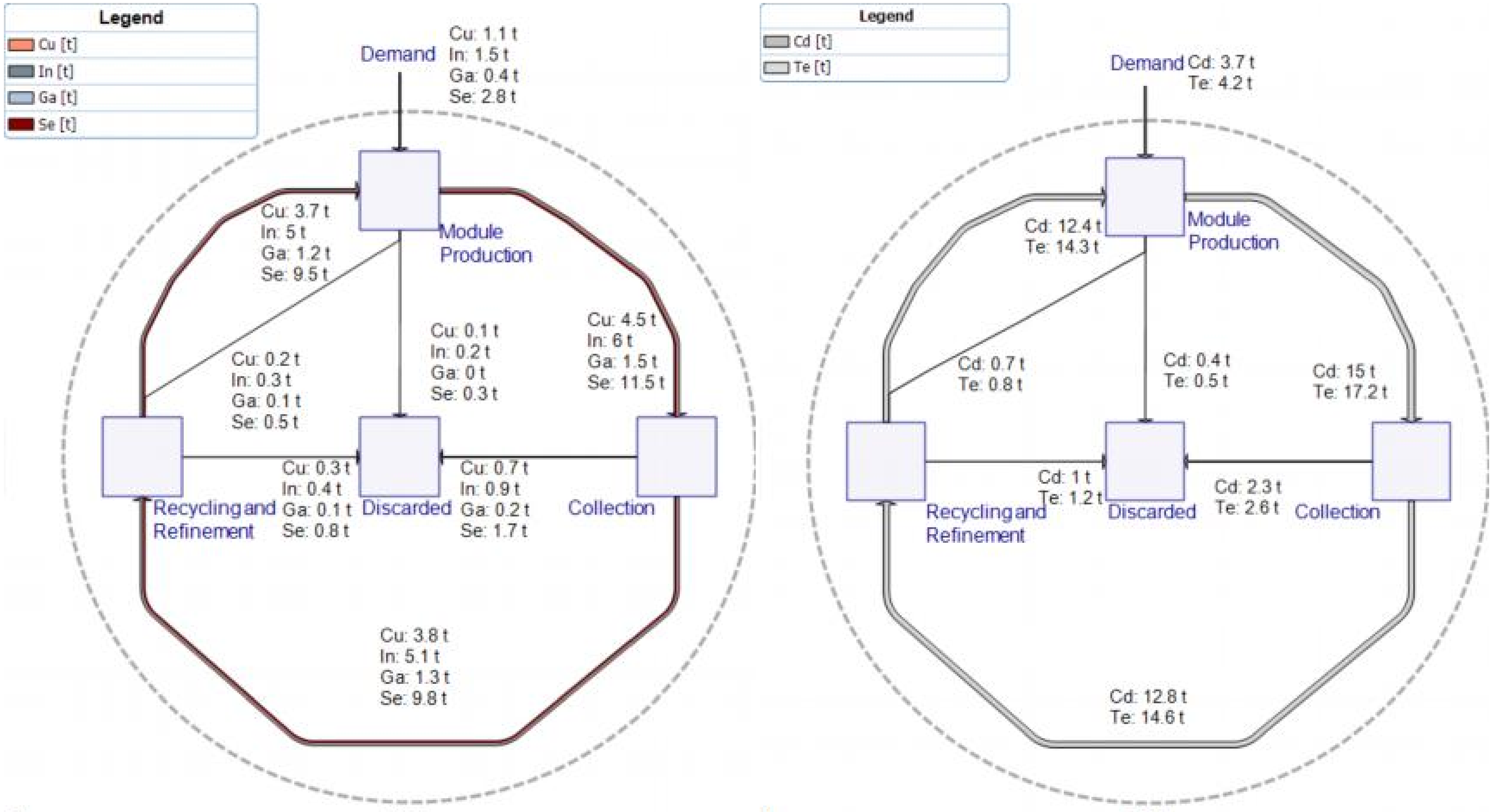
c)

Nb


Legend
Cd [t]
Te [t]
Demand
Cd: 46 t
Te: 52 t
Module Production
Cd: 23 t
Te: 26 t
Cd: 9 t
Te: 11 t
Cd: 13 t
Te: 15 t
Cd: 47 t
Te: 53 t
Cd: 5 t
Te: 6 t
Recycling and Refinement
Discarded
Cd: 28 t
Te: 32 t
Collection
Cd: 19 t
Te: 21 t

d)

Nb



e) YMI

f) YMI

Figure A-1 a-f): Material flows along the life-cycle of CIGS- and CdTe-PV in the "Make it better (Mib)", "Not bad (Nb)" and "You made it (Ymi)" scenario in t/GW

A.5 Lifetime probabilities

Figure A-2 shows the probability that a module is scraped with a service life of t years, computed with formula (1-5) either using the Weibull or the normal distribution function with the mode μ=30 years and the standard deviation σ=3.5 years.

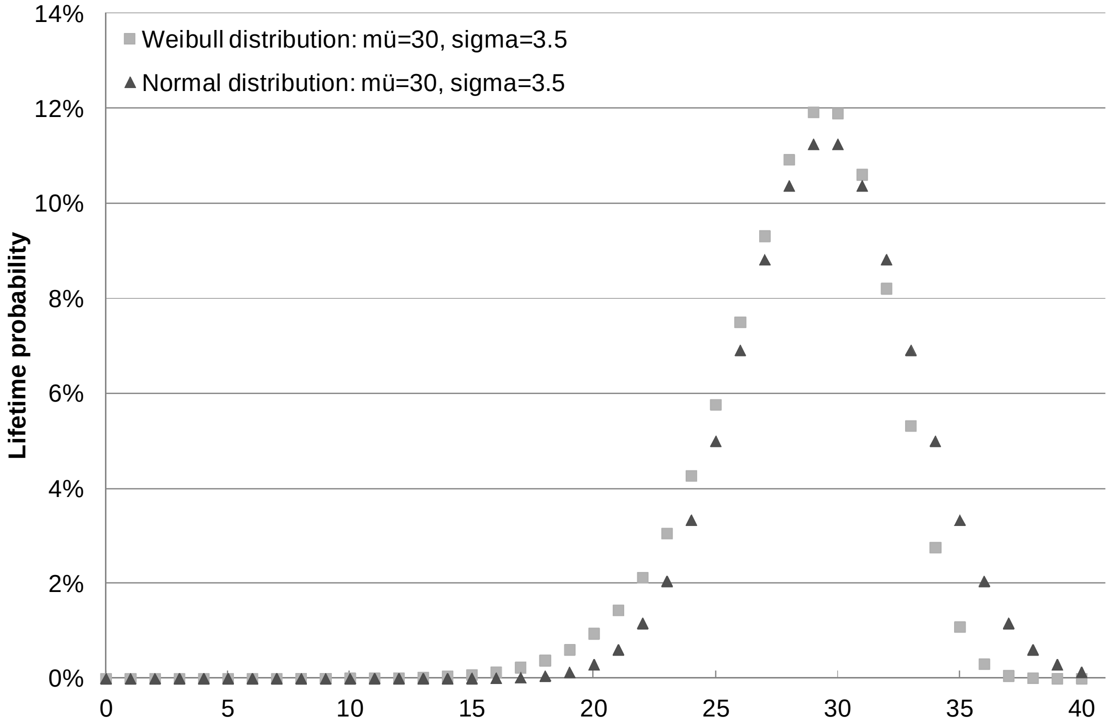


Figure A-2: Lifetime probabilities of CdTe-PV modules

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LEBENSLAUF VON MAX MARWEDE

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