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Environmental impacts of recycling crystalline silicon (c-SI) and cadmium telluride (CDTE) solar panels

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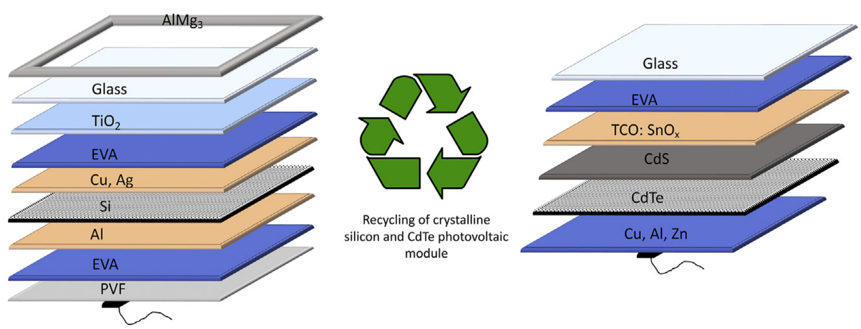
HIGHLIGHTS

- Recycling phase of PV panels has minor impact on entire lifecycle impacts of PVs
- Thermal methods are more eco-friendly than chemical and mechanical methods
- Recovering of Ag, Al, Si and glass in c-Si should be prioritized for c-Si PVs
- Recovering of Te, Cu, and glass should be prioritized for CdTe PVs

GRAPHICAL ABSTRACT



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ABSTRACT

There has been a substantial growth in the deployment of solar photovoltaic (PV) panels in the past couple decades. Solar PVs have a life span of about 25 years and much of the deployed PVs will soon reach their end of life (EoL). It is now timely to plan for the EoL of PVs to recover valuable materials and recycle PV modules sustainably. The goal of this study was to analyze the environmental impacts of different recycling methods for crystalline silicon (c-Si) and CdTe panels. A life cycle assessment (LCA) was performed for delamination and material separation phases of recycling solar panels. The LCA results showed that the recycling of c-Si and CdTe PVs contribute 13–25% and 3–4%, respectively to the entire PV lifecycle impacts. Also, for both c-Si and CdTe PVs, the thermal-based recycling methods resulted in lower environmental impacts than chemical and mechanical methods, except for pyrolysis. Nitric acid dissolution used for c-Si PV recycling had the highest impacts among all methods since the material consumption for this method has not been optimized for industrial use. Results from this study suggested that current techniques used in recycling of PVs, produce higher impacts than extraction of Al, Si and glass for c-Si and extraction of glass for CdTe. Lastly, this study identified which materials to prioritize for highest economic and environmentals benefits from recycling. These will be Ag, Al, Si, and glass in c-Si modules, and Te, Cu, and glass in CdTe modules.

1. Introduction

Solar photovoltaic (PV) is one of the most promising renewable energy technologies: it is clean, reliable, versatile, silent and abundant

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(Hosseinian Ahangharnejhad et al., 2019; Yan et al., 2017). However, for PVs to be truly sustainable, a special emphasis should be put in minimizing the environmental burden from the production, operation and end of life (EoL) of PV systems (Celik et al., 2017b; Ren21, 2014). Many researchers explored the life cycle environmental impacts of the energy supplied from PVs (Celik et al., 2018; Celik et al., 2017a, 2017b; Serrano-Lujan et al., 2015). Prior work mainly focused on impacts resulting from the production and use of the PV panels and omitted the impacts from the EoL phase of PV technologies (Celik et al., 2016; Espinosa et al., 2015; Gerbinet et al., 2014). This is a problem because PV systems are increasing in number all over the world and reached a total installed capacity of around 403 GW at the end of 2017 (IEA PVPS, 2018). Because of this growth, the cumulative global PV waste reached over 250,000 tons by the end of 2017. The PV waste will range between 1.7 and 8 million tons by 2030 and 60 to 78 million tons by 2050 (International Energy Agency, 2017). The increasing waste from PV panels can be a significant environmental problem. If not collected and properly recycled, EoL of solar PV may lead to leaching of metals. For example, one study (Nover et al., 2017) found that after 360 days, 1.4% of lead from c-Si and 62% of Cd from Cadmium Telluride (CdTe) PV panel pieces were released into water based solutions. However, if PVs are properly collected and recycled, the metals and other materials can be recovered and be a valuable resource instead of causing environmental damage.

With the promise of recovering materials and reducing manufacturing costs of PV panels there has been some recent interest in environmental analysis of EoL of PVs. These studies suggest that recycling PV panels is less environmentally burdensome than landfilling (Cucchiella et al., 2015; Faircloth et al., 2019; Giacchetta et al., 2013; Held, 2009; Lunardi et al., 2018a, 2018b). One study noted the potential concern about the use of toxic substances such as dichlorobenzene during the chemical recycling treatment (Lunardi et al., 2018a, 2018b). Another study suggested that CdTe recycling methods may require lower energy and have lower environmental impacts than c-Si recycling methods (Vellini et al., 2017). One of the key questions for recycling of solar panels is whether recovering materials is better for the environment compared to extracting and using virgin materials. Several recent studies did suggest that the environmental impacts from recycling are less than using virgin materials but how much less has been uncertain and one study even found that recycling may lead to higher impacts than using virgin materials (Bogacka et al., 2017; Eskew et al., 2018; Perez-Gallardo et al., 2017; Vellini et al., 2017). One reason for this uncertainty is that there are different recycling processes and the environmental impacts from each may vary greatly. There is one study that reported the end point impacts of different c-Si recycling processes but this paper left out electrothermal heating and pyrolysis c-Si recycling methods, did not report on thin film recycling methods, and also did not provide the midpoint impact results (e.g. global warming and toxicity) that can be used to interpret the different effects of the recycling process on different environmental issues (Lunardi et al., 2018a, 2018b).

In summary, the majority of the works reviewed focus on cradle to gate environmental impacts of PV technologies using life cycle assessment. A few of the studies touch the environmental impacts of PV recycling technologies. The novelty of the proposed manuscript, however, is to analyze and compare the environmental impacts of different recycling methods for crystalline silicon (c-Si) and CdTe panels. In our previous works we provided life cycle inventories of PV technologies. So, this work will be a complimentary analysis on the works we published earlier and gives a complete picture of entire life cycle impacts of PV technologies.

In addition, we adressed the literature gaps by studying the following three: i) Which of the different c-Si and CdTe PV recycling techniques are better for the environment? ii) How do the impacts from recycling compare to the impacts from extracting and producing virgin solar panel materials? iii) Which of the solar panel materials have the higher economic and environmental impacts and would lead to greater benefits if recovered? To answer these questions, we used the life cycle assessment (LCA) method. We developed LCA models for multiple recycling processes based on ISO 14040/14044 standards (ISO, 2006a, 2006b).

2. Methods

2.1. Goal and scope

The goal of our attributional LCA was to evaluate the environmental impacts of different recycling methods for both c-Si and CdTe panels in relation to virgin materials. To achieve this goal, the available recycling methods for CdTe and c-Si solar panels were identified. There are three main stages of PV recycling; (1) delamination, (2) material separation, and (3) material extraction and purification (Lunardi et al., 2018a, 2018b; Marwede et al., 2013; Smith and Bogust, 2018; Strachala et al., 2017; Tao and Yu, 2015; Xu et al., 2018). The scope of this study covered delamination and material separation for both c-Si and CdTe. After material separation, for c-Si modules, >90% of the PV material is recovered (glass, Al and Si) whereas for CdTe >95% of the PV material is recovered (glass). A PV system is composed of a PV panel and a balance of system (BOS). The BOS includes wires, switches, a mounting system, fuse bodies, fuse holders, one or many solar inverters, a battery bank and battery charger (Eskew et al., 2018). This study only considered the recycling of the PV module and did not include recycling of the BOS. The BOS was not included because its design varies greatly depending on whether it is mounted on the ground or on a rooftop and whether it is for c-Si or thin films (Nawaz and Tiwari, 2006).

The functional unit for this LCA was the recycling of 1m^2 of PV panel waste. Most of the prior LCA studies on EoL of solar PV panels used this functional unit (Berger et al., 2010; Bogacka et al., 2017; Held, 2009; Müller et al., 2005; Rocchetti and Beolchini, 2015; Vellini et al., 2017) while a couple studies used unit weight of the waste (1 kg of waste) (Latunussa et al., 2016; Stolz and Frischknecht, 2016) or unit electricity generated (1kWh) (Espinosa et al., 2015; Li et al., 2017). The functional unit selected was area because it allows a straightforward comparison between different PV panels. Area increases linearly with the amount of material within a panel. It is not affected by the different types of materials that may be used in different PV systems and is also not affected by insolation and efficiency parameters that add additional uncertainty to the kWh functional unit. Also, since the function of the study is to evaluate the environmental impacts of different recycling methods for both c-Si and CdTe panels in relation to virgin materials this function would be attained by comparing the impacts per m^2 from the different recycling methods.

The life cycle impact assessment (LCIA) was calculated from the TRACI (Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts) model (Enviromenmental Protection Agency - EPA, 2012). TRACI generates the LCIA in 10 impact categories. Following the approach of Celik et al. (2017a, 2017b) the impact categories were normalized to the manufacturing of the PV panels so as to be able to compare across different impact categories. Normalization is an optional step of LCA to rank the impacts of a system according to ISO 14040/44 (ISO, 2006a, 2006b). Selecting manufacturing of PV panels as a reference point is meaningful because their impacts are well known in the literature; tens of LCA studies were performed to analyze cradle-to-gate solar PV impacts since the beginning of 1990s. In addition, by comparing the manufacturing impacts to the recycling of PVs, one can see how much EoL management of PVs contributes to the entire life cycle impacts of PV panels. Weighting which is an optional step in LCA was not performed and hence all impact categories were assumed to have equal importance.

2.2. PV structure and waste composition

Before explaining the recycling processes and life cycle inventory, it is important to first understand the structure and composition of PV panels which is what we present in this section. Forecasting the volumes and material composition of this PV waste is a relatively new area of research filled with many uncertainties (Peeters et al., 2017; Santos and Alonso-García, 2018). Part of the uncertainty comes from the variability among manufacturers and the rapid change in the technology (Mahmoudi et al., 2019). Yet, averaging data from multiple sources (Bekkelund, 2013; Domínguez and Geyer, 2017; Frischknecht et al., 2015; Jungbluth and Flury, 2012; Sander et al., 2007a, 2007b; Stolz et al., 2016), we estimated the expected mass composition of the PV waste. An average c-Si panel (Fig. 1-a) has a weight to area ratio of 13.7 kg/m^2 whereas the average CdTe (Fig. 1-b) has a weight to area ratio of 16.8 kg/m^2 (Domínguez and Geyer, 2017).

Glass makes up the largest percentage of mass in both c-Si (68%) and CdTe (92%) panels. The primary purpose of the glass is to transmit as much sunlight as possible into the panel. It also enables encapsulation against damaging external factors, such as water and dirt. The aluminum frame has the second highest mass percentage of c-Si PVs (17%) and the frame also includes Mg in the form of aluminum alloy ($AlMg_3$) (Domínguez and Geyer, 2017). CdTe panels do not have an aluminum frame because the solar cells are sandwiched between two pieces of glass and their structure uses sturdier backsheets that don't warrant a frame. The next highest percentage of mass contribution of both PVs come from the ethylene vinyl acetate (EVA) layer. The EVA is a transparent polymeric resin designed to protect the delicate solar cell regions from moisture, dirt, ice, and other conditions expected during operation. The EVA is also used as an adhesive between the glass and the Si wafer. In c-Si, EVA accounts for ~7% of the total mass and it sandwiches the cells whereas in CdTe panels EVA accounts for 4% of mass and it is right below the glass substrate.

In c-Si panels, Si is the light absorber layer; it takes 4% of the total mass and is connected to the backsheet by soldering copper wires onto them. A backsheet is the last layer at the bottom of the c-Si solar PV panel and is typically made of a polymer or a combination of polymers such as polyvinyl fluoride (PVF) (Bradley, 2015). It protects against ultra-violet radiation, humidity and vapor penetration, dryness, wind, dust, sand, and chemicals (Roekens-Guibert, 2007). A junction box is attached to the backside of the panel for electrical connection. Ag in combination with Cu, Ni and Fe make up the electrical connections (1.5% of the total mass) (Grandell and Thorenz, 2014). Ag also helps conduct the gathered electricity out of the Si cell for storage or consumption. The superior conductivity of Ag increases the potential sunlight captured, energy conducted, and total power that is ultimately collected in a solar cell.

In frameless CdTe panels, CdTe is the light absorber layer (Wang et al., 2011) and it takes up 0.12% of the total mass. Its purpose is to absorb light and generate charge carriers. The absence of frame in CdTe PVs not only reduces cost but also helps with electrical isolation of the panel (Ridge et al., 2017). Having metal in contact with glass can provide an unwanted conduction path for leakage currents. Frameless panels are referred to as laminates (Eiffert et al., 2009). The substrate is the material on which the CdTe solar cell layers are deposited (Eiffert et al., 2009). It is usually made of glass and occupies about 95% of the mass of the whole solar panel. CdTe panels have a front and back contact which takes up 3% of the total mass of the panel. The *front* and back contacts are responsible for reducing series resistance for current flowing from the solar cells.

2.3. PV recycling techniques

Through a comprehensive literature review, we identified 10 delamination techniques identified. Six of these were for c-Si (Bruton et al., 1994; Doi et al., 2001; Doni and Dughiero, 2012; Frisson et al., 2000; Kim and Lee, 2012; Wang et al., 2012) and four were for CdTe (Berger et al., 2010; Giacchetta et al., 2013). We identified two material separation techniques, one for c-Si (Klugmann-Radziemska et al., 2010) and one for CdTe (Marwede et al., 2013; Wang and Fthenakis, 2005). The processes compiled are shown in Fig. 2 (for c-Si) and Fig. 3 (for CdTe). In section 2.3 we provide an overview of these processes. An in-depth description of each of the processes is provided in the Supporting Information.

2.3.1. c-Si recycling techniques

In the recycling of c-Si PV panels there is a frame which needs to be removed before the sandwich layer-like structure is dismantled. The process begins with the disassembly of the Al frame and junction box (Del Pero et al., 2019). The frame is frequently disassembled manually because the size, profile and fastening vary between manufacturers.

The next step is the removal of the EVA layer to separate the glass from the Si cell (delamination). During the delamination stage the waste PV panels enter as a whole and by the time they leave, the EVA has been separated from the glass components. The delamination methods are split into chemical and thermal. The chemical methods

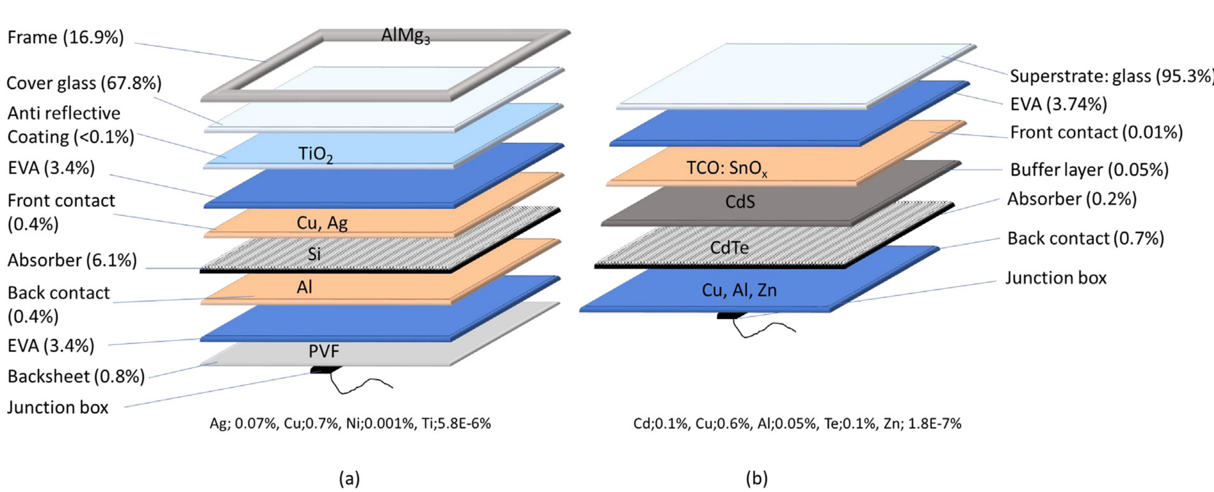

Fig. 1. Typical PV structure of (a) c-Si and (b) CdTe PV panels with percentage mass compositions. The percentage mass compositions are an average of data from six different sources (Bekkelund, 2013; Domínguez and Geyer, 2017; Frischknecht et al., 2015; Jungbluth et al., 2012; Sander et al., 2007a, 2007b; Stolz et al., 2016). EVA: Ethylene Vinyl Acetate, TCO: Transparent Conducting Oxide, PVF: Poly Vinyl Fluoride.

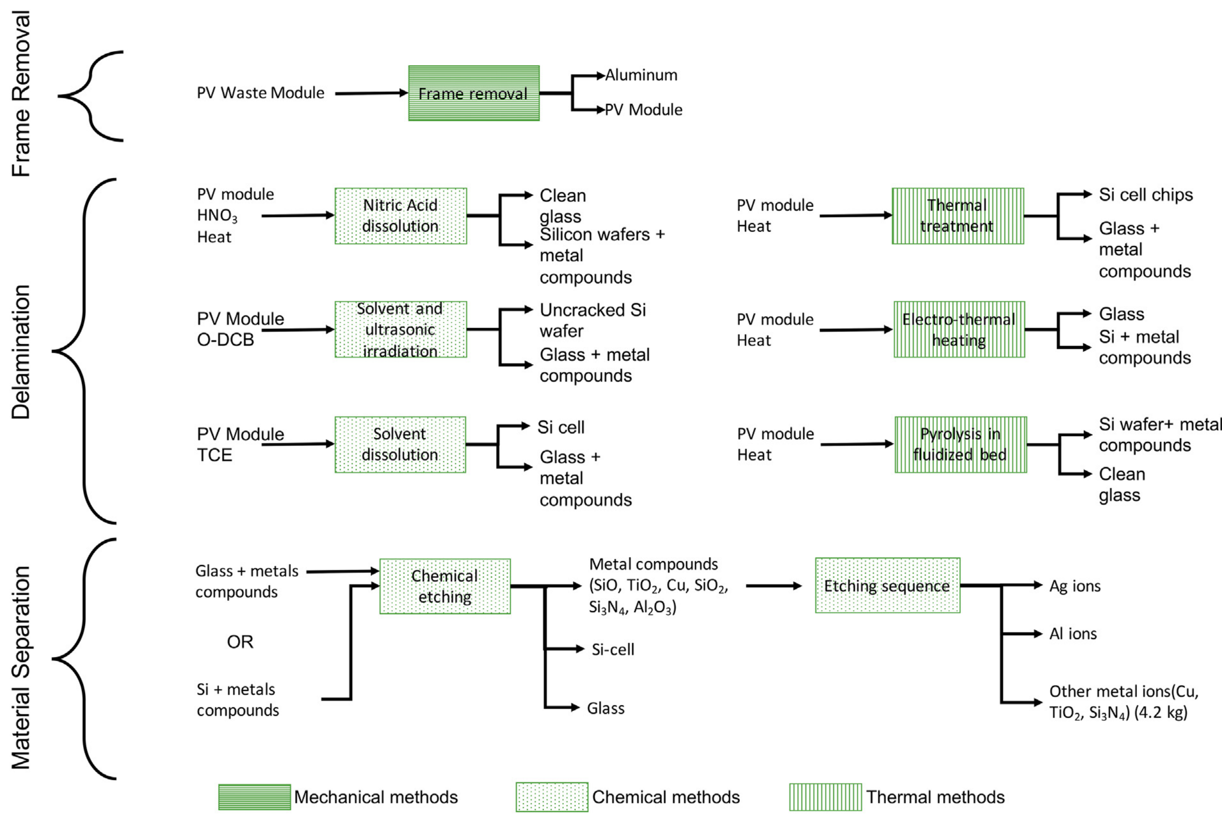

Fig. 2. Delamination and material separation methods for c-Si. Material inputs for each method are shown in Table 1.

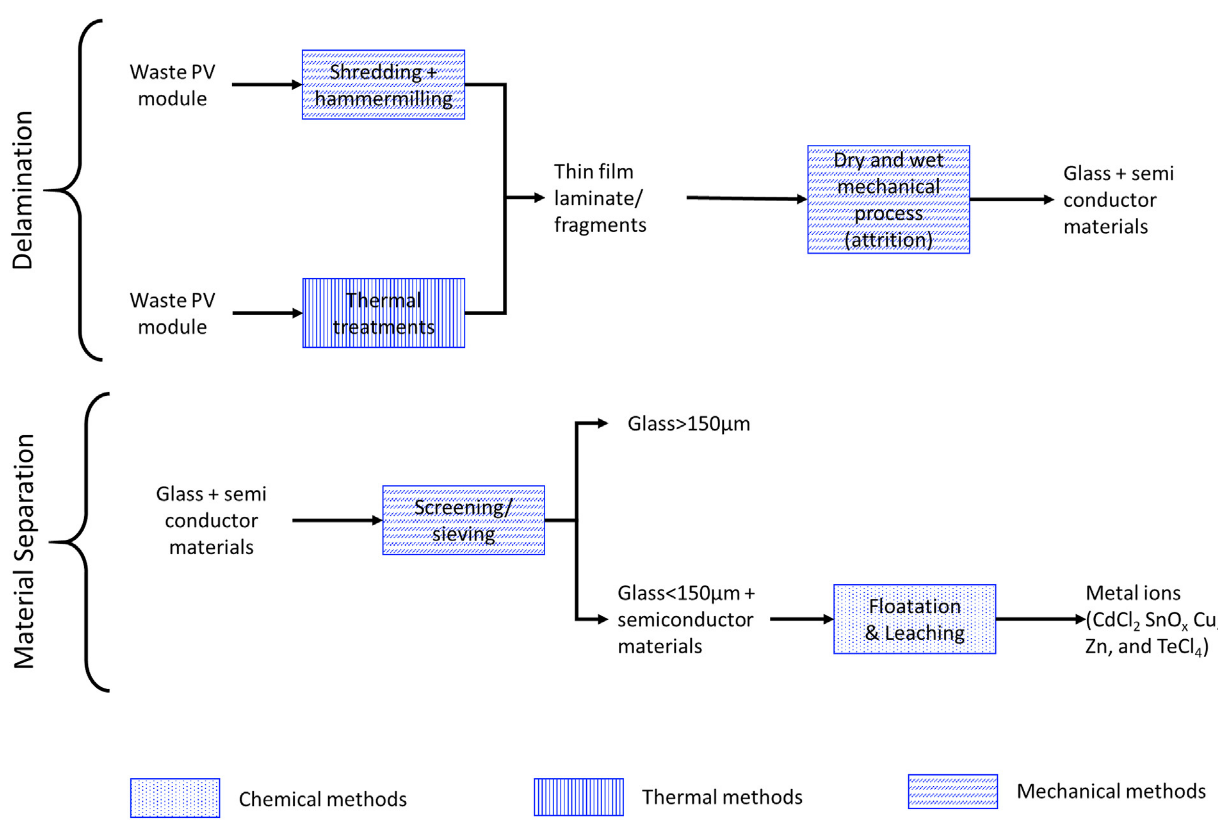

Fig. 3. Delamination and material separation methods for CdTe PV panels. Material inputs for each method are shown in Table 1.

include using nitric acid dissolution, solvent and ultrasonic irradiation and solvent dissolution whereas the thermal methods are; thermal treatment, electro-thermal heating and pyrolysis in fluidized bed. The nitric acid dissolution, pyrolysis in fluidized bed, and electro thermal heating methods all produced clean glass as one output and a combination of silicon and metal compounds as the other output. Solvent and ultrasonic irradiation, solvent dissolution and thermal treatment produced silicon cell chips as one output and a combination of glass and metal compounds as the other output. After delamination, the glass components, the c-Si cell and metal compounds proceed to the material separation stage.

There is only one method of material separation for c-Si and that is chemical etching. Chemical etching uses a combination of nitric, hydrofluoric and ethanoic acid in the presence of bromine gas. The chemical etching process helps to separate glass from the metal compounds and Si cells.

From literature, some material extraction methods for c-Si modules were found (Ardente et al., 2019) (Dias et al., 2016). However, the scope of this paper covers only the delamination and material separation stages which recover over 90% of the PV materials thus material extraction was not included the final step.

2.3.2. CdTe recycling techniques

During thin film delamination the laminate enters as a whole, and it is broken down into fragments using two main methods; mechanical and thermal methods (Marwede et al., 2013; Tao and Yu, 2015). The mechanical methods are laser irradiation, shredding and hammermilling and hotwire cutting. There is currently no industrial information on the process for laser irradiation and hotwire cutting and hence a life cycle analysis could not be performed for these two methods. The only thermal method is thermal treatment which requires heating the panels in lab scale furnace at 500 °C. The thin film fragments proceed to the dry and wet mechanical process (attrition) which separate the EVA from the glass and semiconductor material. The delamination step for CdTe is a bit longer because thin film panels have a more complex structure (due to their thin pairing of layers).

Material separation for thin films on the other hand involves several interlinked processes. It starts out with attrition. Attrition is a wet mechanical process using shear and frictional forces on the surface of the particles to be separated. During attrition the thin film fragments are divided into glass, EVA and semiconductors. This product is then taken through screening/sieving whereby glass >150 μm and EVA are sieved out. Glass smaller than 150 μm and semiconductor materials are passed through a floatation process. Thereafter, the product is taken through leaching/dry etching which results into metal compounds ($CdCl_2$ and $TeCl_4$). The leaching process requires sulfuric acid and hydrogen peroxide. For this study, it should be noted that impacts from floatation and attrition were added directly to leaching. They were added because floatation and attrition are prerequisite steps to leaching and thus are a part of the material separation step.

From literature five different material extraction methods for thin films were found; electrolysis, ion exchange + electro-winning, liquid-liquid extraction precipitation and oxidation reduction (Goozner et al., 1997; Mezei et al., 2008; Sander et al., 2007a, 2007b; Wang and Fthenakis, 2005). However, the scope of this paper covers only the delamination and material separation stages which recover over 95% of the PV materials thus the final step was not included in this study.

2.4. Life cycle inventory

Life cycle inventory (LCI) data, including material inputs and electricity inputs for the recycling processes were compiled using GaBi 8.1 software and the Ecoinvent v3.3 database. The LCI for the different recycling processes is shown in Table 1. Either electricity or a chemical or both are used in each process. Some studies (Doni and Dughiero, 2012; Wang et al., 2012) that were used to generate the life cycle inventory were lab based and data from these studies was extrapolated to represent industrial data. This extrapolation was carried out so that the results could be compared with other industrial level results. Extrapolation from lab to industrial level was done by multiplying with an electricity conversion use factor of 0.2% obtained from (García-Valverde et al., 2010). The use factor is introduced because the equipment at lab scale is not being used to maximum capacity as it would otherwise be in industry. The recycling yield of these materials can range from 20 to 100% as shown in Table 2.

Metals used in PV systems can be classified in five categories of materials: base (nonferrous metals that are neither precious metals nor noble metals), precious metals, hazardous or toxic metals, critical metals (metals essential for high-technology and green applications, but their supplies are susceptible to economic and political issues) and other materials (e.g. glass and EVA) (Domínguez and Geyer, 2017). Critical materials identified in Table 2 is based on Department of Energy's 2011 (Bauer et al., 2011) report which follows Graedel's (Graedel et al., 2012) approach. This approach defines the criticality of the materials as a function of three variables such as vulnerability to supply restriction, supply risk and environmental implications. Any attempt to recycle critical metals will support the global market for secondary raw materials (Domínguez and Geyer, 2017).

The material weights and recovery yields for modeling of the production of virgin materials are shown in Table 2. Impacts from virgin materials for c-Si were modeled for glass, Al and Si since the recycling methods analyzed in this study can recover only those components. For the CdTe, impacts from virgin materials were modeled for only glass because the recycling methods analyzed in this study can recover only glass (which occupies 95% of the module).

3. Results and discussion

3.1. Environmental impacts of different methods of recycling c-Si PV modules

Fig. 4 shows the total normalized environmental impacts of PV panels from cradle-to-gate life cycle phases (named as c-Si manufacturing), the different EoL management options of PV recycling, and the extraction phase of the virgin materials used in the PV panels. The normalization was performed assuming all impact categories implicitly have equal importance (1 c-Si manufacturing impact unit). Since the recycling methods covered in this study extract only glass, Al and Si, the bar on the far right of Fig. 4 (virgin material extraction phase) contains impacts from glass, Al and Si. Our results indicate that the solvent and ultrasonic irradiation, solvent dissolution, thermal treatment, electrothermal heating and pyrolysis all had impacts in the range of 13 to 20% of the total manufacturing impacts while the nitric acid dissolution had impacts of about 33% of the total manufacturing impacts. These results showed that recycling phase of c-Si PVs will contribute 15–35% more impacts to cradle-to-gate environmental impacts of c-Si PVs which implies the impact of recycling on the entire life cycle impacts of c-Si PVs varies 15–25% depending on chosen recycling technique. Results obtained in this study are consistent with those of (Li et al., 2017) who developed an LCA model to compare environmental impacts from different stages of the PV life cycle; manufacture, installation, use and EoL (recycling) for c-Si solar panels. The EoL results were expressed in percentages and it was revealed that manufacturing impacts were far much greater than recycling impacts for all impact categories. For GWP, manufacturing impacts accounted for about 83% of the total impacts and EoL accounted for 15% (Li et al., 2017). Considering acidification potential, manufacturing accounted for 97% and EoL 2%. Also, another interesting similarity was the highest impacts in recycling were

Table 1
Life cycle inventory showing the processes, material inputs, amounts and outputs for 1m^2 panel. The status of the recycling processes are commercial scale *, pilot scale %, and lab scale #.

	Step of recycling	Recycling processes and their status	Materials	Inputs (per m^2)	Outputs	Advantages	Disadvantages
c-Si	Delamination	Nitric acid dissolution% (Bruton, 2020)	HNO_3 Electricity	46.2 kg 0.45 kWh	Glass, metal compounds, wafers and EVA	Complete removal of EVA and metal coating on the wafer. – Possible to recover intact cells	-Causes cell defects due to inorganic acid. – Generates harmful emissions and wastes
		Solvent and ultrasonic irradiation# (Kim and Lee, 2012)	$C_6H_4Cl_2$ Electricity	46.2 kg 7.14 kWh	Glass, metal compounds, wafers and EVA	Complete removal of EVA	-Expensive process and produces harmful emissions and wastes.
		Solvent dissolution# (Doi et al., 2001)	C_2HCl_3	46.2 kg	Glass, metal compounds, wafers and EVA	Complete removal of EVA, recovery of glass and less cell damage compared to HNO_3 dissolution	-Produces harmful emissions and wastes
		Thermal treatment* (Wang et al., 2012)	Electricity	0.45 kWh	Glass, cell chips and metal ribbons	Full removal of EVA, possible recovery of intact cell and direct reuse of wafers, simple and low-cost process.	Requires high energy inputs and produces harmful emissions.
		Electrothermal heating# (Doni and Dughiero, 2012)	Electricity	4.17 kWh	Glass, metal compounds, wafers and EVA	Ensures easy removal of glass and does not generate emissions from EVA burning.	Slow process.
		Pyrolysis % (Frisson et al., 2000)	Electricity	25 kWh	Glass, metal compounds, wafers and EVA	EVA burns with practically no residues.	Slow process and thermal stress lead to glass breakage.
	Material separation	Chemical etching* (Klugmann-Radziemska et al., 2010)	HNO_3 HF CH_3COOH Br gas	5208 ml 3125 ml 3125 ml 62.5 ml	Glass, Metal compounds, Si- cells	Recovery of high purity materials and it is also a simple and efficient process.	Uses chemicals thus produces liquid wastes.
CdTe	Delamination	Thermal treatments* (Berger et al., 2010)	Electricity	40 kWh	Thin film laminate fragments	Full removal of EVA, possible recovery of intact cell	Requires high energy inputs and produces harmful emissions.
		Shredding & hammermilling* (Giacchetta et al., 2013)	Electricity	2.2 kWh	Thin film laminate fragments	Can recycle either intact panels, broken panels or manufacturing scrap.	No removal of dissolved solids
	Material separation	Attrition and floatation* (Marwede et al., 2013)	Electricity	0.04 kWh	Glass & semiconductor materials	No usage of chemicals. Clean glass	Recovered materials have to be further enriched by chemical or mechanical methods
		Leaching* (Wang and Fthenakis, 2005)	H_2SO_4 H_2O_2	1.4 kg 1.4 kg	Metal compounds ($CdCl_2$ and $TeCl_4$)	Complete removal of metals from glass. – Further extraction of metals from solution possible	Encapsulation of organic materials in glass. High use of chemicals. – Generates of acidic fumes

from global warming, and acidification just like in this study (Li et al., 2017).

The chemical-based techniques such as nitric acid dissolution, produces higher impacts compared to the thermal-based techniques (Fig. 4). The main reason for the high impacts is because the nitric acid dissolution method uses large quantities of chemicals (about 7-46 kg of nitric acid) since it is a lab scale/pilot scale and as such are not optimized for large scale industrial use. Also, the upstream processes required for nitric acid production involve the release of more substances such as volatile organic compounds (VOCs) and particulates to the air as compared to upstream processes for electricity production. These substances may have a negative effect on local air quality such as photochemical smog, while certain emissions, such as carbon dioxide (CO_2), nitrous oxide (N_2O) (Ullmanns, 1991), ozone and water vapor, may act as “greenhouse gases,” contributing to the effect of global warming. Also, other gases, such as sulfur dioxide and oxides of nitrogen, may contribute to the formation of acid precipitation (“acid rain”). Thus, the higher values of acidification, global warming, smog air and human health particulate matter for the methods that use high chemicals as compared to methods that use electricity.

Table 2
Summary of PV material components, percentage compositions (Bekkelund, 2013; Domínguez and Geyer, 2017; Frischknecht et al., 2015; Jungbluth et al., 2012; Sander et al., 2007a, 2007b; Stolz et al., 2016) and recycling yields (Domínguez and Geyer, 2019). Precious (Domínguez and Geyer, 2019),$^{\Psi}$ toxic and hazardous (Domínguez and Geyer, 2019)$^{\Phi}$ and critical (Bauer et al., 2011)^{S} metals are shown with symbols and the remaining metals content is made up from base metals.

	c-Si			CdTe		
Material composition	[kg/m^2]	[%]	Recycling yield [%]	[kg/m^2]	[%]	Recycling yield [%]
Ag$^{\Psi}$	1.06E-2	0.08	95	–	–	–
Al	2.32E+0	16.9	100	8.85E-3	0.05	100
Cd$^{\Phi}$	–	–		2.00E-2	0.12	95
Cr^{S}	–	–		3.00E−3	0.02	20
Cu	1.06E-1	0.77	100	1.10E-1	0.68	100
Mg	8.02E-2	0.58	37	–	–	–
Ni	1.63E-4	<0.01	41	–	–	–
Pb$^{\Phi}$	7.20E-4	<0.01	96	8.50E-4	<0.01	96
Si	8.61E-1	6.27	100	5.00E−2	0.30	100
Sn	9.05E-3	0.07	32	2.30E−7	<0.01	32
Te^{S}	–	–	–	2.00E-2	0.12	95
Ti	8.01E-7	<0.01	52	2.30E−8	<0.01	52
Zn	1.20E-6	<0.01	27	3.00E−8	<0.01	27
EVA	9.24E-1	6.73	–	6.10E-1	3.74	–
Glass	9.30E+0	67.8	100	1.60E+1	95.3	100
Total	13.7	100.00		16.8	100.00	

Nitric acid dissolution has higher impacts as compared to the other methods (approximately two times of the other methods) because nitric acid production process generates more impacts than trichloroethylene and dichlorobenzene production processes which are used in solvent dissolution and solvent and ultrasonic dissolution respectively. Thus, nitric acid dissolution has the highest impacts for acidification, smog air and global warming. Solvent and ultrasonic irradiation has relatively high impacts for ecotoxicity and human health particulate air.

Solvent dissolution, thermal treatment, and electrothermal heating all generate relatively lower impacts as compared to nitric acid dissolution and pyrolysis. Chemical etching, a material separation method, produces higher impacts when compared with the delamination methods. Thermal treatment and electrothermal heating have

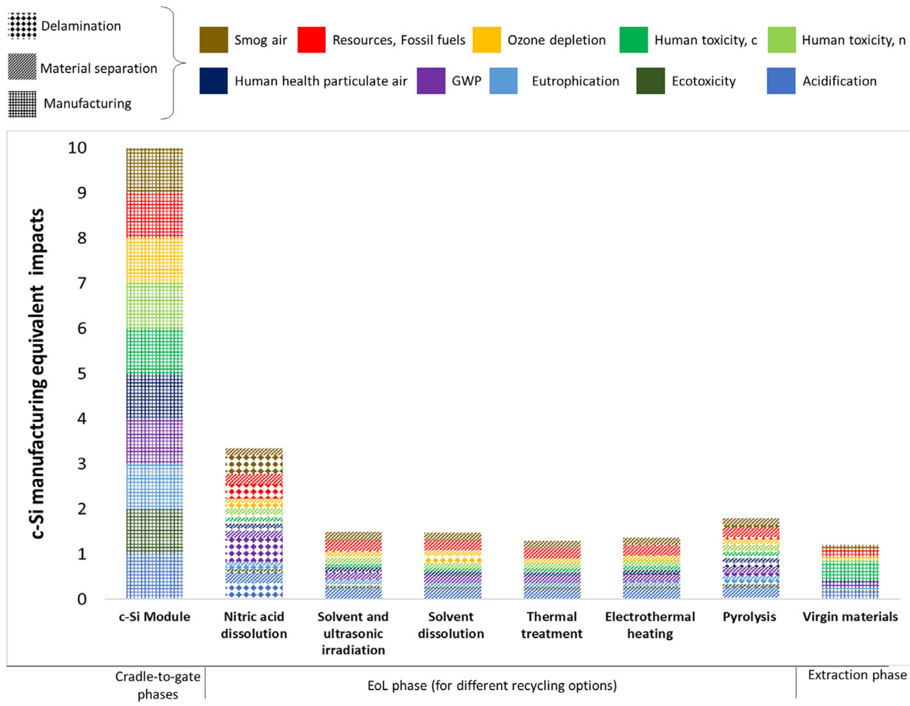

Fig. 4. Comparison of impact results for c-Si delamination with material separation (chemical etching) incorporated into each method and normalized to c-Si manufacturing. Within each impact category, the impact (per m^2 of panel recycled) from each process was divided by the impact from c-Si manufacturing. For c-Si the bar height is unity for each impact category. For ten impact categories, the total impact for c-Si is given as ten units.

lower environmental impacts than the chemical methods, with thermal treatment having the lowest impacts. Their low impacts are attributed to the fact that they utilize only electricity. Pyrolysis has relatively higher impacts than electrothermal heating and thermal treatment because it requires higher energy inputs to reach the required high temperatures.

3.1.1. Comparison of environmental impacts of recycling with impacts from virgin material extraction for c-Si modules

If recovering materials through recycling is more environmentally impactful than extracting those materials from virgin resources, the recycling process would be redundant. To check whether recycling of the materials used in c-Si PVs is more environmentally friendly than extraction of virgin materials, a comparison of the environmental impacts of different recycling options with the one due to the extractions of virgin materials to be used in c-Si PVs (EoL phase vs extraction phase comparison in Fig. 4) was carried out. One point to remember is that impacts shown in the extraction phase are impacts from extraction of glass, Al and Si only. This is because the recycling methods covered in this study are only able to produce glass, Al and Si.

To offer a direct comparison, material amounts and their average recycling yields from different recycling techniques, shown in Table 2, were used. For example, c-Si PVs contains 2.32 kg/m^2 of Al in PV panels and 100% of this amount can be recovered by recycling. The recoverable amounts for each material were multiplied with their respective impacts due to extraction (which were taken from EcoInvent database). These results are shown in the far-right bar in Fig. 4, referred as virgin materials. Results show that all recycling methods for c-Si produce impacts that are higher than impacts from virgin material extraction. This means that the current recycling methods are not environmentally sustainable. Also, considering the fact that the methods analyzed in this study only produce glass, Al and Si, then that would mean that if further processing were to be added to extract the rest of the metals (such as Ag) that are in solution form then the impacts from the recycling methods would even be higher.

On comparing our findings with literature, it was revealed that one study (Bogacka et al., 2017) showed that there is a small environmental relief from raw materials recovery during the recycling process. It also suggests that the level of relief would even be lower if it weren't for the adopted assumptions related to the level of recovery (90% recovery rate for Cu, glass and Si and 100% for Al) and not forgetting the fact that energy consumption was not included.

3.2. Environmental impacts of different methods of recycling CdTe PV modules

Fig. 5 shows the environmental impacts from cradle-to-gate life cycle phases of CdTe PV panels, the different EoL management options of CdTe PV recycling, and the extraction phase of the virgin materials used in CdTe PV panels. Both recycling methods produce very low impacts (25–30 times less) as compared to impacts from CdTe PV manufacturing (Briese et al., 2019). This result implies that the contribution of recycling phase on the entire life cycle impacts of CdTe PVs is minor (3–4%) depending on chosen recycling method. Thermal treatment produced less impacts than shredding and hammer milling mainly because the thermal treatment process requires less electricity than the shredding and hammer milling process. Less electricity consumption results into less impacts. This is harmonious with a study by (Berger et al., 2010) which carried out a life cycle assessment for recycling of thin film PV panels using thermal and mechanical methods. Berger et al. compared these results with a none recycling scenario. According to their results, thermal treatment produced less impacts than mechanical treatment. For example, in the case of GWP, thermal treatment produced 55% of the impacts from mechanical treatment.

Another study (Dwarakanath et al., 2016) carried out a life cycle assessment for different recycling alternatives for CdTe PV panels and ranked them according to their impacts. According to their ranking, the most environmentally friendly method was thermal treatment followed by mechanical treatment. The use of organic solvents was ranked the worst. In terms of impact categories, results for climate

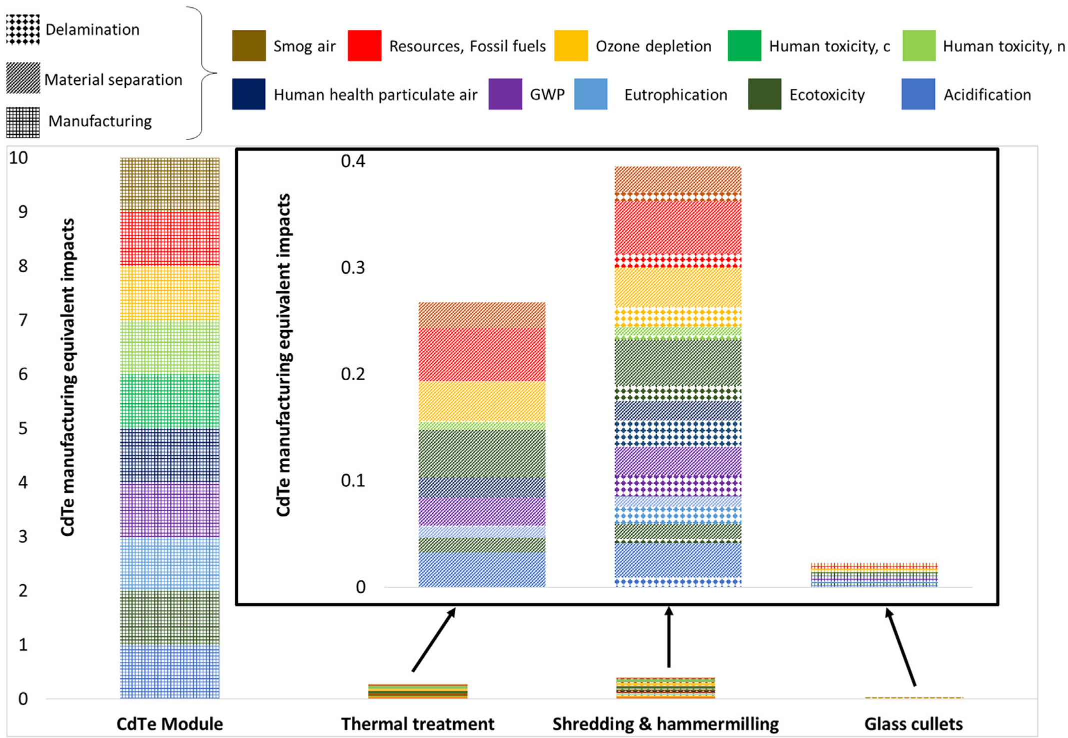

Fig. 5. Comparison of impact results for CdTe delamination with material separation impacts incorporated and normalized to CdTe manufacturing. Within each impact category, the impact (per m^2 of panel recycled) from each process was divided by the impact from CdTe manufacturing. For thin films the bar height is unity for each impact category. For ten impact categories, the total impact for CdTe is given as ten units.

change, fossil depletion and ozone depletion are very similar with results in this study. Overall, their findings state that thermal treatment produces less impacts than mechanical treatment similar to this study.

Material separation for thin films is composed of interlinked processes; floatation, attrition and leaching. Even after material separation results are incorporated into the two delamination methods, impacts are still very low. Thermal treatment with material separation incorporated comes to a total of 0.27 thin film equivalent manufacturing impacts whereas shredding and hammermilling comes to a total of 0.39 thin film equivalent manufacturing impacts as shown in Fig. 5 inset. Floatation and attrition utilize low electricity and leaching utilizes low chemical mass input and hence the low impacts.

3.2.1. Comparison of environmental impacts of recycling with impacts from virgin material extraction for CdTe modules

Fig. 5 also provides a comparison of recycling impacts with impacts from virgin material production (extraction phase). It should be noted that impacts from virgin material production consists of impacts from glass only since the recycling processes covered in this study only recover glass and the rest of the components are ions in solution form.

It is revealed that impacts from both thermal treatment and shredding and hammermilling with material separation incorporated are higher than impacts from virgin material production. Thus, the analyzed recycling methods for CdTe are not environmentally sustainable.

Digging further into the literature, studies that had modeled avoided impacts as well were found. Two studies (Bogacka et al., 2017; Perez-Gallardo et al., 2017) assumed that all substances used to produce PV panel from virgin material were replaced with recycled ones. In other words, they assumed 100% recycling yield rate. The materials considered were Ag, Al, Cu, Si and solar glass. One of the studies (Perez-Gallardo et al., 2017) revealed that 94 kg CO_2/m^2 was avoided through use of recycled materials instead of virgin materials for c-Si panels. The same study also revealed that 52 kg CO_2 was avoided though use of recycled materials instead of virgin materials for CdTe panels. However, the other study (Bogacka et al., 2017) showed that the environmental relief caused by raw materials recovery during the recycling process is quite small. It also suggests that the level of relief would even be lower if it weren't for the adopted assumptions related to the level of recovery and not forgetting the fact that energy consumption was not included.

3.3. Economic and environmental benefits of recovering materials from recycling

Using the recycling yields in Table 2, an analysis of which metals in PV panels one should focus on to offer an environmentally friendly and economically feasible PV recycling was carried out. In other words, recovering which metals provide the economic and environmental benefits for our society? This analysis was performed for two reference points such as per kg of the materials recycled and per unit area of PV panel.

Fig. 6 shows the cost of virgin materials ($/kg) (Sica et al., 2018) vs GWP ($kgCO_2$ eq/kg) from virgin material production for both c-Si and CdTe panels. For c-Si, Ag was found to be the most expensive and most impactful metal. Thus, the recycling of c-Si PV panels should primarily be planned to recover Ag metal. By this way, more environmental impacts can be avoided, and the cost of remanufacturing can be reduced significantly by limiting the expenses related to the virgin Ag metals. Sn, Ti and Si also have relatively high cost and high impacts. For CdTe panels, the most expensive metal is Te and Mn is found to be the least impactful in both PV technologies.

Fig. 7 shows the cost of virgin materials vs GWP from virgin material production on a per m^2 composition. For c-Si panels, Ag remains to be expensive with high GWP impacts. This is generally because production of Ag produces high GWP impacts. Al, unlike in Fig. 6 where it had moderate cost and impacts it, now has high costs and high impacts. This is because of the high mass/m^2 of Al used in c-Si panels. This trend is similar for all other elements such as Si and glass. Hence, both costs and

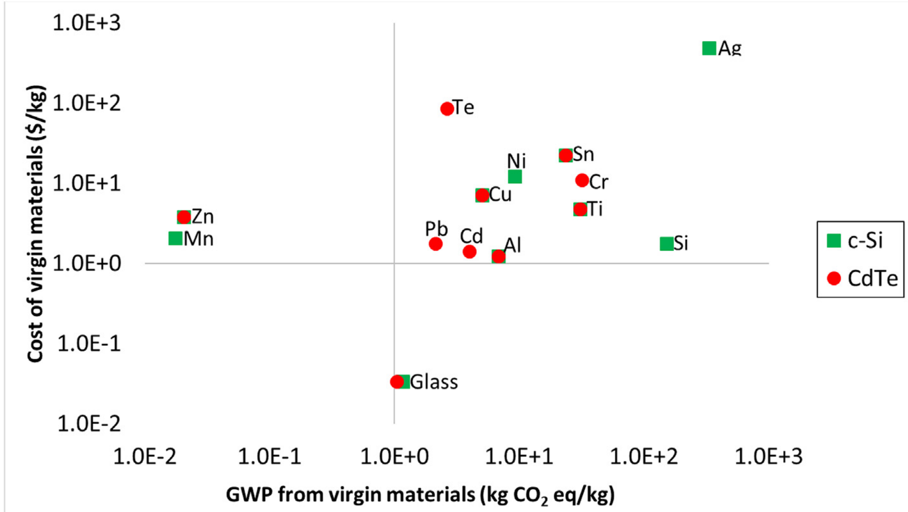

Fig. 6. Cost of virgin materials ($/kg) Vs GWP from virgin materials kgCO$_2$/kg, expressed in logarithmic scale.

impacts of virgin materials are highly dependent on the mass/m^2 used in the c-Si panels. The most impactful elements are Al, Si, glass.

and Ag. For CdTe, Cu and Te are the most expensive elements whereas glass is the most impactful. Glass is the most impactful element because it occupies about 94% of the CdTe panel. Zn is the cheapest and has the lowest GWP. Thus, recycling of PV panels one should aim at recovering expensive and impactful metals such as Ag, Al, Cu, Si, glass and Te.

The results from this study were compared with literature and were found to be consistent with this study. One study (Peeters et al., 2017) carried out a predictive model to predict the materials that will appear in emerging waste streams of PV panels. In terms of monetary value of each of the components in a PV panel they proved that the most economic value in silicon-based PV panels' waste stream comes from the Ag and Al. They also modeled the avoided environmental impacts from recycling, and it was shown that most avoided impacts are from recycling Ag, Al and Si.

3.4. Comparison of environmental impacts of recycling c-Si with impacts from recycling CdTe modules

The aim of this study was to compare impacts from recycling c-Si modules with impacts from recycling CdTe modules and determine which of the two technologies' recycling techniques are more environmentally friendly. In comparing c-Si recycling to CdTe recycling a comparison was made for delamination methods and another for material separation methods. Results were normalized to c-Si manufacturing impacts (Fig. S1). For delamination methods, specifically those that utilized electricity only (thermal treatments and shredding and hammermilling), results were very similar for the two technologies. However, when a comparison was made for CdTe delamination methods with c-Si delamination methods that utilize chemicals it was found that CdTe recycling produced significantly less impacts as compared to c-Si delamination methods. In terms of material separation, c-Si produced significantly higher impacts than CdTe. This is mainly because c-Si material separation utilizes more mass of chemicals than CdTe.

4. Conclusions

The aim of this paper was to analyze the environmental impacts of the different PV recycling techniques used in the EoL management of c-Si and CdTe PV wastes and determine if it is environmentally worthwhile to recycle with an aim of material recovery or to obtain virgin materials from the earth. Six methods of delamination of c-Si were

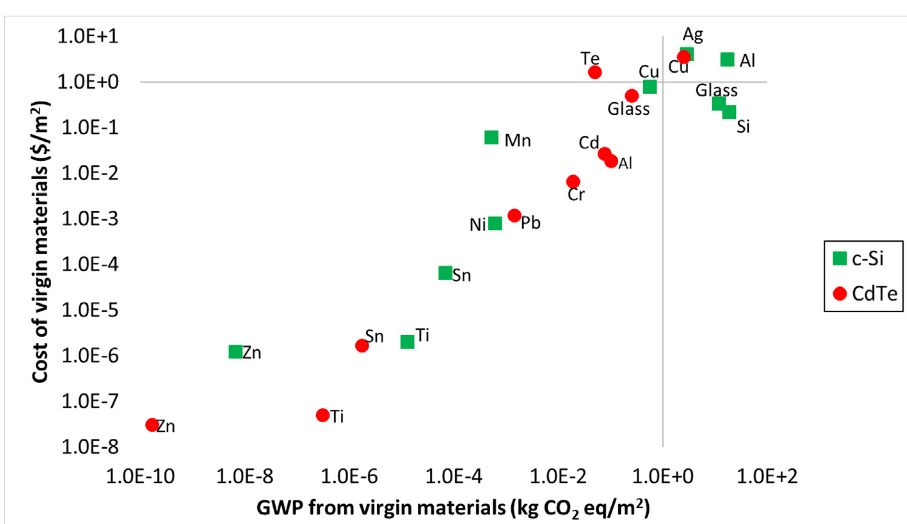

Fig. 7. Cost of virgin materials ($/m^2) Vs GWP from virgin materials kgCO$_2$/m^2, expressed in logarithmic scale.

analyzed; nitric acid dissolution, solvent and ultrasonic irradiation, pyrolysis, solvent dissolution, thermal treatment and electrothermal heating. Our LCA analysis revealed that the chemical-based processes such as nitric acid dissolution, solvent and ultrasonic irradiation and chemical etching produce higher impacts compared to the thermal methods. The major reason for this is because the chemical-based methods are lab/pilot scale and are not optimized for industrial scale. Our findings suggest that current PV recycling techniques analyzed in this study, produce higher impacts than extraction of Al, Si and glass for c-Si and extraction of glass for CdTe. It would be interesting to compare impacts from these chemical methods once their data is available for industrial scale.

In comparing c-Si recycling to CdTe recycling techniques, it was revealed that delamination methods, specifically those that utilized electricity only (thermal treatments and shredding and hammermilling), results were very similar for the two technologies. However, for delamination techniques that utilize chemicals it was found that CdTe recycling produced significantly less impacts as compared to c-Si. In terms of material separation, c-Si produced significantly higher impacts than CdTe. This is mainly because c-Si material separation utilizes more mass of chemicals than CdTe.

In this study, specifically for c-Si panels, Ag is the most expensive metal followed by Al, Cu, glass and Si. These same elements produce the highest GWP impacts on a per m^2 basis. For CdTe panels, the most expensive elements are Te, Cu and glass and these were also the most impactful metals. Cd, Al and Cr also produce relatively high impacts and high cost. From the analysis of the metals' costs vs impacts, metals with higher mass in the PV panels were the ones with high GWP. Thus, the GWP of production of virgin materials directly depends on the amount of the metal is used in the panel. Thus, recycling methods should aim at recovering expensive and impactful metals such as Ag, Al, Cu, Si, glass and Te.

CRediT authorship contribution statement

Thomas Maani: Methodology, Software, Visualization, Writing - original draft. **Ilke Celik:** Conceptualization, Supervision, Data curation. **Michael J. Heben:** Supervision, Investigation. **Randall J. Ellingson:** Supervision, Investigation. **Defne Apul:** Conceptualization, Supervision.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.138827.

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