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Institute of Geochemistry, Mineralogy and Mineral Resources

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Ekaterina Mikhaylova

The behaviour of solar panel components after improper deposition in soils

Chování komponent solárních panelů po nevhodném uložení v půdách

Bachelor’s thesis

Supervisor: Prof. RNDr. Martin Mihaljevič, CSc.

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Declaration of Authorship

I hereby proclaim that I wrote my bachelor thesis on my own under the leadership of my supervisor and that the references include all resources and literature I have used. Neither this work nor a substantial part of it was submitted to obtain another or the same academic degree.

In Prague, 09.05.2022 Signature_____________

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Abstract

The interest in renewable energy resources has been growing exponentially since the beginning of the 20th century and now more countries are heading towards a replacement of non-renewable resources. Considering an average lifespan of a solar panel being 25 years we are about to start facing large-scale solar waste production. Management of such waste is an issue of utmost importance due to heavy metal components used in solar panels. Countries without strict regulations for electronic waste are likely to dump broken panels to landfills. In case the glass encapsulant is damaged heavy metals can leach into the soil and contaminate it. Numerous heavy metal ions like lead, cadmium or chromium are mobile in soils and can travel quickly. This bachelor's thesis explores the factors affecting the mobility and sorption of heavy metals in soils and presents studies focused on leaching of solar panel components under various simulated conditions.

Keywords

Solar panels, solar cells, renewable energy, photovoltaics, leaching, heavy metals

Abstrakt

Zájem o obnovitelné zdroje energie od počátku 20. století exponenciálně roste a nyní více zemí směřuje k náhradě neobnovitelných zdrojů. Vezmeme-li v úvahu, že průměrná životnost solárního panelu je 25 let, je zřejmé, že v blízké budoucnosti začneme čelit velké produkci solárního odpadu. Nakládání s takovým odpadem je otázka nejvyšší důležitosti kvůli těžkým kovům používaných v solárních panelech. Země bez přísných předpisů pro elektronický odpad pravděpodobně ukládají rozbité panely na skládky. V případě poškození ochranného skla mohou těžké kovy prosakovat do půdy a kontaminovat ji. Četné těžké kovy jako olovo, kadmium nebo chrom jsou mobilní v půdě a mohou se rychle pohybovat. Tato bakalářská práce zkoumá faktory ovlivňující mobilitu a sorpci těžkých kovů v půdách a představuje studie zaměřené na vyplavování komponent solárních panelů za různých simulovaných podmínek.

Klíčová slova

Solární panely, solární články, obnovitelná energie, fotovoltaika, loužení, těžké kovy

Table of Contents

1. Introduction

Since the second half of the 20th century, the development of solar cells and photovoltaics has been growing rapidly with the significant event of Germany's Renewable Energy Sources Act from the year 2000 creating a solar market in Europe (Krewitt and Nitsch, 2003). Solar energy is renewable, readily available, and does not pollute the environment – these are the reasons behind its increasing popularity. According to predictions made by the International Energy Agency (2019) the increase in the distributed solar photovoltaic (PV) capacity between the years 2019 and 2024 is projected to be up to 250 %. Gautam et al. (2021) have concluded that up to 2.95 billion of such waste can be expected from 2020 to 2047 in India only. However, such great numbers can also be a cause for concern. Considering the long shelf-life of a solar panel (20 – 30 years) and the start of its significant development being in the 2000s, large-scale solar waste management has not yet been a problem humans as a society had to deal with. Due to the toxic heavy metal components, solar panels fall into the hazardous waste category, hence why proper end-of-life management of such components has become a significant aim in reducing the negative effects on the environment, especially soil and groundwater (Xu et al., 2018).

With the growing population, the demand for energy, food, and thus land grows as well. Every day more land is cleared for crop production or industrial activities. A study done by the University of Basel, the European Commission Joint Research Centre and the Centre for Ecology & Hydrology (CEH, UK) states that up to 36 billion tons of soil are lost every year. Soil is a non-renewable resource that acts as the sink for all atmospheric deposition as well as being a habitat for many organisms. That is why contamination of soils by heavy metals has been a growing concern over the past few years. Even though most heavy metals are already present in the environment from natural sources, the biggest contribution comes from anthropogenic activities such as mining, smelting, or improperly managed industrial waste. Heavy metals are persistent and can bioaccumulate, hence why most soil remediation techniques can be so costly and time-consuming (Friedlová, 2010).

European Union is one of the few regions where solar waste is being regulated in the legislation – the WEEE (waste electrical and electronic equipment) directive making it a must to recover and recycle such waste (BIO Intelligence Service, 2011). A review by Nain and Kumar (2022) presents a summary of various guidelines for end-of-life solar waste management. The

Resource Conservation and Recovery Act from the United States focuses on hazardous waste management specifically based on the leaching of dangerous substances. As for other countries, in China PV waste unfortunately does not fall into the category of electronic waste, hence why no specific regulations have been set. Unfortunately, the sustainable recycling of solar panel components is not at a stage where it can be used widely due to it not yet being cost-effective. Overall, however, many countries are aiming towards establishing clear guidelines for solar waste management considering its increase in production over the last two decades.

This thesis aims to assess the behaviour of solar panel components, such as arsenic (As), cadmium (Cd), lead (Pb) and chromium (Cr) compounds, after improper deposition in soils. Generally, since these components are enclosed in tempered glass leaching of such elements does not occur during normal operation, however, once the structure is broken is when it becomes a hazard to the environment. In the theoretical part mobility of heavy metals and factors affecting it, such as soil pH and organic matter content, will be discussed. In the practical part, several studies on heavy metal leaching from solar panels will be presented and compared, and their results evaluated. Finally, various remediation and end-of-life techniques will be offered.

2. Solar panels – structure and components

A solar panel is made up of multiple solar cells. A solar cell is made up of semiconductor material (crystalline silicone) and the current is transmitted by silver conductors. There are three generations of solar cells. The first one is crystalline silicone (c-Si) represented by monocrystalline or polycrystalline cells. The second generation is referred to as thin film represented by amorphous silicon (a-Si) cells, cadmium telluride (CdTe) cells, and copper indium gallium selenide (CIGS) cells. Finally, the third-generation cells are concentrator photovoltaics and emerging technologies, such as dye-sensitized cells (DSSCs) (Xu et al., 2018). Some studies assume the fourth generation of organic (OPVs) and inorganic photovoltaics, while some consider them a subset of the third generation (Nain and Kumar, 2022). These generations differ in cell efficiency and environmental compatibility.

The structure of a crystalline silicone (c-Si) solar cell, the one most widely used on the market, is quite simple as seen on Figure 1. The semiconductors are sealed between EVA (ethylene vinyl acetate) foil and are enclosed in tempered glass from the top and the bottom is covered by PVF (polyvinyl fluoride). The frame is made of aluminium (Sodhi et al., 2022). The difference between a monocrystalline and a polycrystalline cell can be deduced from their names – the first group is made from a single silicone crystal and the second one uses multiple crystals that are melted together (Kippelen and Brédas, 2009).

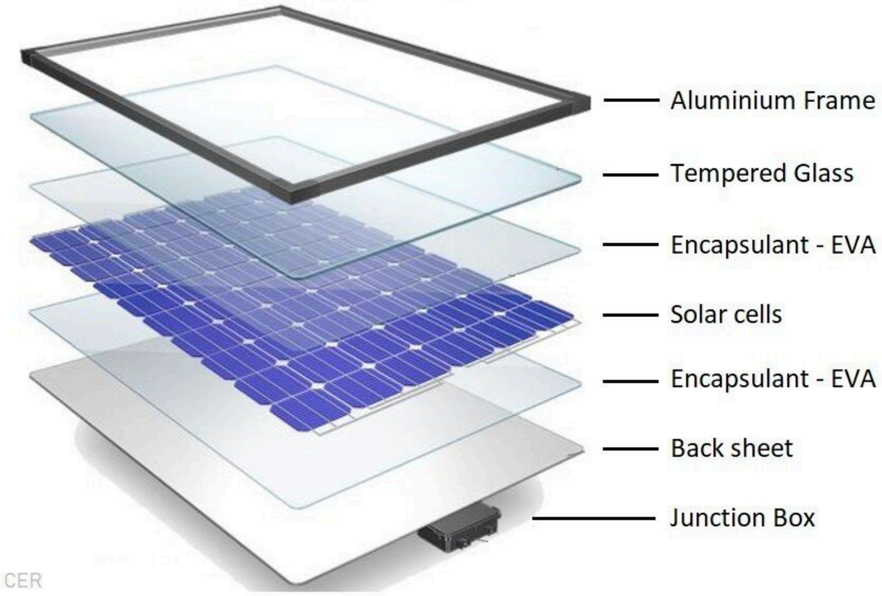

Figure 1: The structure of a c-Si solar cell (Svarc, 2020).

The distinction between a c-Si and a-Si cell can also be deduced from the name. Silicon atoms in amorphous cells are grouped randomly, without a clearly defined shape or form. Additionally, the retrieval of amorphous silicon is a much easier process compared to the crystalline one. The cell is made of amorphous silicon layers with a reflective back layer of aluminium and the whole structure is enclosed in glass (Karzazi and Arbouch, 2014). The CdTe cells contain a CdS (cadmium sulphide) and CdTe layer with the back made from a copper layer (Berger et al., 2010). As it is with crystalline silicone modules, CdTe panels are also enclosed in EVA and glass. The CIGS cells have two layers of CdTe and (absorber) and CdS (window layer), molybdenum (Mo) layer (back contact). This cell structure is also enclosed in glass (Karzazi and Arbouch, 2014).

As for the third and fourth generation, concentrator PVs, specifically dye-sensitized solar cells (DSSCs), are made of a dye sensitizer, semiconductor, electrolyte, and electrode. The components include titanium dioxide (TiO_2), platinum (Pt), iodine (I), and nickel (Ni) (Sharma et al., 2018). The OPVs cells are made from two indium tin oxide (ITO^-) electrodes and two organic semiconductor layers (Kippelen and Brédas, 2009). These cells contain compound similar to the structure of perovskite like methylammonium lead halide ($CH_3NH_3PbCl_3$ for example) (Kwak et al., 2020).

The main reason why a solar panel gets disposed is physical damage usually from natural causes such as strong wind or hail (Jordan and Kurtz, 2012). The most dangerous to the environment components of the solar panel, Pb, or Cd, cannot be removed unless the whole structure is shredded. Weight-wise most of the solar panel is made of glass, however, it unfortunately cannot be reprocessed due to heavy metal impurities. That is why the disposal of damaged solar panels is strongly inadvisable in landfill conditions as these contaminants can leach and pollute the soil (Shellenberger, 2018).

3. Heavy metal mobility in soils

3.1. Physical and chemical properties of heavy metals/metalloids

Generally, heavy metals are defined as chemical elements of high atomic weight (above 23) and specific density above 5 gcm^{-3} (Kafka and Punčochářova, 2002). They are used to describe a group of metals and metalloids that can pose a risk to the environment. They occur naturally in the environment in various concentrations from processes like weathering of rocks. However, anthropogenic activities such as mining can increase those concentrations (Nedelkoska and Doran, 2000). The issue with heavy metals is that in case the concentration increases above normal values, it can affect the microbial communities in the soil, specifically their numbers, diversity, and microbial activity. Additionally, some heavy metals can bioaccumulate and are persistent which is one of the reasons why their abnormal amounts in soils are so dangerous (Friedlová, 2010). Another reason for the great environmental concern of heavy metal pollution is the fact that they are not biodegradable, and their removal and soil remediation is an expensive and timely processes.

3.1.1. Arsenic

One of the main toxic metalloids that can be found in solar panels is arsenic (As). Arsenic is a metalloid found in group 5 and period 4 of the periodic table. It occurs in various oxidation states −III, 0, III, V, the As (III) being the more toxic one. The main inorganic forms are trivalent and pentavalent. As (V) usually presents itself in oxidating environments in the form of arsenate ($As_3O_4^-$). As (III) is more prevalent in reducing conditions as arsenite (AsO_3^{3-}). Metalloids such as As usually form covalent bonds meaning that their negative toxicological effects do not appear straight away. These bonds are typically formed with organic groups. An example of such a compound is methylated forms of As which can be extremely toxic (Briffa et al., 2020). In plants As affects all plants tissues as well the uptake of C, N and S (Zemanová et al., 2021). The main source of As in soils is generally considered to be geological. Nevertheless, lately anthropogenic contribution from mining or industrial waste has been increasing (Tóth et al., 2016).

3.1.2. Cadmium

Cadmium (Cd) is another heavy metal that is used in solar panels, specifically thin film. In the periodic table it is situated in group IIB. Its main oxidation state is Cd (II) and in nature it is mostly found as trace element. During the event of contamination, the concentration of Cd can increase more than a thousand times. One of the most significant properties of Cd is its ability to influence toxicity of other metals such as zinc (Zn) or copper (Cu) (Kafka and Punčochářová, 2002). Nowadays, Cd contamination of soils is an increasing problem due to it being highly mobile and thus absorbable by plants (Zhang et al., 2021). When Cd gets into the soil it can affect the growth and metabolism of plants (Štofejová et al., 2021). As it is with As, the main sources of Cd pollution include mining activities and industrial waste.

3.1.3. Chromium

Chromium (Cr) is a transition metal of group 6 and period 4 of the periodic table. Its atomic mass is 51.99 and it occurs in oxidation states of 0, II, III, and VI. It is naturally present in Earth's lithosphere: rocks and volcanic eruptions. It adsorbs to clayish materials or organic matter. In soils it is present as Cr (III), which is insoluble and thus not mobile, however pH and organic matter can influence that. Chromium can bioaccumulate to some extent, however it does not biomagnify. In plants Cr affects growth and development as well as photosynthesis (Shanker et al., 2005). Most of Cr comes from anthropogenic sources which include mining or agricultural wastes (ATSDR, 2012).

3.1.4. Copper

Copper (Cu) is one of the components used in a copper indium gallium selenide (CuInGaSe2, CIGS) cell, a type of thin-film solar cell. It is a transition metal with atomic weight of 63.55. Its oxidation states include 0, I and II. Copper is naturally present in the environment in various minerals such as chalcopyrite ($CuFeS_2$). The release of this chemical element can be accounted to both natural (volcanic eruptions) and anthropogenic activities (mining). When released to soils, Cu can adsorb to organic compounds or clay minerals. Its bioaccumulation and biomagnification abilities are poor compared to other heavy metals. However, in case the concentration in plants is too high it can negatively affect plant growth and leaf discoloration (Yruela, 2005). Overall, pH does not determine the mobility of Cu as much as the organic content does (ATSDR, 2004).

3.1.5. Lead

Lead (Pb) in solar panels is used for bonding solar panel components together. It is a metal from group IV and period 6 in the periodic table. It presents itself in oxidation states of 0, II and IV with Pb (II) being the most stable and tends to form complex compounds with organic matter in soils. The anthropogenic sources of lead include mining activities and chemical industry. Lead has a smaller natural concentration in soils and thus its mobility is relatively small (Makovníková et al., 2006). For this reason, plants generally do not end up absorbing much Pb, unless its concentrations are extremely high, however even in this case the intake is minimal (Wuana and Okieimen, 2011). If Pb does end up absorbed by plants, it is stored in the roots and thus can cause toxicity (Štofejová et al., 2021). If the disposal of the solar cell was to follow a worst-case scenario (cracking of the glass encapsulant and acidic rain) $CH_3NH_3PbI_3$ ($MAPbI_3$) perovskite would decompose into HI and PbI_2 and release CH_3NH_2 (Billen et al., 2019).

3.1.6. Zinc

Zinc (Zn) is used as coating in solar panels in order to increase their efficiency or as a semiconductor in dye-sensitized solar cells (Vittal and Ho, 2017). It is a metal of atomic mass 65.38 and its main oxidation state is II. Zinc forms bonds with organic and inorganic compounds, however it does not bioaccumulate and biomagnify in flora. Excess Zn in plants causes curling of leaves and death of leaf tips (Rout and Das, 2003). Anthropogenic sources of Zn include mining and it is naturally found in Earth's lithosphere (ATSDR, 2005).

3.2. Natural amounts and limits of heavy metals in soils

As stated above some amounts of heavy metals are present in the Earth's crust and have no significant negative effects on the environment. They are released by chemical weathering during the dissolution of minerals containing heavy metals or metalloids (Brown et al., 1999). In nature heavy metals can be found in their pure forms or as salts. The average concentrations of heavy metals in the lithosphere obtained from the Agency for Toxic Substances and Disease Registry (ATSDR) is presented in Table 1. Table 2 contains the maximum permissible limits (MPL) of heavy metals in soil set by the World Health Organization (WHO, 1996).

Table 1: Average concentrations of heavy metals/metalloids in the Earth's crust (ATSDR, 2004-2012).

Heavy metal/metalloid	Average concentration ($mgkg^{-1}$)
As	3.4
Cd	0.1 – 0.5
Cu	5 – 70
Cr	37
Pb	40
Zn	36

Table 2: Maximum permissible limits of heavy metals/metalloids in soil (WHO, 1996).

Heavy metal/metalloid	MPL ($mgkg^{-1}$)
As	30
Cd	0.8
Cu	36
Cr	100
Pb	85
Zn	50

3.3. Sorption and mobility of heavy metals in soils and its factors

Heavy metals in soils are present in soils in solid state (immobile) or as aqueous specie (mobile). Soil can immobilise certain chemicals such as heavy metals and the ability to do so is defined by physical and chemical properties such as pH, water content or organic matter content (Dube et al., 2001). The most important processes affecting heavy metal mobility and thus their bioavailability in soils are adsorption, complexation, and redox processes (Makovníková et al., 2006). The reason for the soil's ability to participate in adsorption or desorption properties is the presence of colloidal particles, mainly clay and hydrous oxides. These compounds can form a negative charge on their surface and thus attract cations. Additionally, the presence of calcium (Ca) and magnesium (Mg) was shown to affect the mobility of heavy metals in soils. The reason for that is that Ca and Mg occupy the adsorption positions making the heavy metals precipitate instead. Generally, the ability of a certain cation to adsorb is determined by its atom radius and valency. Hence, metals with lower valency and smaller radius (e.g. Pb) will form weaker bonds than the ones with higher valency and greater radius (e.g. Cd). (Kachova, 2015). Additionally, various geochemical forms of heavy metals in soils determine their mobility and bioavailability. The six forms are water soluble, exchangeable, carbonate bound, Fe-Mn oxide bound, organic matter bound, which are all non-residual, and residual. The most mobile forms are water soluble and exchangeable ones (Ogundiran and Osibanjo, 2015). Overall, it can be assumed that the greater the contamination and the higher the concentration of heavy metals in the soil, the greater the leaching will be.

3.4. The behaviour of lithogenic, pedogenic, and anthropogenic metals in soils

Lithogenic material comes from the Earth's crust. The mobility of such elements depends on their stability and physical and chemical properties. They tend to form less-mobile compounds, however their mobility can be changed with changing soil conditions. More mobile metals, such as Zn and Cd, mainly occur bound on organic matter, while less mobile ones (e.g. Cr) occur as stable oxides and silicates. Pedogenic material comes from both natural and human activities and its distribution in the soil depends on the soil processes. Anthropogenic material comes from human activities. This group tends to be the more easily mobile under most soil conditions, however it depends on its chemical form at the time of leaching (Kabata-Pendias, 1993).

3.5. The effect of soil pH on heavy metal mobility

The pH scale is used to determine the acidity of solution. It is represented by a negative logarithm of the concentration of the hydrogen ion. The pH of soils is measured in suspension soil and water (H_2O) or potassium chloride (KCl) solution. Generally, a solution is considered acidic when the pH is below 7 and basic when it is above pH 7.

Value of pH can not only be used to analyse soil mobility but also to measure the degree of soil contamination as it is when heavy metal pollution is expressed as concentration. Heavy metals are present in soils in the form of organic or inorganic compounds. The relationship between soil pH and heavy metal mobility follows a positive correlation: as the pH of the soil decreases, the amount of H^+ protons which can displace heavy metals increases. Thus, in more acidic soil environments the mobility of heavy metals is increased. For example, Cd starts to mobilize at pH 5 and lower (Sintorini et al., 2021). Makovníková et al. (2006) states that Cd becomes the most mobile and hence the most bioavailable at pH 4.5 – 5.5, hence in alkaline soils its mobility is decreased. Moreover, in alkaline conditions Cd precipitates on clay minerals. Overall, Cd is assumed to be the most mobile heavy metal in soils due to its weaker bounds. Metals like Cu, Pb and Zn are bound more strongly and hence are generally less mobile (Janoš et al., 2010).

A study done by Król et al. (2020) further proves the relationship between the pH and the metal mobility in soils. The highest concentrations were observed at pH 3 for Cd, Cu, Zn and at pH 4 for Pb. It is accounted to the dissolution and desorption reactions. On the other hand, with increased pH less metal leaching was observed: at pH 8 for Cr and at pH 9 for Cu. This happens due to the sorption and precipitation reactions. The relationship between soil pH and metal concentration is seen on Figure 2.

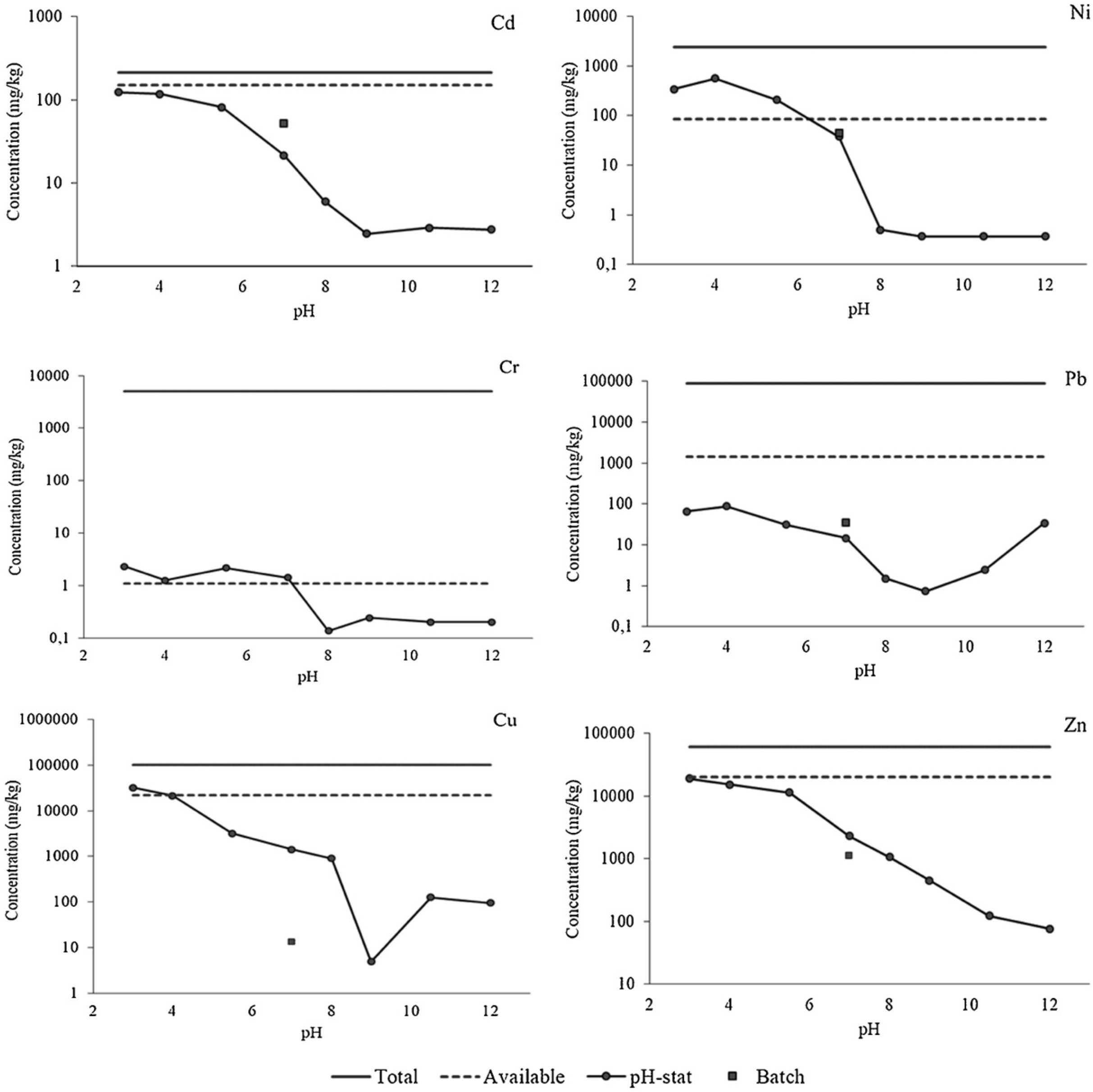

Figure 2: The relationship between soil pH and metal concentration (Król et al., 2020b)

The redox potential (Eh) is closely tied to the pH of the environment. A higher Eh value points to reduction reaction, meaning higher metal mobility (Kicińska et al., 2022). Monitoring the redox potential is important the toxicity of certain elements varies with their oxidation states – for example Cr (VI) is much more toxic and more mobile than Cr (III) (McLean and Bledsoe, 2015). As mentioned above, the main forms of As in soils are arsenate (AsO_4^{3-}) and arsenite (AsO_2^-) with latter one being more toxic. Anion AsO_4^{3-} tends to form insoluble compounds with Al, Ca, and Fe. Maximum adsorption of arsenate by kaolinite has been concluded to occur at pH 5 and at pH 3-4 by aluminium oxides. As for arsenite, adsorption by kaolinite happens in the range of pH 3 to 9 and at pH 7 by iron oxides. At high Eh values As (V) is more abundant and the mobility is low. With decreasing Eh, the amount of As (III) increases and so does the mobility (McLean and Bledsoe, 2015).

3.6. The effect of organic matter content on heavy metal mobility

Soil organic matter (SOM) is made up of non-living biological material in soil. It has been concluded that greater volume of organic matter in soil helps lower the uptake of heavy metals by plant roots (Aigberua, 2018). Giacalone et al. (2015) states that the mobility of heavy metals depends on the type of the bond to a SOM. Generally, strong sorption reactions between metal ions and soil particles are responsible for limiting the bioavailability of the contaminants. The most significant components of SOM are humic and fulvic acids due to their various binding sites and specific structure. Additionally, chelate compounds immobilize heavy metal contaminants and prevent them from spreading further down the soil profile. Since the most organic matter can be found in the topmost humus layer of the soil, it is safe to assume that the highest concentration of heavy metals will be found there. This assumption was proven by the results from a study done by Pikuła and Stępień (2021) where it was shown that the concentration of heavy metals in upper layers (A horizon) was greater than in lower layers (B horizon), nevertheless, some amounts of heavy metals were found even below the depth of 50 cm. Additionally, a study done by Lo et al. (1992) has concluded that removing the organic matter had a direct effect on decreasing the adsorption of Cu and Cd. From these results it can be concluded that organic content and heavy metal mobility have a negative correlation, where increasing SOM contents will decrease the degree of leaching.

3.7. Interaction of heavy metal pollutants with a solid mineral phase of soil

The mobility of heavy metal pollutants in soils is affected by compounds they create with the solid mineral phase. Makovníková et al. (2006) provide an example of Pb being less mobile and hence less bioavailable when it is present in the form of galenite (PbS) or pyromorphite ($Pb_5(PO_4)_3(Cl, OH, F)$). Clay minerals are one of the main components of soil which affect heavy metal mobility. For instance, kaolinite ($Al_2Si_2O_5(OH)_4$) can adsorb 6.8–12.58 mgg^{-1} of Cd and 7.75–13.32 mgg^{-1} of Pb (Li et al., 2022). In their study Covelo et al. (2007) showed Fe oxides mainly sorbing Pb and Cd, while Mn oxides preferred Pb and Cu. Such great adsorption abilities of clay minerals allow them to be a cheap and environmentally friendly alternative to more harsh soil remediation techniques that are being used nowadays.

4. Results from leachate studies

Since the beginning of the 21st century the fate of old solar panels has been a topic of interest for many studies, specifically the possibility of leaching of heavy metals into the environment. In order to test such process landfill conditions are simulated and the behaviour of solar metal components is observed in short-term or long-term periods. Short-term tests are done in very harsh conditions, whereas long-term tests focus on delamination caused by slow physical degradation of the solar panel (Nain and Kumar, 2022). A summary of various leachate studies is presented in chapters 4.1 for first- and second-generation solar cells and 4.2 for third- and fourth-generation solar cells. The main results of these studies are presented in Table 3 and Table 4 respectively, however the concentration of leachates will not be present due to different conditions of each experiment.

4.1. First- and second-generation solar cells

An experimental investigation by Tammaro et al. (2016) focuses on thin-film (a-Si, CdTe and CIGS) and c-Si panels manufactured from 1985 to 2012 whose end-of-life management followed a “worst-case” scenario – being crushed and abandoned in the environment. Samples of obtained solar panels (26 c-Si, 8 a-Si, 3 CdTe and 1 CIGS) were crushed to smaller pieces of 0.5 to 3 cm^2 and a leaching solution of pure water was used. This is a short-term study that was performed and measured over 24 hours. The value of pH and electrical conductivity was measured to identify the degree of leaching from each panel.

The pH of leachates measured was 7-8 (neutral or slightly basic) and electrical conductivity was 8–34 μS/cm which signifies a low salt concentration. The results were compared to the Italian law limits for Waste disposal in landfill for Inert (IW). For c-Si panels over half of them (65%) were concluded to be inert with only one out of 26 samples not exceeding any limits and 4 exceeding the limits only for one metal. Lead was the metal that leached the most (17 out of 26 panels) and Cd leached from 5 panels. Overall, most c-Si leachates contained Pb, Sb and Cd with high concentrations of Al. Thin-film panels have shown to be more dangerous to the environment in comparison to c-Si with 10 out of 12 samples exceeding the IW limits for Al, Cr, Cd and Pb. It is worth to note that a decreasing trend in the Pb and Cd concentrations was observed in more recent c-Si solar panels, while for thin-film panels no time trend was observed and variations in results were accounted to the different technologies. The unfiltered data for the maximum concentrations of metals leached in are summarized in Table 3.

Table 3: Maximum concentrations of metals leached in mg/l. Concentrations marked "BDL" are below the detection limit.

Cell type	Al	Cr	Cu	Cd	Pb	Zn
c-Si	1.32	0.01	0.04	0.02	61.4	0.14
a-Si	1.03	0.48	0.07	0.003	0.78	0.37
CdTe	0.54	0.005	0.004	1.42	0.02	0.04
CIGS	0.06	BDL	0.67	0.08	0.05	0.70

Another study that focuses on the first- (mono- and polycrystalline) and second-generation solar panels (a-Si and CIGS), was done by Nain and Kumar (2020) where the behaviour of metals was tested in real landfill leachate and synthetic solutions. Four different solar panels of size 15 by 15 cm were put in three glass trays containing synthetic solutions of pH 4 (representing rainwater), 7 (representing groundwater) and 10 (representing seawater) and one real landfill leachate of pH 7.6 in broken and intact states for a period of one year. Overall, this experiment has shown minimal leaching of solar panel components under most conditions with the exception of rainwater solution. CIGS panels have shown to be the most stable in various pH conditions with a neglectable metal release. Interestingly enough, the solution in which the least leaching happened was the real landfill solution. Additionally, the study has concluded that the state the solar panels are disposed in (broken vs. intact) has a positive correlation to the amount of toxic metals released into the environment. Nain and Kumar (2021) have also investigated the possibility of metal leaching from third-generation solar panels, where they have concluded that the metal loss factors are smaller for first-generation PVs for Pb, Cd and Cu than for third-generation PVs. The maximum concentrations of metals leached in broken state under rainwater conditions (except for CIGS – unbroken) are summarized in Table 4.

Table 4: Maximum concentrations of metals leached in mg/l. Concentrations marked "ND" were not detected. Concentrations marked "NM" were not measured for that specific sample.

Cell type	As	Ag	Al	Cr	Cd	Pb	Zn
mono-Si	0.003	18.4	NM	2.08	0.007	NM	0.75
poly-Si	ND	0.06	NM	1.63	ND	NM	0.27
a-Si	0.003	NM	18.0	NM	0.001	NM	0.19
CIGS	0.002	0.006	5.23	0.11	0.75	0.008	0.01

A similar study done by Nover et al. (2017) compared long term leaching of photovoltaic modules of four different solar cells: c-Si, a-Si (amorphous silicon), CdTe and CIGS. Samples of 5 x 5 cm were taken and similarly to the other studies pH of 3, 7 and 11 were used to imitate various environmental conditions. This experiment was performed over 360 days to evaluate the behaviour of solar components in more realistic conditions. At the end of the experiment, it was found that in acidic solution 1.4% of Pb leached from c-Si modules, 62% of Cd from CdTe modules and 43% of Zn leached from CIGS modules. Additionally, the study showed a significant difference between short-term (1 day) and long-term (360 days) leaching with amount of Cd released being up to 500 times greater. The greatest leaching was observed in lowest pH values. The maximum concentrations of metals leached are summarized in Table 5.

Table 5: Maximum concentrations of metals leached in mg/l. Concentrations marked "ND" were not detected.

Cell type	Al	Cd	Cu	Mo	Pb	Zn
c-Si	72.0	ND	0.27	ND	0.45	ND
a-Si	ND	ND	16.1	ND	ND	ND
CdTe	ND	18.6	4.59	18.62	ND	ND
CIGS	ND	0.08	8.93	1.44	ND	13.2

Sharma et al. (2021) have evaluated heavy metal leaching under simulated landfill conditions from polycrystalline solar panels and the effects of the damaged glass encapsulant on this process. The tests used were the Toxicity Characteristic Leaching Procedure (TCLP) test to imitate disposal in municipal solid waste landfill conditions, the Synthetic Precipitation Leaching Procedure (SPLP) test to imitate open land disposal and the pH static leaching procedure test to imitate the waste being mixed with other types of waste. Samples of both new and aged solar panels of size 15 by 15 cm were obtained and cut into smaller pieces of less than 1 cm. This is also an example of a short-term experiment which took 18 ± hours.

The results from the TCLP test suggest a higher amount of metals leached from solar panels without the glass encapsulant. As for the solar panel components, levels of Pb (9.3 mg/l) were observed at a value above the TCLP limits of 5 mg/l for aged and new solar panels without the encapsulant. Al, Zn, and Cu have also shown elevated numbers, however they did not pass the limits. The results from the SPLP and the pH static leaching procedure tests were in accordance with the TCLP test results, where levels of Pb were above the limits and the panels without the glass cover had leached more.

4.2. Third- and fourth-generation solar cells

Considering the fact that third- and fourth-generation solar cells are a new and emerging technology, not many practical studies have yet focused on the fate of the components of such cells, however theoretical heavy metal release potential has been evaluated.

Brun et al. (2016) assessed the leachates from CIGS and organic photovoltaic cells (OPV). The cells were put through physical damage and then exposed to various solutions representing acidic rain, lake water, and seawater over the period of four months. In acidic rain conditions Cu, molybdenum (Mo), and Zn leached in higher amounts from the CIGS cells. For OPV cells only Cu and Zn showed elevated values. In lake water conditions the metal leached the most from a CIGS cell was Mo and from the OPV cell – Zn. As for seawater conditions CIGS released Fe and Mo and OPV – Ag and Zn. The study concludes that CIGS cells pose a higher environmental risk due to their components having greater leaching potential.

Zimmermann et al. (2013) have conducted a similar experiment where metals and metalloids leached from CIGS and OPVs were observed in model natural waters (seawater, lake water and acidic rain) over the period of 123 days. The results showed Se, Mo and Cd leaching from CIGS in high amounts, while OPVs released minimal amounts of pollutants (Zn only in lake water conditions). The comparison of the main results by Brun et al. and Zimmermann et al. for maximum concentrations of metals leached under acidic conditions are summarized in Table 6.

Table 6: Maximum concentrations of metals leached in μg/l. Concentrations marked "ND" were not detected.

Cell type	Al	Cd	Cu	Mo	Zn
CIGS (Brun et al.)	10	21	57	59	52
CIGS (Zimmermann et al.)	9.2	16.7	<0.7	949.6	27.9
OPV (Brun et al.)	ND	ND	14	ND	87
OPV (Zimmermann et al.)	<0.7	<0.7	<0.7	<0.7	3.9

The work by Espinosa et al. (2016) aimed to evaluate the environmental impacts of end-of-life OPVs in rain runoff and soil sequestration scenarios. During the first experiment (rain-runoff) 3 samples of OPVs, damaged and intact, were placed in the solar park area and rainwater was collected for 6 months (April – October). For the second experiment 4 samples of OPVs were buried in the soil. The rain-runoff experiment has resulted in some damage to model samples. An elevation of Ag and Zn levels was observed. Similar results were observed during the soil sequestration experiment, where higher leaching of Ag and Zn was observed in broken up samples. Overall, the concentrations of leachates did not exceed the limits set by the WHO.

In their study Kwak et al. (2020) have compared the potential environmental risks of various solar cell types. For perovskite-based solar cells Pb and I can leach into the soil. The results of several studies agree that Pb and I have the greatest leaching potential, especially under simulated rainfall conditions (acidic). Specifically, a study done by Benmessaoud et al., (2016) showed leaching of over 90% I and over 6% Pb. Additionally, Kwak et al. (2021) show that Pb from PbI_2 tends to be the most leachable component of perovskite solar calls with concentration of 0.28 $mgkg^{-1}$.

4.3. Discussion

The leachate studies play an important role in detecting the risks of improper utilization of solar panels, helping create new regulations for solar waste management and monitoring current processes. Additionally, the findings of the form of heavy metal pollutants and their quantity in soil aid in determining proper remediation technologies.

The results from leaching studies are in accordance with the theoretical concepts of the factors affecting heavy metal mobility in soils. If the end-of-life management happens to follow a worst-case scenario and a solar panel ends up in a landfill, it should be kept intact. In the event of breakage of glass encapsulant, the degree of leaching is much higher since the components are not protected from the outside world anymore. Although the concentrations of leachates may seem small, it must not be neglected that such pollutants are very toxic, hence even a small amount can be very dangerous to the environment.

It was indeed proven that heavy metal mobility and pH value follow a positive correlation with the solution causing greater leaching being rainwater due to its lower pH. In landfill leachate conditions metal release was observed to be minimal. The amount of organic content was also proven to immobilize some heavy metals due to their ability to make covalent bonds. For this reason, organic additives can be used as a remediation approach.

For first-generation PVs a decrease in heavy metal leachability can be observed over a period of time, which is due to a technological development, studies of negative effects of toxic metals on the environment and replacement of such elements with more environmentally friendly components. For later generations this trend was not observed, which was accounted to different technologies used for different solar cell types. Although newer solar cells brought improvements in energy efficiency and adaptability to the environment, some studies show that c-Si solar panels tend to be less dangerous to the environment. While most studies focus on the first two solar cell generations due to them dominating the market, there is not much research done on the a-Si panels perhaps due to its decline in popularity in the last few years. As for the actual heavy metal pollutants, while Cd was concluded to be the most mobile and Cu – the least, levels of Pb were the ones which exceeded the limits set by various organizations worldwide.

Overall, the abundance of heavy metals in the leachate tends to follow this order: Cu > Cd > Pb > Al > Te > Ag > Zn > Cr (Fytianos et al., 1998).

A study done by Nain and Kumar (2020b) evaluated ecological as well as human risks of heavy metals leaching from end-of-life solar panels. As for human health risk, the main pathways of exposure are ingestion and dermal contact. Understandably, younger population, specifically children, are more prone to such exposure, while for adults it is less likely. Overall, it was concluded that the risk for most of the metals was acceptable with the exception of Pb from c-Si panels, meaning that unless solar panels are indeed disposed following worst-case scenario large-scale, they should not pose a great risk to the environment. Additionally, the worst-case scenario itself is thought to be quite unlikely since a substantial amount of acidic rain is needed to leach large quantities of mental pollutants.

Most of the studies propose the need for metal leaching assessment under more long-term and realistic landfill conditions as well as new improvements in solar cell manufacture preventing such occurrences. In their study Billen et al. (2019) state that going forward coming up with substitutes for heavy metals (replacing lead in perovskite cells) would be the most environmentally friendly option. Many believe that because solar cells do not display high metal leachability in short-term (a few days) tests it does not mean that it will not occur later on. Kumar and Alappat (2004) were the first to propose an index which could predict the potential for pollution by leaching – the Leachate Pollution index, which is currently being used in many studies analysing the safety of solar panels. Additionally, due to most studies focusing on first-generation solar cells, more research should be done on third- and possibly fourth-generation cells.

5. Remediation techniques

There are many different remediation technologies, which include physical, chemical, and biological approaches, however they unfortunately can be quite expensive, long, and overall inconvenient. This is due to the fact that heavy metal cannot be broken down and can only be removed. As mentioned above, some metals are essential for life on Earth, while some can be toxic even at the smallest concentrations. That is why despite all the nuisances, soil remediation must be taken seriously.

A review by Rajendran et al. (2022) introduces various remediation approaches and evaluates them. Physical approach focuses on soil displacement – the removal of a contaminated layer. As a result, the amount of metal contaminants is reduced, however this method is not commercially sustainable and time-consuming. Chemical approach, specifically chemical fixation, helps heavy metals adsorb and decrease their availability for plants, unfortunately this method also is not sustainable in a long-term scale. Biological approach, such as in-situ or ex-situ bioremediation, is safe and harmless to the environment, but it cannot be applied to all pollutants and can be extremely slow.

Koptsik (2014) presents two strategies of remediation of soils polluted by heavy metals. The first one being the most preferred option focuses on the reduction of the concentration of pollutants to the maximum permissible level. The second option focuses on managing the effects of the contamination on the environment meaning the reduction of mobility and bioavailability of heavy metals. The specific type of remediation is chosen based on the type of pollutant, the extent of contamination and the budget provided. Soil washing is an in-situ process during which heavy metals are removed using various solutions such as water, strong mineral acids and their salts, weak organic acids, and others. Unfortunately, as a result some soil functions are strongly disturbed or lost. Stabilization of pollutants using sorbents is a type of mild remediation techniques. Natural mineral and organic substances and specific sorbent materials immobilize the heavy metals in soil. Phytoremediation restores soil using plants which absorb the pollutants and is considered effective for large unevenly polluted areas of land.

6. End-of-life recycling

As solar panel components fall into the category of hazardous waste, recycling of its components is a matter of uttermost importance for the environment. In the European Union the export of solar waste is forbidden and instead recovery and recycling are encouraged in the WEEE directive. A great example of a member of the EU that strictly follows this directive is Czech Republic. The WEEELABEX organization prepares the standards and monitors waste-processing facilities, and Retina provides advisor services as well as reprocessing services (Leroy, 2012).

Chowdhury et al. (2020) state that two commercially available techniques for solar panel recycling are being used, however more technologies are being researched. Due to the differences in structures between the various generations of PVS, different recycling strategies must be applied. For c-Si panels the aim is to separate the components from the glass cover and to retrieve the Si cells and other metals. There are physical, chemical, and thermal types of recycling. The physical process involves the removal of the frame and cables and the whole structure is then shredded into small pieces. Afterwards, thermal treatment is applied to recover glass, silicone, and metal fractions. Additionally, organic solvents can be used to break down the EVA layer by melting.

Unfortunately, at the moment the recycling of solar panels and their components is an expensive and time-consuming process. Hence why without strict regulations few countries are motivated enough to properly deal with solar waste. Deng et al. (2019) concluded that as attractive as landfill dumping is due to it being cheap, it is not a sustainable option for the end-of-life management. Additionally, the chemicals used in metal recovery can be quite dangerous to the environment. In their study Chakankar et al. (2019) declare that a more environmentally friendly alternative to chemical leaching should be developed and propose the use of microorganisms (bacteria and fungi). Overall, many researchers agree that not enough attention is given to the potential environmental crisis that improper disposal of solar panels can bring and that more countries worldwide should follow the example that the EU has set and pass stricter regulations.

7. Conclusion

This thesis focused on the behaviour of solar panel components after their improper deposition in soils. The types of solar panels were introduced on the basis of generational development and their structures were presented. Various types of heavy metals/metalloids used, such as Pb, Cd, As, and Zn, were described using their physical and chemical properties. The sorption and mobility of these metals is influenced by different properties of soil. Heavy metals tend to be more mobile in lower pH because of dissolution reactions, while in higher pH the mobility is lower due to sorption. Another factor which can limit heavy metal mobility in soils is the amount of organic matter. Heavy metals tend to form compounds with organic matter and hence are immobilized, which is why more heavy metals are found in the upper layers of the soil profile. Finally, solid mineral phase, such as clay minerals (e.g. kaolinite), of soil also tends to limit heavy metal mobility.

Most of the leaching studies focus mainly on the first two generations of solar cells due to the latter generations being a new and emerging technology. While the first generation (c-Si) seems to follow a trend of improvement in leaching over time, leaching from other solar cells is more technology dependent (tends to vary by manufacturer or type). Lead and Al tend to leach the most, while Zn leached minimally. Cd was shown to be the most mobile in soils and Cu had minimal mobility.

A general end-of-life recycling technique was proposed and evaluated. Nowadays an end-of-life solar panels must be broken down manually and then chemical and thermal processes are used to recover individual components. Unfortunately, it is not the most cheap, fast, or environmentally friendly method, so going forward new improvements should be proposed in order to make this process more attractive for the manufacturers and prevent them from dumping broken components in landfill. In case soil does end up being contaminated by heavy metals, various remediation techniques have to be used, which can further degrade the soil. This also is an expensive and time-consuming process, so avoiding such worst-case scenario is crucial for environmentally-friendly end-of-life solar panel utilization.

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