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Leaching potential of chemical species from real perovskite and silicon solar cells

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ABSTRACT

Despite their many advantages, solar photovoltaic (PV) cells used for electricity generation can have negative environmental impacts. The chemicals necessary for their fabrication can be released into the environment during their disposal or following damage, such as that from natural disasters. The principle objective of this study was to assess the leaching potential of chemical species, primarily heavy metals, from perovskite solar cells (PSC), monocrystalline (MoSC) silicon solar cells, and polycrystalline (PoSC) silicon solar cells under worst-case natural scenarios. In all cases, real solar cells were used as opposed to the pure component. The toxicity characteristic leaching procedure (TCLP) was used to analyze the leachates from PSCs to determine the concentrations of major component species. The results showed that broken PSCs released Si, Pb, Al, As, and Ni under TCLP conditions; lead, a major component of PSCs, was released at around 1.0 mg/L at a pH of 4.93, from both broken and unbroken PSCs. However, the concentrations of these elements in the leachate were within the toxicity characteristic (TC) limits. Encapsulation of the PSCs inhibited the release of hazardous substances, but did not completely eliminate the release of metals. TCLP results from broken MoSCs revealed that metals leached at relatively high levels: Al: 182 mg/L, Ni: 7.7 mg/L, and Cu: 3.6 mg/L. The results from broken PoSCs indicated the release of 43.9 mg/L of Cu and 6.6 mg/L of Pb, which are higher than the TC limits. These high levels may be attributed to the welding materials used on the rear side of crystalline-Si (c-Si) solar cells. This study identifies the importance of encapsulating PSCs and the welding materials on the rear side of c-Si solar cells to minimize the release of toxic substances into the environment.

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1. Introduction

The use of solar photovoltaic (PV) cells is on the rise. The capacity of solar power generation plants worldwide reached approximately 400 GW by the end of 2017 and is expected to increase to approximately 1270 GW and 4500 GW by the end of 2022 and 2050, respectively (Chowdhury et al., 2020; Solar Power Europe, 2020). The main PV technologies available are: i) first-generation crystalline-Si (c-Si); ii) second-generation thin-film

technologies such as cadmium telluride (CdTe), cadmium selenide (CdSe), amorphous-Si (a-Si), and copper indium gallium diselenide (CIGS); iii) third-generation PVs based mainly on dye-sensitized and organic PV cells which are emerging technologies still at pre-developmental stages (Bio Intelligence Service, 2013; Nain and Kumar, 2020; Xu et al., 2018). Although solar cells are considered safe, economical, and convenient (Xu et al., 2018), environmental concerns are increasing because PV systems contain hazardous substances—mainly heavy metals such as cadmium, copper, lead, nickel, tin, and zinc—which can be released into the environment due to defects in manufacturing, accidental damage, and disposal (Celik et al., 2018; Espinosa et al., 2016; Sinha et al., 2012; Yoo et al., 2019; Zapf-Gottwick et al., 2015).

The life span of solar cells is estimated to be 25–30 years for power generation (Chakankar et al., 2019). Waste from PV modules is expected to constitute 60–78 million tons globally by 2050 (IRENA and IEA-PVPS, 2016; Kadro and Hagfeldt, 2017). There is a lack of policy and regulation in leading solar panel manufacturing countries to define the safe disposal of solar panels (Chowdhury

Abbreviations: a-Si, amorphous-Si; BS, broken and stable condition; BT, broken and tumbling condition; c-Si, crystalline-Si; CdSe, cadmium selenide; CdTe, cadmium telluride; CIGS, copper indium gallium diselenide; DI, de-ionized; MoSC, monocrystalline; PCE, power conversion efficiency; PoSC, polycrystalline; PSC, perovskite solar cell; PV, photovoltaic; SPLP, synthetic precipitation leaching procedure method; TC, toxicity characteristic; TCLP, toxicity characteristic leaching procedure; WEEE, waste electrical and electronic equipment; WET, waste extraction test; US, unbroken and stable condition; UT, unbroken and tumbling condition.

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et al., 2020; Lunardi et al., 2018; Sharma et al., 2019). At present, a universally employed recycling process for PV waste is not yet in existence. However, the European Union officially revised the waste electrical and electronic equipment (WEEE) directive so that PV components must be collected and recycled (Chowdhury et al., 2020; Lunardi et al., 2018; Xu et al., 2018). It is the only authority to have such a policy. Active substances from PV module waste may be released into the environment and can be hazardous to the whole ecosystem (Lunardi et al., 2018). Therefore, it is necessary to assess the metals leaching from PVs under various scenarios as well as their impacts on human health and the environment.

A leaching test is usually carried out to assess the potential environmental risk from the toxic substances in a product. Many types of leaching tests are in use, such as the toxicity characteristic leaching procedure (TCLP) method 1311 (USEPA), synthetic precipitation leaching procedure (SPLP) method 1312 (USEPA), 13/JIS K 0102:2013 method (JLT-13; Ministry of Environmental Notice, Japan), DIN EN 12457–4:01–03 (Germany), and the waste extraction test (WET) (Sinha and Wade, 2015; US EPA, 1992, 1994; Zeng et al., 2015; Kim et al., 2018; Chae et al., 2021). Many leaching tests have been conducted on CdTe PV CIGS, c-Si, and a-Si solar cells (Finke et al., 1996; Nain and Kumar, 2020; Ramos-Ruiz et al., 2017; Robinson and Meindl, 2019; Savvilotidou et al., 2017; Sinha and Wade, 2015; Zapf-Gottwick et al., 2015; Zeng et al., 2015).

A perovskite solar cell (PSC) is a type of next-generation solar cell that has been considered a promising PV technology due to its excellent power conversion efficiency along with its very low material cost (Benmessaoud et al., 2016; Jung and Park, 2015; Kim et al., 2016; Zhang et al., 2018). PSCs have a crystal-shaped structure with a general formula of ABX_3 , where A is a cation-like methyl ammonium, ethyl ammonium, or formamidinium; B is lead (Pb) in most cases and in some cases tin (Sn); and X is the halogen, usually iodine (Abate, 2017; Green et al., 2014). Currently, much research effort is being paid to improving PSCs, particularly their power conversion efficiency (PCE) and in determining alternatives to the use of Pb (e.g., replacement with Sn or Ge). However, PSCs with high PCE are usually Pb-based (Su et al., 2020). Though PSCs are efficient and cost-effective, their environmental aspects with respect to the toxicity of lead, the main constituent of most halide PSCs, are not yet well evaluated (Abate, 2017). To the authors' best knowledge, studies on the leaching of hazardous chemical species from real PSCs are scarce. The few studies that have been conducted evaluated the pure components, namely lead compounds, for investigating leaching and environmental impacts. In our study, actual PSCs were used to simulate the environmental impacts due to rain water coming into contact with them (Hailegnaw et al., 2015; Li et al., 2020a,b; Yoo et al., 2019). Recently, the first study on the leaching of toxic substances from defective/discarded real PSCs was reported (Su et al., 2020).

The primary objective of this study was to investigate the leaching of hazardous substances (mainly heavy metals) from real PSCs and commercially available monocrystalline (MoSC) and polycrystalline (PoSC) silicon solar cells. Another objective was to evaluate the effects of different leaching scenarios on metal leaching, such as extraction methods, harsh or stable extraction conditions (including the tumbling of extraction vessels), PSC conditions, and PSC encapsulation.

2. Materials and methods

2.1. Solar photovoltaic cells

This study carried out a total of nine different sets of experimental investigations (seven on PSCs and two on c-Si). Many types of PSCs were obtained from three different PSC research teams

in Korea (Sungkyunkwan University, Korea University, and Seoul National University), as shown in Table 1.

For the leaching evaluation of PSCs, two samples were prepared viz. original or pristine (unbroken) cells and broken cells (Fig. 1 [A] and Fig. 1 [B]). The size of the pristine PSC was 2.5 cm × 2.5 cm × 0.2 cm (length × width × thickness). The PSCs were cut into pieces less than 9.5 mm in length and width to obtain broken cells as required by TCLP method 1311 (US EPA, 1992). To evaluate the effects of cell encapsulation thickness on leaching, three PSC samples with varying encapsulation thicknesses were prepared—0 mm (no encapsulation), 4 mm, and 10 mm. The encapsulating materials used in the PSCs were glass, Al_2O_3 , SiO_2 , and resin.

Commercially available silicon-based solar cells were purchased for the leaching test. Silicon-based MoSC solar cells with dimensions 7.7 cm × 1.8 cm as well as PoSC solar cells were randomly purchased from a solar cell company. Only pieces of Si-PVs less than 9.5 mm in length and width were used for leaching tests with broken MoSC and PoSC solar cells (Fig. 1 [C] and Fig. 1 [D]).

2.2. Preparation of extraction fluid

Two types of extraction solutions were used for the leaching tests viz. USEPA TCLP extraction fluid and ultrapure water. Detailed information on the extraction methods and reagents prepared is presented in Table S1. The extraction fluid (TCLP extraction fluid #1) was prepared in accordance with USEPA, TCLP method 1311 (US EPA, 1992). Briefly, 5.7 mL of glacial acetic acid (Daejung, Korea) was added to 500 mL ultrapure water (Human Corporation) after which 64.3 mL of 1 N NaOH (Samchun, Korea) was added. The solution was then diluted to a volume of 1 L. The pH of the resulting extraction fluid was adjusted to 4.93 ± 0.05 using dilute acid or alkali. Furthermore, de-ionized (DI or ultrapure) water (pH, 5.75 ± 0.05) was used as the control.

2.3. Leaching test

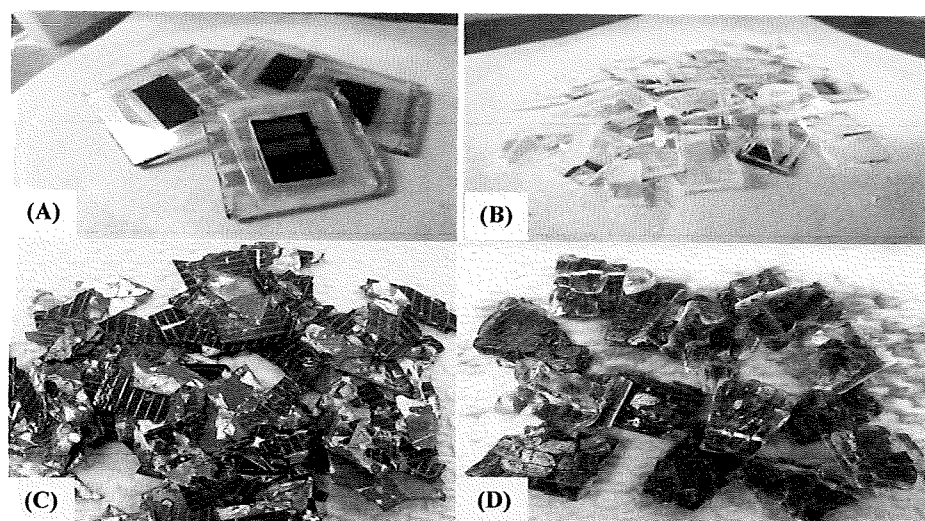
A total of 37 leaching experiments were performed to demonstrate the release of substances from solar cells. Among them, 24 experiments were conducted for PSCs (i.e., PSC1–PSC24), seven experiments for MoSC solar cells (MoSC1–MoSC7), and six experiments for PoSC solar cells (PoSC1–PoSC6; Table 1).

Two types of extraction conditions were evaluated for the TCLP leaching test: the tumbling condition (achieved by tumbling the extraction bottle) and the stable condition. For the tumbling condition, the capped extraction bottles containing a mixture of solar cells and extraction fluid were vertically (end over end) rotated at a constant speed of 30 rpm for 18 ± 2 h using rotatory agitation apparatus (YKZ-08–2, Changsha Yonglekang Equipment Co., Ltd, China), as shown in Fig. S1. For the stable condition, the mixture was left stationary for 18 ± 2 h without tumbling. The resulting mixture was filtered using a 0.7 μ m glass microfiber filter (GF/F, Whatman, China). The pH of the resulting filtrate was measured prior to analysis. All experiments were conducted at ambient laboratory temperature.

The effects of cell condition (pristine or broken), extraction fluid type (TCLP or water), PSC encapsulation thickness, and solar cell type on the leaching of hazardous substances were investigated. To investigate the effect of encapsulation, PSCs containing methylammonium lead iodide ($CH_3NH_3PbI_3$, MAPbI₃) with 10 mm and 4 mm thick encapsulations and PSCs containing formamidinium lead iodide ($HC(NH_2)_2PbI_3$, FAPbI₃) with 0 mm or no encapsulation were used. Furthermore, leaching tests were carried out on broken pieces of both MoSC and PoSC cells.

Table 1
Specifications of perovskite solar cells tested.

Set	Sample	Cell type	Major components	Encapsulation	Manufacturer
Set 1	PSC1, PSC2, PSC3, PSC4, PSC5, PSC6	Perovskites: MAPbI ₃ (PSC)	Al ₂ O ₃ , SiO ₂ , glass, gold, Perovskite, Bathocuproine (BCP), Butyric acid methyl ester (PCBM), NiO ₂	4 mm	Sungkyunkwan University, Korea.
Set 2	PSC7, PSC8, PSC9	Perovskites: MAPbI ₃ (PSC)	Al ₂ O ₃ , SiO ₂ , glass, gold, Perovskite, Bathocuproine (BCP), Butyric acid methyl ester (PCBM), NiO ₂	4 mm	Sungkyunkwan University, Korea.
Set 3	PSC10, PSC11	Perovskites: MAPbI ₃ (PSC)	Al ₂ O ₃ , SiO ₂ , glass, gold, Perovskite, Bathocuproine (BCP), Butyric acid methyl ester (PCBM), NiO ₂	10 mm	Sungkyunkwan University, Korea.
Set 4	PSC12, PSC13, PSC14	Perovskites: MAPbI ₃ (PSC)	Glass, gold, resin, Perovskite, Bathocuproine (BCP), Butyric acid methyl ester (PCBM), NiO ₂	4 mm	Sungkyunkwan University, Korea.
Set 5	PSC15, PSC16, PSC17	Perovskites: MAPbI ₃ (PSC)	Resin, Al ₂ O ₃ , SiO ₂ , glass, gold, Perovskite, Bathocuproine (BCP), Butyric acid methyl ester (PCBM), NiO ₂	4 mm	Sungkyunkwan University, Korea.
Set 6	PSC18, PSC19	Perovskites: FAPbI ₃ (PSC)	SnO ₂ , Perovskite, Spiro/FTO, and gold	0 mm (no encapsulation)	Korea University, Korea
Set 7	PSC20, PSC21, PSC22, PSC23, PSC24	Perovskites: 0.9 FAPbI ₃ + 0.1 MAPbI ₃ (PSC)	Glass, Doped indium tin oxide (ITO), Polytriarylamine (PTAA), Perovskite, C ₆₀ , Bathocuproine (BCP), Cu	0 mm (no encapsulation)	Seoul National University, Korea
Set 8	MoSC1, MoSC2, MoSC3, MoSC4, MoSC5, MoSC6, MoSC7	Monocrystalline Si (Mono c-Si)	Silicon nitride (Si ₃ N ₄), Al, glass, PbSn	0 mm (no encapsulation)	TSEC Co., Taiwan
Set 9	PoSC1, PoSC2, PoSC3, PoSC4, PoSC5, PoSC6	Polycrystalline Si (Poly c-Si)	Si, Al alloy, glass	0 mm (no encapsulation)	Hanwha Q Cells Co., Ltd., Korea

**Fig. 1.** Types of solar PV cells used in the study: (A) unbroken PSCs; (B) broken PSCs; (C) broken MoSC cells; and (D) broken PoSC cells.

2.4. Chemical analysis

The analysis of leachates filtered through a 0.7 μm GF/F (henceforth called leachate or filtrate) was conducted according to the standard TCLP method to identify the leached chemicals. All metals in the leachate except Hg were directly analyzed by inductively coupled plasma mass spectrometry (Agilent 7800, USA), while Hg was analyzed using the direct mercury analyzer (DMA-80, Italy). In addition, the concentrations of CN^- and Cr^{+6} were analyzed using the UV–vis–NIR spectrophotometer (Agilent Cary-5000, USA). A photometer (Spectroquant NOVA 60, Germany) was used to measure ammonium (NH_4^+) ion concentration with the help of NH_4^+ cell test kits. The ion concentrations of all of the leaching metals were measured with the help of their respective calibration curves,

using standard solutions and corrected for the background concentration of blank samples. The leaching tests were carried out for two or more replicates and the data obtained from multiple experiment samples were averaged (except where mentioned otherwise).

3. Results and discussion

The pH of the filtrates was in the range 4.2–5.8, depending on the initial pH of the extraction fluid. Cyanide ion (CN^-) was not detected in any of the leaching tests. The results of the chemical analysis of the filtrate or leachate were compared in terms of the extraction fluid (TCLP/DI water), extraction condition (tumbling/stable), solar

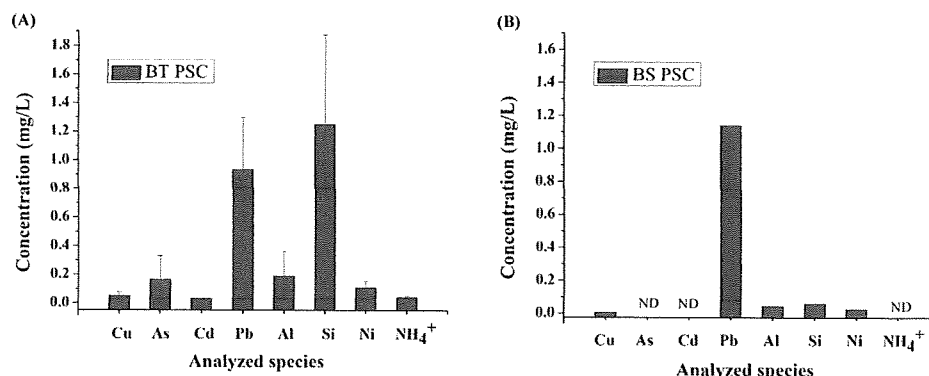
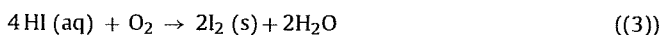
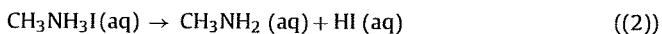
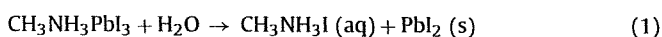


Fig. 2. Leaching of chemical species from broken PSCs using TCLP fluid under (A) tumbling condition (BT PSC) (values \pm SD; $n = 6$) and (B) stable condition (BS PSC) ($n = 1$).

cell condition (pristine/broken), encapsulation thickness (0/4/10 mm), and solar cell type (PSCs/c-Si).

3.1. Chemical species leaching from PSCs

It was observed that the black colored samples of PSC firstly became yellow upon contact with extraction fluid and finally became almost colorless during the leaching tests (Fig. S2). This is due to the removal of CH₃NH₃I (which is deliquescent in nature) by water or the aqueous reagent and the conversion of solar material into PbI₂ (Hailegnaw et al., 2015; Su et al., 2020), as shown in Eqs. (1)–(3). A similar color change was observed for FAPbI₃-type PSCs.



3.1.1. Leaching concentration of species from broken PSCs

Fig. 2 (A) presents the major components leached out from broken PSCs with TCLP extraction fluid, under the tumbling condition (BT: broken and tumbling). This aggressive leaching test is a representative of the worst-case scenario. When leached with acidic TCLP fluid for the tumbling condition, broken PSCs released the highest average amount (in mg/L) of Si (1.248), followed by Pb (0.935), Al (0.192), As (0.166), and Ni (0.108) in the filtered leachate. Cr⁺⁶ and CN[−] were not detected in the leachate, while other species (Cu, Cd, NH₄⁺) were released in low concentrations (<0.05 mg/L). A very low concentration of Hg (0.00013 mg/L) was detected in only one sample. In fact, out of a total of six samples tested under the BT condition, no PSC sample exceeded the toxicity characteristic (TC) limits for hazardous waste (Table S2).

The species released into the TCLP leachate from the broken PSC for the stable condition (BS: broken and stable; Fig. 2 [B]), in the order of highest to lowest concentration are as follows: Pb > Si > Al > Ni > Cu. While As, Cd, Cr⁺⁶, NH₄⁺, and CN[−] were not detected in the leachate, the detected concentration of Hg was very low (0.00014 mg/L). Although leachate concentrations of most metals were significantly lower under the BS condition compared to the BT condition, release of Pb up to 1.15 mg/L, similar to that of the BT condition, was observed. The results imply that it is highly probable that Pb compounds will be leached out into the environment from broken PSCs. The stable condition, where tumbling of the extraction vessel was not carried out, may represent the realistic conditions to which the PSCs will be subject, with accidentally broken PSCs exposed to acidic rain water in a landfill.

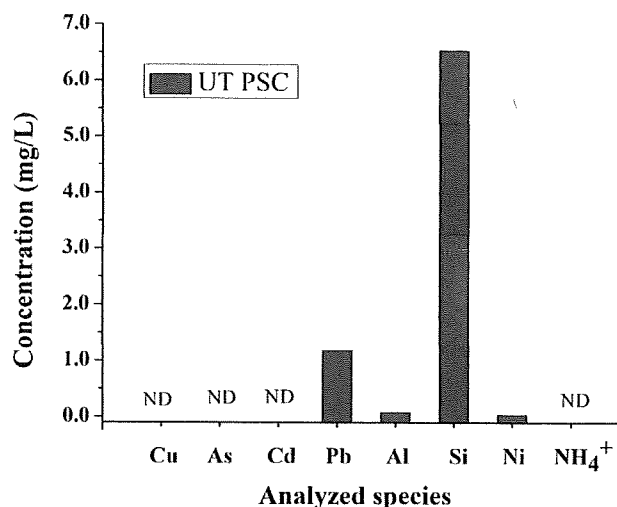


Fig. 3. Leaching of chemical species from unbroken (pristine) PSCs (4 mm encapsulation) under tumbling condition (UT PSC) using TCLP fluid.

3.1.2. Leaching concentration of species from unbroken PSCs

Figs. 3 and 4 show the leaching concentrations of species from unbroken PSCs (4 mm encapsulated). Fig. 3 evaluates leaching under the tumbling condition and Fig. 4 evaluates leaching under the stable condition.

Fig. 3 shows that when leached with TCLP fluid while the vessel is tumbled (UT condition: unbroken and tumbling), the pristine PSCs released elements whose concentrations were in the order: Si > Pb > Al > Ni, while Cu, As, Cd, Hg, Cr⁺⁶, NH₄⁺, and CN[−] were not detected. The concentration of no species exceeded the TC limits for hazardous wastes. The Pb concentration for unbroken PSCs under UT condition was 1.20 mg/L, which is similar to that for broken PSCs under either tumbling or stable conditions. The Si concentration for unbroken PSCs under the tumbling condition was significantly higher than for broken PSCs under the tumbling condition. The results imply that abrasion between large unbroken PSCs resulted in more Si leaching than what occurs in the case of small broken pieces.

Fig. 4 shows that when leached with TCLP fluid under stable conditions, pristine PSCs released the highest average amount (in mg/L) of Pb (1.402), followed by Si (0.092) and Al (0.058) (see Fig. 4 [A]). As, Cd, Cr⁺⁶, and CN[−] were not detected in the leachate, while Cu, Ni, and NH₄⁺ were hardly released (<0.05 mg/L). A very low concentration of Hg (0.00058 mg/L) was detected in only one sample. Fig. 4 (A) shows that Pb was leached up to 1.40 mg/L even from unbroken PSCs at the stable condition (US: unbroken and stable). The results indicate that the acidic TCLP fluid may leach Pb present

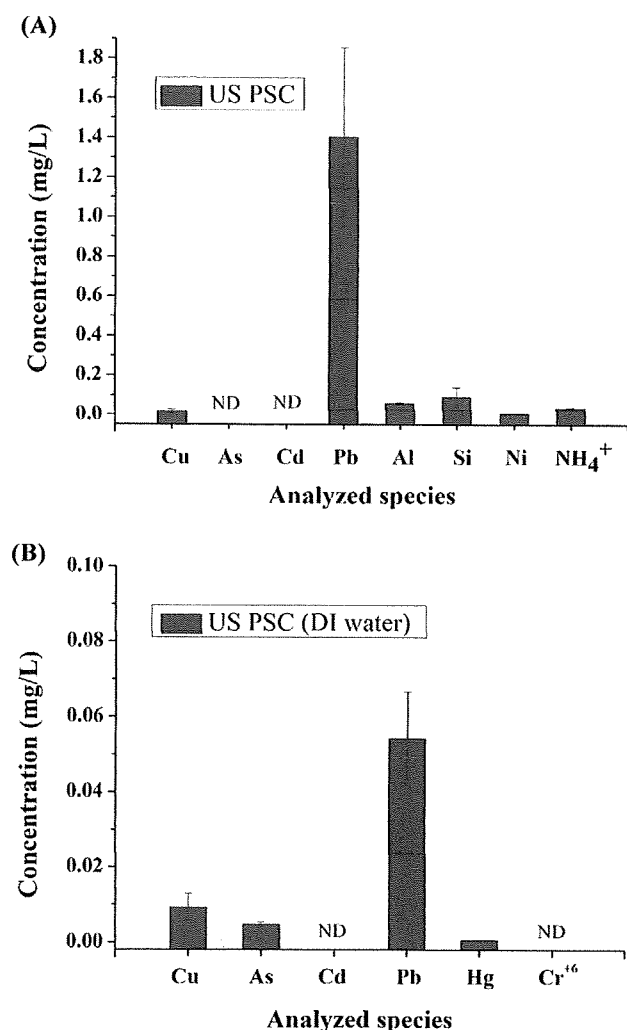


Fig. 4. Leaching of chemical species from unbroken (pristine) PSCs under stable condition (US PSC) using (A) TCLP fluid (values \pm SD; $n = 11$) and (B) DI water (values \pm SD; $n = 5$).

in PSCs under any environmental condition. The overall results of Figs. 3 and 4 imply that the Pb present in PSCs is released at around 1.0 mg/L under all acidic environmental conditions (broken and pristine, tumbling and stable).

Fig. 4 (B) shows the leaching of pristine PSCs using pure water under the stable condition (without tumbling the vessel). The unbroken PSCs released the following chemical species (average value, mg/L): Pb (0.054), Cu (0.009), and As (0.004). Hg was detected in only one sample at very low concentrations (0.0006 mg/L), while Cd, Cr⁶⁺, and CN⁻ were not detected. The leaching concentration of chemical species under DI condition were significantly lower than under all other conditions. Furthermore, it was observed that the probability of chemical species being released is increased when the pH of rain water decreases or if fluid with a lower pH comes into contact with the PSCs. This is in accordance with published literature on different types of PVs (c-Si, a-Si, CdTe, CIGS; Allen et al., 2010; Nain and Kumar, 2020; Nover et al., 2017; Zapf-Gottwick et al., 2015).

3.1.3. Effect of cell encapsulation on leaching from PSCs

Fig. 5 shows the effect of cell encapsulation (thickness: 0, 4, and 10 mm) in PSCs on the leaching of chemical species with TCLP fluid. The amount of Pb, which is a main constituent of PSCs, exhibited

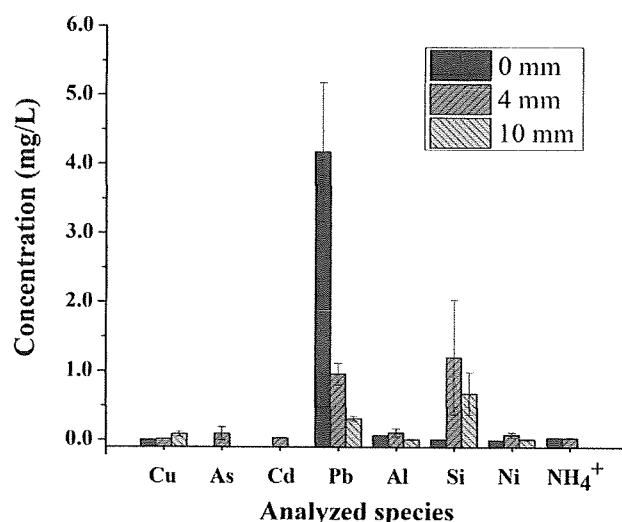


Fig. 5. Leaching of chemical species from PSCs using TCLP extraction fluid for different thicknesses of encapsulation (0 mm or no encapsulation [$n = 2$], 4 mm [$n = 15$], and 10 mm [$n = 2$]).

the highest leaching from cells without encapsulation (0 mm) with a concentration of 4.175 mg/L. The average concentration of Pb released from non-encapsulated PSCs did not exceed the TC limit. However, Pb was observed, albeit at reduced levels compared to the un-encapsulated PSCs, in the encapsulated PSC leachates, with concentrations of 0.959 mg/L and 0.315 mg/L for 4 mm and 10 mm encapsulation, respectively. This clearly indicates that solar cell encapsulation can prevent the release of toxic elements; however, it did not completely prevent the release of metals. Similar results were obtained by Finke et al. (1996) where a glass cover reduced the concentration of leachate from copper indium diselenide by 2–4 times compared to an uncovered cell. This factor will become all the more significant when the use of PSCs becomes widespread, since the compounding harmful effects of small quantity of leachates from a large number of cells, on humans and the environment, cannot be ignored. Thus, it is essential that attention be paid to research on improving the quality of encapsulation in PSCs so that the leaching of toxic substances can be completely prevented without affecting the efficiency of the cells themselves.

Overall, Pb and Si were leached out in higher concentrations because Pb and SiO₂ are the main constituents of PSCs; other species, namely Cu, As, Cd, Hg, Al, and Ni were hardly released. Most detected elements were released in higher amounts from broken PSCs than from unbroken (pristine) PSCs, which is likely because of cell size. The rate of a reaction increases with the area of contact between the reactants; thus, cutting or grinding the PSC into small pieces exposes more particles to the extraction fluid, which increases the chances of collision between them. Moreover, the physical process of grinding or cutting may weaken the attractive forces between the species in the cells, which also facilitates their release. Similar results were obtained for commercial cells (c-Si, a-Si, CdTe, CIGS) in which broken cells or milled pieces released higher amounts of toxic substances compared to pristine cells (Nover et al., 2017; Zapf-Gottwick et al., 2015).

3.2. Leaching results of c-Si cells

3.2.1. Leaching of chemical species from MoSC solar cells

In this study, broken mono c-Si cells were used for the leaching test with acidic TCLP fluid under tumbling and stable conditions. As shown in Fig. 6 (A), Al was released with the highest average concentration in leachate (182.28 mg/L) under the tumbling con-

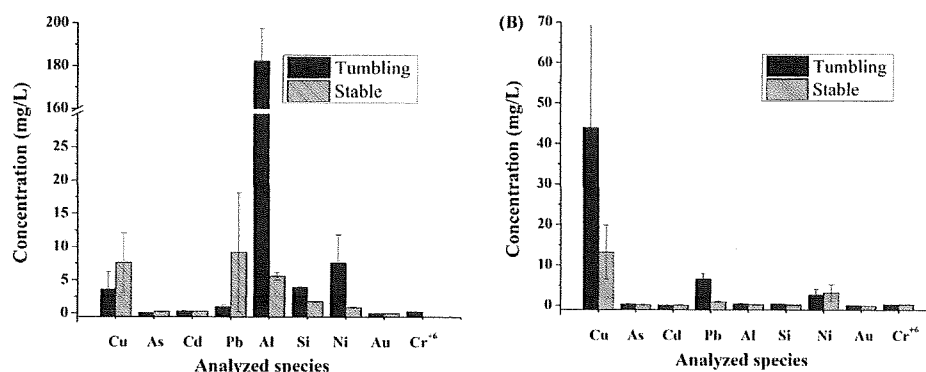


Fig. 6. Leaching of hazardous substances in TCLP fluid. (A) broken MoSC cells under tumbling (values \pm SD; $n = 3$) and stable (values \pm SD; $n = 4$) conditions. (B) Broken PoSC cells under tumbling (values \pm SD; $n = 3$) and stable (values \pm SD; $n = 3$) conditions.

dition. This was approximately 36 times higher than that under the stable condition (5.10 mg/L of Al leached). This is attributed to TCLP tumbling (harsh condition) which is a better representative of the worst-case scenario. Furthermore, a relatively higher amount of Al used in welding on the rear side of the MoSC cell is a cause for the higher amount of Al released in the leachate. Concentrations of 7.66 mg/L and 0.91 mg/L of Ni were detected from tumbling and stable conditions, respectively. The detected average amounts of Cu and Pb in the leachate under the stable condition were 7.603 mg/L and 9.197 mg/L, respectively, which were unusually higher compared to the tumbling condition (3.606 mg/L and 0.995 mg/L, respectively). In broken MoSC cell leaching, the tumbling condition did not always show a higher leaching concentration than the stable condition; some leaching results showed significantly higher concentrations compared to others. One datapoint of both Cu and Pb leaching in the stable condition showed extremely high values. This may be because the composition materials of commercially available c-Si cells were not consistently assembled. The significant factor concerning the leaching results is that broken MoSC cells leach very high levels of metals such as Al, Cu, Pb, and Ni.

Cu is not listed as a hazardous metal in the TC limit guidelines. Pb exceeded the TC limit under the tumbling method; in fact, out of the seven cells tested, only one (MoSC7) showed inordinately high concentrations of Pb (35.93 mg/L). Ni (7.663, 0.910 mg/L) was released in noticeable amounts from MoSC cells under tumbling (7.663 mg/L) and in average amounts under stable conditions (0.910 mg/L). However, other species, namely As, Hg, Au, and Cr^{6+} were hardly released (<0.5 mg/L), were not detected, or their concentrations ranged below the detection limits.

3.2.2. 2. Leaching of chemical species from PoSC cells

The leaching of chemical species from PoSC cells was also tested with broken cells with TCLP fluid under tumbling and stable conditions. Fig. 6 (B) clearly shows that more than 3.3 times more Cu and 6.5 times more Pb were released under the tumbling condition than under the stable condition. The average leaching in mg/L under the tumbling (former value) and stable (latter value) conditions for the PoSC leachate was highest for Cu (43.950; 13.225) followed by Pb (6.579; 1.009), and Ni (2.785; 3.299). In addition, two PoSCs (PoSC2, PoSC3) exceeded the TC limit for Pb. Other species (As, Al, Si, Hg, Au, and Cr^{6+}) were not observed in significant concentrations (<0.5 mg/L) or remained below the detection limit. In contrast, Collins and Ancia (2017) found a very high amount of Al (16.5–348 mg/L) leaching from multi-c-Si cells (or PoSC cells) using TCLP/modified TCLP methods because Al was used as the back contact for the MoSC cells. Sinha and Wade (2015) also found high Pb (3–11 mg/L) in leachate from c-Si PV under the TCLP procedure. Tammam et al. (2016) also reported a higher leaching concentration of Pb from

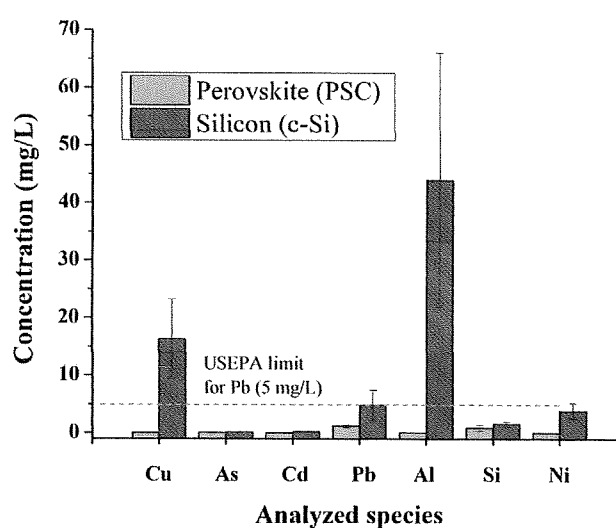


Fig. 7. Comparison of concentrations of hazardous substances leached from PSC ($n = 19$) and c-Si ($n = 13$) solar cells. All data from the use of TCLP extraction fluid for both types of cells are included. The horizontal dashed line represents USEPA's TC regulatory limit for Pb (5 mg/L).

c-Si compared to other elements. Overall, the leaching concentrations of different chemical species from MoSC and PoSC cells were found to be variable (Table S3).

3.3. Comparison of solar cell type on leaching potential: PSC vs c-Si

The leaching of hazardous substances (mainly heavy metals) from two types of PV cells viz. PSC and c-Si cells was compared using the TCLP method (worst-case scenario). As shown in Fig. 7, the c-Si leached significantly higher amounts of chemical species compared to the PSC (see details in Table S3). The hazardous species may leach from the cells into the surrounding environment following exposure to water or soil (Robinson and Meindl, 2019).

A literature survey indicated that perovskite material can pose risks to the surrounding environment due to presence of lead (Babayigit et al., 2016; Li et al., 2020a;b). A recent study revealed the biological impact of lead from halide perovskites (no real PSC was used; instead, its components, $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 were examined). It was observed that plants can uptake lead ten times more effectively if the lead was released into the soil by a perovskite material compared to lead subsequently leaking into the food cycle from other lead contaminants already present in the soil as a result of human activities (Li et al., 2020a;b). It was also revealed that replac-

ing lead with tin (Sn) may be an environmentally-safer alternative (Li et al., 2020a;b); however, the stability of Sn-based PSCs is much worse than Pb-based PSCs (Su et al., 2020). On the other hand, it must be noted that there is a dearth of studies on Pb leaching from real PSCs. In contrast, the results of our study show that c-Si solar cells leached more metals than real PSCs and that the concentrations of Pb released from many c-Si cells exceeded the TC guidelines. This means that c-Si solar cells can be classified as hazardous waste. This study found that the leaching concentrations of heavy metals (mainly Pb) from PSCs were lower than the TC guidelines, indicating that PSCs may be considered a non-hazardous waste.

4. Conclusions

The leaching potential of real PSCs, was clearly demonstrated for an acidic leaching fluid and DI water. For a comparison of the leaching potential, commercially available random c-Si solar cells were also evaluated; the effects of cell condition (broken/unbroken), leaching liquid type (TCLP/DI leaching), agitation level (tumbling/stable), and encapsulation thickness (0, 4, and 10 mm) on metal leaching from solar cells were also investigated.

The leaching results for PSCs showed that Pb (the major component of PSCs) is released at around 1.0 mg/L by an acidic leaching fluid under any condition (broken or pristine, tumbling or stable). These results show that while the encapsulation of PSCs resulted in lower leaching concentrations compared with non-encapsulated PSCs, it did not fully prevent leaching under weak acidic conditions.) More studies on PSC encapsulation methods are needed to understand this aspect better.

On the basis of leaching TC potential, the PSC was found to be safer than the c-Si because major chemical species were leached at higher concentrations from the c-Si cells than the PSCs. A greater number of c-Si cells exceeded the limit for Pb as defined by the TC of USEPA. The high metal leaching potential of c-Si solar cells may be attributed to the welding materials present in c-Si solar cells. Future research must pay attention to environmentally-friendly welding methods for c-Si solar cells and to the identification of significant leaching sources.

The results of this study will help to explore the possible risks to human health and to the environment from the widespread use of solar cells. This can be done by investigating the accidental release level of hazardous substances from solar cells into their surroundings under realistic conditions following defects in manufacturing, accidental damage, and disposal. Future studies investigating the leaching of hazardous species from solar PVs should consider the direct or indirect effects of these species on nearby ecosystems.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.psep.2020.10.035>.

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