



# Cadmium telluride (CdTe) and cadmium selenide (CdSe) leaching behavior and surface chemistry in response to pH and O<sub>2</sub>



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## ABSTRACT

Cadmium telluride (CdTe) and cadmium selenide (CdSe) are increasingly being applied in photovoltaic solar cells and electronic components. A major concern is the public health and ecological risks associated with the potential release of toxic cadmium, tellurium, and/or selenium species. In this study, different tests were applied to investigate the leaching behavior of CdTe and CdSe in solutions simulating landfill leachate. CdTe showed a comparatively high leaching potential. In the Toxicity Characteristic Leaching Procedure (TCLP) and Waste Extraction Test (WET), the concentrations of cadmium released from CdTe were about 1500 and 260 times higher than the regulatory limit (1 mg/L). In contrast, CdSe was relatively stable and dissolved selenium in both leaching tests was below the regulatory limit (1 mg/L). Nonetheless, the regulatory limit for cadmium was exceeded by 5- to 6- fold in both tests. Experiments performed under different pH and redox conditions confirmed a marked enhancement in CdTe and CdSe dissolution both at acidic pH and under aerobic conditions. These findings are in agreement with thermodynamic predictions. Taken as a whole, the results indicate that recycling of decommissioned CdTe-containing devices is desirable to prevent the potential environmental release of toxic cadmium and tellurium in municipal landfills.

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## 1. Introduction

II–VI compounds are a group of materials that have attracted remarkable attention due to their wide range band gaps, which span the spectral region from near-infrared to ultraviolet (Jain, 1993). Cadmium telluride (CdTe) and cadmium selenide (CdSe) are two important members in II–VI family. CdTe has a direct band gap of 1.45 eV, which is very close to the ideal value for solar cells (Birkmire and McCandless, 2010; Choi et al., 2010). It also has high optical absorption coefficient that allows CdTe to absorb >99% of light within about 2 μm film (Birkmire and McCandless, 2010; Choi et al., 2010). These unique electrical and optical properties make it a perfect light absorber. Therefore, CdTe is recognized as the most promising material for cost-effective photovoltaic devices. In fact, CdTe PVs had the second greatest market share with a module production of about 1.8 GW in 2012 (Kranz et al., 2013). CdSe has an intrinsic band gap of 1.74 eV, while it can be tuned from infrared region to the ultraviolet for desired optical and electrical properties

(Chate et al., 2013). CdSe is widely used in solar cells, light emitting diodes (LEDs), and photodetectors (Chate et al., 2013; Khomane and Hankare, 2010).

Despite their popularity in the scientific and technological fields, one major concern about CdTe and CdSe application is the potential risk of hazardous substances release. Firstly, the increasing application of CdTe and CdSe will inevitably result in the release of these materials into environment. For example, according to current regulations, most electronic waste (e-waste) is not classified as hazardous waste in the U.S., therefore, decommissioned CdTe and CdSe modules can be disposed in municipal mixed waste landfills. Secondly, cadmium (Cd) and selenium (Se) are well known toxicants that have been included by the United States Environmental Protection Agency (USEPA) in the list of regulated drinking water contaminants. The maximum contaminant levels (MCL) allowed for cadmium and selenium in drinking water are 0.005 and 0.05 mg/L, respectively. Tellurium in drinking water is not regulated by the USEPA. However, studies have shown that tellurium compounds may cause adverse effects on kidney, liver, gastrointestinal and nervous system (Taylor, 1996; Vij and Hardej, 2012). Therefore, it is important to understand the leaching ability and behavior of these cadmium chalcogenides.

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The purpose of this study is to investigate the leaching behavior of CdTe and CdSe under different redox and pH conditions. To study the effect of aqueous chemistry on CdTe and CdSe dissolution, different batch leaching tests were performed including the Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1992) and Waste Extraction Test (WET) (CCR, 1991a,b) which are standardized methods utilized by the USEPA and the California Environmental Protection Agency (Cal/EPA), respectively, to simulate landfill leaching and determine whether a waste material should be classified as hazardous based on its toxicity characteristics. Pourbaix (potential-pH) diagrams were built to predict the predominant species in aqueous system. X-ray photoelectron spectroscopy (XPS) analyses were applied to study the surface chemistry.

## 2. Materials and methods

### 2.1. Chemicals

CdTe (99.999%) and CdSe (99.999%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Both materials were carefully ground and sieved, and the CdTe and CdSe fractions ranging in size between 120 and 230 U.S. standard meshes (63–125  $\mu\text{m}$ ) were collected for the use in leaching tests. All the leaching solutions were prepared using deionized (DI) water (Milli-Q Water System, Millipore, Billerica, MA, USA).

### 2.2. Standardized leaching tests

This study compared the leaching ability of CdTe and CdSe using both TCLP and WET procedures. Table 1 summarizes the conditions applied in these protocols. All the leaching tests were performed at room temperature using glass serum bottles (20 mL) supplied with 6 mL leaching solution. For this work, the TCLP was run at 0.003 scale, but previous experiments on the reproducibility of results showed no drawback with this approach (Ghosh et al., 2004). However, there is no such data available for WET test. The headspace of the flasks in the TCLP and WET tests was filled with air or  $\text{N}_2$  gas, respectively, as specified in the respective leaching protocols. The test vials were placed vertically in a rotary apparatus (A-R 12, Thumler's Tumbler, Auburn, WA, USA) at 21 rpm for agitation. After incubation, all the extracts were filtered through a 0.45  $\mu\text{m}$  cellulose acetate membrane filter (Whatman) and the filtrates were prepared for analytical determination. All the leaching tests were conducted in duplicate. Negative controls (leaching solution without CdTe or CdSe supplementation) were run in parallel.

### 2.3. Impact of atmospheric oxygen on CdSe and CdTe dissolution

In order to investigate the effect of oxygen on CdTe and CdSe dissolution, modified TCLP and WET leaching tests were performed in which the headspace of the leaching flasks was supplied with an atmosphere  $\text{N}_2$  gas or ambient air, respectively. All other test

conditions and sample preparation procedures were as described above.

### 2.4. Impact of pH on CdSe and CdTe dissolution

The effect of medium pH on the dissolution of CdTe and CdSe was investigated in shaken batch assays using leaching solutions with varying pH values, i.e., 3.5, 5.9 and 9.9 for tests with CdTe, and 3.6, 6.1, 7.0 and 10.5 for tests with CdSe. NaOH (2 and 10 mM) and HCl (2 and 10 mM) solutions were used to adjust the pH of the leaching solutions.

Leaching solutions were first prepared and stored overnight in serum bottles with screw caps to make sure they reached equilibrium. Batch tests were performed in glass serum bottles (160 mL) supplied with leaching solution (100 mL) and CdTe or CdSe at a concentration of 5 mM. After the introduction of solids and medium, the bottles were sealed with rubber stoppers and aluminum caps. In all the experiments, the headspace in each bottle was ambient air. Vessels were incubated in the dark at 30 °C using an orbital shaker (Innova 4300, New Brunswick) at 120 rpm. During the experiment, no further attempts were made to control pH and volume of the solutions. Liquid samples were withdrawn periodically from the test bottles for analysis of pH and metal/metalloid concentration. At the end of the experiment, the concentration of soluble and colloidal Cd, Se and/or Te in the liquid medium was determined. The colloidal concentration of these species was measured by filtering the samples through 1.2  $\mu\text{m}$  and 0.025  $\mu\text{m}$  filters (Millipore) separately. The filtered liquid samples were then analyzed, and the concentration of metal/metalloid in the colloidal fraction was calculated using the following equation:

$$C_{\text{colloidal}} = C_{1.25\mu\text{m}} - C_{0.025\mu\text{m}} \quad (1)$$

All the tests were conducted in duplicate. Controls lacking CdTe and CdSe were run parallel.

### 2.5. XPS

XPS analyses were performed to study the surface chemistry of CdTe and CdSe (See Supplementary Materials section). The samples were prepared using the same procedure as described in the pH effect tests. In this experiment, the initial pH of the leaching solution was set to 3.5. After incubation for 7 days, CdTe and CdSe were separated from the leaching solution in an anaerobic chamber (Type B Vinyl Anaerobic Chamber, Coy Laboratory, Grass Lake, MI, USA) to avoid surface oxidation. Then CdTe and CdSe samples were dried under  $\text{N}_2$  gas for XPS analysis.

### 2.6. Potential-pH (Pourbaix) diagrams

Pourbaix diagrams (also known as potential-pH diagrams) are designed to show domains of predominant species in complex aqueous systems which are predicted based on thermodynamic data. In our study, the STABCAL software (Huang et al., 2002), one integrated Windows program, was used to plot CdTe and CdSe Pourbaix diagrams. Pourbaix diagrams were constructed at Cd, Te and Se activities of 5 mM. For CdTe– $\text{H}_2\text{O}$  and CdSe– $\text{H}_2\text{O}$  system, the following species were considered:

i) Nine cadmium species: CdTe(or CdSe), Cd(s), CdO(s),  $\text{Cd}^{2+}$ ,  $\text{CdOH}^+$ ,  $\text{Cd}(\text{OH})_2(\text{a})$ ,  $\text{Cd}(\text{OH})_2(\text{s})$ ,  $\text{Cd}(\text{OH})_3^-$ ,  $\text{Cd}(\text{OH})_4^{2-}$ .

ii) Thirteen tellurium or selenium species (X: Te, Se):  $\text{X}^{2-}$ ,  $\text{HX}^-$ ,  $\text{H}_2\text{X}$ ,  $\text{X}_2^{2-}$ ,  $\text{X}(\text{s})$ ,  $\text{X}^{4+}$ ,  $\text{XO}_2(\text{s})$ ,  $\text{XO}_3^-$ ,  $\text{HXO}_3^-$ ,  $\text{H}_2\text{XO}_3$ ,  $\text{XO}_4^{2-}$ ,  $\text{HXO}_4^-$ ,  $\text{H}_2\text{XO}_4$ .

**Table 1**  
Summary of the experimental conditions applied in the TCLP and WET procedures.

	TCLP	WET
Solid to liquid ratio (w/w)	1: 20	1: 10
Extraction fluid	Acetic acid, sodium hydroxide (pH = 4.93 $\pm$ 0.05)	Citric acid, sodium hydroxide (pH = 5.00 $\pm$ 0.05)
Headspace	Ambient air	$\text{N}_2$
Extraction period (h)	18	48

## 2.7. Analytical determinations

Prior to the analysis of soluble Cd, Se and Te, liquid samples were centrifuged for 10 min at 13,300 g.  $\text{HNO}_3$  (3% v/v) solution was then added to acidify and dilute the samples. The concentration of Cd, Te and Se species was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2100 DV, Perkin–Elmer, Waltham, MA, USA) at a wave length of 228.802, 238.578 and 196.026 nm, respectively. The detection limit was 0.1  $\mu\text{g/L}$  for Cd, and 10  $\mu\text{g/L}$  for Te and Se.

## 3. Results and discussion

### 3.1. Potential–pH (Pourbaix) diagrams

CdTe and CdSe Pourbaix diagrams are shown in Fig. 1a and b, respectively. The corresponding redox reactions are summarized in Table S1 (Supplementary Section). In Pourbaix diagrams, the dashed lines mark the stability region of water. These stability lines

can be defined using the following equations:

$$\text{Upper Stability Line : } E = 1.23 - 0.059 \text{ pH} \quad (2)$$

$$\text{Lower Stability Line : } E = -0.059 \text{ pH} \quad (3)$$

where  $E$  is the redox potential expressed in volts.

Fig. 1a shows that the potential of CdTe lower stability limits (–0.89 and –1.33 V at pH 0 and pH 14) are lower than that of water, which indicates CdTe is thermodynamically stable in aqueous solution within the whole pH range under reductive conditions. On the other hand, its upper stability limits are in the range of –0.40 to 0.03 V. Therefore, thermodynamic considerations predict that CdTe is readily destabilized under oxidative condition. In addition, as the potential increases, tellurium (Te) species with higher valence states are expected to become predominant in water system.

Fig. 1b shows that CdSe is also very stable under reductive condition. It is interesting to note that the general chemical speciation of CdSe is similar with CdTe. This is conceivable since

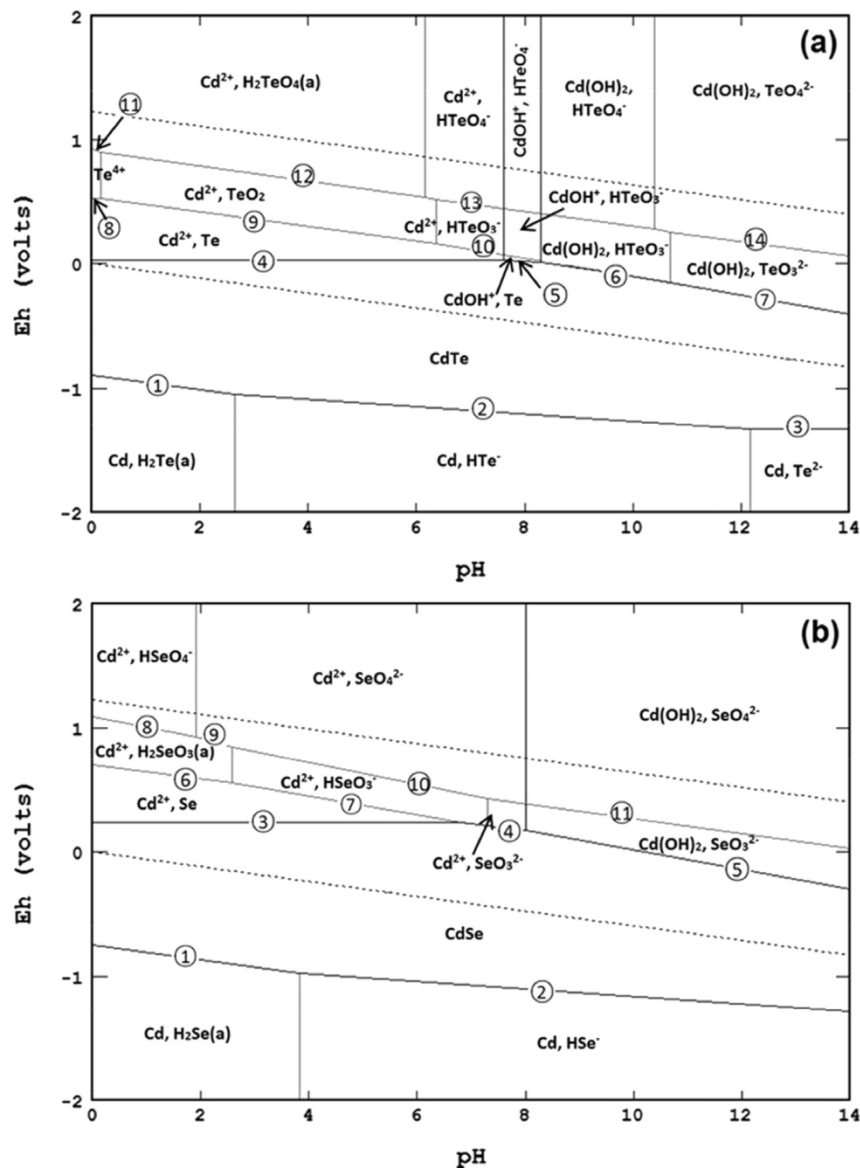


Fig. 1. Pourbaix diagrams for CdTe–H<sub>2</sub>O system (a) and CdSe–H<sub>2</sub>O system (b) at 25 °C. Pourbaix diagrams were constructed at activities of Cd, Te and Se of 5 mM.



both Te and Se belong to the chalcogen group in the periodic table. However, compared to CdTe, CdSe has higher upper stability limits (−0.30 to 0.24 V), indicating a more oxidizing environment is needed to solubilize CdSe.

### 3.2. Standardized leaching tests

In our study, CdTe and CdSe were subjected to USEPA TCLP test and to the California WET test to evaluate their leaching ability. In the TCLP procedure, the concentrations of Cd and/or Se determined in the leachate are compared with toxicity characteristic regulatory limits, while in the WET, the soluble threshold limit concentration (STLC) is applied (CCR, 1991a). The regulatory limits for cadmium and selenium are 1 mg/L in both leaching procedures. Tellurium is not included among the chemicals monitored in the TCLP and WET procedures.

The results of the TCLP and WET tests for CdTe and CdSe are presented in Fig. 2. The concentrations of Cd released from CdTe and CdSe were 1490.9 and 6.5 mg/L under standard TCLP conditions (air headspace) (Fig. 2a and b). For standard WET tests (N<sub>2</sub> headspace), the concentrations of Cd leached from CdTe and CdSe were 260.5 and 5.5 mg/L, respectively (Fig. 2c and d). These values are about 5–1500-fold higher compared to the regulatory limit for Cd. In contrast, the concentrations of dissolved Se released from CdSe in the TCLP and WET leachate, only 0.3 and 0.1 mg/L, respectively, were lower than the regulatory limit. The concentrations of dissolved Te detected in these leachates were 1.1 and 47.0 mg/L, respectively.

The considerably higher dissolution potential observed for CdTe compared to CdSe in both leaching tests is in general agreement with the thermodynamics predictions discussed in the previous section. Likewise, the higher dissolution of Cd from CdTe (nearly

5.7-fold) observed in the conventional TCLP test, which uses an air headspace, compared to the WET test, which is performed under anoxic conditions, is in agreement with the enhanced susceptibility of CdTe to corrosion under oxidative conditions predicted in the Pourbaix diagrams. The concentration of tellurium detected in solution, both in the TCLP and WET tests, was considerably lower than expected based on stoichiometry, which may be due to the lower solubility of Te species compared to Cd under the conditions of these tests. Indeed, metallic tellurium (Te<sup>0</sup>) and TeO<sub>2</sub>, the main corrosion products predicted at moderate redox potentials above the lower stability line (Fig. 1a.) are known to have negligible solubility in water (Greenwood and Earshaw, 1997). TeO<sub>2</sub> shows a minimum in solubility at pH 4.0 (Greenwood and Earshaw, 1997), a value close to that used in the leaching tests (4.93–5.00). In addition, different ligands used in the leaching tests may be responsible for the higher concentration of soluble Te released in the WET test compared to TCLP test (47.0 vs. 1.1 mg/L). This will be discussed further in Section 3.3.

### 3.3. Effect of oxygen and different ligands on CdTe and CdSe dissolution

In our study, the TCLP and WET tests were performed using both air and N<sub>2</sub> headspace to investigate the impact of different redox conditions on CdTe and CdSe dissolution. Comparing the results from different headspace treatments (Fig. 2), it is evident that exposure to atmospheric oxygen has a strong impact on CdTe and CdSe release. For example, in the TCLP test with N<sub>2</sub>, the concentrations of dissolved Cd and Te were 133.1 and 0.5 mg/L, which are about ten times lower than those determined under standard TCLP test conditions where an oxygen atmosphere is used. Similarly, considerably lower levels of dissolved Cd, Te and Se were

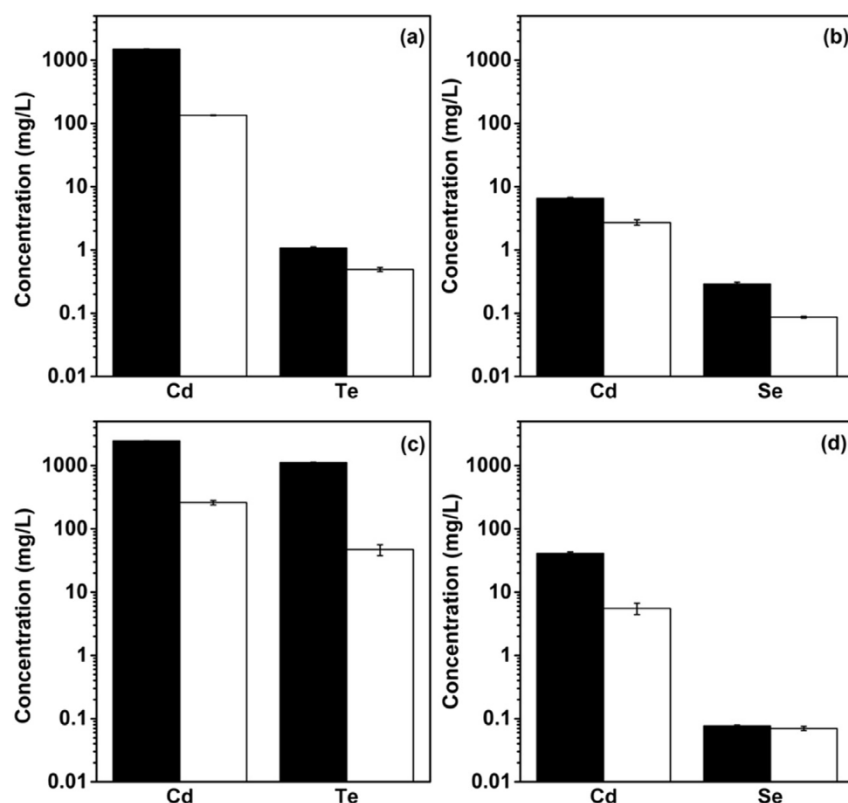


Fig. 2. Concentrations of dissolved Cd, Te and Se released from CdTe or CdSe in the (modified) TCLP and WET leaching tests: (a) CdTe TCLP test; (b) CdSe TCLP test; (c) CdTe WET test; (d) CdSe WET test. Legends: Treatment with ambient air in the headspace (filled columns); treatment using N<sub>2</sub> gas in the headspace (blank columns).

determined in WET assays determined under the prescribed anoxic conditions (N<sub>2</sub> headspace) compared to the leaching under an air atmosphere. These results are agreement with thermodynamic calculations in [Section 3.1](#).

Comparison of the TCLP and WET tests using the same headspace treatment indicates that the concentrations of dissolved Cd and Te in the WET test were higher than in the TCLP test. This trend is particularly evident in the case of Te which reached a concentration of 1116.6 mg/L in the WET leachate compared to only 1.07 mg/L in the TCLP leachate when both assays were performed with air. The higher solubility of Cd and Te in the WET test could partially be due to the higher solid to liquid ratio used (WET 1:10 vs. TCLP 1:20, w/w) and the longer contact times applied (WET 48 h vs. TCLP 18 h). The difference in Cd and Te dissolution might to some extent also be related to the use of different ligands in these assays. One on hand, both acetate and citrate, which are used in the TCLP and WET extraction solutions, respectively, can chelate with Cd forming soluble complexes ([Dakanali et al., 2003](#); [Kefalas et al., 2005](#); [Naidu and Harter, 1998](#)). Whereas acetate is a mono-dentate ligand, citrate is tridentate which may have higher affinity for Cd, resulting in higher cadmium dissolution. Indeed, the logarithm stability constants (log  $\beta$ ) of cadmium acetate and cadmium citrates are 1.93 and 3.15, indicating that citric acid is more aggressive for Cd dissolution ([Naidu and Harter, 1998](#)). For Te, on the other hand, it has been reported that citric acid can be used as solubilizing agent to increase its solubility in aqueous solutions ([Ishizaki et al., 2004](#)).

### 3.4. Effect of pH on CdTe and CdSe dissolution

The dissolution kinetics for Cd and Te from CdTe as a function of the pH value are shown in [Fig. 3a](#) and [b](#). The results demonstrate that pH plays a significant role in the leaching process. Acidic conditions were favored for CdTe leaching, while the dissolution process was largely inhibited under basic environment. In leaching tests performed at the lowest pH value (3.5), the concentration of dissolved Cd reached the peak (20.0 mg/L) at day 3, corresponding to a release of 3.6% (w/w) of the total Cd added into the aqueous phase. At pH 3.5, Te also underwent initially a quick release, and then the dissolved Te started to decrease. The highest concentration of Te detected (9.1 mg/L), which corresponded to a release of 1.4% (w/w) of the total Te added, was determined following incubation for one day.

In contrast with CdTe, CdSe appeared very stable in aqueous solution ([Fig. 3c](#) and [d](#)). Kinetic experiments performed at pH values ranging from 3.6 to 10.5 demonstrated that only low concentrations of Cd were released into solution. The highest Cd release, only 0.9 mg/L after 50 days of incubation, was observed in the most acidic leaching solution (pH 3.6). Selenium dissolution was also very limited and the concentrations of dissolved Se were close to the detection limit of the ICP instrument (10  $\mu$ g/L), at all the pH levels tested. Therefore, the Se data show comparatively large standard deviations.

The concentrations of Cd, Te and Se colloidal particles determined in all leaching solutions were negligible, indicating that the released metal/metalloid species in these kinetic leaching experiments were present as dissolved material.

To the best of our knowledge, published information about the leaching potential of CdTe is very limited. It has been reported that CdTe has a very low solubility product ( $K_{sp} = 9.5 \times 10^{-35}$ ) and long-term transformation study showed 1.5% of Cd species released after 28 days ([Sinha et al., 2012](#)). There is no such data available for CdSe.

### 3.5. CdTe and CdSe surface analyses

The surface chemistry of CdTe and CdSe materials was evaluated using XPS to better understand their leaching behavior in aqueous solutions. [Table 2](#) shows the percent atomic concentration determined on the surface of the samples before and after leaching at pH 3.5 for 7 days. The data indicates that considerable amounts of oxygen had been adsorbed on both CdTe and CdSe surfaces even prior to treatment. This result is in agreement with other XPS studies indicating that cadmium chalcogenides are likely to adsorb oxygen when exposed to atmospheric oxygen ([Katari et al., 1994](#)). The fraction of oxygen determined in CdTe and CdSe was higher after leaching ([Table 2](#)). This is most likely due to release of soluble Cd, Te or Se species and deposition of metalloid oxides such as TeO<sub>2</sub>.

[Fig. 4](#) shows the Cd (3d) and Te (3d) spectra for CdTe samples. The data indicates that the predominant Cd species on the surface of the untreated material was CdTe (404.7 eV) ([Liu et al., 2006](#); [Zhang et al., 2003](#)). On the other hand, the spectra of the leached CdTe samples indicate that in addition to CdTe, another Cd species (406.0 eV) is present on the surface of the material at a comparatively high concentration ([Fig. 4c](#)). One candidate is CdCl<sub>2</sub>, which has been reported to have a binding energy of 405.9 eV ([Briggs and Seah, 1993](#)). However, a chlorine peak was not observed in the survey spectrum of treated CdTe, indicating that most, if not all, of the chlorine was in the aqueous solution. Since there is much oxygen on the CdTe surface, the peak at 406.0 eV might be related to Cd–O or Cd–Te–O complexes, as atoms of higher oxidation state are known to exhibit a higher binding energy.

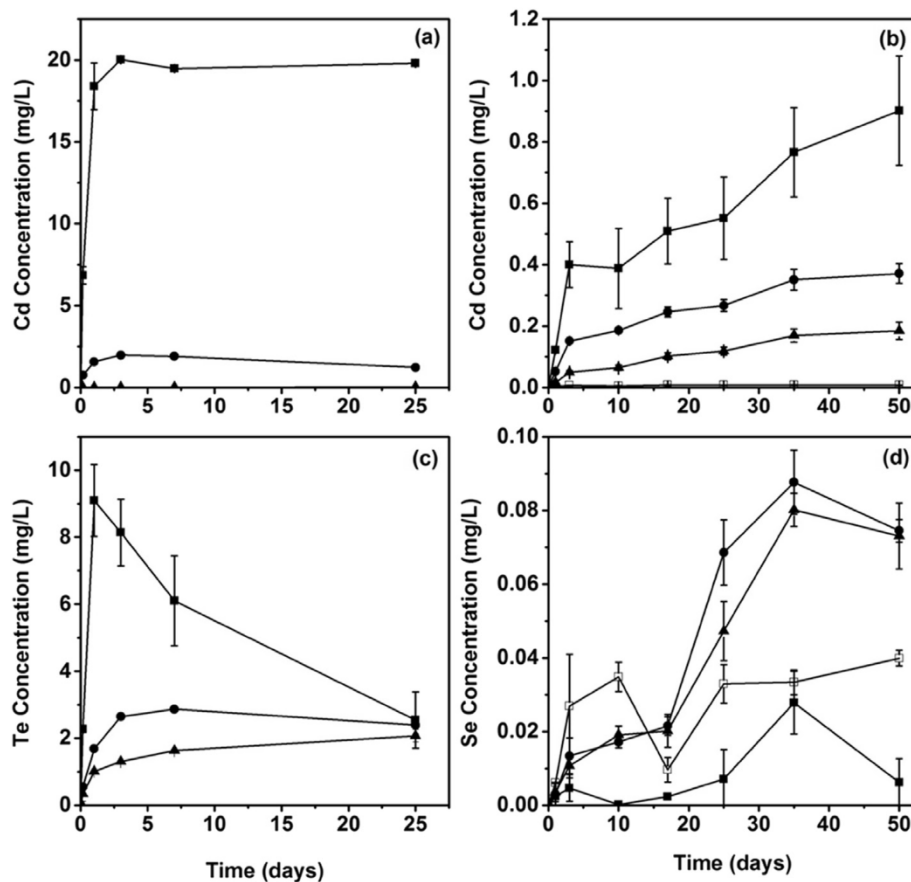
Two dominant tellurium species were present on the surface of the untreated CdTe sample, CdTe (572.0 eV) ([Zhang et al., 2003](#)) and TeO<sub>2</sub> (575.6 eV) ([Garbassi et al., 1981](#)). In addition, a peak with a binding energy of 577.2 eV suggests the presence of some TeO<sub>3</sub> ([Briggs and Seah, 1993](#)). After leaching, the majority of Te was in the form of oxides, mostly TeO<sub>2</sub>, as evidence by the large peak at 575.9 eV in [Fig. 4d](#). These data suggest that CdTe corrosion initially leads to the release of soluble Cd and Te into aqueous solution. Later, residual insoluble Cd and Te species and the deposition of newly formed insoluble oxides (e.g. TeO<sub>2</sub>) prevent CdTe from further dissolution. This hypothesis is confirmed by the results of the kinetic studies shown in [Fig. 3](#), where CdTe dissolution stopped after a quick initial release of Cd and Te. Also it is supported by the sub-stoichiometric levels of dissolved Te, with respect to dissolved Cd, found in all leaching experiments with CdTe ([Fig. 2a](#) and [c](#)).

On the other hand, the XPS results show that compared to CdTe, CdSe is very inert in aqueous solution ([Fig. 5](#)), which is in agreement with the result from all the leaching tests conducted in this study ([Figs. 2b, c and 3b, c](#)) and with the theoretical studies of thermodynamic stability ([Fig. 2b](#)). The predominant Cd and Se species on the surface of untreated and leached CdSe were present as CdSe (404.7 eV and 53.6 eV) ([Polak, 1982](#)).

### 3.6. Implications

Firstly, there was a dramatic difference in the leaching behavior of CdSe and CdTe under simulated landfill conditions. While CdSe was very stable in aqueous solutions, CdTe showed a very high potential for release of toxic Cd and Te. Secondly, the corrosion of these cadmium chalcogenides was enhanced under oxidizing conditions. These observations have important implications for the standardized TCLP and WET leaching tests which prescribe the use of different headspace gases, ambient air atmosphere and N<sub>2</sub> atmosphere, respectively. The most aggressive leaching scenario was provided by a modified WET test in which the N<sub>2</sub> headspace was replaced by air. The enhanced dissolution was not only due to the use of oxidizing conditions but also to the role of citric acid as a





**Fig. 3.** Release of dissolved Cd (a) and Te (c) from CdTe exposed to aqueous solutions adjusted to different initial pH values: pH 3.5 (■); pH 5.9 (●); pH 9.9 (▲), as a function of time. Release of dissolved Cd (b) and Se (d) from CdSe exposed to aqueous solutions adjusted to different initial pH values: pH 3.6 (■); pH 5.9 (●); pH 7.5 (▲); pH 10.5 (□), as a function of time.

**Table 2**

Percent atomic concentration determined by XPS in CdTe and CdSe samples before and after treatment with a leaching solution (pH = 3.5) at room temperature for 7 days.

Sample ID	Atomic concentration (%)			
	O	Cd	Te	Se
CdTe (untreated)	47.6	26.5	25.9	N/A <sup>a</sup>
CdTe (treated)	66.2	12.4	21.3	N/A <sup>a</sup>
CdSe (untreated)	32.1	40.4	N/A <sup>a</sup>	27.5
CdSe (treated)	51.2	25.6	N/A <sup>a</sup>	23.2

<sup>a</sup> Not applicable.

chelating ligand that promoted Te dissolution.

Although some previous studies have claimed that Cd in CdTe is in an insoluble form and thus is likely to have low bioavailability in the environment (Patterson et al., 1994), the results of this study demonstrate that Cd is readily leachable if exposed to the aquatic environment, particularly under acidic pH and/or aerobic conditions. CdTe in thin-film PV cells is encapsulated between thick glass sheets which minimize environmental exposure of CdTe and release of soluble Cd species as demonstrated elsewhere (Steinberger, 1998). Disposal of decommissioned CdTe panels in municipal waste landfills could, however, result in exposure of the CdTe film to the aquatic environment in situations where the physical integrity of the glass casing is compromised. We are not aware of any study evaluating the likelihood of such events in municipal landfills, however, waste disposal and compaction

operations in municipal landfills can be harsh and they are not designed to protect glass sheets used in PVs. Indeed, several TCLP leaching studies have reported release of Cd from broken CdTe panels, with several instances in which the Cd concentration exceeded its TCLP limit of 1.0 mg/L (Cyrus et al., 2014; Moskowitz and Fthenakis, 1991; Patterson et al., 1994). The Cd concentrations reported in those studies ranged from 0.01 to 9.5 mg/L.

Although the TCLP and WET tests are designed to expose the waste to conditions more conducive to toxic leaching than landfill conditions (and establish if the waste can be disposed in a nonhazardous landfill), it is difficult to estimate the actual amount of Cd that could leach during landfilling based on the results of these leaching tests. The simple chemistries and short-term contact times prescribed by the TCLP and WET tests poorly simulate the changing pH and redox conditions, biological activity, long retention time, and organic composition of mature landfills. In this regard it is interesting to note that our results demonstrate that shifts in the prevailing pH and redox conditions in landfills could have a considerable impact on the dissolution of Cd from CdTe. Furthermore, the composition of the leachate could also affect the solubilization of toxic species from CdTe. The results obtained in the leaching tests conducted in this study suggest that the dissolution of tellurium was more favored in the presence of citric acid compared to acetic acid. Although no study to date has considered the impact of microbial transformations on the fate of CdTe in municipal landfills, the ability of some anaerobic microorganisms to reduce soluble tellurium species (e.g. tellurate and tellurite) is well established (Baesman et al., 2007; Basnayake et al., 2001).

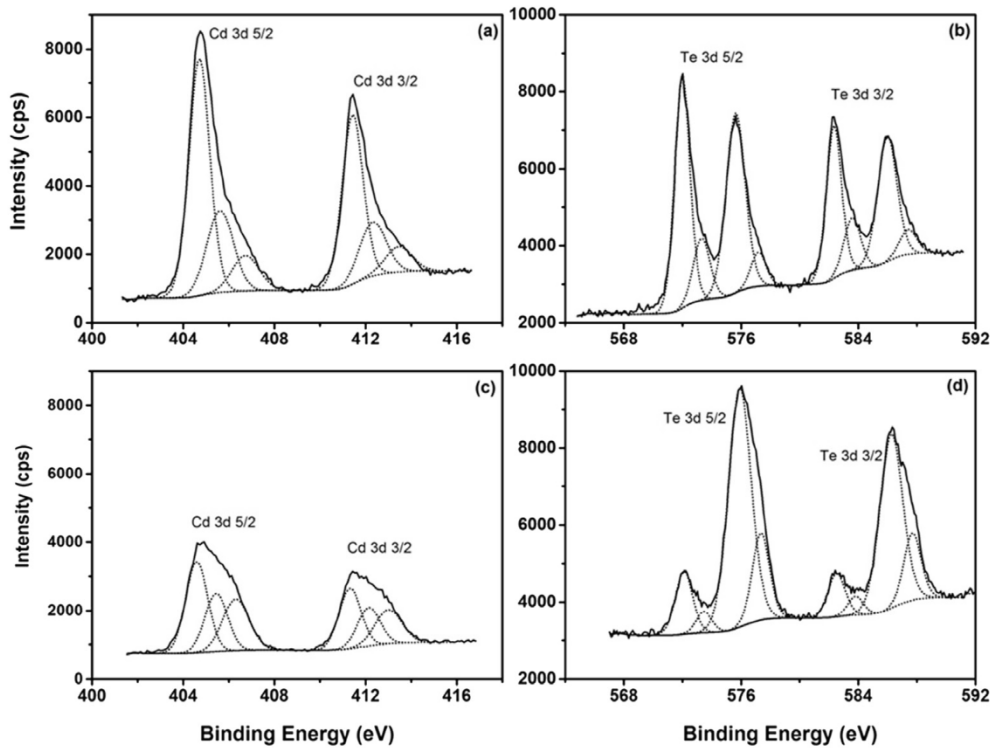


Fig. 4. XPS spectra for untreated and leached CdTe: (a) Cd (3d) spectra for untreated CdTe; (b) Te (3d) spectra for untreated CdTe; (c) Cd (3d) spectra for treated CdTe; (d) Te (3d) spectra for treated CdTe. Legend: XPS results (solid lines); XPS fittings (dashed lines).

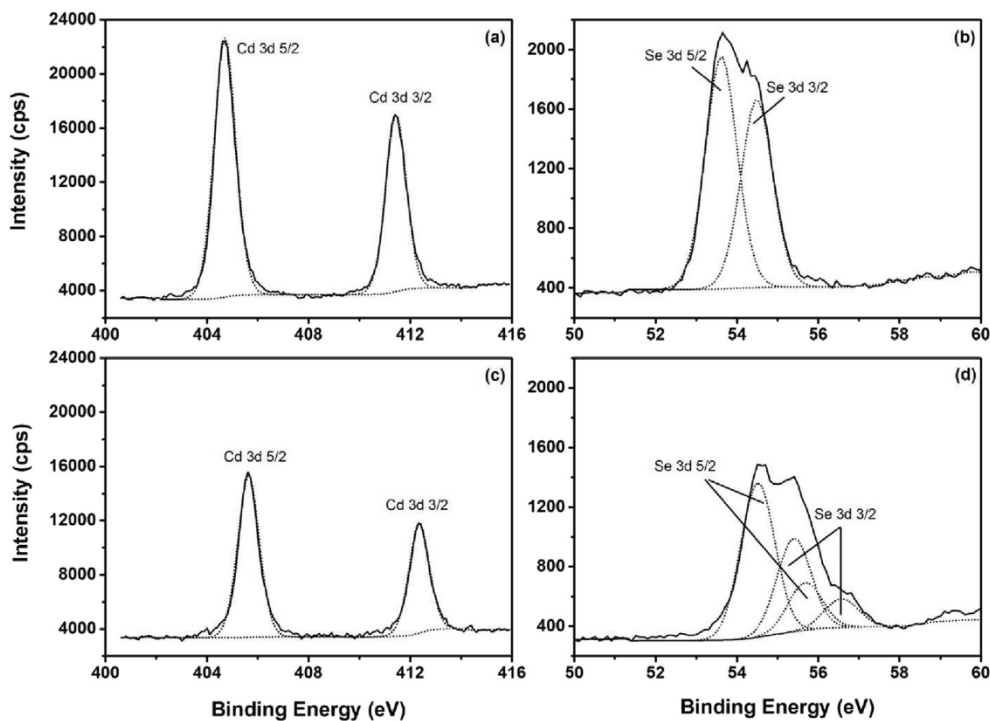


Fig. 5. XPS spectra for untreated and leached CdSe: (a) Cd (3d) spectra for untreated CdSe; (b) Se (3d) spectra for untreated CdSe; (c) Cd (3d) spectra for treated CdSe; (d) Se (3d) spectra.

Since young landfills are rich in anaerobic microbial activity, it is conceivable that such transformations could occur and perhaps have an impact on the fate of CdTe. The ultimate fate and mobility

of Cd and Te released from CdTe will depend on the complex biogeochemistry of the landfill environment.

Taken together the results obtained indicate that recycling of

decommissioned CdTe photovoltaic modules and other electronic waste containing CdTe is desirable to prevent the potential environmental release of toxic cadmium and tellurium in municipal landfills. Moreover, the sustainability of the supply of Te has come into question. Tellurium is now being considered as a strategic element due to its scarcity and increasing application in the energy and electronics sector (Berger et al., 2010; Marwede et al., 2013), and it ranked with the highest concern level by the both US Department of Energy (DOE, 2010) and the UK House of Commons' Science and Technology Committee (2011). Therefore, end-of-life recycling is necessary to prevent the release of toxic materials into environment, but also to allow the recovery of critical resources. Fortunately, recent studies have shown that recycling of decommissioned CdTe panels is feasible (Fthenakis, 2000; Raugei et al., 2012).

#### 4. Conclusions

Our results show that CdTe has comparatively high leaching potential. The release of soluble Cd in the TCLP and WET tests was about 1500 and 260-fold higher, respectively, than the regulatory limit of 1 mg/L. CdTe dissolution behavior indicates that the corrosion initially leads to the release of soluble Cd and Te into aqueous solution, then the residual insoluble Cd and Te species and the deposition of newly formed insoluble oxides (e.g. TeO<sub>2</sub>) prevents CdTe from further dissolution. In contrast, CdSe was found to be relatively stable in all the leaching experiments. In addition, the results of standardized leaching tests indicate that the federal TCLP is more aggressive than the California WET for CdTe and CdSe dissolution. This is mainly due to the different headspace treatment (TCLP: air; WET: N<sub>2</sub>). The aqueous pH also played an important role in the leaching process and acidic conditions favored CdTe and CdSe dissolution. These findings are in agreement with thermodynamic calculations (Pourbaix diagrams) and XPS surface analysis.

The standardized leaching tests (TCLP and WET) applied in this study have their own limitations, therefore, further experiments under conditions that closely represent those found in municipal solid waste landfills (e.g. experiments with real landfill leachate) should be performed to gain a better understanding of the leaching behavior of CdTe and CdSe in actual landfills.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2015.02.033>.

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