Journal of Environmental Management 154 (2015) 78–85

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Cadmium telluride (CdTe) and cadmium selenide (CdSe) leaching behavior and surface chemistry in response to pH and O_2

Chao Zeng*, Adriana Ramos-Ruiz, Jim A. Field, Reyes Sierra-Alvarez

Department of Chemical and Environmental Engineering, University of Arizona, P.O. Box 210011, Tucson, AZ 85704, USA

ARTICLE INFO

Article history:
Received 22 December 2014
Received in revised form
15 February 2015
Accepted 18 February 2015
Available online

Keywords:
Cadmium telluride
Cadmium selenide
Leaching test
Landfill leachate

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.

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 bond 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.

---

* Corresponding author.
E-mail address: chaozeng@email.arizona.edu (C. Zeng).

http://dx.doi.org/10.1016/j.jenvman.2015.02.033

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 μm) 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 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 μm 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 N_2 gas or ambient air, respectively. All other test conditions and sample preparation procedures were as described above.

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	N_2
Extraction period (h)	18	48

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 μm and 0.025 μm 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:

$$C_{colloidal} = C_{1.25\mu m} - C_{0.025\mu m} \tag{1}$$

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 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–H_2O and CdSe–H_2O system, the following species were considered:

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

ii) Thirteen tellurium or selenium species (X: Te, Se): X^{2-}, HX^-, H_2X, X_2^{2-}, X(s), X^{4+}, $XO_2(s)$, XO_3^{2-}, HXO_3^-, H_2XO_3, XO_4^{2-}, HXO_4^-, H_2XO_4.