Thermal detoxification and bloating of chromium(VI) with bentonite

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ABSTRACT
This study stabilizes and bloats Cr(VI)-sorbed bentonite by heating at high temperature. Cr leaching decreases with increasing temperatures. Heating the sample at 1100 °C results in a non-detectable Cr concentration in the leachate, equivalent to a Cr leaching percent less than 0.001% (i.e., Cr TCLP concentration < 0.018 mg of Cr L-1 of leachate). Morphology observed with a scanning electron microscopy indicates the occurrence of sintering of the sample heated at 1100 °C. The heated samples also show the occurrence of a vesicant process at 1100 °C. X-ray absorption spectroscopy results indicate that heating at 500 °C for 4 h can convert approximately 87% Cr(VI) into Cr(III) that is negligibly toxic; Cr2O3 was detected to be the most abundant Cr species. After heating at higher temperatures, namely 900–1100 °C, almost all doped Cr(VI) is reduced to Cr(III) as inferred from the height of the pre-edge peak of XANES spectra and/or from XANES simulation.

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1. Introduction

Despite the significant toxicity of Cr(VI), the use of Cr(VI) in industries is very intensive, ranging from leather tanning and plating to modern electronics manufacturing. Cr(VI) is carcino-genic and mutagenic [1] and considered as one of the 17 most threatening chemicals to human health, according to the US Environmental Protection Agency (USEPA) [2]. It is of high solubility and mobility. Efforts have frequently been made to chemically reduce Cr(VI) to Cr(III). Cr(III) is much less mobile and usually exists as chromium hydroxide precipitate in the natural environment [3].

Bentonite is extensively used as landfill lining to prevent the leachates from contaminating soil and underground water system. It consists of primarily montmorillonite. Using bentonite as a sorbent to remove heavy metals from wastewater is inexpensive compared with other methods, such as ion exchange, sorption by activated carbon, and membrane filtration [4,5]. Bentonite has been employed to remove Cr(VI) or other heavy metals from wastewater [4,5]. Further treatment of the Cr(VI)-containing bentonite is necessary for the environment's sake; it would be safer to chemically reduce Cr(VI) to Cr(III) prior to landfill or recycling. With respect to recycling, because of the vesicant properties of bentonite at elevated temperatures, the Cr(VI)-containing bentonite can be used, in a whole or partially, as a raw material to form a lightweight aggregate through sintering and vesicant processes at high temperatures. During these processes, Cr(VI) can be chemically reduced to Cr(III) which is characterized by great thermal resistance. Low bulk density of the lightweight aggregate always implies good noise and thermal insulations, and less weight loading in construction engineering.

Our previous studies have addressed the potential to use china clay and/or kaolinite as sorbents to immobilize Cr(VI) or other heavy metals under elevated temperatures [6–8]. Chromium silicate and chromium oxide are two main products resulting from chemical reduction of Cr(VI) at 500–1100 °C; both are resistant to leaching of toxicity characteristic leaching procedure (TCLP) [6,8]. Due to the lack of foaming constituents in china clay and kaolinite, the final products obtained by the sintering process are of high density. Therefore, these sorbents alone cannot be used to prepare lightweight aggregates.

Molecular-level information on chromium is very helpful in understanding Cr(VI) immobilization mechanisms, providing information needed for a long-term solution for environmental remediation and waste management [9]. X-ray absorption spectroscopy (XAS) can provide a direct, non-destructive measurement of the chromium oxidation state and molecular environment. It is an informative technique for investigating both bulk crystalline and non-crystalline samples.

Cr(VI) and Cr(III) can be easily distinguished from their pre-edge spectra. Only the former one is characterized by a strong pre-edge peak due to the transition of Cr 1s core electrons to its 3d orbital. This transition is allowed due to the lack of a center of inversion symmetry in the CrO4 tetrahedral structure [10,11]. The height or area of the pre-edge peak of a normalized sample
The spectrum is quantitatively proportional to the ratio of Cr(VI) to total Cr [11].

The objective of this research is to (i) investigate the extent of thermal immobilization of Cr(VI)-containing bentonite samples by the TCLP test [12], (ii) examine the change in the morphology of heated samples, and (iii) study the alteration of the chromium oxidation state in bentonite after heating. We expect to develop a technique to safely treat Cr(VI)-containing bentonite with heat. This technique can increase the potential for recycling the toxic samples as lightweight aggregate.

2. Materials and method

Expressed in oxide forms, the bentonite used in this study mainly consists of 61.26% SiO₂, 21.54% Al₂O₃, 6.97% MgO, 3.65% Fe₂O₃, 1.77% Na₂O, 1.25% CaO, 0.41% K₂O, 0.14% TiO₂, 0.06% P₂O₅, and 6.03% loss on ignition (LOI). The main difference between the bentonite and the previously used china clay [8] is that the china clay contains only 0.90% MgO and 3.50% LOI. After the heating at high temperatures, the china clay contracts in size, while the bentonite swells.

All chemicals used in this study are reagent grade. To prepare the Cr(VI)-containing bentonite, a mixture of 0.75 L of 0.513 M CrO₃ aqeous solution and 0.5 kg of dry bentonite powder (< 50 mesh size) was placed in a polyethylene bottle that rotated end-to-end at a speed of 30 revolution/min for 2 days. Then the mixture was de-moisturized at 105 °C for 3 days. The de-moisturized sample contains 37.1 mg of Cr g⁻¹ of sample. It was sequentially ground, mixed, and thermally treated by heating at 500–1100 °C for 4 h in stagnant air in a covered crucible, which was placed inside an electrically heated cubic oven. The heated samples were subjected to (i) chromium leaching test according to the TCLP method [12], (ii) morphology observation using a scanning microscope (SEM, XL-40 FE-SEM, Philips, Netherlands), and (iii) determination of the change in Cr oxidation state by the use of XAS.

The TCLP method is designed to determine the mobility of analytes in wastes under glacial acetic acid environment [12]. After the TCLP extraction, the slurry was pressure filtered. The filtrate was digested with HNO₃, filtered, and the Cr concentration in each TCLP leachate was determined in triplicate. The TCLP leachate concentration (unit: mg/L Cr) can be converted into a Cr leaching percentage by multiplying it with 20 L/kg and then dividing with 37.1 mg of Cr g⁻¹ of heated sample [12].

3. Results and discussion

Fig. 1 depicts the degree of Cr TCLP leaching, in terms of percent, from the Cr(VI)-containing bentonite samples heated at various temperatures. Heating the sample at higher temperature leads to considerably less Cr leaching. Compared with a previous report that has used china clay as a sorbent [8], the Cr leaching values from the 500–900 °C heated bentonites are always greater than the corresponding leaching values of the heated, Cr(VI)-containing, china clay. Cr leaching percent is 65.50 ± 0.90% for the sample dried at 105 °C; it remarkably decreased to 14.40 ± 0.01% for 500 °C sample, 2.17 ± 0.004% for 700 °C, 0.0800 ± 0.0004% for 900 °C, and less than 0.001% for the 1100 °C sample. Our previous report has demonstrated that the total Cr mass is conserved before and after such high-temperature heating [8], thus the decrease in Cr leaching in this study should not result from a loss of Cr vaporization at elevated temperatures.

Fig. 2 shows the SEM morphology from the samples heated at 105, 500, and 1100 °C. The 1100 °C sample morphology appears to be much smoother than the other two samples. This indicates an occurrence of sintering reaction at 1100 °C, thus we believe that sintering is partially responsible for the results of non-detectable Cr leaching (see Fig. 1). Furthermore, during the experimentation stage, only the 1100 °C sample was observed to show the vesicant phenomenon with an apparent particle density of 1.38 g cm⁻³; an obvious expansion in size was observed when the heated sample was removed from the heating unit at the end of heating. Note that sintered/bloated minerals with an apparent particle density <1.80 g cm⁻³ can be considered as lightweight aggregates for civil engineering purpose.

The simulations of the XANES for the heated bentonites with reference XANES spectra are shown in Fig. 3. The reference percentages resulting from the XANES simulation process are shown in each panel. The XANES spectra of the sample dried at 105 °C can be successfully modeled with 15% Cr(OH)₃+66% HCrO₄⁻+19% CrO₃. The 500 °C XANES can be satisfactorily fitted with 80% Cr₂O₃+7% Cr(OH)₃+13% CrO₃. Approximately 87% of the doped Cr(VI) is chemically decomposed into Cr(III) with a release of O₂ after the heating at 500 °C. Cr(OH)₃ exists in a smaller percent in the 500 °C sample than in the 105 °C sample, 7% versus 15%. This is attributed to the decomposition of Cr(OH)₃ into Cr₂O₃ and H₂O at a higher temperature.
Regarding the 900–1100 °C samples, Cr(OH)₃ is absent in both samples. The simulation for the 900 °C sample XANES is quite satisfactory and results in a Cr species distribution of 100% Cr₂O₃. However, the modeling of the 1100 °C XANES with the references is unsuccessful; note that the open-circle curve which represents 100% Cr₂O₃ is simply overlapped with the 1100 °C sample XANES for comparison, and the white-line region (i.e., approximately the region of 6006–6014 eV) is considerably different between the 1100 °C sample and Cr₂O₃. This implies that references other than Cr₂O₃, Cr(OH)₃, HCrO₄⁻, and CrO₃ are needed to improve the simulation. We believe that the needed references may be Cr₂O₃·(Al₂O₃)ₓ, Cr₂O₃·(MgO)ₓ, and/or others, but at present they are not commercially available. Although the simulation for the 1100 °C sample is not satisfactory, the 1100 °C sample XANES does show that the doped Cr(VI) has been chemically reduced to Cr(III) because the Cr(VI) pre-edge peak disappears.

4. Conclusion

Heating Cr(VI)-containing bentonite at higher temperature leads to considerably less Cr leaching with an acetic acid-based aqueous solution. After heating at 700–1100 °C for 4 h, Cr concentration in the TCLP leachates is < 5 mg of Cr L⁻¹ of leachate, which is the regulatory threshold set by the Taiwan Environmental Protection Administration. Only the sample heated at 1100 °C shows both the occurrence of sintering and vesicant processes, and its particle density is 1.38 g cm⁻³; thus this sample can be incorporated in cement to produce lightweight aggregate-containing cement for civil engineering usage.

Nearly 100% transformation of chromate to Cr(III) is observed for the 900 and 1100 °C samples. The Cr transformation, along with the sintering reaction, occurring at 1100 °C is suggested to be responsible for the extremely low Cr leaching from these heated samples.

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