Study of calcium/lead apatite structure type for stabilising heavy metals

Dong, Zhili; White, Timothy John; Wei, B.

2001

Dong, Z. L., Wei, B., & White, T. J. (2001). Study of Calcium/Lead Apatite Structure Type for Stabilising Heavy Metals. Materials Research Society Symposium Proceedings, 658..

<https://hdl.handle.net/10356/79928>

<https://doi.org/10.1557/PROC-658-GG6.33>

© 2000 Materials Research Society. This paper was published in Materials Research Society Symposium Proceedings and is made available as an electronic reprint (preprint) with permission of Materials Research Society. The paper can be found at the following DOI: <http://dx.doi.org/10.1557/PROC-658-GG6.33>. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 22:21:01 SGT

Study of Calcium/Lead Apatite Structure Type for Stabilising Heavy Metals

Z.L.Dong, B.Wei and T.J. White

Dept. Solid State Characterisation & Materials Processing, Environmental Technology Institute,
18 Nanyang Drive, Singapore 637723, SINGAPORE

ABSTRACT

(Ca_xPb_{10-x})(VO₄)₆F₂ apatites were synthesised and their microstructures were studied using powder X-ray diffraction, scanning electron microscopy and transmission electron microscopy before and after leach testing. X-ray diffraction showed that the apatites were hexagonal with $a \approx 10\text{\AA}$ and $c \approx 7\text{\AA}$. During the leach test, Pb was released into the solution more slowly than Ca, which is desirable as the immobilisation of Pb is of importance. The experimental results also showed that V was almost undetectable in the leaching test solutions. In the (Ca₇Pb₃)(VO₄)₆F₂ pellet, Ca and Pb distributions were not homogenous from one grain to another. Microstructural evidence from scanning electron microscopy revealed that the dissolution via development of etch pits began at grain boundaries and inside grains, and progressed faster in Ca rich regions. These results suggest that apatites of high Pb to Ca ratio are more durable.

INTRODUCTION

Solid Waste Incineration (SWI) processes generate bottom ash and fly ash, as well as flue gas. The fly ash normally contains heavy metal oxides, such as PbO and V₂O₅, and other hazardous compounds [1,2]. One way to reduce the impact of fly ash on the environment is to stabilise the toxic species before disposal. The tailored addition of extra materials can promote the formation of more durable structure-types, eg., olivine, apatite, spinel and anhydrite structures [2-5].

This investigation is focused on the formation of apatite structures containing the heavy metals Pb and V, and the leaching characteristics of the ceramic pellets. The results of the investigation can be applied not only to incinerator ash stabilisation, but also to other industrial solid wastes.

EXPERIMENTAL DETAILS

Apatites of composition (Ca_xPb_{10-x})(VO₄)₆F₂ were synthesised from AR grade CaO, CaF₂, V₂O₅ and PbO powder mixtures by firing at 800°C for more than 10 hours. The apatites so obtained were pressed into pellets and heat treated again at 800°C.

Leach tests were performed to determine the mechanism of dissolution and the leach rate of each element in the pellets. The leach solution used was TCLP prescribed acetic acid of pH 2.88. The concentrations of Pb, V and Ca released into solution were measured using wavelength dispersive X-ray fluorescence spectrometer (XRF) after periods of 3, 5 and 7 days. A Siemens D5005 X-ray diffractometer (XRD), JSM-5310LV scanning electron microscope (SEM) and

JEM-3010 transmission electron microscope (TEM) were used for structural characterisation prior to and after leach tests.

RESULTS AND DISCUSSION

Formation of apatite structure

Apatite is a general term for crystalline materials with the composition of $A_{10}(BO_4)_6X_2$. In this study, $(Ca_9Pb_1)(VO_4)_6F_2$, $(Ca_7Pb_3)(VO_4)_6F_2$ and $(Ca_5Pb_5)(VO_4)_6F_2$ pellets were obtained by firing the oxide mixtures at 800°C. SEM results revealed that higher Ca containing pellets tended to form two phases, whereas lower Ca content pellets yielded single-phase apatite. The backscattered electron images of the slightly polished pellet surfaces are shown in Figure 1.

Figure 1. Backscattered electron images from three different pellets: (a) $(Ca_5Pb_5)(VO_4)_6F_2$, (b) $(Ca_7Pb_3)(VO_4)_6F_2$, (c) $(Ca_9Pb_1)(VO_4)_6F_2$. The bright regions in (b) and (c) have higher Pb concentrations than the dark regions.

X-ray diffraction analysis revealed that the apatite structure formed using these heat treatment conditions. For the two-phase apatite sample, no split diffraction peaks could be detected as the compositional variations of these apatites were not large enough to give this effect. The XRD pattern and HRTEM image from apatite $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ with lattice parameters $a \approx 10\text{\AA}$ and $c \approx 7\text{\AA}$ are given in Figures 2 and 3 respectively. Rietveld simulation and refinement of the XRD pattern has been completed using a two-phase assemblage with each component having slightly different Ca/Pb ratios and lattice parameters [6].

Figure 2. Diffraction patterns from $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ pellet showing apatite structure.

Figure 3. HRTEM image taken from zone axis $[0001]$ of hexagonal $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$. The diffraction pattern was taken from the upper part of the image.

Leaching characteristics of apatite pellet

A leach test was performed on the $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ pellet (see Figure 4). The data indicated that leach losses of V and Pb were much slower than that of Ca. A possible explanation is that some solid phase(s) containing Pb and V might precipitate and the concentrations of the corresponding elements in the leach solution reduced, although it should be noted that precipitates were not observed by SEM. More accurate leach liquid analysis will be conducted for the other apatite pellets and the results will be presented in subsequent paper.

Figure 4. Concentrations of Ca, Pb and V in the solutions after different leaching intervals.

The microstructure of the same pellets after leaching was examined again using SEM (see Figure 5). For single-phase apatite $(\text{Ca}_5\text{Pb}_5)(\text{VO}_4)_6\text{F}_2$, etch pits were observed on the polished surface. Grain boundaries also dissolved preferentially. It was likely that the etch pits penetrated along particular crystallographic direction(s)/plane(s).

For the two-phase apatite sample $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$, the etch pits in the dark regions were already connected, so pull-out morphology was observed. The bright regions in the same apatite pellet (Figure 5 (b)) demonstrated similar etch pit morphology as the single-phase pellet (Figure 5(a)). The experimental evidence suggests that the Pb rich areas (bright regions) dissolved much more slowly than the Ca rich areas (black regions). Pb rich areas were more durable. Further work will be carried out with the aid of TEM to better understand the stabilisation mechanism for different toxic species.

Figure 5. SEM observation of pellet surfaces after leach test:
 (a) $(Ca_5Pb_5)(VO_4)_6F_2$, (b) $(Ca_7Pb_3)(VO_4)_6F_2$.

CONCLUSIONS

$Ca_xPb_{10-x}(VO_4)_6F_2$ apatite structure was formed by firing oxide mixtures at 800°C. During leach testing in acetic acid, Pb and V were extracted more slowly than Ca. Precipitation of Pb- and V-rich phases was not observed with SEM.

The dissolution rate is faster in Ca rich regions than in Pb rich regions. Apatites of high Pb to Ca ratio are more stable. The potential to accommodate more Pb in this type of apatite minimises the addition of CaO, which in turn reduces the volume of waste for final disposal.

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Dr. Karin Laursen for her assistance in XRF analysis and to ETI for supporting this project.

REFERENCES

1. S.Auer, H.J.Kuzel, H.Pollmann and F.Sorrentino, "Investigation on MSW fly ash treatment by reactive calcium aluminates and phases formed", *Cement and Concrete Res.*, **25** (6), 1347 (1995).
2. T.J.White and I.A.Toor, "Synthetic mineral immobilization technology for the stabilization of incinerator ashes", *The 1995 International Incineration Conference*, Seattle, May 1995.
3. J.V.Bothe Jr. and P.W.Brown, "Apatite formation in the $CaO-PbO-P_2O_5-H_2O$ system at $23^\circ \pm 1^\circ C$ ", *J. Am. Ceram. Soc.*, **83** (3), 612 (2000).

4. P.Zhang and J.A.Ryan, "Transformation of Pb(II) from cerrusite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH", *Environ. Sci. Technol.*, **33** (4), 625 (1999).
5. P.Zhang and J.A.Ryan, "Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite", *Environ. Sci. Technol.*, **33** (4), 618 (1999).
6. T.J.White, Z.L.Dong and B.Wei, "X-ray Rietveld simulation and refinement of calcium lead apatite system used for stabilization of toxic metals", to be published.