

The use of cement to control the mobility of heavy metals in wastes:

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Cement is often used to stabilise nuclear and non-nuclear wastes. The aim is to reduce the release of potential contaminants to the environment. These contaminants may be radionuclides or ionic species of metals and metalloid components. Understanding their binding in the cement matrix enables us to optimise prediction of the behaviour of cement/waste mixes.

Studies show that in hydrated cementitious matrices, metal mobility is generally low due to physical factors, such as a low permeability, and by geochemical binding within the cement matrix. There appear to be three basic types of binding mechanism. A metal ion may (i) be bound in the alkaline cement matrix as an oxide, mixed oxide or other solid phase, (ii) sorbed onto surfaces or (iii) be incorporated into hydrated cement minerals. The precipitation of heavy metal containing solid phases does seem to be a limiting factor with regard to the second and third mechanisms. However, for heavy metals that are sufficiently soluble in basic media, such as Zn, Pb or Cr(VI), incorporation in hydrated cement minerals appears to be significant.

Calcium silicate hydrate ($\text{CaOSiO}_2 \cdot x\text{H}_2\text{O}$ or CSH) is the most abundant component of hydrated portland cement (~60%), has a large capacity for ion uptake and is thus a prime candidate for heavy metal binding. Basic Ca sulphoaluminates such as monosulphate ($3\text{CaOAl}_2\text{O}_3\text{CaSO}_4 \cdot 12\text{H}_2\text{O}$) or ettringite ($3\text{CaOAl}_2\text{O}_3 \cdot 3(\text{CaSO}_4) \cdot 32\text{H}_2\text{O}$) also have a potential for heavy metal uptake. Their structures are relatively tolerant of substitution without a change in structure. A number of ions are reported to substitute at the different sites in ettringite, namely divalent cations such as Pb^{2+} , Cd^{2+} or Zn^{2+} for Ca^{2+} , trivalent cations such as Cr^{3+} , Ni^{3+} or Co^{3+} in place of Al^{3+} and diverse anions in exchange for SO_4^{2-} .

The different processes that control the solubility of heavy metal and metalloid ions in contact with cement minerals can be illustrated by the example of cement stabilised municipal solid waste incinerator air pollution control residues. Here it is probable that dissolved Zn concentrations are controlled by sorption to CSH. Less soluble heavy metal cations, such as Ni^{2+} and Cu^{2+} may be immobilised as $\text{Ni}(\text{OH})_2$ and CuO respectively, and the solubility of MoO_4^{2-} and WO_4^{2-} are probably controlled by their respective Ca metallates. Components that are highly soluble in the basic pH range, such as Pb(II), may be incorporated in CSH or ettringite.

The Thermal Stability of Hydrogen in Feldspars

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Introduction

Feldspars are the most common crustal minerals, and contain fluid inclusions and trace amounts of structural OH, H_2O , and NH_4^+ . Trace H in feldspars could be used as a record of fluid history, but to do this an understanding of the behavior of each species at temperatures of geologic interest is needed. Infrared (IR) spectroscopy is a sensitive method for determining speciation of H, and, when calibrated, can be used to determine the concentration of individual hydrous species. We investigated the thermal stability of structural OH and H_2O and fluid inclusions in feldspars from a variety of geological environments at 1 bar using IR spectroscopy.

Methods

For samples containing structural H, polarized IR spectra were taken parallel to principal optical directions on polished slabs. Unpolarized spectra were used for samples containing fluid inclusions. Polarized spectra were summed to determine total band area. Absolute concentrations of H were determined using the IR calibration from Johnson and Rossman (2001) for structural species and the absorption coefficient of water for fluid inclusions. Samples were dehydrated in air.

Results

The diffusion coefficient (D) of H at 1000°C in plagioclase containing structural OH is estimated to be $1\text{--}2 \times 10^{-12} \text{ m}^2/\text{s}$ using a one-dimensional diffusion model for an infinite slab. This is similar to the D ($2.2 \times 10^{-11} \text{ m}^2/\text{s}$) determined at 900°C for adularia containing structural H_2O (Kronenberg et al. 1996). The D determined for plagioclase suggests the retention of initial [OH] by volcanic feldspars could range from >90%–0% depending on the transport time (hours to weeks) during an eruption at 1000°C. Natural volcanic phenocrysts contain low but variable amounts of OH (0 to 300 ppm wt. H_2O).

Upon heating a pegmatitic albite from Brazil to 300°C, the intensity of a band due to fluid inclusions (3440 cm^{-1}) decreases and absorbance at 3050 cm^{-1} increases. No such transformation is observed in other feldspars. Fluid inclusion water is lost from plutonic feldspars by 700°C. The high concentration of fluid inclusions in plutonic feldspars (up to 2 wt% H_2O) is much larger than the concentration of structural OH in plagioclase or H_2O in microcline (up to 0.14 wt% H_2O). Fluid inclusions in plutonic feldspars must be principally derived from hydrothermal fluids.

References

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Kronenberg, A.K., Yund, R.A., and Rossman, G.R. (1996) *Geochim. Cosmochim. Acta* 60, 4075–4094.