

Crystal Chemistry of Trace Metals in Cementitious Hydraulic Binders

J. Rose, I. Moulin, A. Masion, J.Y. Bottero (CEREGE, France) and P.M. Bertsch (U. of Georgia)

Abstract No. rose9797

Beamline(s): X23A2

The use of hazardous waste as fuel for the kilns in the cement industry leads to an enrichment of the clinkers (cement) in heavy metals whose concentration can reach 2000 ppm [1]. To assess the environmental risks linked to the use of these materials, it is essential to study of the physico-chemical stability of these metals in hydrated hydraulic binders. Hydration of cements lead to the dissolution of the primary cement phases followed by the precipitation of new hydrated phases. Thus, the metals trapped in the anhydrous phases are also dissolved. Standard leaching tests performed on cements manufactured with hazardous waste have revealed low levels of soluble metals; however, the total metal release was dependent on cement and secondary hydrate phase composition [1]. Thus, to predict the long-term metal leaching behavior and associated environmental and human health risks associated with metal release, it is crucial to determine the crystallographic sites of the heavy metals in the clinker.

Our recent studies [2-5] coupling different spectroscopic techniques (NMR, XAS) enabled us to determine the crystallographic site of Pb and Zn in cement during a separate hydration of each phase constituting a cement. Lead has a high affinity for calcium silicate and ferro-aluminate phases (hydrated C3S and hydrated C4AF). In the case of the hydration of C3S, lead is incorporated within the matrix of the new mineral (CSH for Calcium Silicate Hydrates) through Si-O-Pb linkages [2-4]. In the case of hydrated C4AF Pb is directly linked to the mineral and Fe-O-Pb linkages have been detected[2]. For these two phases and due to the low Pb concentrations (2000 ppm), no cluster with a Pb-oxide like structure has been detected. In the case of Zn and calcium silicate interaction, it appears that Zn can be linked at the end of the silica chains constituting the CSH but also a certain amount of Zn can be incorporated within the Si tetrahedra chains during the hydration of C3S[2,5]. No special affinity has been observed between Zn and the Calcium aluminate phase. Small clusters with the hydroxyzincate mineral structure have been identified.

This study revealed the powerful nature of the combination of NMR and XAS to determine the crystallographic site of trace/dilute metal in hydrated cement phases.

Acknowledgments: We wish to acknowledge the helpful assistance of J. Woicik on X23A2.

References:

- [1] E.W. Kleppinger. "Cement clinker: an environmental sink for residues from hazardous waste treatment in cement kilns." *Waste Management*, 13(8), 553-572, 1993.
- [2] I. Moulin. "Spéciation de Pb, Cu, Zn, Cr (III) et Cr(VI) dans les hydrates de ciment". Ph.D. Thesis, University Aix-Marseille III (France), 1999.
- [3] I. Moulin, W.E.E. Stone, J. Sanz, J.Y. Bottero, F. Mosnier and C. Haehnel. "Pb and Zn retention during hydration of C3S: a study by sorption isotherms and ²⁹Si NMR Spectroscopy". *Langmuir*, 15, 2829-2835, 1999.
- [4] J. Rose, I. Moulin, J.L. Hazemann, A. Masion, P.M. Bertsch, J.Y. Bottero, F. Mosnier and C. Haehnel. "X-ray absorption spectroscopy study of immobilization processes for heavy metals in calcium-silicate-hydrates : 1. Case of lead." *Langmuir*, *In press*.
- [5] J. Rose, I. Moulin, A. Masion, P.M. Bertsch, J.Y. Bottero, F. Mosnier and C. Haehnel. "X-ray absorption spectroscopy study of immobilization processes for heavy metals in calcium-silicate-hydrates : 2. Case of zinc." *Langmuir*, *Submitted*.