U and Pb isotope ratios in manganese nodules by MC-ICP-MS

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Isotope ratios of U and Pb were measured in two groups of manganese nodules from the Cambrian Timna Formation, Israel. The division into two groups was based on petrographical, major and trace element geochemistry (Bar-Matthews, 1987). The first group (A) of nodules is composed mainly of pyrolusite and hollandite, with Mn, Ba, Pb and U concentrations of 45-50%, 1-2.5%, 0.1-0.8% and 500-3500 ppm respectively. The second group (B) was formed by alteration of the former, and contains mainly coronadaite, with Mn, Ba, Pb, and U concentrations of 9-30%, 0.2-5%, 1-2.5% and 60-150 ppm respectively.

Samples were dissolved in $HNO_3 + H_2O_2$ and measurements were obtained on the acid soluble fraction using the "Nu Instrument" MC-ICP-MS. Two sets of analyses were performed, with and without matrix separation. For Pb analyses, measurements were carried out with Meinhard nebulizer, and thallium ($^{205}Tl/^{203}Tl=2.3875$) was added to enable correction for mass discrimination. U was measured using an Aridus system with microconcentric nebulizer (MCN). Mass discrimination was corrected using U internal standard $^{238}U/^{235}U=137.88$.

The results obtained from the matrix-separated and unseparated samples were identical, with a slightly better (2σ) precision for the separated sample of $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ 60-80ppm; $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ~30ppm and $^{234}U/^{238}U$ 0.2-0.4%.

The isotopic results support the distinction between the two groups. On a $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot the nodules from group A have higher and variable ratios compared with the nodules of group B. Both groups fall probably on a mixing line (Fig. 1). $^{234}U/^{238}U$ in group A nodules fall close to the equilibrium values of 54.887 (Cheng et al., 2000), whereas in group B nodules the values fall usually below this value.
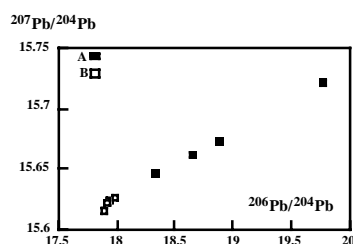
References

Bar-Matthews M., (1987) *Geol. Mag* **124,** 211-229
Cheng H. et al., (2000) *Chem. Geol.* **169,** 17-33

Use of surface analysis, solid-state spectroscopy, and geochemical modelling to characterize phosphate-stabilized wastes

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Chemical stabilization of inorganic wastes can reduce leachability of heavy metals through formation of geochemically stable and insoluble precipitates. Understanding the immobilization reaction, the reaction products, and the leaching behaviour of the treated material is crucial for a mechanistic understanding of the process.

Our group has focused on phosphate stabilization of various MSW ashes, electric arc furnace dusts, smelter dusts, mine tailings, and metal-contaminated sediments. The approach typically characterizes both the untreated and the treated wastes before and after aggressive leaching with the Dutch NEN 7341 Availability Leach Test. A variety of bulk spectroscopic techniques (petrography, SEM-WDS, SEM-EDAX, XRD, STEM-XRM, MAS-NMR and EXAFS) are used to characterize untreated residues and metal phosphate reaction products. XPS is particularly useful in identifying surface species where leaching first occurs. SIMS can identify reaction mechanisms (sorption, surface precipitation to pre-existing phases, discrete phase precipitation) via depth profiling of discrete reactant particle agglomerates. pH-static leaching coupled with the geochemical thermodynamic equilibrium modelling with MINTEQA2 can confirm chemical stabilization and solid phase control of leaching. MINTEQA2 databases have been extensively modified to include many metal phosphate solids and ideal solid solutions for better applicability.

Immobilization mechanisms almost always involve precipitation of discrete metal phosphate crystalline solids or solid solutions. Apatite family (e.g., $Ca_5(PO_4)_3OH$) minerals for Cd and Pb and tertiary metal phosphates (e.g. $Zn_3(PO_4)_2$) for Zn, Cu, and Cd are typical reaction products; these phases are very insoluble and are present after the treated residues have been subjected to aggressive leaching. Work is ongoing on the application of apatite-based reactive barriers for waste containment and plume interception.