Radioiodine Speciation in Cementitious Environments

Daniel I. Kaplan[1], Chen Xu[2], Peng Lin[2], Dien Li[1], Kathleen Schwehr[2], Kazuya Tanaka[3], Toshihiko Ohnuki[4], Peter H. Santschi[2]

[1] Savannah River National Laboratory, Aiken, South Carolina 29808, United States
[2] Department of Marine Science, Texas A & M University at Galveston, Galveston, Texas 77553, United States
[3] Japan Atomic Energy Agency, Ibaraki, Japan
[4] Tokyo Institute of Technology, Tokyo, Japan

Iodine-129 is the key risk driver in many existing low-level waste cementitious waste repositories. The objective of this study was to determine iodine speciation in cementitious materials (cement/fly ash) with slag (Grout$_{+slag}$) and without slag (Grout$_{-slag}$) and its impact on iodine immobilization. When iodide (I^-) or iodate (IO_3^-) was added to the Grout$_{-slag}$, >50% of the desorbed iodine transformed into organo-iodine (org-I_{aq}). This transition was undetectable in the Grout$_{+slag}$ samples. Fly ash is a likely source for the organic carbon (~1 wt-% is total organic carbon). When 4-iodoaniline (a proxy for org-I) was added to either grout sample, about 40% of the desorbed iodine had transformed into IO_3^- and 10% into I^-. Desorption K_d values ([I_{solid}]/[I_{aq}]) for Grout$_{-slag}$ amended with: I^- was 6.1 L/kg, iodate was 30.6 L/kg, and organoiodine was 32.3 L/kg. Desorption K_d values for Grout$_{+slag}$ samples were consistently greater than those for the Grout$_{-slag}$ samples. Grout$_{+slag}$ amended with: I^- was 7.5 L/kg, iodate was 121.8 L/kg, and organoiodine was 42.1 L/kg. Iodine K-edge XAS analyses of the solids revealed essentially no iodine speciation transformations after a 1-month curing time, irrespective of whether slag was or was not included in the grout mix. The differences in iodine speciation between solid and aqueous phase may in part be attributed to the analyses describing two different fractions that are likely not in equilibrium. The aqueous iodine, the much smaller fraction, would be much more prone to speciation transformations induced by aqueous chemical conditions. A majority of the solid phase iodine appears to be incorporated in the grout mineral structure, presumably in the sulfate or Ca-SiO_4-hydrate phases, which would limit speciation changes in response to the aqueous phase chemistry. Together, these studies of cementitious materials demonstrate for the first time, that: 1) the form that aqueous iodine is added to the dry mix of grout, impacts immobilization, 2) iodine adsorption testing underestimates actual desorption rates, and 3) a large fraction of iodine may be strongly immobilized as part of the grout mineral structure.