Abstract

Recently, iron slag and coal fly ash materials which are by-products from steelmaking and power industries, respectively are widely recycled as construction materials. However, these alkaline wastes could generate alkaline pore water and source of hazardous anions such as arsenic and selenium during the weathering and internal dissolution of the source material. During the hydration of these alkaline materials, Ca-bearing minerals such as ettringite and hydrocalumite, even though they can act as major sorbing solids for anionic species, they are only stable at alkaline condition and cannot ensure the long-term immobilization of toxic anions. Due to this paucity of stable mineralogical host for anionic species during the chemical weathering of alkaline waste, the need to develop a novel technology in limiting the leachability of toxic elements from the source materials is necessary.

Chapter 1 discusses the background and research objectives of this study and the related literatures which support the basis of the experiments undertaken. Natural attenuation of anionic species such as arsenate in antigorite, borate in brucite and serpentine phases and silicate in hydrotalcite minerals were reported in several investigations. These Mg-bearing minerals are stable in a wide range of pH compared to Ca-bearing minerals discussed previously. The need to investigate the generation of these minerals as major sorbing solids for anions during the use and disposal of alkaline waste materials by controlling their pore water chemistry must be considered. On the other hand, the initially very high pH and the rapid neutralization of slag and coal fly ash during weathering could lead to the observed widespread formation of amorphous aluminosilicates since neutralization reduces the solubility of Al and Si. This condition will promote further the precipitation of these constituents in the pore water solutions. Hence, the role of these amorphous phases as chemical barriers for anionic species must be investigated as well. In this context, the aim of this study is to determine the ideal pore water chemistry that can generate effective anion scavengers during the weathering of alkaline wastes at low temperature. The generation of various mineral phases in Mg-Si-Al at alkaline condition and Si-Al system at circum-neutral pH conditions and their geochemical interaction with arsenate As(V) and selenate Se(VI) were investigated in order to ensure the safe removal and encapsulation of toxic anions during the entire utilization and disposal of alkaline waste materials.

In Chapter 2, the general importance of various mineral phases formed at different Mg-Si-Al ratios in ambient condition and their corresponding sorption behavior of arsenate at hyperalkaline condition was examined. The coprecipitation and surface adsorption behavior of arsenate in the mineral phases formed was evaluated and compared in order to determine whether arsenic can be irreversibly fixed within the mineral structure. In Mg-Si-Al system, various mineral phases were generated at hyperalkaline pH condition such as amorphous material, hydrotalcite, smectite, brucite, serpentine and gibbsite and their relative formation was mainly influenced by the Mg, Si and Al concentration. The interaction of these mineral phases with arsenate revealed that only hydrotalcite and serpentine formed at low Si ratio showed high uptake capacity and irreversible fraction of sorbed arsenate.

Chapter 3 presents the extent to which arsenate and selenate can be taken up by Mg-bearing minerals with different Mg/Al ratios under low Si concentration during and after mineral formation considering the corresponding effects of temperature and initial As and Se concentration in their sorption behavior. The sorption mechanisms of arsenate and selenate were examined by XAFS analysis to give account of their local coordination environment. The experimental results indicated that the sorption capacity and irreversibility of arsenic with high Al-content hydrotalcite and serpentine phases increased significantly at higher temperature. The irreversible fraction of arsenic was mainly retained by inner-sphere complex with Mg in the octahedral site for brucite, hydrotalcite and serpentine phases though Al as fit cannot be excluded as well. The probability for arsenate to replace silicate in the tetrahedral site of serpentine phases may also contribute for the irreversibility of arsenic retention. On the other hand, selenate sorption was much lower compared to arsenate and showed decreasing removal efficiency with temperature and mainly retained by outer-sphere complexation. The observed smaller amount of selenate irreversibility in high Al content hydrotalcite and serpentine phases could
be attributed to the increase in the layer charge as Al substitutes for Mg in the octahedral site for hydrotalcite and serpentine which leads to its higher affinity.

In Chapter 4, the results of a preliminary study in controlling the pore water chemistry of coal fly ash and granulated blast furnace slag by MgO addition to induce the precipitation of hydrotalcite/serpentine with ideal Mg/Al ratio was investigated in order to confirm the ideal pore water chemistry obtained in the previous experiments. Arsenate extraction experiments were also conducted to determine if the formation of hydrotalcite or serpentine after the mineralogical transformation of slag and coal fly ash could lessen the leachability of arsenic during hydration. Based on the results, significant decrease in the amount of leached arsenic from TFA and GBFS after MgO addition was observed. The formation of secondary hydrotalcite phases after hydration experiments could possible account for arsenic immobilization.

Chapter 5 takes in to consideration the effect of Al/Si ratio on the formation of amorphous and short-range ordered minerals and uptake of arsenate by these minerals phases at circum-neutral pH condition. The results revealed that only allophane-like materials formed at relatively lower Si/Al ratio showed high sorption capacity and irreversible fraction for arsenate. The results of XAFS analysis showed that arsenate was retained by allophane via inner-sphere complexation. The irreversible fraction of sorbed arsenate by allophane could be attributed to the possibility of arsenate incorporation by replacing Si in the tetrahedral sheet of allophane along the defect sites and the inner-sphere complexation of arsenate on the allophane surface.

In chapter 6, the role of allophane in controlling the mobility of arsenate and selenate considering the effect of its Si/Al ratio was evaluated. The results showed that allophane-like materials exhibited high affinity for arsenate compared to selenate. Only arsenate showed significant irreversible fraction supporting its inner-sphere complexation with the aluminol group while selenate was mainly retained via outer-sphere complexation which is rather weak in controlling selenate mobility at circum-neutral pH condition.

Chapter 7 presents the summary and concluding remarks as well as a short outlook for future necessities and suggestions of research. In overall, this study provided the bases for the development of novel remediation method for the long-term sequestration of hazardous oxyanions such as arsenate and selenate during the entire utilization and disposal of slag and coal fly ash materials as well as in alkaline waste disposal environment by Mg-bearing minerals. The control of the pore water chemistry of the source materials to generate anion scavengers particularly hydrotalcite (in alkaline condition) and allophane (in near neutral pH condition) with ideal Mg, Si and Al ratio must be considered to ensure the safety removal and encapsulation of toxic anions. In order to further develop and apply this method using real alkaline waste materials under actual environmental conditions, the major aspects that needs to be considered are the conduct of column experiments which is closer to actual environmental condition, the use of thermodynamic modeling to calculate the saturation indices in alkaline waste pore solution and the development of a geochemical model to determine the rate of consumption of alkaline waste materials so that the evolution of the solid phase assemblage and pore solution during the weathering of alkaline waste can be controlled and predicted.