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Leaching Behavior of Coal Combustion Products and the Environmental Implication in Road Construction

by

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| 16. Abstract The use of coal fly ash in road base and sub-base applications can provide better properties and performance, and is superior to it being otherwise disposed and becoming a possible environmental liability. Understanding the metal leaching behavior for various fly ashes can help the construction industry and the energy industry in selecting the environmentally benign fly ash for road construction and for other beneficial use applications, and determining the long term environmental impact of fly ash during road construction. Coal fly ash contains many regulated cationic and oxyanionic elements such as antimony, arsenic, barium, boron, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, and selenium. Due to the implantation of several new air emission control regulations, future fly ash may contain elevated concentrations of volatile trace elements especially oxyanionic elements. Since oxyanionic elements have greater mobility in the environment, being less studied previously, and are generally more toxic than cationic elements, understanding the leaching behavior of oxyanionic elements from fly ash is significant in determining the potential environmental impact of fly ash during disposal or beneficial use, selecting the appropriate fly ash for road construction, and developing methods to control the leaching of oxyanionic elements. This research becomes more urgent due to the implementation of more stringent arsenic standards in drinking water that will become effective in January 2006. This research will focus on the leaching behavior of 6 major oxyanionic elements, antimony, arsenic, boron, chromium, molybdenum, and selenium, for various fly ashes under different management scenarios, using both batch and column experiments. Mathematical models will be developed to quantify the leaching behavior of these elements. Speciation of these oxyanionic elements will be determined using the most advanced Perkin-Elmer HPLC-ICP-MS system available at MST. | | | |
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1. Sample collection and characterization:

Two samples were collected and characterized: Ash NRT #169 and #170. The loss-on-ignition (LOI) and moisture content were measured based on the gravimetric method. The LOI was based on the weight loss at 550 °C for samples dried at 103 °C. All measurement were conducted with 3 replicates, at the mean is reported.

The total composition of major elements and some trace elements for these two samples were analyzed with XRF (X-LAB 2000, SPECTRO Analytical Instruments GmbH & Co. KG). The detection limit of XRF was approximately 10 ppm (mg/kg). Those elements undetectable with XRF and those lighter than Na (including Cd, Hg, B, Be and Li) were analyzed with complete acid digestion followed by ICP-OES, ICP-MS or mercury analyzer.

Complete digestion method was developed for ash digestion, using Multiwave 3000 (Anton Paar USA). The results for standard ash 1633b were in the acceptable range.

2. Equilibrium based assessment:

Leaching of major and trace cationic elements (Ca, Al, Si, Mg, Fe, K, Na, Sr, Mn, Ba, Zn, Ni, Cu, Cr, Co, Be, Pb, Tl, Cd and Ag) and anionic elements (B, V, Mo, Se, As and Sb) under different pH conditions were determined based on the batch method. Ca displayed the highest leachability among all the elements, partially due to the high Ca content of these ashes. The sharp decrease of Ca concentration at pH greater than 12 may be caused by precipitation of $\text{Ca}(\text{OH})_2$. The three major elements Al, Si and Fe showed a typical leaching behavior as cationic metals. Their leaching generally was negligible at alkaline pH conditions, but increased significantly as pH is decreased to below certain level, which was 4 here for these three elements. Similar leaching behavior was observed for other elements including Mn, Zn, Cu, Co, Cr, Pb, Be, Tl and Cd. The remarkable release of these elements at low pH might be caused by not only surface desorption, but also by acid dissolution, because significant amount of acid was used to reduce pH for these two ashes.

The leaching results of K and Na indicated that they were in soluble phase in entire pH range, and the sharp increase at lowest pH was caused by particle dissolution, similarly with Li, Re, Mg and Ba. However Mg and Ba concentration were decreased at high pH, which might be due to the precipitation of $\text{Mg}(\text{OH})_2$ and BaSO_4 . Re concentration in solution was very low. Both Ni and Sr leaching decreased with increase of pH, but not as low as other cationic metals at high pH conditions. Ag displayed the least leaching potential (< 10 ug/L). For most cationic elements, ash NRT #169 exhibited much higher leaching potential than NRT #170.

B has the highest leachability among the oxyanionic elements. Its leaching slightly increased with decrease of pH, and a sharp increase was observed at the lowest pH point. All other five anionic elements shown exhibited similar leaching behavior, with a minimum release in pH range between 4 and 6, and increased release at lower and higher pH conditions.

The leaching results of other anions showed that sulfate concentration in leachate was much higher than chloride. For ash NRT #169, the concentrations of both sulfate and chloride kept consistent at neutral and alkaline pHs. However, when pH was greater than 11, chloride concentration started decreasing and sulfate concentration started increasing. Ash NRT #170 showed a similar trend in the same pH range, except that both anions displayed an increased concentration below pH 5. Fluoride showed the lowest leachability among the three anions, which was less than 10 ppm at all pHs. Fluoride leaching from ash NRT #170 followed the same trend with sulfate. Ash NRT #169 performed similarly at acidic and neutral pH, but demonstrated a sharp decrease of fluoride concentration as pH was elevated from 11 to 12, which may be due to coprecipitation.

Mercury leaching results from two ashes indicated that the maximum leaching concentration for ash NRT # 169 was ten times higher than that of ash NRT #170, although both were below 200 ng/L. TDS concentrations in fly ash leachates as a function of pH were determined. The variation of TDS with pH followed exactly the same trend with that of Ca, indicating that calcium salt was the primary component in total dissolved solids.

The TOC in fly ash leachate was analyzed using TOC5050A (SHIMADZU Corporation). Considering the samples had high IC and very low purgeable organic carbon, TOC concentrations were actually determined by measuring NPOC (Non-Purgeable Organic Carbon). Samples were acidified by adding HCl to pH 2 to 3, CO₂ free air was sparged through the sample to eliminate the IC component. The TC remaining in the sample afterwards was measured to determine total organic carbon. TOC concentration in the leachate was within the range of 1 mg/L to 5 mg/L at various pH conditions. TOC leaching was enhanced at both low and high pHs. For ash NRT #169, change of S/L ratio has no significant effect on the TOC leaching, while ash NRT #170 displayed markedly increased TOC release at S/L of 1:5.

Metal leaching under different S/L ratios at natural pH (12.5 for ash NRT #169 and 12.2 for NRT #170) showed that, among major elements (in ppm level), Ca, K, Na, B and Sr have higher concentrations compared with others. Among the trace elements (in ppb level), Cr, Mo and Ba have higher concentrations. For some elements, the soluble concentration increased with increase of S/L ratio, such as B, K, Na, Sr, Mo, Ba and Se. This may be because these elements tend to be in soluble phase at the natural pH condition. Other elements showed an opposite trend, such as As and V. This may be caused by the decrease of other elements which can form precipitation with them. Other elements have relatively constant concentration, such as Ca and Al, which may indicate there leaching is a dissolution controlled process.