Chemical reactions of bottom ash with CO₂-saturated water (TVA-Test)

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The TVA test was created by the Federal Office for the Environment for the classification of waste materials according to the legislation "TVA" (BAFU 1999), which supplies threshold values for several toxic organic and inorganic constituents. The batch eluate test is performed in two parts. Anionic constituents are extracted in pure water, whereas cations, especially heavy metals, are extracted using CO_2 -saturated water. The water is continuously flushed with gaseous carbon dioxide, so that the system is continuously at equilibrium with CO_2 . The added carbonic acid lowers the pH-value of pure water to 4 and to about 6.5 for municipal solid waste incineration (MSWI) bottom ash samples (the solid to liquid ratio is 1:10). The pH of MSWI bottom ash extracted with distilled water yields typical values of 11. In this study, the role of carbonic acid was investigated by means of experimental work and by geochemical modelling using PHREEQC (Parkhurst and Appelo 1999). Two titration experiments with bottom ash samples were performed, using different acids with the same pH-value of 4: CO_2 -saturated water (carbonic acid) and 10^{-4} M nitric acid (HNO₃).

Even if CO_2 -saturated water is a weak acid, it is able to lower the pH-buffering capacity of the bottom ash eluate much stronger than nitric acid. 50 ml of CO_2 -saturated water per gram of bottom ash is sufficient to lower the pH-value down to 6.8. By adding 50 ml/g 10^{-4} M HNO₃ to the sample, the pH-value decreases only to about 9.6.

The reasons for this behaviour are the provoked carbonation reactions of pHcontrolling phases like ettringite, hydrocalumite, portlandite and amorphous phases by CO₂. Nitric acid on the other hand decomposes these phases completely and they buffer the pH-value during dissolution.

PHREEQC modelling showed, that due to the large input of CO_2 carbonate phases become oversaturated and precipitate. This effect is strongest when stopping the CO_2 -flux after the test, because of the increasing pH-value that occurs while the CO_2 starts to degas. The precipitation of carbonates is favoured by low pressure and therefore attention has to be paid while filtrating the eluate. Further, immediate acidification of the eluate avoids carbonate precipitation due to CO_2 -degassing.

In the experiment it was observed, that calcite starts to precipitate just after filtrating the eluate. It incorporates large amounts of heavy metals like Zn, Cu, Pb and Cd, lowering the concentrations in the eluate.

For comparison column experiments of several samples (bottom ash and filter ash) were performed, running for several weeks. The solid to liquid ratio was kept equal to the TVA-test (1:10 per day). Data of column test experiments are better indicators for the leaching behaviour of waste material in deposits than batch experiments. However, the TVA test data of the same samples showed, that the heavily contaminated samples dissolved likewise more heavy metals and that the overall ranking equals that of the column tests.

REFERENCES

Bundesamt für Umwelt (BAFU) 1990: Technische Verordnung über Abfälle (TVA). Parkhurst, D.L. and Appello C.A.J. 1999: User's guide to PHREEQC (version 2)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geol. Surv. Water Resour. Inv. Rep. 99-4259, 312pp.