

Potential groundwater contamination from pulverised fuel ash (PFA)

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In coal-fired power stations the ash produced either falls to the base of the furnace (furnace bottom ash, FBA) or is carried through the combustion chambers as fine-grained particulate matter (pulverised fuel ash, PFA). Approximately 80% of the ash produced is PFA. Both FBA and PFA are used in the construction industry but there is an excess production of PFA necessitating disposal in lagoons, land-fill sites and mounds. In 1990 48.6×10^6 tonnes of coal were used in UK power stations (Central Statistical Office 1992) producing about 10×10^6 tonnes of PFA, just over half of which was not marketed. In the future there may be less PFA in the UK, to be disposed of and disposal sites are carefully engineered to reduce the risk of groundwater contamination. However, on older disposal sites there is the possibility of long-term weathering reactions influencing groundwater composition. It is this aspect which has been of particular interest to us. Furthermore, elsewhere in the World the production of coal for power generation is rapidly increasing, particularly in China and India, and there is the threat of both short and long term weathering reactions adversely influencing groundwater composition.

The chemical composition of PFA is similar in some respects to the normal mudrocks associated with coals. This is because the same detrital minerals are present in the coal. In addition, however, there are elements associated with the organic matter and the diagenetic minerals, which means that some elements are concentrated greatly in excess of the background detrital levels.

PFA consists of minerals, glass and sublimates. Quartz, mullite and hematite/magnetite are the main minerals present. Reaction rates involving these minerals in groundwater systems will generally be slow. Reaction rates for the aluminosilicate glass will be faster and the sublimates could be readily soluble. Thus not only are elements concentrated in PFA but elements are associated with reactive phases.

The potential impact of PFA on groundwaters has been recognised for a number of years. Column and batch leaching studies have been undertaken in the laboratory to simulate the

natural environment (van der Sloot *et al.*, 1982; Roy and Griffin, 1984; Fruchter *et al.*, 1990). Field based studies have mainly concentrated on PFA lagoons because of the high initial water content and the rapid release of elements into solution (Dreesen *et al.*, 1977; Talbot *et al.*, 1978). Fewer studies have involved PFA mounds and particularly paying attention to the longer term changes. This has been the focus of the present work.

The study is based on a PFA mound adjacent to a major UK power station. The mound is constructed by lateral tipping onto a permeable layer of FBA overlying impermeable boulder clay. As the mound reaches the planned height top soil is added and the land is returned to agricultural use. It is therefore possible to sample PFA on the mound dating back to 1975. PFA samples were taken from a number of boreholes down to a depth of approximately 4 m. Borehole samples were spun in the laboratory on a high-speed centrifuge to remove porewaters which were analysed by a combination of AA (flame and furnace) ICP-AES and Dionex ion chromatography. Not only are the concentrations of interest, but also how concentrations vary as a function of depth. Increasing concentrations with depth are indicative of continued reaction between PFA and the infiltrating porewater. The achievement of constant concentrations with depth provides evidence of equilibrium, whereas decreasing concentrations could be due to the introduction of an element from an external source. Analyses of the PFA itself provide confirmation of the porewater trends. Loss of an element in solution is detected in the whole rock analysis provided that a significant fraction has been removed in the time available.

The weathered PFA from the disposal site has been compared with the fresh PFA using X-ray diffraction and the SEM to detect changes attributable to weathering. Substantial differences have not been detected between fresh PFA and PFA emplaced in 1978. Reaction products were not detected with certainty, although a reduction in the proportion of the sub-micron fraction was noted in the weathered ash.

Equilibrium calculations have been performed

TABLE 1. Porewater analysis from PFA emplaced in 1975 and subjected to natural weathering on the PFA disposal mound. The analysis shown is for a sample at a depth of 4.0 m within the PFA mound (Element concentrations mg/l and *µg/l, Eh: mv)

Ca	Mg	Na	K	Fe	Al	Si	B	Ba	Cd	Co	Cr
608	363	52	137	0.09	0.03	0.2	13	0.1	0.05	0.10	0.15
Cu	Li	Mn	Ni	Pb	Sr	Zn	Mo	As*	Se*	Hg*	Cl
0.01	1.6	0.00	0.13	0.59	2.4	0.02	2.5	80	37	< 5.0	145
NO ₃	SO ₄	pH	Eh								
634	4023	8.26	409								

on the porewater data using WATEQ4F (Ball *et al.* 1987). The porewater Ca and SO₄ concentrations reach constant values with depth and the equilibrium calculations confirm that saturation with respect to gypsum has been achieved. Concentrations of Ba and Sr also achieve constant values with depth and coprecipitation of these elements with the SO₄ is one possibility. The calculations also suggest that aqueous Cu is near to equilibrium with a crystalline Cu oxide. In general, however, few of the elements in the porewaters achieve constant values with depth, implying lack of equilibrium with a solid phase and this is confirmed by the equilibrium calculations. Some attenuation of elements could be achieved by adsorption reactions with Fe-Mn oxides and secondary phases; that is the mobility of some elements may be restricted by reaction within the PFA.

A porewater analysis from a PFA sample at a depth of 4.0 m in a borehole from the disposal mound is given on Table 1. This PFA was deposited in 1975. These analyses therefore provide an indication of likely contribution to groundwater from a thin blanket of older PFA. Concentrations for many elements do increase as a function of depth in the Barlow Mound and concentrations could be extrapolated for greater depths provided that equilibrium calculations signified undersaturation. However, concentrations in solution will be not only a function of time but also of the infiltration rate.

References

- Ball, J. W., Nordstrom, D. K. and Zachman, D. K. (1987) WATEQ4F-A personal computer FORTRAN translation of the geochemical model WATEQ2 with revised database. *U.S. Geological Survey Open-file report* 87-50., 108p.
- Central Statistical Office. 1992. Annual abstract of statistics.
- Dreesen, D. R., Gladney, E. S., Owens, J. W., Perkins, B. L., Wienke, C. L. and Wangen, L. E. (1977) Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from a coal fired power plant. *Environmental Science & Technology*, **10**, 1017-9.
- Fruchter, J. S., Rai, D. and Zachara, J. M. (1990) Identification of solubility-controlling solid phases in a large fly ash field lysimeter. *Environmental Science & Technology*, **24**, 1173-9.
- Roy, W. R. and Griffin, R. A. (1984) Illinois basin coal fly ashes. 2. Equilibria relationships and qualitative modeling of ash-water reactions. *Environmental Science & Technology*, **18**, 739-42.
- Talbot, R. W., Anderson, M. A. and Andren, A. W. (1978) Qualitative model of heterogeneous equilibria in fly ash pond. *Environmental Science & Technology*, **12**, 1056-61.
- van der Sloot, H. A., Wijkstra, J., Van dal, A., Das, H. A., Slania, J., Dekkers, J. J. and Wals, G. D. (1982) Leaching of trace elements from coal solid waste. ECN-120., *Netherlands Energy Research Foundation*. 201p.