

**SPECIATION OF
ARSENIC AND SELENIUM DURING
LEACHING OF FLY ASH**

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Omslag : Vliegaswolk bij uitbarsting Etna 1989
Foto: Dineke Sall

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**SPECIATIE VAN
ARSEEN EN SELEEN GEDURENDE DE
UITLOGING VAN VliegAS**

(met een samenvatting van het Nederlands)

PROEFSCHRIFT

Ter verkrijging van de graad van doctor aan de Universiteit Utrecht op
gezag van de Rector Magnificus, Prof. dr. J.A. van Ginkel, ingevolge het
besluit van het College van Dekanen in het openbaar te verdedigen op
maandag 4 december 1995 des namiddags te 12.45 uur

door

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geboren op 26 mei 1965 te Utrecht

Promotor: Prof. Dr. C.H. van der Weijden
Co-promotor: Dr. R.N.J. Comans

Voor Hans
In herinnering aan Jetty

*'Hier wordt gener waarheid gezegd,'
riep professor Prlwytzkofski uitzinnig.
'Hier wordt der wetenschap gepleegd.'*

Maarten Toonder
De gekikkerde vorst, 1977

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SPECIATION OF ARSENIC AND SELENIUM DURING LEACHING OF FLY ASH

Introduction and overview

CHAPTER 1

SPECIATION OF AS AND SE DURING LEACHING OF FLY ASH Introduction and overview*

Introduction

Combustion residues, such as coal fly ash and municipal solid waste incinerator (MSWI) bottom ash, are a subject of environmental concern because they contain high concentrations of hazardous elements (CARLSON AND ADRIANO, 1993; THEIS AND GARNER, 1990). Large amounts of combustion residues are produced worldwide. For example, in 1992 360 millions of tons of coal fly ash were produced worldwide (MANZ, 1995). Combustion residues are mostly disposed of, but they are also used in construction materials (MANZ, 1995). In order to protect the environment, disposal or usage must be carried out under safe conditions. Therefore, it is necessary to quantify the potential release of hazardous components under different environmental circumstances.

This thesis focuses on the leaching of As and Se from coal fly ash. As and Se are in principle toxic elements, which leach in relatively high quantities from combustion residues (MATTIGOD *et al.*, 1990). In this chapter, the leaching processes of combustion residues are first discussed in general. Secondly, the major chemistry and mineralogy of coal fly ash are considered. This is followed by a brief review of the environmental chemistry of As and Se. Finally, the behaviour of As and Se in fly ash as studied in this thesis is described and an overview of the following chapters is given.

*Partly Published as: VAN DER HOEK, E.E. AND COMANS, R.N.J. (1994) Speciation of As and Se during leaching of fly ash. In *Waste Materials in Construction II*. Proceedings of the International Conference on Environmental Implications of Construction with Waste Materials, Goumans, J.J.J.M, Van der Sloot, H.A. and Aalbers, Th.G. (Eds.), Elsevier, Amsterdam, The Netherlands, p. 467-476.

Leaching processes of combustion residues

Leaching tests have been applied in order to quantify the release (leaching) of contaminants from combustion residues. Single batch leaching tests are often used because of their simplicity, but the results of these tests depend upon the experimental conditions (VAN DER SLOOT, 1988). Better predictions can be obtained by using more extensive tests, such as the Dutch standard leaching test (a combination of column and batch leaching tests at different liquid to solid ratios (L/S) and pH values; VAN DER SLOOT, 1988).

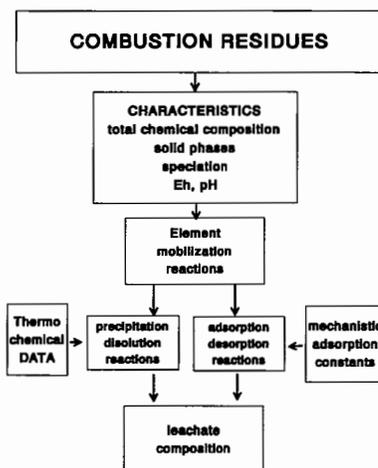


Fig. 1 Schematic framework of leaching processes from combustion residues

Fig. 1 shows the schematic framework of the leaching processes of combustion residues. The leaching behaviour of combustion residues is controlled by the elemental composition. Although there is high variability in the elemental composition of combustion residues, all these residues are composed of high temperature solids and are metastable at low temperatures in water (EARY *et al.*, 1990). The geochemical reactions which describe the processes between the solid and the aqueous phase are dissolution/precipitation and adsorption/desorption. These geochemical reactions depend upon the pH, redox potential (Eh) and the speciation reactions.

A systematic leaching behaviour has been observed for coal fly ash (DE GROOT *et al.*, 1989), MSWI bottom ash (VAN DER SLOOT, 1991), and also for *waste construction products* (VAN DER SLOOT, 1991). This systematic leaching

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behaviour has been shown to be a function of major element concentration, pH (DE GROOT *et al.*, 1989; VAN DER SLOOT, 1991) and Eh (COMANS *et al.*, 1991). The dependency observed for leaching is in accordance with the dependency of the geochemical reactions.

However, it is difficult to translate the results of leaching tests (also those of the more extensive tests) into the actual release of (hazardous) elements in the environment. A number of processes that influence the actual release have often been neglected, e.g. the Eh (VAN DER SLOOT, 1991) and weathering processes such as carbonation (SCHRAMKE, 1992; SAKATA, 1987) and clay formation (WARREN AND DUDAS, 1984; ZEVENBERGEN *et al.*, 1993). These underlying processes have to be known in order to obtain a better judgement regarding the (long-term) chemistry of combustion residues. This knowledge can be applied to all types of waste under different environmental conditions.

The precipitation/dissolution reactions of the major elements can be calculated using thermodynamic data, viz. complexation and solubility constants. It has been observed in a number of studies that major element leaching is generally controlled by dissolution/precipitation reactions. In a column leaching experiment, WARREN AND DUDAS (1985) showed the dissolution and precipitation of a number of solid phases from an alkaline coal fly ash. FRUCHTER *et al.* (1990) modelled the major element concentrations in leachates of coal fly ash by means of solubility reactions. COMANS *et al.* (1993) also succeeded in modelling the major element leaching in MSWI bottom ash with solubility reactions. For example, it was observed in the modelling studies of FRUCHTER *et al.* (1990) and COMANS *et al.* (1993) that the aluminium concentrations in the leachates are in equilibrium with amorphous $\text{Al}(\text{OH})_3$ at low pH and with gibbsite at high pH.

Trace element leaching can sometimes be modelled by precipitation reactions. Leaching of Cd in MSWI bottom ash could partly be described in equilibrium with otavite, CdCO_3 (COMANS *et al.*, 1993). Where other trace elements, such as As and Se, are concerned, leaching cannot be modelled by solubility

Speciation of As and Se during leaching of fly ash

relations. It is more likely that adsorption and desorption reactions control the leaching behaviour (WARREN AND DUDAS, 1985; FRUCHTER *et al.*, 1990; COMANS *et al.*, 1993). These sorption processes have to be identified and the parameters of the reactions have to be known, in order to model the leaching process.

The sorption reactions have still not been identified in combustion residues. More knowledge about sorption reactions can be obtained from sediments and soils. In these systems sequential extractions have mostly been used to obtain qualitative information about the type of sorption process (SALOMONS AND FÖRSTNER, 1984). The *sequential* extractions have an operational character and, therefore, no sorption parameters which are required in order to model the reactions, can be obtained. On the other hand, *single* step extractions can be useful for obtaining model parameters (BELZILE AND TESSIER, 1990).

To model the leaching of As and Se, the speciation of these elements during leaching has to be known. The term 'speciation' refers to the distribution of As and Se among different chemical forms (species) in the aqueous phase and on the solid. Thus, in this thesis speciation is used to differentiate between for example species of As and Se in different valency states present in solution and also between solid structures in which As and Se are present on the fly ash matrix. As indicated above, leaching of trace elements, such as As and Se, depends mainly on sorption reactions. Therefore, the sorption reactions controlling the oxyanion leaching from fly ash must be identified. The results of this study can also be used to understand the leaching behaviour from other combustion residues, because of the fundamental approach and the systematic leaching behaviour of combustion residues in general.

Coal fly ash

The composition of coal fly ash depends upon the composition of the coal, the type of boiler, the precipitator and the FGD (flue gas desulphurization)

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installation (NATUSCH AND TAYLOR, 1980). The greatest part of coal fly ash is produced by coal-fired plants using pulverized fuel (HELMUTH, 1987). In these boilers the temperatures rise to 1500°C, while in fluidized bed boilers, also frequently used, temperatures are approximately 850°C (TAUBER, 1987). Fly ashes from fluidized bed boilers have a different composition and structure from fly ashes derived

from pulverized coal boilers, due to of the different temperatures and the different grain size of the coal. In order to bind SO₂, additions are sometimes made to the coal while burning. These additions obviously alter the fly ash composition. In 1993, in 22 countries, 80 % of the FGD was carried out with wet scrubbers after precipitation of the fly ash (SOUD, 1994) and, therefore, the fly ash composition was not influenced by FGD. In the Netherlands, all coal-fired plants use wet scrubbers as FGD installation.

Coal may be divided into different classes, ranging from peat, brown coal, lignitic coal, bituminous coal to anthracite. These classes refer to the degree of coalification (HELMUTH, 1987). The mineral fraction of the coal determines which minerals are formed in the fly ash (MATTIGOD *et al.*, 1990). The dominant presence of phyllosilicates and quartz in the mineral fraction of coal is reflected in the observed predominance of glass, mullite and quartz. The frequently reported Fe-sulphides, Fe-carbonates, Fe-sulphates and Fe-oxides in coal account for the presence of Fe-oxides in fly ash. Also, the presence of alkaline earth carbonates in coal is reflected in the presence of Ca and Mg-oxides in fly ash (MATTIGOD *et al.*, 1990).

Table 1: Major element composition of coal fly ash

Element	reported range (MATTIGOD <i>et al.</i> , 1990)	range of 50 Dutch coal fly ashes (VAN DER SLOOT <i>et al.</i> , 1985)
Al (%)	0.1-20.9	7-18
Ca (%)	0.1-22.2	0.5-6.0
Fe (%)	1-27.6	2.5-8.0
K (%)	0.17-6.7	0.4-3.6
Mg (%)	0.04-7.7	0.25-2.3
Na (%)	0.01-7.1	0.08-0.96
S (%)	0.04-6.4	0-0.7
Si (%)	1.0-31.8	19-23

Speciation of As and Se during leaching of fly ash

The major element composition of coal fly ash is given in Table 1. The range of Al, Fe and Ca concentrations in the fly ashes are within the range of the concentrations found in soils (MATTIGOD *et al.*, 1990). In our study we mainly used the fly ash of bituminous coal from pulverized-coal plants, because this is the predominantly produced in the Netherlands (VAN DER SLOOT *et al.*, 1983). The range in composition of 50 different fly ashes produced in the Netherlands (VAN DER SLOOT *et al.*, 1985) is also included in Table 1. Fly ash from bituminous coal consists for 70-80 %, of an amorphous Al,Si glass phase. The most important minerals are quartz, mullite, magnetite and hematite (MCCARTY *et al.*, 1988)

The trace elements, such as As and Se, are preferentially associated with smaller fly ash particles and are, therefore, probably enriched at the surface (NATUSCH AND TAYLOR, 1980; MELJ, 1989). Surface enrichment can be explained by the condensation of elements, which are volatilized during combustion, onto solid particles at different rates and in varying amounts as the combustion gases cool down (EARY *et al.*, 1990). In a submicroscopic model, DUDAS AND WARREN (1987) described coal fly ash particles as hollow and solid spheres. These spheres consist of an internal amorphous glass layer with minor and trace elements and an external glass layer with more available salts and trace elements. The amount of trace elements present in the internal glass layer is probably not available for leaching (NATUSCH AND TAYLOR, 1980; DUDAS AND WARREN, 1987).

Brief overview of environmental chemistry of As and Se

In the natural environment, the partitioning of trace elements between the aqueous phase and the solid phase is determined by the speciation of these elements (BUFFLE, 1988). Very similar processes are likely to take place during the leaching of combustion residues because, similar to soils and sediments, these materials can be seen as an assemblage of different minerals (EARY *et al.*, 1990; MATTIGOD *et al.*, 1990). The behaviour of oxyanions in the

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natural environment has been extensively studied, as shown below, and can tell us more about the leaching behaviour of oxyanions from fly ashes. As and Se can appear in a number of valency states. The valency state influences, the toxicity of the oxyanions. For example, the toxicity of As(III) is higher than that of As(V) (GESAMP, 1986). During the formation of fly ash, large amounts of oxygen are present and the fly ash leachates are, therefore, probably oxidic. In the oxidic natural environment As and Se are generally present as oxyanions (CUTTER, 1992), which dependent on the pH, can be protonated (Table 2). Organic species of As and Se are frequently present in sediments and soils (e.g. NRIAGU, 1994; NEAL AND SPOSITO, 1991), but because in coal fly ash only minor amounts of organic species are present these species are less important for these systems. As and Se are often associated with (iron) hydroxides in sediments and soils (BELZILE AND TESSIER, 1990; MAHER, 1984; NEAL *et al.*, 1987). It has been shown that clay minerals and calcium carbonates are important for the retention of As and Se in soils at pH-values above 8 (GOLDBERG AND GLAUBIG, 1988a; 1988b).

Table 2: Oxyanionic species of As and Se in oxidic environment

Arsenate		Arsenite	
$\text{Log}(\text{AsO}_4^{3-})$	$\text{Log}(\text{HAsO}_4^{2-}) = \text{pH} + 11.6$	$\text{Log}(\text{AsO}_3^{3-})$	$\text{Log}(\text{HAsO}_3^{2-}) = \text{pH} + 13.4$
$\text{Log}(\text{HAsO}_4^{2-})$	$\text{Log}(\text{H}_2\text{AsO}_4^-) = \text{pH} + 6.8$	$\text{Log}(\text{HAsO}_3^{2-})$	$\text{Log}(\text{H}_2\text{AsO}_3^-) = \text{pH} + 12.1$
$\text{Log}(\text{H}_2\text{AsO}_4^-)$	$\text{Log}(\text{H}_3\text{AsO}_4) = \text{pH} + 2.2$	$\text{Log}(\text{H}_2\text{AsO}_3^-)$	$\text{Log}(\text{H}_3\text{AsO}_3) = \text{pH} + 9.2$
Selenate		Selenite	
$\text{Log}(\text{SeO}_4^{2-})$	$\text{Log}(\text{HSeO}_4^-) = \text{pH} + 1.9$	$\text{Log}(\text{SeO}_3^{2-})$	$\text{Log}(\text{HSeO}_3^-) = \text{pH} + 8.0$
		$\text{Log}(\text{HSeO}_3^-)$	$\text{Log}(\text{H}_2\text{SeO}_3) = \text{pH} + 2.5$

The mobility of oxyanions in soils and sediments depends upon the valency state, in addition to other factors such as the pH. MASSCHELEYN *et al.*, 1991 conclude that in general arsenate is more strongly retained than arsenite, while selenite is more strongly retained than selenate. This shows that the valency state influences the sorption affinity. For instance, PIERCE AND MOORE (1982) observed a lower sorption affinity for arsenite than for arsenate

Speciation of As and Se during leaching of fly ash

on amorphous iron oxide. HAYES *et al.* (1987) observed a much lower sorption affinity for selenate than for selenite on goethite.

Speciation of As and Se in fly ash leachates: overview of the thesis

As stated above, the valency state influences the toxicity, the mobility in the environment and the sorption behaviour of the oxyanions. Therefore, it is necessary to determine the valency state of As and Se in fly ash leachates.

In **Chapter 2**, studies determining the speciation of As, Se and Sb in fly ash leachates are reviewed. No general conclusion about the speciation of oxyanions could be drawn from these studies. In order to determine the valency state of As, Se and Sb, a number of analytical methods were tested as described in Chapter 2. The speciation of the oxyanions in 5 fly ash leachates at different pH-values was measured with these tested methods. It appeared that only small amounts of As(III) and Se(VI) were present in the fly ash leachates after 24 hours of leaching.

Since no precipitation/dissolution processes were found to control As and Se concentrations in fly ash leachates, sorption reactions were studied for their possible role in controlling As and Se leaching. In **Chapter 3**, an attempt was made to find the possible controlling sorbents. The leaching of As and Se from an alkaline and an acidic fly ash as a function of pH was compared which sorption of arsenate and selenite on different minerals, hematite, mullite, portlandite and ettringite, which are generally present in the fly ash matrix. It is shown that leaching of As and Se from acidic fly ash can be described by sorption on iron oxide, while leaching from alkaline fly ash seems to be controlled by sorption on an alkaline Ca-phase.

The reversibility of the sorption processes is important for the actual release (leaching). Therefore, the reversibility of the sorption processes of arsenate

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and selenite on the different minerals was studied. There was a difference between the sorption of arsenate and selenite on mullite, portlandite and hematite in that arsenate sorption was, in general, less reversible, especially on hematite. This may explain the lower availability of As relative to Se leaching.

In Chapter 3 it was shown that sorption on iron oxide is important in controlling the leaching of As and Se from acidic fly ash. An attempt was made to model this process in **Chapter 4**. Leaching experiments were followed by extractions of iron (hydr)oxides, in order to obtain the amount of As, Se and Fe involved in the sorption reaction. In addition, isotopic exchange experiments were performed in order to focus on the exchangeable As and Se on the fly ash surface. The leaching of As and Se from acidic fly ash was described with a simplified model of surface complexation for the sorption on amorphous iron (hydr)oxide.

In view of the importance of iron (hydr)oxide in controlling the leaching processes of As and Se, the sorption reversibility of arsenate, selenite and molybdate on hematite and amorphous iron (hydr)oxide are further described in **Chapter 5**. Arsenate was sorbed less reversibly on the iron (hydr)oxides, while selenite was sorbed reversibly with respect to changes in the pH. The pH at which the oxyanion is sorbed is crucial in controlling its sorption reversibility on iron (hydr)oxides.

In **Chapter 6** the knowledge gathered in the earlier chapters, is used to describe the processes controlling As and Se leaching from fly ash under natural conditions. For this purpose samples of solids and pore water were taken from an 11 year old, naturally weathered, fly ash at different depth in a lysimeter and were studied both experimentally and by geochemical modelling. The potentially important sorbents for As and Se, amorphous iron (hydr)oxide and alkaline Ca-mineral ettringite, are shown to be present and likely to be in equilibrium with the pore waters. Lysimeter profiles, pH dependent leaching experiments and extraction of As, Se, and Fe in the

weathered fly ash, as well as the modelling results, confirm that As and Se leaching from the fly ash, especially in the upper section of the lysimeters, is likely to be controlled by sorption on amorphous iron (hydr)oxide. Alkaline Ca-minerals such as ettringite may contribute in controlling the leaching process of As and Se in the lower section of the lysimeter.

References

- BELZILE, N. AND TESSIER, A. (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments, *Geochim. Cosmochim. Acta* **54**, 103-109.
- BUFFLE, J. (1988) *Complexation reactions in aquatic systems: An analytical approach*, Ellis Horwood Limited, Chichester, England.
- CARLSON, C.L. AND ADRIANO D.C. (1993) Environmental impacts of coal combustion residues, *J. Environ. Qual.* **22**, 227-247.
- COMANS, R.N.J., VAN DER SLOOT, H.A., HOEDE, D. AND BONOUVRIE, P.A. (1991) Chemical processes at a redox/pH interface arising from the use of steel slag in the aquatic environment. In *Waste materials in construction, Proceedings of the international conference on environmental implications of construction with waste materials*, Maastricht (eds) Goumans, J.J.J.M., van der Sloot, H.A., Aalbers, Th, G. Elsevier, Amsterdam, 243-255.
- COMANS R.N.J., VAN DER SLOOT, H.A., AND BONOUVRIE, P.A. (1993) Geochemical reactions controlling the solubility of major and trace elements during the leaching of municipal solid waste incinerator residues. In *VIP-32 Municipal Waste Combustion Proceedings of an international specialty conference*, Williamsburg, Virginia, 667-680.
- CUTTER, G.A. (1992) Kinetic control on metalloid speciation in seawater. *Marine Chem.* **40**, 65-80.

CHAPTER 1

- DE GROOT, G.J., WIJKSTRA, J., HOEDE, D. AND VAN DER SLOOT, H.A. (1989) Leaching characteristics of selected elements from coal fly ash as a function of acidity of the contact solution and the liquid/solid ratio. In *Environmental aspects of stabilization and solidification of hazardous and radioactive wastes* (eds. P.L. Côté and T.M. Gilliam) ASTM STP 1033, American Society for Testing and Materials, Philadelphia, 170-183.
- DUDAS, M.J. AND WARREN, C.J. (1987) Submicroscopic model of fly ash particles, *Geoderma* **40**, 101-114.
- EARY, L.E., RAI, D., MATTIGOD, S.V. AND AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements, *J. Environ. Qual.* **19**, 202-214.
- FRUCHTER, J.S., RAI, D. AND ZACHARA, J.M. (1990) Identification of solubility-controlling solid phases in a large fly ash field lysimeter, *Environ. Sci. Technol.* **24**, 1173-1179.
- GESAMP (1986) (IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint group of experts on the scientific aspects of marine pollution) Review of potentially harmful substances- arsenic, mercury and selenium, *Rep. Stud. GESAMP* **28**.
- GOLDBERG, S. AND GLAUBIG, R.A. (1988a) Anion sorption on a calcareous, montmorillonitic soil-selenium, *Soil. Sci. Soc. Am. J.* **52**, 954-958.
- GOLDBERG, S. AND GLAUBIG, R.A. (1988b) Anion sorption on a calcareous, montmorillonitic soil-arsenic, *Soil. Sci. Soc. Am. J.* **52**, 1297-1300.
- HAYES, K.M., PAPELINS, C. AND LECKIE, J.O. (1987) Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces, *J. Colloid Interface Sci.* **125**, 717-726.
- HELMUTH, R. (1987) Fly ash in cement and concrete, Portland Cement association, Skokie, Illinois.
- MAHER, W.A. (1984) Mode of occurrence and speciation of arsenic in some pelagic and estuarine sediments, *Chemical Geology*, **47**, 333-345.
- MANZ, O.E. (1995) Worldwide production of fly ash and utilization in concrete and other productions. In *proceedings of the 5th CANMET/ACI international conference on fly ash, silica fume, slag & natural pozzolans in concrete*, (ed) Malhotra, V.M., Milwaukee, Wisconsin.

Speciation of As and Se during leaching of fly ash

- MASSCHELEYN, P.H., DELAUNE, R.D. AND PATRICK, JR, W.H. (1991) Arsenic and selenium chemistry as affected by sediment redox potential and pH. *J. Environ. Qual.* **20**, 522-527.
- MATTIGOD, S.V., RAI, D., EARY, L.E. AND AINSWORTH C.C.(1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the mayor elements, *J. Environ. Qual.* **19**, 188-201.
- MCCARTY, G.J., MANZ, O.E., JOHANSEN, D.M. AND STEINWAND, S.J. (1988) X-Ray Diffraction Analysis of fly ash. In *Advances in X-ray Analysis.* **31** (eds Barrett, C.S., Gilfrich, R.J., Russ, J.C., Richardson, Jr, J.W. and Predecki, P.K. Plenum Publishing Corporation, 331-342.
- MEIJ, R. (1989) Tracking trace elements at a coal-fired plant equipped with a wet flue-gas desulphurisation facility, *Kema Scientific & Technical Reports* **7**, 267-339.
- NATUSCH, D.F.S. AND TAYLOR, D.R. (1980) Environmental effects of western coal combustion. Part IV. Chemical and physical characteristics of coal fly ash. U.S. Environmental Protection Agency Rept. *EPA 600/3-80-094*.
- NEAL, R.H. AND SPOSITO, G.(1991) Selenium mobility in irrigated soil columns as affected by organic carbon amendment. *J. Environ Qual.* **51**, 1161-1165.
- NEAL, R.H., SPOSITO, G., HOLTCLAV., K.M. AND TRANA, S.J. (1987) Selenite adsorption on alluvial soils: I. Soil composition and pH effects, *Soil Sci. Soc. Am. J.* **51**, 1161-1165.
- NRIAGU, J.O (1994) *Arsenic in the environment. Part 1 Cycling and characterization*, John Wiley & Sons, inc, New York.
- PIERCE, M.L. AND MOORE, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* **16**, 1247-1253.
- SAKATA, M. (1987) Movement and neutralisation of alkaline leachate at coal ash disposal sites, *Environ. Sci Technol.* **21**, 771-777.
- SALOMONS, W. AND FÖRSTNER, U. (1984) *Metals in the hydrocycle*, Berlin, Springer Verlag.
- SCHRAMKE, J.A.(1992) Neutralization of alkaline coal fly ash leachates by CO₂(g), *Applied Geochem.* **7**, 481-492.
- SOD, H. N. (1994) *FGD installations on coal-fired plants*, IEA Coal Research, IEACR/71, London.

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- TAUBER, C. (1987) *Spurenelementen in flugaschen: Kohle-Kraftwerk-Umwelt*, Verlag TÜV Rheinland.
- THEIS, T.L. AND GARNER, K.H. (1990) Environmental assessment of ash disposal, *C.R.C. Crit. Rev. Environ. Control*, **20**, 21-24.
- VAN DER SLOOT, H.A. (1988) Leaching procedures for waste materials and waste products, *Hazardous Waste: Detection control, Treatment* (Ed) Abbou, R., Elsevier Science Publishers B.V., Amsterdam, 637-649.
- VAN DER SLOOT, H.A. (1991) Systematic leaching behaviour of trace elements from construction materials and waste materials. In *Waste materials in construction, Proceedings of the international conference on environmental implications of construction with waste materials*, Maastricht (eds) Goumans, J.J.J.M., van der Sloot, H.A., Aalbers, Th.G., Elsevier, Amsterdam, 19-37.
- VAN DER SLOOT, H.A., WEYERS, E.G., HOEDE, D. AND WIJKSTRA, J. (1985) Physical and chemical characterization of pulverized-coal ash with respect to cement-based applications, *ECN-178*, Netherlands Energy Research Foundation, Petten.
- VAN DER SLOOT, H.A., ZONDERHUIS, J. AND MEIJ, R. (1983) Sporelementen in steenkool en steenkoolas, *Energiespectrum* **7**, 318-325.
- WARREN, C.J. AND DUDAS, M.J. (1984) Weathering Processes in relation to leachate properties of alkaline fly ash, *J. Environ. Qual.* **13**, 530-538.
- WARREN, C.J. AND DUDAS, M.J. (1985) Formation of secondary minerals in artificially weathered fly ash, *J. Environ. Qual.* **14**, 405-410.
- ZEVENBERGEN, C., BRADLY, J.P. VAN DER WOOD, T., BROWN, R.S., VAN REEUWIJK, L.P. AND SCHUILING R.D. (1993) Weathering as a process to control the release of toxic constituents from MSWI bottom ash. In *Geology and Confinement of toxic waste, Proc. of the Int. Symp. Geoconfine '93*, Montpellier, France, 591-595.

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DETERMINATION OF As, Sb AND Se SPECIATION IN FLY ASH LEACHATES

CHAPTER 2

DETERMINATION OF As, Sb AND Se SPECIATION IN FLY ASH LEACHATES*

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Abstract

Several studies have been carried out to determine the speciation of As and Se in fly ashes in order to understand the leaching behaviour of these elements and have reported widely varying results. Many of these studies make use of pH-selective hydride generation with sodium tetrahydroborate to determine the speciation of As. We found that these methods gave unreliable results for the speciation in fly-ash leachates. In this study the valency states of As, Sb and Se are determined by speciation methods which were specially tested for fly-ash leachates. Coprecipitation with dibenzylidithiocarbamate appeared to be a good method to determine As(III) and Sb(III) in fly ash leachates. It was possible to obtain the total leached amount of As and Sb by a one-step hydride generation method. Precipitation of Se(IV) on activated carbon appeared to be the most adequate of the methods tested in this study for Se. Only minor amounts of the more toxic and mobile oxyanions of As(III), Sb(III) and Se(VI) were leached from the five fly ashes investigated in this study.

Key Words: speciation, As, Se, Sb, fly ash, valency state, leaching.

*In press in: *Intern. J. Environ. Anal. Chem.*

Introduction

Leaching of oxyanions from fly ash in landfills or after reuse in construction materials is of environmental concern (CARLSON AND ADRIANO, 1993). As, Sb and Se can appear in the environment in a number of valency states, i.e. As as As(V), As(III), As(0) and As(-III); Sb as Sb(V), Sb(III), Sb(0) and Sb(-III); and Se as Se(VI), Se(IV), Se(0), and Se(-II). In oxic aqueous systems As, Sb and Se appear mostly as oxyanions (CUTTER, 1992). The valency state is an important factor for the behaviour of the elements in the environment. For example, the toxicity of As(III) (GESAMP, 1986) and Sb(III) (BERMAN, 1980) is higher than that of their pentavalent species. In addition to other parameters, the valency state also determines the sorption behaviour and, hence, the mobility in the aquatic environment. Dependency on valency state has also been shown for the sorption of As(III) and As(V) on amorphous iron (hydr)oxide (PIERCE AND MOORE, 1982) and for the sorption of Se(IV) and Se(VI) on goethite (BALISTRIERI AND CHAO, 1987) and amorphous iron (hydr)oxide (HAYES *et al.*, 1987; BALISTRIERI AND CHAO, 1990).

This study was performed in the framework of a larger programme in which the leaching of oxyanions from fly ash is investigated. We have shown that leaching of As and Se from fly ash is sorption controlled (VAN DER HOEK *et al.*, 1994). Therefore, it is important to know the valency state of the oxyanions during leaching. There have been a number of studies in which the speciation of As, Sb and Se in fly ashes has been determined. A review is given in Table 1.

Table 1 shows that there is a great discrepancy in the speciation results for both As and Se. This discrepancy may be attributed to the use of different fly ashes and leaching methods (leaching medium, leaching time, liquid/solid ratio, temperature and, consequently, in the amount leached). Another factor that can contribute to the discrepancy is the use of different methods for the determination of the speciation. For instance, WADGE AND HUTTON (1987) and HANSEN *et al.* (1984) noted recovery problems for the determination of As(III).

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Furthermore, storage of the fly ash and of the leachate may alter the elemental speciation; for example, As(III) on the solid may be oxidized to As(V) during storage (TURNER, 1981).

Table 1: Speciation of As, Sb and Se in fly ash and fly ash leachates

Ref	fly ash (FA)	leaching method*	speciation method	speciation results	percentage leached
1	oil ash	none, solid state speciation	EXAFS and XANES	mainly As(V)	-
2	coal FA > 3 y old	pH 3,7,11, 50 g/l leaching over time	HG-AAS, SnCl ₂ As(III)/As(T)	50 % As(III) conc As(III) 749 µg/l	-
3	coal FA > 1 y old	pH 10.8, > 1 g/ml serial batch leaching	HPLC-GFAAS, DMAA, MMAA, As(V), As(III), rec 60%	only As(V), other species ND	1 % As(T)
4	coal FA	in seawater, pH 8-10, 1-1000 g/l, leaching over time	HG-NAA, NaBH ₄ Sb(III)/Sb(V) As(III)/As(V)	As(III) 40-70 % Sb(III) 20-80 % < 70 µg/l As(III)	0.05-18 % As(T), 0.6-15 % Sb(T)
5	coal FA kept under air	0.2 M NaOH, 40 g/l, several days	HG heteropoly blue NaBH ₄ , rec As(III) 60 %	50 % As(III) < 15 µg/l	-
6	coal FA oil FA	1 M Na citrate pH 5, 5-25 g/l, 16 hrs	HG-AAS, NaBH ₄ As(III)/As(V) rec As(III) 96 %	< 2 % As(III) < 150 µg/l As(III)	80-90% As(T)
7	coal FA fresh	in seawater, pH 9.1-8.6, 20 g/l, analyzed instantaneously	HG-AAS NaBH ₄ As(III)/As(T)	< 33 % As(III) 45 µg/l As(III)	8-16% As(T)
8	coal FA fresh and old	pH 3-12, 20 g/l leaching over time	HG-AAS NaBH ₄ As(III)/As(T)	As(III) < 22 µg/l (fresh fly ash) As(III) 350 µg/l	1-15% As(T)

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Table 1: Speciation of As, Sb and Se in fly ash and fly ash leachates

Ref	fly ash (FA)	leaching method*	speciation method	speciation results	percentage leached
9	FA SO ₂ -removed: 1) Ca-based 2) Na ₂ CO ₃	0.5 NaOH, 1 g/ml, 4 hrs	ion chromatography > 0.05 mg/l Se(IV)/Se(VI)	Se(T) 7-11 mg/kg 1) all Se(IV) 2) all Se(VI)	-
10	garbage incinerator residue e.g. FA	0.1 M HCl, Se(IV+VI) 3 M acid-70°C Se(IV+VI+0), 2-4 g/l	HG-AAS Se(IV) Se(VI+IV) after 4 M HCl 110°C standard addition	no Se(0) Se(VI) < 3 µg/l	-
3	1) coal FA 2) refuse FA >1 y old	pH 10.8, > 1 g/ml serial batch leaching	fluorimetry Se(IV) DAN-extract, Se(VI+IV) after 120°C HCl	1) Se(VI) ND 2) Se(IV)/Se(VI) 0.19/0.05 µg/g	30 % Se(T) 6 % Se(T)
11	5 FA	Se(IV+VI+0) in 70 % HClO ₄ , Se(IV+VI) in water, 2 g/l	HG-AAS Se(IV) Se(VI+IV) after 12 M HCl	no Se(VI) ≈ 70 % Se(IV) ≈ 30 % Se(0)	70 % Se(T)
4	1 coal FA	in seawater, pH 8-10, 1-1000 g/l, leaching over time	NAA Se(IV) reduction ascorbic acid Se(VI+IV) after 6 M HCl 100°C	all Se(IV)	10-70 % Se(T)

*leaching medium, pH, solid/solution ratio, leaching time and temperature

EXAFS = Extended X-ray Adsorption Fine Structure, XANES = X-ray Absorption Near Edge Structure, HG = hydride generation, AAS = atomic adsorption spectroscopy, HPLC = High Performance Liquid Chromatography, GFAAS = Graphite Furnace-AAS, NAA = Neutron Activation Analysis, rec = recovery, ND = not detectable, DMAA = dimethylarsonic acid, MMAA, monomethylarsonic acid and DAN = 2,3 diamionaphthalene Ref = 1= SILK *et al.* (1989), 2= ALBERTS *et al.* (1988), 3 = WADGE AND HUTTON (1987), 4 = VAN DER SLOOT *et al.* (1985), 5 = HANSEN *et al.* (1984), 6 = SILBERMAN AND HARRIS (1984), 7 = BRESLIN AND DUEDALL (1983), 8 = TURNER (1981), 9 =NISS *et al.* (1993), 10 = ERICZON *et al.* (1989), 11= QUIN (1985).

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The literature, summarized in Table 1, does not allow general conclusions to be drawn concerning the speciation of As, Se and Sb in fly ash. The intention of this study was to measure the speciation of As, Se and Sb in leachates of a number of distinctly different fly-ash samples, using methods which are validated for each of these three elements in the leachates.

We also studied the influence of storage conditions of the fly ash and of the leachates on the measured speciation. As and Se leaching (VAN DER HOEK *et al.*, 1994) and valency state (CUTTER, 1992) are strongly dependent on the pH. The pH can be imposed by the fly ash but also by external environmental conditions. Therefore, the fly ashes used in this study varied in their "natural" pH values and were leached within a pH-range of pH 4 to 12.

Methods

Fly ashes

The alkaline fly ash used in this study was obtained from the power plant "Stignæsværket" in Denmark. This material was also used in two earlier studies (VAN DER HOEK *et al.*, 1994; VAN DER SLOOT *et al.*, 1991). The acidic fly ash, the neutral fly ash and the fresh alkaline fly ash originated from the power plant "Amercentrale" in the Netherlands. The acidic fly ash was also used in an earlier study (VAN DER HOEK *et al.*, 1994). The neutral fly ash had already been used by VAN DER SLOOT *et al.* (1991). The brown coal fly ash originated from a fluidized bed installation in Homberg, Germany. The fly ashes were chosen for their different pH (acidic, neutral and alkaline), storage time (varying between 30 days and 8 years) and storage conditions (air or N₂). Table 2 shows the "natural" pH, storage time and conditions and composition of the fly ashes as determined with ICP-AES and hydride generation (HG) - AAS.

Leaching

Suspensions of 96 g/l fly ash (VAN DER HOEK *et al.*, 1994) in nanopure de-ionized water were prepared in acid-cleaned pyrex or teflon (PFA) vessels and leached at three different pH values of approximately 4, 7, and 12. Two of these pH values were set by adding acid or base; the third value was the "natural" pH of the fly ash suspension, which was obtained without any additions. The pH of the set values was kept constant within 0.2 pH units by a pH-stat, that added 1 M NaOH or 1 M HCl when necessary.

The solutions were continuously stirred at room temperature by a magnetic stirrer and after 24 hours samples were taken and filtered through 0.45 µm membrane filters (Schleicher and Schüll, cellulose nitrate). During leaching the vessels were open to the atmosphere in order to enable O₂ and CO₂ to react with the fly ash, as would occur under "natural" circumstances. The filtrate was acidified (pH < 2) with supra-pure HCl (Merck). Preliminary experiments indicated no significant changes in either total-concentrations or valency state of As, Sb and Se in the leachates between 90 minutes and 24 hours of leaching.

Table 2: Composition of the fly ashes

	Acidic FA	Neutral FA	Alkaline FA	Alkaline (Fresh) FA	Brown Coal FA
pH	4.24	8.9	11.9	12.1	11.5
storage	1 y, air	8 y, air	5 y, air	30 d, N ₂	30 d, N ₂
As	9.1 µg/g	55.8 µg/g	23.0 µg/g	25 µg/g	8.0 µg/g
Sb	3.44 µg/g	16.6 µg/g	3.6 µg/g	3.5 µg/g	1.3 µg/g
Se	3.7 µg/g	41.3 µg/g	7.9 µg/g	13.8 µg/g	14.7 µg/g
Si	31.8 %	30.7 %	26.2 %	25.1 %	6.25 %
Al	9.9 %	10.2 %	12 %	12.5 %	3.28 %
Fe	3.0 %	3.1 %	3.7 %	3.16 %	6.38 %
Ca	0.2 %	1.16 %	2.2 %	2.58 %	31.3 %
Mg	0.11 %	0.5 %	0.83 %	0.61 %	5.2 %
S	0.08 %	-	14 %	0.15 %	4.24 %

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Testing of speciation methods

Several methods are available to determine the speciation of As, Se and Sb. We assume that no organic species of the oxyanions are present in fly ash because of the high temperatures at which coal combustion takes place. This is confirmed by the observations of WADGE AND HUTTON (1987) who have been unable to detect organic species of As in fly ash leachates. Therefore, we have considered only methods for analysis of the non-volatile inorganic species of As, Se and Sb in solution. Hydride generation has generally been applied for this purpose (Table 1). In this study a hydride generation method, a coprecipitation method and a precipitation method have been tested and are described below.

Hydride generation method

The speciation method for As, Sb and Se of HOEDE *et al.* (1987), developed for seawater samples, was tested for fly ash leachates. This method is based on a reaction of As, Se and Sb ions with sodium tetrahydroborate (NaBH_4) to form volatile hydrides. As(V) and Sb(V) species react only at low pH values ($\text{pH} < 1$) whereas the trivalent species also react at higher pH values ($\text{pH} < 5$) (BRAMAN *et al.*, 1972). Volatile hydrides can only be formed from Se(IV) and, therefore, the speciation of Se can only be obtained after reducing Se(VI) to Se(IV) in a separate sample and measuring the total Se concentration (VAN DER SLOOT *et al.*, 1982).

To determine the speciation of As and Sb, the procedure was divided into two steps (HOEDE *et al.*, 1987):

1. Determination of As(III) and Sb(III):
20-30 ml leachate solution was acidified with HCl to pH 2. 10 % (w/v) NaBH_4 was added slowly to the leachate at 1 ml/min over a 3-min period to form the hydrides. Because of the instability of the NaBH_4 -solution (HOEDE *et al.*, 1987) this solution was aged for at least 0.5

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hours, prior to its addition. The hydrides were continuously purged from the leachate by a carrier gas (N_2 , 750 ml/min), followed by trapping of the water ($-20^\circ C$), and subsequent collection of the hydrides on a carbon absorber. The carbon absorber was changed to proceed with step 2;

2. Determination of As(V) and Sb(V):

The solution was further acidified with concentrated HCl to obtain a concentration of 4 M HCl. Five ml of a mixture of 0.6 M potassium iodide/10 % (w/v) ascorbic acid was also injected. Subsequently, $NaBH_4$ was added to the leachate for 20 minutes at a flow rate of 1 ml/min. After 10 minutes, another 5 ml of the 0.6 M potassium iodide/10 % (w/v) ascorbic acid mixture was injected. The hydrides were collected on the fresh carbon absorber as described under step 1.

To determine Se(IV), the same procedure as in step 2 was followed except for the addition of the potassium iodide/ascorbic acid mixture.

Coprecipitation

Another method to determine As(III) and Sb(III) is the coprecipitation method of VAN ELTEREN *et al.* (1989). This method is based on coprecipitation of As(III) and Sb(III) with dibenzylthiocarbamate (DBDTC). DBDTC is known to react with a number of metals and metalloids (LINDNER *et al.*, 1978). The coprecipitation method has been developed for sea and surface waters (VAN ELTEREN *et al.*, 1989). However, in fly-ash leachates high concentrations of metals and metalloids are present and therefore a higher concentration of DBDTC is needed than in the original method.

After optimization for fly ash leachates, the final procedure was as follows:

1. Determination of As(III) and Sb(III):

30 ml leachate was acidified to pH 2 (HCl) and 1.5 ml 1 % DBDTC (1 g in 100 ml methanol) was added. After 10 min. the coprecipitate was collected on a 0.45 μm filter (Schleicher and Schüll, cellulose nitrate) and rinsed with 0.01 M HCl;

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2. Determination of As(V) and Sb(V):

The As(V) and Sb(V) present in the filtrate were reduced to their trivalent species by reaction with 1 ml 20 % (w/v) potassium iodide and 1 ml 25 % (w/v) sodium thiosulphate for 20 min. Subsequently, the procedure for As(III) and Sb (III) was repeated.

It is also possible to determine Se(IV) in water by coprecipitation with DBDTC (SALEH *et al.*, 1990). The difference with the above method is that the coprecipitate is collected on a 1 μm filter immediately after adding the DBDTC; 100 mg of phenolphthalein may be added as a supplementary coprecipitant for stabilization of the Se(IV)-DBDTC complex.

Precipitation of Se(IV)

We also tested the method of MASSEE (1977) to determine Se(IV). In this method Se(IV) is reduced to Se(0) with ascorbic acid and adsorbed on activated carbon. After this method was optimized for fly ash leachates, the procedure was as follows:

1. Determination of Se(IV):

25 mg activated carbon and 2 ml ascorbic acid solution (10 % w/v) were added to 30 ml fly ash leachate at $\text{pH} < 2$ (HCl). After 20 min the leachate was filtered through a 0.45 μm membrane filter (Schleicher and Schüll, cellulose nitrate) which was evenly covered another 50 mg of activated carbon;

2. Determination of total-Se:

Total Se was determined after reducing Se(VI) to Se(IV) in a separate sample: 20-30 ml fly ash leachate was acidified with concentrated HCl to obtain a concentration of 6 M HCl and was refluxed for 30 min. After reduction the above procedure for Se(IV) was applied except that 150 mg activated carbon and 3 ml ascorbic acid were added.

Radiotracers

Radiotracers were used to check the recovery of the speciation methods. Carrier-free $^{75}\text{Se(IV)}$, $^{75}\text{Se(VI)}$ and $^{125}\text{Sb(V)}$ were obtained from Amersham and

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$^{73}\text{As(III)}$ from Isotopen Dienst Benelux. $^{125}\text{Sb(III)}$ was obtained by reduction of $^{125}\text{Sb(V)}$ with ascorbic acid in 4 M HCl and $^{73}\text{As(V)}$ by oxidation of $^{73}\text{As(III)}$ with 25 % H_2O_2 in 4 M HCl. The speciation of the radiotracers was checked by the speciation method of van ELTEREN *et al.* (1989) and MASSEE *et al.* (1977) in test solutions of 0.05 M NaNO_3 , with and without added carrier.

The radiotracers were added individually to fly ash leachates and the speciation methods were carried out according to the procedures given above. The remaining radioactivity in the end product (on a filter or on a carbon absorber) was measured with a 3 inch NaI(Tl) well-type detector (LKB-wallac, 1282 Compugamma) relative to a standard containing 100 % of the initially added radioactivity.

Recovery of the speciation methods

Table 3 shows the measured recoveries of different As, Sb and Se species. Clearly, the recoveries of both As(III) and As(V) using the hydride generation method are very low. Attempts to improve the recovery of As(III) in step 1 by changing the carrier gas flow rate or the amount of NaBH_4 were unsuccessful. Lowering leachate pH to values < 1 gave better recoveries. However, lowering pH did not only increase the recovery of As(III) in step 1, but also that of As(V), thus lowering the method's potential to measure the species separately. Quantitative recovery of both As(III) and As(V) can, however, be obtained by using step 2 direct.

A low recovery of As(III) has also been noted in similar studies with hydride generation of arsine (AsH_3) from fly ash leachates using sodium tetrahydroborate (WADGE AND HUTTON, 1987; HANSEN *et al.*, 1984). Only SILBERMAN AND HARRIS (1984) found a recovery > 96 % in 1 M sodium citrate leachates, although in one fly ash leachate they also found a recovery of only 72 %. An explanation for the low recovery may be the preferential reduction of transition metals and subsequent interaction of the metal precipitate with the arsine (WELZ AND MELCHER, 1984).

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On the basis of the As results above and the fact that As(III) and Sb(III) show both a high recovery using the DBDTC coprecipitation method (see below), the hydride generation method was not further tested for Sb(III). Step 2 of this method was, however, tested for its recovery of Sb(V), which was $100 \pm 2\%$. Although hydride generation appears to be not suitable for speciation measurements of As and Sb in fly ash leachates, the direct use of step 2 can serve as a means to determine the total concentrations of As and Sb.

Table 3: Recovery of As, Sb and Se species from fly ash leachates

	As(III)	As(V)	Sb(III)	Sb(V)	Se(IV)	Se(VI)
HG step 1	< 45%	< 5%	n.d.	n.d.	n.d.	n.d.
HG step 2	$3 \pm 1\%$	$20 \pm 6\%$	n.d.	n.d.	n.d.	n.d.
HG step 2	$100 \pm 2\%$	$100 \pm 4\%$	n.d.	$100 \pm 2\%$	< 5%	n.d.
direct						
DBDTC	$95 \pm 7\%$	$0.3 \pm 0.1\%$	$91 \pm 5\%$	$2 \pm 1\%$	< 60%	n.d.
coprecip. step 1						
DBDTC coprecip. step 2	n.d.	90 %	n.d.	< 1 %	n.d.	n.d.
Precipitation on activated carbon, step 1	n.d.	n.d.	n.d.	n.d.	$100 \pm 2\%$	$0.2 \pm 0.2\%$
Precipitation on activated carbon, step 2	n.d.	n.d.	n.d.	n.d.	$100 \pm 1\%$	$100 \pm 4\%$

HG = hydride generation; n.d. = not determined; methods used for final measurements are highlighted

The recovery of Se(IV) from fly ash leachate was < 5 % using the hydride generation method, even when helium was used as a carrier gas (VAN DER SLOOT *et al.*, 1982). Hydride generation of Se(IV) is known for its inherent problems caused by the presence of oxygen (VAN DER SLOOT *et al.*, 1982) and, therefore, we did not attempt to further optimize this method.

The recovery of As(III) and Sb(III) from leachates of five fly ashes after

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coprecipitation with DBDTC was $95\pm 7\%$ and $91\pm 5\%$, respectively. After reduction, the recovery from acidic fly ash leachate was 90% for As(V) and $< 1\%$ for Sb(V). Probably the potassium iodide/sodium thiosulphate mixture is not strong enough to reduce Sb(V) to Sb(III). For Se(IV) the coprecipitation with DBDTC gave very low recoveries ($< 60\%$). Therefore, this method is considered not suitable for the determination of Se(IV) and Sb(V) in fly ash leachates.

Precipitation of Se(IV) from different fly ash leachates on activated carbon using ascorbic acid gave recoveries of $100\pm 2\%$. The recovery of Se(VI) after reduction in 6 M HCl was $100\pm 4\%$.

Sample preservation

The speciation of As, Se and Sb in the samples may change during storage of the leachates. TURNER (1981) found that As(III) concentrations in filtered fly ash leachates did not alter for 33 days when frozen (dry ice) or kept at 4°C . Leachates with As(III) stored at 4°C in 0.1% (w/v) ascorbic acid were only stable for 48 hours. DE LA CALLE-GUNTIÑAS *et al.* (1992) found that Sb(III) in water did not oxidize when samples were stored at $0-4^{\circ}\text{C}$. When stored at 4°C in 1% (w/v) ascorbic acid, Sb(III) had decreased after 1 month and the solutions had turned yellow. VENGHOUT AND AGEMIAN (1980) found that Se(VI)/(IV) in water could be stored for 125 days at pH 1.5 in polyethylene containers at either 4°C or at room temperature.

We tested the storage of As(III/V), Sb(III/V) and Se(IV/VI) in acidic fly ash leachates for 1 d in polyethylene containers, with and without ascorbic acid, and either at room temperature or at 4°C . We found that As(III) and Sb(III) were best preserved in 0.1% (w/v) ascorbic acid at 4°C . After 24 hours, recoveries of 96% and 90% , respectively, were obtained, while without ascorbic acid these recoveries were 5% lower. As(V) and Sb(V) were not reduced in the presence of 0.1% (w/v) ascorbic acid. Apparently, sample storage in ascorbic acid only has a beneficial effect during short storage periods. We observed a lower recovery of Se(IV) (a loss of up to 30%) in

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ascorbic acid, probably as a result of the reduction of Se(IV) to Se(0). At 4°C and without addition of ascorbic acid, Se(IV) and Se(VI) could be preserved for 24 hours (recoveries > 97%).

Final methods

After we leached the fly ashes, the acidified and filtered leachates were divided in four subsamples: one for As(III) and Sb(III) determination, one for total-As and -Sb determination, one for Se(IV) determination and one for total-Se determination. All subsamples were preserved as described below. The analyses of As(III), Sb(III) and Se(IV) were performed within 1 day of sampling and the total concentrations were measured within 1 week.

Based on the testing and optimization of methods described in the previous section, the following approach was chosen for the determination of As, Sb and Se speciation in fly ash leachates. As(III) and Sb(III) in the fly-ash leachates were determined using coprecipitation with DBDTC. We used step 2 of the hydride generation method for the determination of total-As and Sb concentrations. Se(IV) and total-Se were determined by the precipitation method with ascorbic acid. Leachate samples for Se(IV) determination were stored at 4°C and samples for As(III) and Sb(III) were preserved by addition of ascorbic acid (final concentration of 0.1 %) and storage at 4°C.

The analyses of the filters and the carbon absorbers were performed with neutron activation analysis (NAA). The samples were packed in polyethylene containers. In order to correct for possible flux differences among the samples, iron flux monitors were applied. Irradiation of the As and Sb samples was carried out for 2 hours at a neutron flux of $3 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$ and of the Se samples for 6 hours at a neutron flux of $4 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$. After approximately 3 days the As and Sb were counted for 2000 s on a Ge(Li) detector coupled to a multi-channel analyzer. After approximately 12 days the Se samples were counted for 4000 s on the same device. The cooling period of 3 or 12 days is selected on the basis of the background radiation of the samples and decay of

the measured isotopes. More details are given in VAN ELTEREN *et al.* (1989), VAN DER SLOOT *et al.* (1982) and SALEH *et al.* (1990). Detection limits were approximately 1 and 0.5 µg/l for As and Sb, respectively, depending on the presence of Na which is largely responsible for the background in NAA. The detection limit for Se was approximately 2 µg/l.

All chemicals used were analytical-reagent grade. The hydrochloric acid applied was suprapure (Merck). The activated carbon used as absorber and for the determination of Se was prepared according to VAN DER SLOOT *et al.* (1980), by carbonization of very pure PVC (polyvinylidene chloride) in a nitrogen atmosphere.

Results and Discussion

In Table 4 the leaching results of As(III), As(V), Sb(III), Sb(V), Se(IV) and Se(VI) are presented for five fly ashes after 24 hours of leaching. The percentages of these species in the leachates are presented in Figs. 1, 2 and 3, respectively. In all fly ash leachates, except for the fresh alkaline fly ash, the amounts of As(III) and Sb(III) are negligible. The highest amounts were found after leaching the fresh alkaline fly ash at acidic pH. Most of the Se leached from the coal fly ashes was Se(IV). There is a large variation in the Se(VI) concentrations because the differences between the concentrations of total-Se and Se(VI) were small relative to the analytical error. Se(VI) exceeded Se(IV) only in the low and neutral pH leachates of the acidic fly ash and in the leachates of the brown coal fly ash. Total-Se leached in these special cases was, however, lower than 50 µg/l. Also the relative amount leached was negligible (Fig. 3). The highest concentration for all 3 oxyanions is leached from neutral fly ash in the order Se > As > Sb. The results shown in Figures 1-3 imply that Se is the most mobile of these oxyanions. Almost no As, Sb and Se were leached from brown coal ash.

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As and Sb speciation

As(III) is expected to be leached better than As(V), because it is less strongly retained by geological materials (e.g. PIERCE AND MOORE, 1982; FROST AND GRIVIN, 1977). Therefore, if only a small percentage of As is leached as As(III), the relative amount of As(III) on the fly ash surface is likely to be small as well. Although little is known about the relative mobility of Sb(III) and Sb(V), the behaviour may be comparable with that of As (CUTTER, 1992).

Some authors (e.g. WU AND CHEN, 1987; NATUSCH AND TAYLOR, 1980) have predicted that As in fresh fly ash is present as As(III). Those authors hypothesize that only oxides are formed during the burning of coal and that, theoretically, only As_2O_3 precipitates.

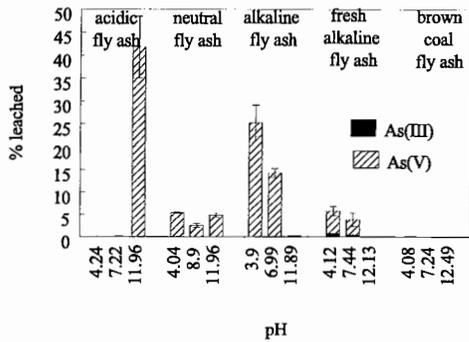


Fig. 1: As(III) and As(V) leached from 5 different fly ash samples at acidic (pH ≈ 4), neutral (pH ≈ 7-9) and alkaline (pH ≈ 12) conditions. Percentages are relative to the total-As present in the ashes.

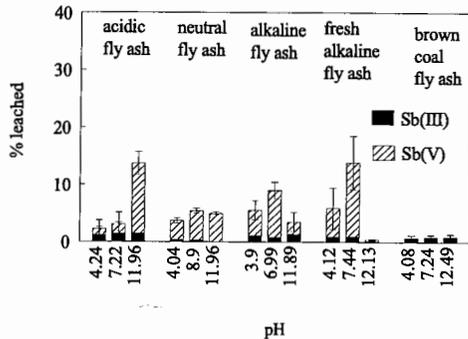


Fig. 2: Sb(III) and Sb(V) leached from 5 different fly ash samples at acidic (pH ≈ 4), neutral (pH ≈ 7-9) and alkaline (pH ≈ 12) conditions. Percentages are relative to the total-Sb present in the ashes.

Determination of As, Sb and Se speciation

These calculations, based on boiling and melting points, take into consideration that, during the burning of powder coal, temperatures can rise to 1600°C and that the fly ash is precipitated on an electrostatic precipitator (ESP) at approx. 200°C (HELMUTH, 1987).

Table 4: Speciation of As, Sb and Se in the leachate after 24 hours at different pH-values ($\mu\text{g/l}$, $n = 2$)

	pH	As(III)	As(V)	Sb(III)	Sb(V)	Se(IV)	Se(VI)
Acidic fly ash	4.2	0.0±0.2	1.0±0.3	3.8±4.6	3.7±5.0	4.2±3.4	5.8±5.1
	7.2	0.0±0.8	0.6±1.2	4.7±6.4	5.5±6.7	16±4	5.7±5.5
	12.0	0.0±0.2	365±58	4.8±5.6	40.4±6.7	294±16	3±23
Neutral fly ash	4.0	0.0±0.2	287±6	6.4±5.3	52.6±6.7	394±20	49±31
	8.9	0.0±0.3	133±22	4.2±5.0	82.0±7.2	423±22	662±34
	12.0	0.0±0.1	262±24	0.6±1.8	77.9±4.7	2087±107	197±157
Alkaline fly ash	3.9	0.0±0.2	557±87	3.8±4.7	15.1±5.7	203±11	18±17
	7.0	0.0±0.1	315±23	2.7±3.1	28.3±5.0	234±13	8±19
	11.9	0.0±0.4	5±0	4.4±5.2	7.6±5.6	79±6	11±9
Fresh alkaline fly ash	4.1	17.6±1.1	121±23	3.0±0.5	16.7±12.2	588±16	-2±97
	7.4	11.1±0.8	81±35	3.2±0.4	43.3±15.9	481±25	28±28
	12.1	0.0±0.0	1±1	0.5±0.0	1.0±0.3	108±3	49±5
Brown coal fly ash	4.1	0.2±0.4	0±0.4	0.9±0.5	0±0.5	1.8±0.0	21.0±1.0
	7.2	0.1±0.3	0±0.3	1.1±0.5	0±0.5	2.2±0.3	38.5±1.3
	12.5	0.1±0.2	0±0.2	1.1±0.6	0±0.6	2.1±0.1	19.8±1.6

However, considering these temperatures, metal arsenates can also precipitate (WEAST *et al.*, 1983). The latter hypothesis is in agreement with the measurements of As in the gas stream before and after the ESP by HAYNES *et al.* (1982) and MELJ (1993), respectively. Both studies suggest that only small amounts of As_2O_3 are present on the solid surface. In addition to As, HAYNES *et al.* (1982) have measured also Sb and suggest the formation of metal antimonates.

Our results that As and Sb are leached mainly as As(V) and Sb(V) are consistent with the hypotheses of HAYNES *et al.* (1982) and MELJ (1993). We

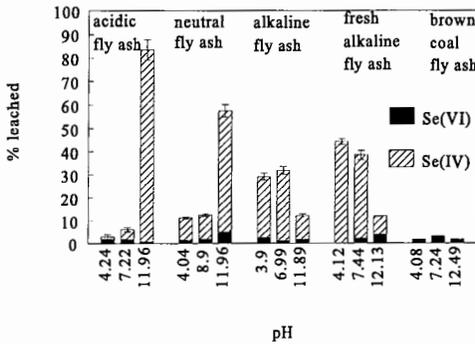


Fig. 3: Se(VI) and Se(IV) leached from 5 different fly ash samples at acidic (pH ≈ 4), neutral (pH ≈ 7-9) and alkaline (pH ≈ 12) conditions. Percentages are relative to the total-Se present in the ashes

and Sb(III) present in fly ash is likely to be small and is dependent on fly ash composition (MEIJ, 1993), age and storage conditions.

Se speciation

Thermodynamic calculations by ERICZON *et al.*(1989) for the possible species precipitated on garbage incinerator residues indicate that in these systems (800-250°C) SeO₂ is the most stable species. However, according to these calculations, the formation of hexavalent Se remains possible.

We found that most of the Se in the fly ash leachates was in the form of Se(IV). Selenate (Se(VI)) is less strongly retained on geological materials than selenite (Se(IV) (COWAN *et al.*, 1990)) and is, therefore, expected to be more available for leaching. The small percentage of Se(VI) measured in the leachates suggests that a minor amount of hexavalent Se is present on the fly

have measured, however, minor amounts of As(III) and Sb(III) (Table 4) in the leachates of the fresh alkaline fly ash. These valency states were not measured in the other leachates. Possibly, minor amounts of As(III) and Sb(III) present in the fly ash are oxidized to the pentavalent states during storage. TURNER (1981) found high concentrations of As(III) only in leachate of a fresh fly ash. Therefore, the amount of As(III)

ash surface, in accordance with the calculations of ERICZON *et al.* (1989) and the general findings summarized in Table 1.

QUIN (1985) and ERICZON *et al.* (1989) have applied extractions with strong acids to measure Se(0) in fly ash (Table 1). It is, however, likely that other mineral phases, e.g. iron oxides, dissolve from the fly ash matrix in these strong acids. Trace elements, such as Se, can be enclosed in those minerals (EARY *et al.*, 1990). Therefore, we believe that strong acid extractions cannot be used to obtain reliable measurements of Se(0) in fly ash.

In contrast with the other fly ashes, Se(VI) was the dominant species leached from the brown coal fly ash. This difference in Se speciation may be related to the addition of calcium carbonate in the fluidized bed installation in which the brown coal was burned. Calcium carbonate is generally added to fluidized bed installations in order to bind the SO₂ (TAUBER, 1987). This addition also explains the high Ca-content of this fly ash. NISS *et al.* have (1993) also found that only Se(VI) was leached from fly ash in cases where the combustion gas was treated with Na₂CO₃ to remove SO₂. The addition of carbonates during the burning process may, therefore, affect the speciation of Se on the fly ash.

Concluding remarks

A review of the literature, summarized in Table 1, does not allow general conclusions to be drawn concerning the speciation of As, Sb and Se in fly ash.

In many studies a pH-selective hydride generation method with sodium tetrahydroborate was used to determine the speciation of As. We found that this method gives unreliable results for the speciation in fly ash leachates; but that it can be used to obtain the total leached amount of As and Sb. DBDTC coprecipitation appears to be a good method to determine As(III) and Sb(III) in fly ash leachates.

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Precipitation on activated carbon was found to be a reliable method to quantitatively extract Se(IV) from fly ash leachates. Se(VI) was determined by subtraction of Se(IV) from total-Se. Due to the low concentrations of Se(VI) the latter approach resulted, however, in a large analytical error.

The major oxyanionic species leached from fly ash are As(V), Sb(V) and Se(IV). Only minor amounts of the more toxic and mobile species As(III), Sb(III) and Se(VI) are leached. Fly ash composition, additions for flue-gas desulphurization and storage conditions may affect the speciation of leachable As, Sb and Se in fly ash.

Acknowledgement

The authors like to thank Prof. Dr. C.H. van der Weijden for carefully reading an earlier draft of the manuscript, F.P. Bakker for performing the NAA-measurements and M. Jorris for performing a number of the laboratory experiments.

References

- ALBERTS, J.J., WEBER, M.J. AND EVANS, D.W. (1988) The effect of pH and contact time on the concentration of As(III) and As(V) in coal ash systems. *Environ. Technol. Lett.* **9**, 63-70.
- BALISTRERI, L.S. AND CHAO, T.T. (1987) Selenium adsorption by goethite. *Soil. Sci. Soc. Am. J.* **51**, 1145-1151.
- BALISTRERI, L.S. AND CHAO, T.T. (1990) Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. *Geochim. Cosmochim. Acta* **54**, 739-751.
- BERMAN, E. (1980) *Toxic metals and their analysis*, Heyden, London.
- BRAMAN, A.S., JUSTEN, L.W. AND FOREBACK, C.C. (1972) Direct totalization-spectral emission type detection system for nanogram amounts of arsenic and antimony. *Anal. Chem.* **44**, 2195-2199.

- BRESLIN, V.T. AND DUEDALL, I.W. (1983) The behavior of fly-ash derived arsenic in seawater, *Marine Chem.* **13**, 341-355.
- CARLSON, C.L. AND ADRIANO D.C. (1993) Environmental impacts of coal combustion residues. *J. Environ. Qual.* **22**, 227-247.
- COWAN, C.E., ZACHARA, J.M. AND RESCH, C.T. (1990) Solution ion effects on the surface exchange of selenite on calcite. *Geochim. Cosmochim. Acta* **54**, 2223-2234.
- CUTTER, G.A. (1992) Kinetic control on metalloid speciation in seawater. *Marine Chem.* **40**, 65-80.
- DE LA CALLE-GUNTIÑAS, M.B., MADRID, Y. AND CÁMARA, C. (1992) Stability study of total antimony, Sb(III) and Sb(V) at trace level. *Fresenius J. Anal. Chem.* **334**, 27-29.
- EARY, L.E., RAI, D., MATTIGOD, S.V. AND AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements. *J. Environ. Qual.* **19**, 202-214.
- ERICZON, C., PETTERSON, J., ANDERSSON, M. AND OLIN, A. (1989) Determination and speciation of selenium in end products from a garbage incinerator. *Environ. Sci. Technol.* **23**, 1524-1528.
- FROST, R.R. AND GRIVIN, R.A. (1977) Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. *Soil. Sci. Soc. Am. J.* **41**, 53-57.
- GESAMP (1986) (IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint group of experts on the scientific aspects of marine pollution) *Review of potentially harmful substances- arsenic, mercury and selenium*, Rep. Stud. GESAMP **28**.
- HANSEN L.D., SILBERMAN, D., FISHER, G.L. AND EATOUGH, D.J. (1984) Chemical speciation of elements in stack collected, respirable-size, coal fly ash. *Environ. Sci. Technol.*, **18**, 181-196.
- HAYES, K.M., PAPELINS, C. AND LECKIE, J.O. (1987) Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces. *J. Colloid Interface Sci.* **125**, 717-726.

CHAPTER 2

- HAYNES, B., NEVILLE, M., QUANN, R.J. AND SAROFILM, A.D. (1982) Factors governing the surface enrichment of fly ash in volatile trace species., *J. Coll. Interface Sci.* **87**, 266-278.
- HELMUTH, R. (1987) *Fly ash in cement and concrete*, Portland Cement association, Skokie, Illinois.
- HOEDE, D., WIJKSTRA, J. AND VAN DER SLOOT, H.A. (1987) *Dissolved trace oxyanions and trace elements in suspended matter and sediments in indonesian waters*. Datareport of the ECN participation in the snellius II expedition. ECN-203, Netherlands Energy Research Foundation, Petten.
- LINDNER H.R., SELTNER, H.D. AND SCHREIBER, B. (1978) Use of dibenzylthiocarbamate as coprecipitant in the routine determination of 12 heavy metals in pharmaceuticals by X-ray fluorescence spectroscopy. *Anal. Chem.* **50**, 896-899.
- MASSEE, R., VAN DER SLOOT, H.A. AND DAS, H.A. (1977) The determination of selenium in water samples from the environment, *J. Radioanal. Chem.*, **35**, 157-165.
- MELJ, R. (1993) The distribution of trace elements during the combustion of coal. Chapter VI In. *Environmental Aspects of trace elements in coal*, Swaine, D.J. and Goodarzi, F. (Eds.) Kluwer Academic Publishers, Dordrecht.
- NATUSCH, D.F.S. AND TAYLOR, D.R. (1980) *Environmental effects of western coal combustion*. Part IV. Chemical and physical characteristics of coal fly ash. U.S. Environmental Protection Agency Rept. EPA 600/3-80-094.
- NISS, N.D., SCHARBRON, J.F. AND BROWN, T.H. (1993) Determination of selenium species in coal fly ash extracts. *Environ. Sci. Technol.* **27**, 827-829.
- PIERCE, M.L. AND MOORE, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **16**, 1247-1253.
- QUIN, T.A. (1985) *Chemical speciation of selenium in fly ash*. Ph.D Thesis, University of California Riverside.
- SALEH, A.I., WOITTEZ, J.R.W., WALSH, G.D. AND DAS, H.A. (1990) Determination of Se(IV) in water by neutron activation analysis after coprecipitation of metal dibenzylthiocarbamate with phenolphthalein. *J. Radioanal. Nucl. Chem.* **140**, 357-363.

Determination of As, Sb and Se speciation

- SILBERMAN, D. AND HARRIS, W.E. (1984) Determination of arsenic(III) and arsenic(V) in coal and oil fly ashes. *Intern. J. Environ. Anal. Chem.* **17**, 73-83.
- SILK, J.E., HANSEN, L.D., EATOUGH D.J., HILL, M.W., MANGELSON N.F., LYTLE, F.W. AND GREERGOR, R.B. (1989) Chemical characterization of vanadium, nickel, and arsenic in oil fly-ash samples using EXAFS and XANES spectroscopy. *Physica B* **158**, 247-248.
- TAUBER, C. (1987) *Spurenelementen in flugaschen: Kohle-Kraftwerk-Umwelt*, Verlag TÜV Rheinland.
- TURNER, R.R. (1981) Oxidation state of arsenic in coal ash leachate, *Environ. Sci. Technol.* **15**, 1062-1066.
- VAN ELTEREN, J.T., DAS, H.A., DE LIGNY, C.L. AND AGTERDENBOS, J. (1989) Determination of arsenic(III/V) in aqueous samples by neutron activation analysis after sequential coprecipitation with dibenzylidithiocarbamate. *Anal. Chim. Acta* **222**, 159-167.
- VAN DER HOEK, E.E., BONOUVRIE, P.A. AND COMANS, R.N.J. (1994) Sorption of As and Se on mineral components of fly ash: relevance for leaching processes. *Applied Geochem.*, **9**, 403-412.
- VAN DER SLOOT, H.A., HOEDE, D., ZONDERHUIS, J. AND MELJER, C. (1980) *Preparation of pure active carbon*. ECN-80, Netherlands Energy Research Foundation, Petten.
- VAN DER SLOOT, H.A., HOEDE, D., KLINKERS, TH.J.L., DAS, H.A. (1982) The determination of arsenic, selenium and antimony in rocks, sediments, fly ash and slag. *J. Radioanal. Chem.*, **71**, 463-478.
- VAN DER SLOOT, H.A., WIJKSTRA, J., VAN STIGT, C.A. AND HOEDE, D. (1985) Leaching of trace elements from coal ash and coal-ash products. In *Wastes in the ocean 4*, (eds. Duedall, I.W., Kester, D.R., Park, P.K., Ketchum, B.H.) pp.467-499, John Wiley & Son, U.S..
- VAN DER SLOOT, H.A., DE GROOT G.J., HOEDE, D. AND WIJKSTRA, J. (1991) *Mobility of trace elements derived from combustion residues and products containing these residues in soil and groundwater*, Netherlands Energy Research Foundation, ECN-C-91-059.

CHAPTER 2

- VENGHOUT, C. AND AGEMIAN H. (1980) Preservation and stability of inorganic selenium compounds at ppb levels in water samples. *Anal. Chim. Acta* **113**, 237-245.
- WADGE, A AND HUTTON, M. (1987) The leachability and chemical speciation of selected trace elements in fly ash from coal combustion and refuse incineration. *Environ. Poll.* **48**, 85-99.
- WEAST, R. C., ASTLE, M. J. AND BEYER, W. H. (eds) (1983) *CRC Handbook of chemistry and physics*, 64 th edition, U.S.A., ISBN -0-83493-0464-4.
- WELZ, B. AND MELCHER, M. (1984) Mechanism of transition metal interferences in hydride generation atomic absorption spectroscopy. Part 2. Influence of the valency state of arsenic on the degree of suppression caused by copper, iron and nickel. *Analyst* **109**, 573-575.
- WU, E.J. AND CHEN, K.Y. (1987) *Chemical form and leachability of inorganic trace elements in coal fly ash* EPRI-EA-5115, Electric Power Research Institute, Palo Alto, California.

3

SORPTION OF AS AND SE ON MINERAL COMPONENTS OF FLY ASH:

Relevance for leaching processes

CHAPTER 3

**SORPTION OF AS AND SE ON MINERAL COMPONENTS OF FLY
ASH: Relevance for leaching processes***

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Abstract

To improve our understanding of As and Se leaching from fly ash it is necessary to know the underlying geochemical processes. It has been previously suggested that sorption processes may control the partitioning of these trace elements during leaching of fly ash. In natural systems, such as soils and sediments, As and Se have been shown to interact with iron oxides at acidic pH, with a CaCO_3 at alkaline pH and with clay-minerals at neutral pH. By analogy, we compared the leaching of As and Se from fly ash with the sorption of arsenate and selenite on hematite, portlandite and mullite. It was possible to describe the leaching of As and Se from acidic fly ash with a simplified model of surface complexation with iron oxides. The apparent adsorption constants calculated from the leaching experiments resembled those calculated from our sorption experiments with hematite and values published for amorphous iron oxide. The leaching of As and Se from alkaline fly ash was compared with the sorption of arsenate and selenite on portlandite. A Ca-phase was shown to control the leaching process. Portlandite was shown to be an important sorbent for arsenate and to a lesser extent for selenite, at $\text{pH} > 12.4$. The affinity of arsenate and selenite for mullite was low. Maximum sorption was reached in the neutral pH ranges, similar to the interactions of oxyanions with kaolinite. Sorption reversibility of arsenate on all three minerals considered in this study was less, or at least

*Published in: *Applied Geochemistry* (1994) **9**, 403-412.

slower, than that of selenite. This feature may partly explain that the fraction of As available for leaching from fly ash is generally lower.

Introduction

Oxyanionic species of As and Se show significant and pH-dependent leaching from fly ash (RAI *et al.*, 1987; VAN DER SLOOT *et al.*, 1985) and can, after disposal in the environment, affect the quality of ground and surface waters. The underlying mechanisms controlling oxyanion leaching are still unknown. It is to be expected that these mechanisms are strongly related to the major element chemistry of fly ash. In a leaching study involving more than 50 different coal fly ashes, DE GROOT *et al.* (1989) have shown that the pH of fly ash suspended in water depends on the major element composition and may range from 4 to 12.5. In addition, major elements control the solubility of many trace elements in aqueous systems by precipitation/dissolution mechanisms. Finally, major elements constituting primary or secondary mineral substrates may limit aqueous concentrations of trace elements by sorption processes (STUMM AND MORGAN, 1981).

The leaching of major elements from fly ash is controlled by solubility (FRUCHTER *et al.*, 1990; MATTIGOD *et al.*, 1990). FRUCHTER *et al.* (1990) have also shown, however, that the leaching of trace elements such as As and Se could not be modelled on the basis of solubility. WARREN AND DUDAS (1988) have suggested that adsorption and coprecipitation, especially on secondary minerals, may be important in controlling the partitioning of trace elements between fly ash and leachate. For modelling purposes it is necessary to identify the sorption processes which control leaching. Following an approach which is frequently being used in studies on contaminant sorption in soils and sediments (as reviewed in TESSIER, 1991 and DAVIS AND KENT, 1990) we compare sorption of As and Se on model sorbents with their leaching from the heterogeneous fly ash matrix. Our aim in this study is to find the type of

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sorbent(s) controlling leaching, rather than to identify single sorption reactions. Below we discuss potential sorbents for As and Se in fly ash.

The solid structure of coal fly ash consists for 50 to 80 % of amorphous Si,Al-glass. In addition, the most important mineral phases are quartz, mullite, hematite and magnetite (NATUSCH AND TAYLOR, 1980). During weathering, secondary precipitates such as amorphous iron oxide, calcite and gypsum are formed (WARREN AND DUDAS, 1985). As and Se do not have a high affinity for glass and quartz (VAN DER HOEK, unpublished results; XU *et al.*, 1991). The affinity for mullite is, to the best of our knowledge, unknown. However, DUDAS AND WARREN (1987) have proposed a submicroscopic model of fly ash in which the particles contain a thin shell of mullite near the surface. Because of its potentially large surface area in fly ash, mullite cannot be excluded as a relevant sorbent mineral.

Metal (hydr)oxides, such as those of iron, are known to sorb oxyanions strongly in a pH-dependending manner (HINGSTON, 1981). In natural heterogeneous solid systems, such as soils and sediments, arsenic has often been shown to be associated with iron (hydr)oxides (AGGET AND ROBERTS, 1986; BELZILE AND TESSIER, 1990). DE GROOT *et al.* (1989) have observed low aqueous concentrations of As and Se in leachates of acidic fly ash. By analogy to natural systems, we hypothesize that the leaching of As and Se from acidic fly ash is controlled by sorption on iron (hydr)oxide. After a thorough review of the literature, Mattigod *et al.* (1990) concluded that both hematite and magnetite are the principal iron bearing minerals in unweathered fly ash (MATTIGOD *et al.*, 1990). Hematite is known to strongly sorb oxyanions (PARFITT, 1978; BREEWSMA, 1973; TURNER AND KRAMER, 1991 and AYLMOORE *et al.*, 1967). We could find no studies concerning the sorption behaviour of oxyanions on magnetite. Therefore, we have selected hematite as a model sorbent for the purpose of this study.

Iron (hydr)oxides do not sorb oxyanions at highly alkaline pH (HINGSTON, 1981). Nevertheless, alkaline fly ash generally releases only minor amounts of

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As and Se at high pH (DE GROOT *et al.*, 1989). To explain this leaching behaviour, other sorbent phases have to be considered. DE GROOT *et al.* (1989) observed a strong decrease in leaching of oxyanions above pH 12. Furthermore, the authors claim that it is mainly the CaO-content that determines the alkaline character of fly ash. We suspect that sorption on a Ca-phase may control the leaching of As and Se from alkaline fly ash. Lime has been observed as the most common Ca-phase in unweathered fly ash (MATTIGOD *et al.*, 1990). Upon leaching, hydration of lime will form portlandite. Hence, portlandite was chosen as a model alkaline calcium sorbent.

The reversibility of sorption reflects the ability of the adsorbed contaminant to be leached by the aqueous phase under changing conditions and is, therefore, pertinent for the environmental question. Therefore, an assessment of the reversibility of As and Se on model sorbents was included in this study. In recent literature (SPOSITO, 1986), the term *adsorption* has a specific mechanistic meaning. The term *adsorption* has, however, also a more general usage, by which it refers to a forward sorption process. This usage is adopted below because its convenience for discussion of sorption reversibility.

Sorption of As and Se is strongly dependent on the valence state of the oxyanionic species (PIERCE AND MOORE, 1982; HAYES *et al.*, 1987). VAN DER SLOOT *et al.* (1985) have shown that selenium leaches from fly ash almost entirely as selenite. Both arsenite and arsenate have been observed to leach from fly ash, more than 70 %, however, being in the form of arsenate (VAN DER SLOOT *et al.*, 1985; TURNER, 1981). SILBERMAN AND HARRIS (1984) and WADGE AND HUTTON (1987) observed total-As in fly ash leachates to consist for over 93 % of arsenate.

In summary, we compare below the leaching of As and Se from an acidic and an alkaline fly ash, over a large pH region, with the sorption behaviour of arsenate and selenite on the model sorbents hematite, portlandite and mullite.

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Materials and Methods

Materials

The alkaline fly ash used in this study was obtained from the power plant "Stignæsværket" in Denmark. This material was chosen because it was also used in a mobility study supported by the EC (VAN DER SLOOT *et al.*, 1991). The acidic fly ash used in this study was obtained from the Dutch Fly Ash Corporation and originated from the power plant "Amercentrale" in the Netherlands. Both ashes were selected on the basis of their pH when suspended in water (Table 1). The concentrations of the most important elements in these fly ashes are shown in Table 1.

pH*	Alkaline fly ash		Acidic fly ash	
	%	mg/kg	%	mg/kg
Total concentration				
Si	26.2		31.6	
Al	12.0		9.3	
S	14.0			812
Fe	3.74		2.87	
Ca	2.19			1975
As		23.0		9.69
Se		7.9		3.54

*) Suspension of 100 g/l in deionized water

Iron(III)oxide (Baker grade) and $\text{Ca}(\text{OH})_2$ (Baker grade) were used in this study and identified by X-ray diffraction analysis as hematite and portlandite, respectively. The specific surface area (BET-analysis) of hematite was $9.18 \text{ m}^2/\text{g}$ and the specific surface area of portlandite was $9.1 \text{ m}^2/\text{g}$. Mullite (> 99.9 % chemically pure, $\text{Al}_6\text{Si}_2\text{O}_{13}$) was prepared by high temperature synthesis from Al_2O_3 and SiO_2 and obtained from Baikowski Chimie. The mullite batch contained < 2 % $\alpha\text{-Al}_2\text{O}_3$, as identified by X-ray diffraction analysis. The specific surface area (BET-analysis) was $3 \text{ m}^2/\text{g}$.

Arsenate and selenite stock-solutions ($\text{pH} < 2$) were prepared from As_2O_5 and SeO_2 Titrisol standard solutions of 1000 $\mu\text{g}/\text{l}$ (Merck). A mixture of $^{73/74}\text{As}$ -radiotracer was obtained from "Isotopen Dienst Benelux" as AsI_3 (40 MBq/mg As) in water. $^{73/74}\text{Arsenate}$ was prepared by oxidation of AsI_3 with H_2O_2 and

Sorption of As and Se on mineral components of fly ash

concentrated HCl. ⁷⁵Selenite-radiotracer (188 MBq/mg Se) was purchased from Amersham. All other chemicals used were analytical/reagent grade. All suspensions and solutions were diluted with "nanopure" deionized water.

Leaching experiments

Suspensions of 95 g/l of acid fly ash or 96 g/l alkaline fly ash in deionized water were prepared in acid-cleaned polyethylene 200 ml vessels. The pH was set to pre-determined values in the range of 4 to 12.5, by adding 1 M NaOH or 1 M HNO₃, and was adjusted a few times during the first few hours of equilibration. Similar to standard leaching tests, contact of the suspensions with the atmosphere was not avoided. After the vessels were continuously tumbled for 24 hours at room temperature, the pH was measured and the suspensions were filtered over a 0.45 µm filter (Schleicher and Schüll, cellulose nitrate). The filtrate was acidified (pH < 2) with supra-pure HNO₃ (Merck) and aqueous concentrations of As, Se, Fe and Ca were measured by hydride AAS or by ICP-AES.

Sorption experiments with hematite or mullite

100 ml suspensions of 1.0 g/l hematite were equilibrated for at least one week in acid-cleaned 250-ml polyethylene reaction vessels with a solution of either NaOH or HNO₃, and NaNO₃ in order to vary the pH from 3 to 12.5 and to maintain the ionic strength at 0.05 M. Arsenate or selenite stock-solution and radiotracer were added to the equilibrated hematite suspensions. The As and Se concentrations were ± 100 µg/l after addition of stock and tracer solutions. The radioactivity in the suspensions was > 50 Bq/ml. During equilibration and during the sorption experiments, the suspensions were shaken in a reciprocating shaker at 22°C.

At distinct times, 2 ml subsamples were taken and the pH was measured and readjusted if necessary. During subsampling, the suspensions were continuously stirred to maintain a constant solid/liquid ratio. The subsamples

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were centrifuged for 30 minutes at 2000 x g and 1 ml of the supernatant was transferred to a polyethylene counting-vial containing 10 μ l of concentrated HNO_3 . The radioactivity was measured on a 3 inch NaI(Tl) well-type detector (LKB-wallac, 1282 Compugamma) relative to a standard containing 100 % of the initially added radioactivity.

After two weeks the pH in every vessel was changed to a value of 12 in order to induce desorption. This pH was chosen, because the prior adsorption experiments indicated no sorption of arsenate and selenite on hematite at $\text{pH} \geq 12$. Subsamples were taken at distinct times and treated as described above.

The above procedure was also followed for the sorption experiments with mullite, using 50 ml suspensions of 96 g/l.

Sorption experiments with portlandite

During equilibration, all the vessels containing portlandite were kept under a nitrogen atmosphere in a glove box to prevent the formation of CaCO_3 by atmospheric CO_2 . Portlandite was equilibrated in solutions containing $\text{Ca}(\text{NO}_3)_2$, NaOH , or NaNO_3 , or a combination, in order to vary the pH from 12 to 13.8 and to maintain the ionic strength at 1.0 M. After one day of equilibration, the solutions were centrifuged. The portlandite-saturated supernatants were transferred to acid-cleaned 90-ml Teflon (PFA) reaction vessels and fresh portlandite was added to obtain suspensions of 1.0 g/l and 96 g/l. These suspensions were equilibrated for at least 1 week. The suspensions of 1 g/l were used for arsenate sorption and the suspensions of 96 g/l for selenite sorption, because of the large difference in affinity for portlandite observed in preliminary experiments. During the equilibration and the sorption experiments, the suspensions were continuously tumbled at room temperature.

Sorption of As and Se on mineral components of fly ash

Selenite or arsenate stock-solution and radiotracer were added to the equilibrated portlandite suspensions. The As and Se concentrations in suspensions after addition of stock and tracer solution were 58.5 µg/l and 124 µg/l, respectively. Subsamples were taken and treated as described for the hematite experiments, with the pH measured in a second 2 ml subsample.

Desorption was induced after 2 weeks of sorption. The remainder of the suspensions was centrifuged for 30 minutes at 2000 x g in acid-cleaned Teflon (FEP) centrifuge tubes and the solids were separated from the supernatant. About 5 % of the supernatant was left at the bottom of the tube to prevent removal of the solid and was corrected for. The particles were resuspended in equal volumes of the same saturated solutions without selenite or arsenate. At distinct times subsamples were taken and treated as described above.

As will be discussed below in the Results and Discussion, a few preliminary experiments were performed to study the sorption of arsenate and selenite on 1 g/l and 10 g/l ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) at pH 10.2 (pH after synthesis) following the procedure described above for hematite and mullite. Ettringite was prepared according to method III of ODLER AND ABDUL-MAULA (1984).

Speciation measurements

During a few selected sorption experiments, the speciation of As and Se was tested before and after the interaction with hematite and portlandite using sodium dibenzylthiocarbamate methods of VAN ELTEREN *et al.* (1989) and SALEH *et al.* (1990). All arsenic was present as As(V) and hence as arsenate. All selenium was Se(IV) and hence selenite.

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Results and Discussion

Leaching from fly ash

Fig. 1 and Fig. 2 show As and Se leaching patterns of the acidic and alkaline fly ash, respectively, presented as the percentage remaining on the solid. All solutions were undersaturated with respect to iron arsenate, iron selenite and calcium selenite as calculated with MINTEQA2 (FELMY *et al.*, 1984). The solubility product of $\text{Ca}_3(\text{AsO}_4)_2$ is still a matter of discussion and $\log K_{\text{sp}}(\text{Ca}_3(\text{AsO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{AsO}_4^{3-})$ have been reported in a range between -18.16 (WAGEMANN, 1978) and -21.9 (SADIQ, 1990). However, even with the lower solubility product of SADIQ (1990), $\text{Ca}_3(\text{AsO}_4)_2$ is still calculated to be undersaturated during leaching of the alkaline fly ash. Recently, REARDON *et al.* (1993) have suggested that arsenate solubility in alkaline waste porewaters is controlled by basic calcium arsenate $(\text{Ca}_4(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O})$. These authors do not, however, report a solubility constant for this phase. In separate experiments with 75000 $\mu\text{g/l}$ As and portlandite-saturated solution

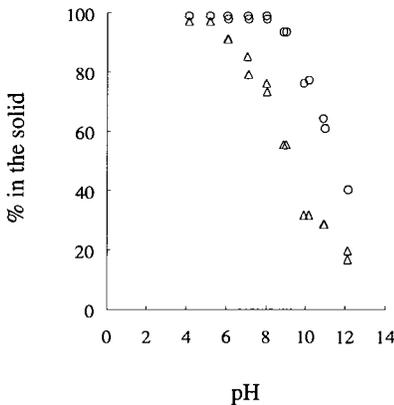


Fig. 1: Percentage of As (\circ) and Se (Δ) remaining in the solid after leaching from acidic fly ash as a function of pH.

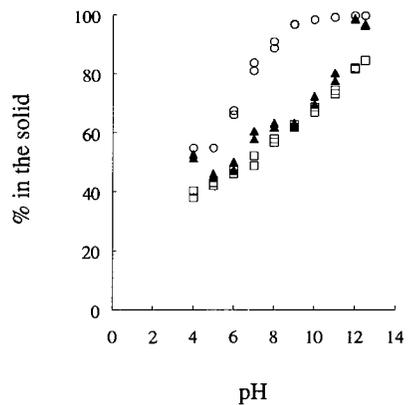


Fig. 2: Percentage of As (\circ), Se (\blacktriangle) and Ca (\square) remaining in the solid after leaching from alkaline fly ash as a function of pH.

Sorption of As and Se on mineral components of fly ash

we have not been able to identify the formed precipitate, with XRD-analysis, in contradiction to REARDON *et al.* (1993).

In the acidic fly ash, the aqueous As and Se concentrations increase with pH up to concentrations of 550 $\mu\text{g/l}$ and 280 $\mu\text{g/l}$, respectively. The pattern (Fig. 1) is qualitatively similar to anion sorption curves on hydrous metal oxides (HINGSTON, 1981). A higher pH is required to release the same percentage of As as that of Se, indicating that As has a stronger association with the solid controlling the aqueous concentrations of As and Se.

In the alkaline fly ash the aqueous As and Se concentrations increase with decreasing pH up to concentrations of 1000 $\mu\text{g/l}$ and 360 $\mu\text{g/l}$, respectively. The concentration/pH relationship of aqueous As and Se in alkaline fly ash is opposite to that of acidic fly ash. Hence, it appears that a different process controls the partitioning of As and Se during leaching of alkaline fly ash. To illustrate the interrelationships during leaching, the amount of Ca remaining in the solid is also given in Fig. 2. The leaching of Se parallels the leaching of Ca. From pH 10 downwards Se is leached even in direct proportion to Ca. The leaching of As follows the leaching of Ca only at low pH. The relevance of portlandite and other secondary Ca-minerals for the leaching pattern in Fig. 2 will be discussed below.

DE GROOT *et al.* (1989) observed a retention of As and Se in both acidic and alkaline fly ash at their natural pH. However, the above results show that large amounts of As and Se can be leached when applying a pH opposite to the natural pH of the fly ash.

Sorption experiments with Hematite

Fig. 3 shows the sorption of arsenate and selenite on hematite as a function of pH. No change in sorption is observed between 2 hours and 14 days indicating that maximum sorption of arsenate and selenite was reached within 2 hours. The sorption edge of arsenate is located at higher pH than that of selenite,

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indicating a higher affinity of arsenate for the hematite surface. The sorption curves of selenite and arsenate on hematite resemble those of selenite (BALISTRERI AND CHAO, 1990) and arsenate (PIERCE AND MOORE, 1982) on amorphous iron oxide.

Reversibility

The reversibility of the sorption process was tested after two weeks of adsorption (Fig 4.). Selenite sorption seems almost completely reversible with respect to pH. After 2 hours desorption at pH 12, 10 % of the selenite, initially sorbed at low pH-values, was still retained. After 17 days all selenite was in solution. BALISTRERI AND CHAO (1987) have found that selenite adsorption on goethite was also reversible with respect to the pH within a 24 hours time period.

The desorption of arsenate was very slow and incomplete (Fig. 4). After 4 weeks desorption at pH 12 38 % remained sorbed. An explanation of this effect may be the incorporation of arsenate in hematite at low pH-values (VAN DER HOEK *et al.*, 1995). In the leaching experiments, 79 % of Se and only 57 % of As, is released within 24 hours from the acidic fly ash at high pH. When the acidic fly ash is suspended in water, at the start of a leaching experiment, the pH is ~ 4. It takes about an hour to adjust the pH from this original value to 12. During this period, As may interact irreversibly with iron oxides. Therefore, the lower availability of As for leaching may result from its limited sorption reversibility. A fraction of the As (and Se) may also be fixed in other

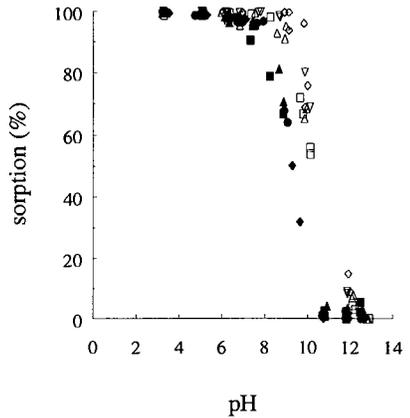


Fig. 3: Percentage of arsenate (open symbols) and selenite (closed symbols) sorption on hematite (1 g/l) as a function of pH. Equilibration times are 2 hrs (\square), 1 d (\triangle), 2 d (\circ), 1 week (\diamond) and 2 weeks (∇). Total-As = 125 $\mu\text{g/l}$ and total-Se = 112 $\mu\text{g/l}$

Sorption of As and Se on mineral components of fly ash

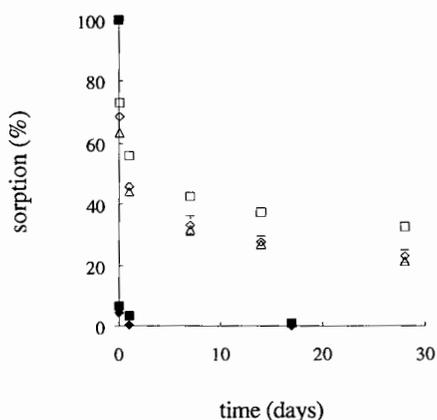


Fig. 4: Desorption of arsenate (open symbols) and selenite (closed symbols) from hematite at pH 12 ± 0.3 . Prior to desorption, the oxyanions were adsorbed for two weeks at initial pH 3 (□), pH 5 (◇) and pH 7 (△).

minerals in the fly ash matrix. To test this hypothesis two leaching experiments were performed with acidic fly ash. In the first experiment the pH was adjusted immediately (within 30 sec.) to pH 12 and in the second the pH was adjusted to pH 12 after 1 hour of reaction with water without pH adjustment (pH \approx 4). Selenium was leached for 76 ± 1 % in experiment 1 and for 68 ± 2 % in experiment 2, whereas for As these values were 64 ± 2 % and 41 ± 4 %, respectively. These results show that during leaching of As, irreversible sorption can occur and may lead to a 10 to 20 % lower availability for leaching.

Sorption on hematite compared with leaching from acidic fly ash

The sorption curves of arsenate and selenite on hematite (Fig. 3) closely resemble the leaching of these elements from acidic fly ash as presented in Fig. 1. The affinity of arsenate for hematite is higher than that of selenite, which is in agreement with the observed affinities for the solubility controlling solid during leaching.

Hypothesizing that As and Se in fly ash are associated with iron oxide, we can describe as a comparative exercise, the partitioning of these anions between fly ash and solution and between hematite and solution in terms of a simplified version of the surface complexation model (TESSIER, 1991):

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where *K_A is an apparent overall equilibrium constant, \equiv refers to surface sites and x is the average number of protons involved in the reaction.

If we assume low surface coverage, we can relate the concentration of free sites to that of iron oxide:

$$\{\equiv\text{FeOH}\} \approx N\{\text{Fe-oxide}\} \quad (3)$$

where N is the number of moles of adsorption sites per mole iron oxide (BELZILE AND TESSIER, 1990).

This leads to:

$$K_A = N^*K_A[\text{H}^+]^x = \{\equiv\text{FeH}_{x+1}\text{AsO}_4^{x-1}\} / (\{\text{Fe-oxide}\}\text{H}_2\text{AsO}_4^-) \quad (4)$$

$$K_A = N^*K_A[\text{H}^+]^x = \{\equiv\text{FeH}_x\text{SeO}_3^{x-1}\} / (\{\text{Fe-oxide}\}\text{HSeO}_3^-) \quad (5)$$

where K_A is an apparent overall equilibrium constant which is a function of pH. Following the above hypothesis, we relate the concentration of adsorbed As and Se to their total concentrations in fly ash:

$$\{\equiv\text{FeH}_{x+1}\text{AsO}_4^{x-1}\} = f\{\text{Fly ash-As}\} \quad (6)$$

$$\{\equiv\text{FeH}_x\text{SeO}_3^{x-1}\} = f\{\text{Fly ash-Se}\} \quad (7)$$

where f is the fraction of the total concentration of As or Se which remains in the fly ash. Not all As and Se are leached from the acidic fly ash at pH 12 (Fig. 1), whereas at this pH no As and Se are sorbed on hematite at pH 12 (Fig. 3). As mentioned earlier, the lower availability of As for leaching may partly result from its lower sorption reversibility, and a fraction of the As and

Sorption of As and Se on mineral components of fly ash

Se may also be fixed in other minerals in the fly ash matrix. Therefore the fraction, f , was varied between the total concentrations ($f = 1$) in the fly ash, to the fraction available at pH 12 ($f = 0.6$ and $f = 0.8$ for As and Se, respectively).

Taking the logarithm of Eqn (4) or Eqn (5) leads to

$$\text{Log } K_A = \text{Log}(N \cdot K_A) - x \text{ pH} \quad (8)$$

where x refers to the proton stoichiometry.

With $\{\equiv\text{FeH}_{x+1}\text{AsO}_4^{x-1}\}$, $\{\equiv\text{FeH}_x\text{SeO}_3^{x-1}\}$, {Fe-oxide} and the concentrations of the species H_2AsO_4^- and HSeO_3^- , K_A can be calculated. The latter concentrations were calculated in MINTEQA2 using the total dissolved concentration of As or Se from the sorption experiments with hematite and from the leaching experiments with acidic fly ash. For selenite, the dissociation constants of COWAN (1988) were used in the MINTEQA2 calculations ($\text{HSeO}_3^- = \text{H}^+ + \text{SeO}_3^{2-}$, $\text{p}K=8.04$ and $\text{HSeO}_3^- + \text{H}^+ = \text{H}_2\text{SeO}_3$, $\text{p}K=-2.46$).

To obtain a value for {Fe-oxide}, we extracted the iron oxide component from 1 g fly ash with 50 ml 2 M HCl (30 min at 96°C; CHAO AND ZHOU, 1983). This method showed 17 to 18 % of the total Fe to be extractable. Although we believe that this value constitutes a fair estimate of the amount of iron participating in the sorption process, we performed modelling calculations using input values ranging from 1-50 % of the total Fe. The K_A -values obtained at different pH-values are shown in Fig. 5a and Fig. 5b. The error bars in these figures indicate the variation in K_A arising from modelling calculations using different fractions of total Fe, As, and Se, involved in the reaction (see above). The values calculated for the acidic fly ash agree within approximately one order of magnitude with the K_A -values for hematite. Above pH = 10 the values for Se on fly ash deviate from those on hematite. Another process is, therefore, likely to control the leaching of Se above pH 10. The linear regression parameters for $N \cdot K_A$ and x (Eqn 8.) are:

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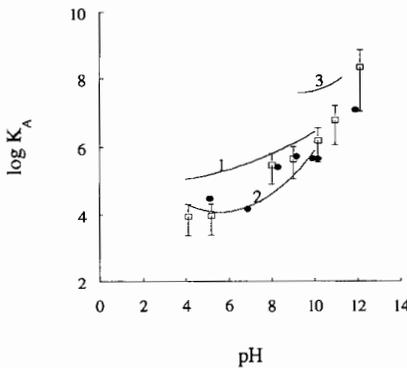


Fig. 5a: Leaching data of acidic fly ash and sorption data on hematite modelled as surface complexation of arsenate on iron oxide. K_A is the apparent overall equilibrium constant. (□) Leaching data; error bars represent variation of the amount of Fe and As involved in the surface reaction (see text for further details). (●) hematite data with a total-As of 1.67 μM and total-Fe of 12.5 mM. Lines represent amorphous iron oxide. Line 1 (total-Fe 42 μM and total-As 0.67 μM) and Line 2 (total-Fe 42 μM and total-As 13,3 μM) were calculated with data from PIERCE AND MOORE (1982). Line 3 (total-As = 5 μM and total-Fe = 1 mM) was calculated with data from LECKIE *et al.* (1980).

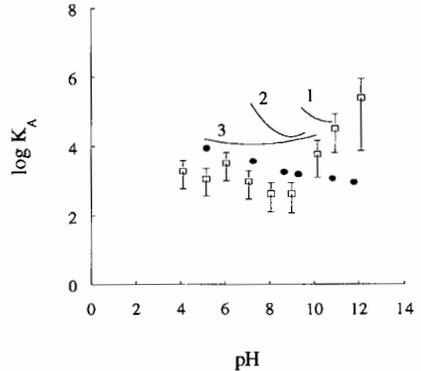


Fig. 5b: Leaching data of acidic fly ash and sorption data on hematite modelled as surface complexation of selenite on iron oxide. K_A is the apparent overall equilibrium constant. (□) Leaching data; error bars represent variation of the amount of Fe and Se involved in the surface reaction (see text for further details). (●) hematite data with a total-Se of 1.43 μM and total-Fe of 12.5 mM. Lines represent amorphous iron oxide. Line 1 (total-Fe 148 μM and total-Se 0.68 μM) and Line 2 (total-Fe 1483 μM and total-Se 0.68 μM) were calculated with data from BALISTRERI AND CHAO (1990). Line 3 (total-Se = 5 μM and total-Fe = 1 mM) was calculated with data from LECKIE *et al.* (1980).

$$\log K_A(\text{As, fly ash}) = -0.5\text{pH} + 1.4 \quad (9)$$

$$\log K_A(\text{As, hematite}) = -0.4\text{pH} + 2.1 \quad (10)$$

$$\log K_A(\text{Se, fly ash, pH} < 10) = 0.15\text{pH} + 4.0 \quad (11)$$

$$\log K_A(\text{Se, hematite}) = 0.15\text{pH} + 4.6 \quad (12)$$

Sorption of As and Se on mineral components of fly ash

There is a fair correspondence between the parameter values of fly ash and hematite for As and Se, respectively.

For comparison, K_A -values were calculated from published laboratory studies of arsenate sorption on amorphous iron oxide (PIERCE AND MOORE, 1982; LECKIE *et al.*, 1980) and of selenite sorption on amorphous iron oxide (BALISTRIERI AND CHAO, 1990; LECKIE *et al.*, 1980). For these calculations $\{=FeH_{x-1}AsO_4^{x-1}\}$, $\{=FeH_xSeO_3^{x-1}\}$ and the dissolved concentrations of As and Se were estimated graphically from the published adsorption curves. The K_A -values of As on hematite and acidic fly ash obtained in this study are close to those for amorphous iron oxide. The K_A -values of Se on amorphous iron oxide are higher than those for hematite and fly ash (Fig. 5b). Amorphous iron oxides possess more binding sites than hematite (DAVID AND KENT, 1990) and are, therefore, better adsorbents. It is possible that amorphous iron oxides are formed as a secondary precipitate during fly ash leaching (DUDAS AND WARREN, 1987). Our results do not allow conclusions as to the particular type of iron oxide involved in As and Se binding in fly ash. It is, however, possible to describe the leaching of As and Se by sorption on either crystalline or amorphous iron oxide.

Sorption experiments with Mullite

Fig. 6 shows the sorption of arsenate and selenite on mullite as a function of pH. No change in arsenate and selenite sorption was observed between 1 d and 18 d indicating maximum sorption was obtained within 1 d. Arsenate and selenite have a sorption maximum around pH 6. Mullite ($Al_6Si_2O_{13}$) in fly ash arises from kaolinite ($Al_2Si_2O_5 \cdot H_2O$) after heating at high temperatures ($> 900^\circ C$) (RAASK, 1980; TAYLOR, 1987). The crystal structure of mullite is orthorhombic and the surface contains AlO-groups and SiO-groups (DEER *et al.*, 1966). For metal oxides it is known that the oxygen atoms, which are shared by more than one metal cation, are not fully coordinated and hold a residual negative charge. After reaction with water the surface is hydrolyzed (TAYLOR, 1987). By analogy, it is reasonable to assume that hydroxyl groups

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are present on the mullite surface. Sorption of oxyanions on metal (hydr)oxides can be modelled by ligand exchange (PARFITT, 1978), which is the principle of surface complexation modelling (HINGSTON, 1981). Sorption of arsenate and selenite on kaolinite has also been successfully modelled by ligand exchange with aluminol surface groups (GOLDBERG AND GLAUBIG, 1988a; 1988b). Although the structure of mullite differs from that of the clay mineral kaolinite (DEER *et al.*, 1966), the types of aluminol groups are likely to be similar. The difference in structure

and charge distribution on kaolinite and mullite can affect the sorption affinity, but the type of sorption process is likely to be the same. It seems therefore reasonable to assume that arsenate and selenite sorption on mullite is also controlled by ligand exchange and hence to compare the pH-dependent sorption curves in Fig. 6 with those published for kaolinite (GOLDBERG AND GLAUBIG, 1988a; 1988b; FROST AND GRIFFIN, 1977).

The shapes of the sorption curves (Fig. 6) resemble the curves of arsenate and selenite sorption on kaolinite, in that a sorption maximum is formed around pH 5-6 (GOLDBERG AND GLAUBIG, 1988a; 1988b; FROST AND GRIFFIN, 1977). Both GOLDBERG AND GLAUBIG (1988a; 1988b) and FROST AND GRIFFIN (1977) have found that more arsenate than selenite is sorbed at pH > 5. In this study we observe the same for mullite, which indicates a higher affinity of arsenate for the mullite surface. The decrease in arsenate and selenite sorption at low pH is remarkable and seems to be a general feature for Al-containing solids, such as amorphous Al(OH)₃ (ANDERSON *et al.*, 1976), kaolinite (GOLDBERG AND

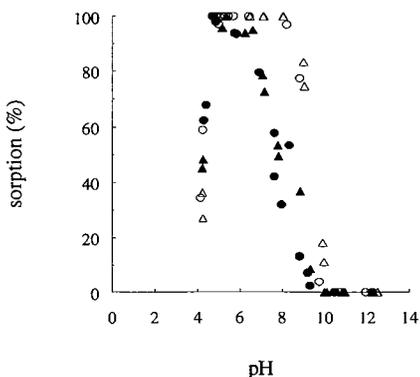


Fig. 6: Percentage of arsenate (open symbols) and selenite (closed symbols) sorption on mullite (96 g/l) as a function of pH. Equilibration times are 1 d (○) and 18 d (□). Total-As = 125 µg/l and total-Se = 112 µg/l.

GLAUBIG, 1988a; 1988b; FROST AND GRIFFIN, 1977) and mullite (Fig. 6). ANDERSON *et al.* (1976) have related this decrease to the dissolution of amorphous $\text{Al}(\text{OH})_3$. Kaolinite is known to dissolve incongruently to gibbsite, $\text{Al}(\text{OH})_3$, (STUMM AND MORGAN, 1981), which has a similar pH-dependent solubility. ROY AND GRIFFIN (1984) have suggested the same dissolution mechanism for mullite. Therefore, the decrease in arsenate and selenite sorption on mullite at low pH (Fig. 6) may well be caused by the dissolution of the sorbent mineral.

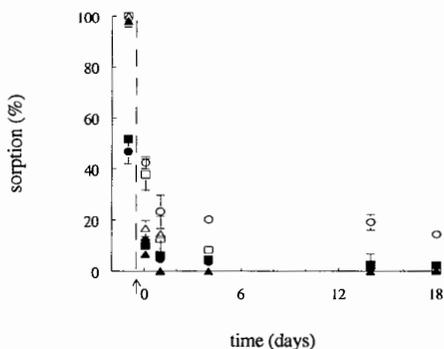


Fig. 7: Desorption of arsenate (open symbols) and selenite (closed symbols) from mullite at $\text{pH } 12 \pm 0.3$. Prior to desorption, the oxyanions were adsorbed for 18 d at initial pH 4 (\circ), pH 5 (Δ) and pH 8 (\square). The arrow shows the start of desorption.

Except for arsenate originally sorbed at pH 4, the sorption process for both elements is almost completely reversible with respect to pH (Fig. 7). The kinetics of desorption is, however, considerably slower than the adsorption kinetics. It takes about two weeks to desorb virtually all arsenate and selenite from mullite. In view of the similar sorption behaviour of arsenate and selenite at low pH, it is unclear why about 15-20 % of arsenate adsorbed at pH 4 is retained, whereas all selenite is desorbed.

The affinity of arsenate and selenite for mullite is low in comparison to that for iron oxides. This difference implies that mullite can only play an important roll in arsenate and selenite leaching from fly ash with low available iron at intermediate pH-values (5-8).

Sorption experiment with Portlandite

Fig. 8 shows sorption of selenite and arsenate over time and as a function of

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pH. Selenite sorption was studied at a total concentration of 124 µg/l Se and 96 g/l portlandite (Fig. 8). For arsenate (Fig. 8) these values were 58.5 µg/l and 1 g/l, respectively. These experiments were performed at a constant ionic strength of 1.0 M. A large amount of portlandite was used in the selenite experiments, because of the low sorptive affinity in comparison to arsenate.

All experiments were undersaturated with respect to calcium selenite as calculated with MINTEQA2. With the possible exception of the experiments at pH 12-12.5, and using the lowest reported solubility product (SADIQ, 1990) the experiments were also undersaturated with respect to $\text{Ca}_3(\text{AsO}_4)_2$.

Fig. 8a and b show that selenite sorption on portlandite is significantly slower than arsenate sorption. Arsenate and selenite sorption decreases with pH. Maximum sorption of the oxyanions was reached at pH 12. This pH-dependency may be due to competition of OH^- and/or to the fact that the portlandite surface becomes more negatively charged. Arsenate has a

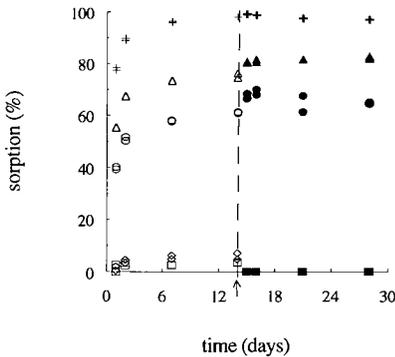


Fig. 8a: Adsorption (open symbols) and desorption (closed symbols) of selenite on 96 g/l portlandite, at pH 11.98 (+), pH 12.55 (Δ), pH 12.8 (○), pH 13.55 (◇) and pH 13.81 (□), I = 1.0 M and total-Se = 124 µg/l. The arrow shows the start of desorption.

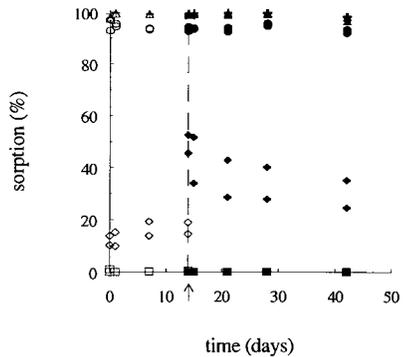


Fig. 8b: Adsorption (open symbols) and desorption (closed symbols) of arsenate on 1 g/l portlandite, at pH 11.98 (+), pH 12.55 (Δ), pH 12.8 (○), pH 13.55 (◇) and pH 13.81 (□), I = 1.0 M and total-As = 58.5 µg/l. The arrow shows the start of desorption.

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considerably higher affinity for portlandite than selenite; the distribution coefficient (K_d) of selenite on portlandite (pH 12.8, I = 1.0 M) after 14 days adsorption is 0.02 ml/g while that of arsenate is 20 ml/g.

The sorption of selenite seems to be reversible (Fig. 8a). Since separate experiments (not shown) have indicated that the isotherm is linear between 10 and 10,000 $\mu\text{g/l}$ Se, reversible sorption should result in the same sorption percentage during both adsorption and desorption. Desorption of arsenate (Fig. 8b) at pH 13.6 is slow and incomplete after at least 4 weeks. The uncertainty in the measurements at the other pH-values (at extremely high or low percentage in solution) does not allow a definite conclusion as to the reversibility of the sorption process.

Leaching from alkaline fly ash compared to sorption on Ca-phases

In alkaline fly ash the leaching of As and Se follows the leaching of Ca (Fig. 2). It is therefore feasible that, upon contact of alkaline fly ash with water, As and Se sorb on a Ca-phase which dissolves at lower pH. MINTEQA2 calculations on 100 g/l fly ash suspensions at the "natural" pH of 12.4 (Table 1) indicate that the solution is likely to be in equilibrium with portlandite. This mineral has been shown to strongly sorb arsenate (Fig. 8b). The affinity of selenite for portlandite is much less.

Calcite and gypsum have also been identified as secondary precipitates during fly ash leaching (WARREN EN DUDAS, 1985). MINTEQA2 calculations suggest that the fly ash leachates are not in equilibrium with calcite and atmospheric- CO_2 . FRUCHTER *et al.* (1990) could model the calcium and sulphate leaching from fly ash with gypsum solubility. The fly ash leachates in this study are calculated to be close to gypsum solubility. Both calcite and gypsum have been considered to be relevant adsorbates, but preliminary experiments have indicated a low affinity of arsenate and selenite for these minerals ($K_d < 4$ ml/g). This low affinity for calcite is in contradiction to results of

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GOLDBERG AND GLAUBIG (1988a, 1988b), but in agreement with observations by COWAN *et al.* (1990).

Although portlandite can strongly bind arsenate, and to a lesser extent selenite, this mineral cannot control the oxyanion leaching at pH-values below 12.4 (Fig. 2). Nevertheless, this study (Fig. 2) suggests that there is likely to be an association with an alkaline Ca-phase at pH-values lower than 12.4.

Another Ca-phase which can be formed during fly ash leaching is ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, (SIMONS AND JEFFERY, 1960; DE GROOT *et al.*, 1989). Experiments recently performed in our laboratory have shown a strong sorption of arsenate and selenite on ettringite (Fig. 9) Even at only 1 g/l of ettringite selenite is sorbed for 40 %, whereas arsenate is almost totally sorbed at both 10 g/l and 1 g/l of ettringite. These first results suggest that sorption of As and Se on ettringite may well contribute in controlling the leaching of these oxyanions from alkaline fly ash. Experiments are ongoing to investigate the role of ettringite in controlling the release of oxyanions from alkaline waste materials.

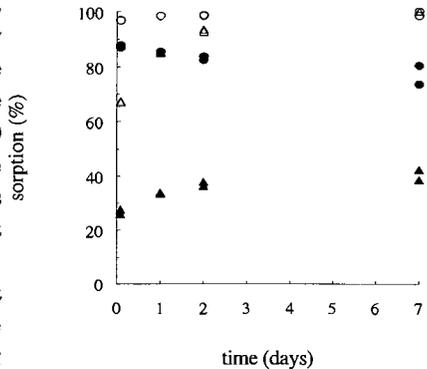


Fig. 9: Percentage of arsenate (open symbols) and selenite (closed symbols) sorption on ettringite. Ettringite equilibrated for one week at 1 g/l (Δ), and 10 g/l (\circ) with 100 $\mu\text{g/l}$ arsenate and 100 $\mu\text{g/l}$ selenite at pH 10.2.

Concluding remarks

As and Se leaching from acidic fly ash at pH-values between approximately 4 and 10 can be described by a simplified model of surface complexation with

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iron oxides in fly ash. Our results do not allow conclusions as to the particular type of iron oxide involved. The precise amounts of available iron oxide and As and Se involved in this sorption process are still unknown. To distinguish between crystalline and amorphous iron oxide and to obtain better model parameters we have started a study involving selective extractions of iron oxides from acidic fly ash.

For alkaline fly ash it is likely that a Ca-phase controls the leaching of As and Se. At pH >12.4, portlandite strongly sorbs arsenate and to a lesser extent selenite. Certainly for arsenate, this mineral cannot be excluded as the solubility controlling solid at strongly alkaline pH. Sorption of arsenate and selenite on ettringite may contribute in controlling their leaching from alkaline fly ash.

Mullite may be a relevant adsorbent mineral in the neutral pH range, similar to the interactions of oxyanions with kaolinite in natural systems.

On all three minerals considered in this study sorption reversibility of arsenate differed from that of selenite. Especially on hematite, selenite was sorbed reversibly to a much larger extent than arsenate, which could explain the observations (EARY *et al.*, 1990) that the fraction of As available for leaching from fly ash is generally less than that of Se.

Acknowledgement

We thank Prof Dr. C.H. van der Weijden and Dr. H.A. van der Sloot for critically reading an earlier draft of the manuscript.

CHAPTER 3

References

- AGGET, J. and ROBERTS, L.S. (1986) Insight into the mechanism of accumulation of arsenate and phosphate in hydro lake sediments by measuring the rate of dissolution with ethylenediaminetetraacetic acid, *Environ. Sci. Technol.* **20**, 183-186.
- ANDERSON, M.A., FERGUSON, J.F. and GAVIS, J. (1976) Arsenate adsorption on amorphous aluminum hydroxide, *J. Colloid Interface Sci.* **54**, 391-399.
- AYLMORE, L.A.G., KARIM, M. and QUIRK, J.P. (1967) Adsorption and desorption of sulfate ions by soil constituents, *Soil Sci.* **103**, 10-15.
- BALISTRERI, L.S. and CHAO, T.T. (1987) Selenium adsorption by goethite, *Soil. Sci. Soc. Am. J.* **51**, 1145-1151.
- BALISTRERI, L.S. and CHAO, T.T. (1990) Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide, *Geochim. Cosmochim. Acta* **54**, 739-751.
- BELZILE, N. and TESSIER, A. (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments, *Geochim. Cosmochim. Acta* **54**, 103-109.
- BREWSMA, A. (1973) Adsorption of ions on hematite (α -Fe₂O₃), PhD Thesis, Landbouwhogeschool Wageningen, The Netherlands.
- CHAO, T.T. and ZHOU, L. (1983) Extractions techniques for selective dissolution of amorphous iron oxides from soils and sediments, *Soil Sci. Soc. Am. J.* **47**, 225-232.
- COWAN, C.E. (1988) Review of selenium thermodynamic data, Electric Power Research Institute EA-5655.
- COWAN, C.E., ZACHARA, J.M. and RESCH, C.T. (1990) Solution ion effects on the surface exchange of selenite on calcite, *Geochim. Cosmochim. acta* **54**, 2223-2234.
- DEER, W.A., HOWIE, A.R. and ZUSSMANN, J. (1966) *An introduction to the rock forming minerals*, Wiley, New York.

Sorption of As and Se on mineral components of fly ash

- DAVIS, J.A. and KENT, D.B. (1990) Surface complexation modeling in aqueous geochemistry, in *Mineral-water interface geochemistry* (Eds. M.F. Hochella, and A.F. White) Reviews in mineralogy 23, Mineralogical Society of America, Washington, 177-248.
- DE GROOT, G.J., WIJSTRA, J., HOEDE, D. and VAN DER SLOOT, H.A. (1989) Leaching characteristics of selected elements from coal fly ash as a function of acidity of the contact solution and the liquid/solid ratio. In *Environmental aspects of stabilization and solidification of hazardous and radioactive wastes* (eds. P.L. Côté and T.M. Gilliam) ASTM STP 1033 pp. 170-183, American Society for Testing and Materials, Philadelphia.
- DUDAS, M.J. AND WARREN, C.J. (1987) Submicroscopic model of fly ash particles, *Geoderma* **40**, 101-114.
- EARY, L.E., RAI, D., MATTIGOD, S.V. and AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements, *J. Environ. Qual.* **19**, 202-214.
- FELMY, A.R., GIRVIN, D.C. and JENNE, E.A. (1984) MINTEQA A computer program for calculating aqueous geochemical equilibria. Environmental Protection Agency, Office of research and development, Rept. EPA 600/3/84/032.
- FROST, R.R. and GRIFFIN, R.A. (1977) Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals, *Soil. Sci. Soc. Am. J.* **41**, 53-57.
- FRUCHTER, J.S., RAI, D. and ZACHARA, J.M. (1990) Identification of solubility-controlling solid phases in a large fly ash field lysimeter, *Environ. Sci. Technol.* **24**, 1173-1179.
- GOLDBERG, S., and GLAUBIG, R.A. (1988a) Anion sorption on a calcareous, montmorillonitic soil-selenium, *Soil. Sci. Soc. Am. J.* **52**, 954-958.
- GOLDBERG, S., and GLAUBIG, R.A. (1988b) Anion sorption on a calcareous, montmorillonitic soil-arsenic, *Soil. Sci. Soc. Am. J.* **52**, 1297-1300.
- HAYES, K.M., PAPELIS, C. and LECKIE, J.O. (1987) Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces, *J. Colloid Interface Sci.* **125**, 717-726.

CHAPTER 3

- HINGSTON, F.J. (1981) A review of anion adsorption. In *Adsorption of inorganics at solid-liquid interfaces*, (eds. M.A. Anderson and A.L. Rubin) Chap. 2, pp. 51-91 Ann Arbor Sci. Publ., Michigan.
- LECKIE, J.O., BENJAMIN, M.M., HAYES K., KAUFMAN G. and ALTMANN S.(1980) Adsorption/Coprecipitation of trace elements from water with iron oxyhydroxide. Final Report EPRI CS-1513, Palo Alto, CA.
- MATTIGOD, S.V., RAI, D., EARY, L.E. and AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the mayor elements, *J. Environ. Qual.* **19**, 188-201.
- NATUSCH, D.F.S. and TAYLOR, D.R. (1980) Environmental effects of western coal combustion. Part IV. Chemical and physical characteristics of coal fly ash. U.S. Environmental Protection Agency Rept. EPA 600/3-80-094.
- ODLER, I. and ABDUL-MAULA, S. (1984) Possibilities of quantitative determination of the Aft-(Ettringite) and AFm-(Monosulphate) phases in hydrated cement, *Cem. Concr. Res.* **14**, 133-141.
- PARFITT, R.L. (1978) Anion adsorption by soils and soil materials, *Adv. Agron* **30**, 1-50.
- PIERCE, M.L. and MOORE, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* **16**, 1247-1253.
- RAASK ,E. (1980) Quartz, sulphates and trace elements in pf ash, *J. Inst. Energy* **70**, 70-75.
- RAI, D., AINSWORTH, C.C., EARY, L.E., MATTIGOD, S.V. and JACKSON, D.R. (1987) Inorganic and organic constituents in fossil fuel combustion residues. Electric Power Research Institute Rept. EPRI EA-5176 vol. 1.
- REARDON, E.J., WARREN C.J. and HOBBS, M.Y. (1993) Reduction of trace element concentrations in alkaline waste porewaters by dedolomitization, *Environ. Sci. Technol.* **27**, 310-315.
- ROY, W.R. and GRIFFIN, R.A. (1984) Illinois basin coal fly ashes. 2 Equilibria relationships and qualitative modeling of ash-water reactions, *Environ. Sci. Technol.* **18**, 739-742.
- SADIQ, M. (1990) Arsenic chemistry in marine environments: a comparison between theoretical and field observations, *Marine Chemistry* **31**, 285-297.

Sorption of As and Se on mineral components of fly ash

- SALEH, A.I., WOITTEZ, J.R.W., WALS, G.D. and DAS, H.A. (1990) Determination of Se(IV) in water by neutron activation analysis after coprecipitation of metal dibenzylthiocarbamate with phenolphthalein, *J. Radioanal. Nucl. Chem.* **140**, 357-363.
- SILBERMAN, D. and HARRIS, W.E. (1984) Determination of arsenic(III) and arsenic (V) in coal and oil fly ashes, *Intern. J. Environ. Anal. Chem.* **17**, 73-83.
- SIMONS, H.S. and JEFFERY, J.W. (1960) An X-Ray study of pulverised fuel ash, *J. Appl. Chem.* **16**, 328-336.
- SPOSITO, G. (1986) Distinguishing adsorption from surface precipitation. In *Geochemical processes at mineral surfaces* (eds. J.A. Davis and K.F. Hayes), pp. 217-228. ACS symposium series 323. American Chemical Society, Washington DC.
- STUMM, W. and MORGAN, J.J. (1981) *Aquatic Chemistry*, 2nd Edition, John Wiley, New York.
- TAYLOR, R.M. (1987) Non-silicate oxides and hydroxides. In *Chemistry of clays and clay minerals* (ed Newman, A.C.D.) Longman Scientific & Technical.
- TESSIER, A. (1991) Sorption of trace elements on natural particles in oxic environments. In *Environmental Particles* (eds. Buffle, J. and van Leeuwen, H.P.) Chap. 11, pp. 425-455 Lewis Publishers.
- TURNER, L.J. AND KRAMER, J.R. (1991) Irreversibility of sulfate sorption on goethite and hematite, *Water, Air and Soil Poll.* **63**, 23-32.
- TURNER, R.R. (1981) Oxidation state of arsenic in coal ash leachate, *Environ. Sci. Technol.* **15**, 1062-1066.
- VAN DER HOEK, BOOTS, B.J. AND COMANS R.N.J. (1995b) Experimental observations on sorption reversibility of arsenate, selenite and molybdate on hematite and amorphous iron (hydr)oxide to be published.
- VAN DER SLOOT, H.A., DE GROOT G.J., HOEDE, D. and WJKSTRA, J. (1991) Mobility of trace elements derived from combustion residues and products containing these residues in soil and groundwater, Netherlands Energy Research Foundation, ECN-C-91-059.

CHAPTER 3

- VAN DER SLOOT, H.A., WIJKSTRA, J., VAN STIGT, C.A. and HOEDE, D. (1985) Leaching of trace elements from coal ash and coal-ash products. In *Wastes in the ocean 4*, (eds. Duedall, I.W., Kester, D.R., Park, P.K., Ketchum, B.H.) pp.467-499, John Wiley & Sons, U.S..
- VAN ELTEREN, J.T., DAS, H.A., DE LIGNY, C.L. and AGTERDENBOS, J. (1989) Determination of arsenic(III/IV) in aqueous samples by neutron activation analysis after sequential coprecipitation with dibenzylidithiocarbamate, *Anal. Chim. Acta* **222**, 159-167.
- WADGE, A and HUTTON, M. (1987) The leachability and chemical speciation of selected trace elements in fly ash from coal combustion and refuse incineration, *Environ. Poll.* **48**, 85-99.
- WAGEMANN, R. (1978) Some theoretical aspects of stability and solubility of inorganic arsenic in the freshwater environment, *Water Res.* **12**, 139-145.
- WARREN, C.J. and DUDAS, M.J. (1985) Formation of secondary minerals in artificially weathered fly ash, *J. Environ. Qual.* **14**, 405-410.
- WARREN, C.J. and DUDAS, M.J. (1988) Leaching behaviour of selected trace elements in chemically weathered alkaline fly ash, *Sci. Total Environ.* **76**, 229-246.
- XU, H., ALLARD, B. and GRIMVALL, A. (1991) Effects of acidification and natural organic materials on the mobility of arsenic in the environment, *Water, Air and Soil Poll.* **57-58**, 269-278.

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MODELLING AS AND SE LEACHING FROM ACIDIC FLY ASH BY SORPTION ON IRON (HYDR)OXIDE IN THE FLY ASH MATRIX*

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Abstract

The sorption of As and Se on iron (hydr)oxide in acidic fly ash is studied as a possible process controlling the leaching of these contaminants. Following controlled leaching experiments with an acidic fly ash, sorption of As and Se is investigated both on crystalline and amorphous iron (hydr)oxide, using partial chemical extractions and isotopic exchange experiments. Virtually all As and Se at the fly ash surface, which is potentially available for leaching, is shown to be associated with hydroxylamine extractable "amorphous" iron (hydr)oxides in the fly ash matrix. Isotopic exchange experiments suggest that at pH < 10 the oxyanions are partly coprecipitated with secondary-formed amorphous iron (hydr)oxide, a process reducing their availability. The leaching of As and Se from acidic fly ash is described by a simplified model of surface complexation on amorphous iron (hydr)oxide, taking the limited availability of iron-associated As and Se into account. This approach is shown to constitute a useful tool to model sorption-control of contaminant leaching from waste materials.

Introduction

The availability of particle-bound trace elements is pertinent to the environmental question as it controls both the mobility in aquatic systems and the uptake by biota. In soils and sediments, trace element availability is often controlled by sorption processes (e.g. BUFFLE, 1988 and references

*Accepted for publication in: *Environ. Sci. Technol.*

therein). For combustion residues, such as fly ash, similar controlling processes have recently been suggested (e.g. WARREN AND DUDAS, 1985; FRUCHTER *et al.*, 1990; EARY *et al.*, 1990; VAN DER HOEK *et al.*, 1994).

In an earlier study we showed that the pH-dependent leaching of As and Se from acidic fly ash was consistent with the pH-dependent sorption of these oxyanions on iron oxides in model laboratory experiments. Geochemical modelling of the leachates did not indicate any precipitation/dissolution reactions involving As or Se. The results suggested that the leaching of As and Se was sorption-controlled and that iron (hydr)oxide was the probable controlling sorbent (VAN DER HOEK *et al.*, 1994). Both crystalline and amorphous iron (hydr)oxides may play a key-role in controlling the leaching process. Hematite and magnetite have been identified as the most important crystalline iron-bearing minerals in coal fly ash (MATTIGOD *et al.*, 1990), whereas WARREN AND DUDAS (1985) have shown that during leaching amorphous iron (hydr)oxides can form as secondary minerals.

Surface complexation models have been developed to quantitatively describe adsorption of trace elements on hydrous oxide surfaces. Laboratory studies on pure metal (hydr)oxides (e.g. on amorphous iron (hydr)oxide, DZOMBAK AND MOREL *et al.*, 1990) have shown that sorption processes can be successfully described by surface complexation. In natural systems not all parameters and reactions necessary for the surface complexation model are known (HONEYMAN AND SANTSCHI, 1988). Therefore, the sorption processes in natural systems are often modelled with an apparent overall surface reaction. Using such a simplified surface complexation model, BELZILE AND TESSIER (1990) showed that dissolved concentrations of As in sediment pore waters were controlled by sorption on amorphous iron (hydr)oxide.

In a first attempt to model the leaching of As and Se from acidic fly ash, using the simplified surface complexation approach (VAN DER HOEK *et al.*, 1994), assumptions were made concerning the amount of Fe, As and Se involved in the sorption process. Consequently, the modelling results depended strongly on the assumptions made. Furthermore, the iron

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(hydr)oxide sorbent was not identified, which made comparison with sorption data in the literature difficult.

In this study we investigate the surface processes between aqueous As and Se, and the iron (hydr)oxides in fly ash in more detail. Partial chemical extractions are used to obtain the necessary parameters for the surface complexation model and to differentiate between interactions with "crystalline" and "amorphous" iron (hydr)oxides. In referring to extracted iron (hydr)oxide phases we use quotation marks to indicate the operational character of the partial chemical extraction procedures. Isotopic exchange experiments are performed to focus on exchangeable As and Se at the fly ash surface. It will be shown that the isotopically exchangeable amount of As and Se is likely to be completely associated with the iron (hydr)oxides in fly ash. These values are, therefore, included in the simplified surface complexation model to calculate sorption parameters which are more realistically compared with laboratory sorption data in the literature. We outline the theoretical basis for our surface complexation approach below.

Surface complexation modelling

A simplified surface complexation model was used to investigate whether As and Se leaching as a function of pH can be described by sorption on iron (hydr)oxide. In the model, the sorption/leaching process is described as follows (VAN DER HOEK *et al.*, 1994; BELZILE AND TESSIER, 1990):



where \equiv represents the surface sites, x the proton stoichiometry and $*K_A$ the apparent overall sorption constant.

Assuming low surface coverage, we can relate the concentration of surface sites to the concentration of iron:

$$\{\equiv\text{FeOH}\} \approx N\{\text{Fe-oxide}\} \quad (3)$$

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where N is the number of moles of adsorption sites per mol iron (hydr)oxide (BELZILE AND TESSIER, 1990). This leads to:

$$K_A = N \cdot K_A [H^+]^x = \{=FeH_{x+1}AsO_4^{x-1}\} / \{Fe\text{-oxide}\} [H_2AsO_4^-] \quad (4)$$

$$K_A = N \cdot K_A [H^+]^x = \{=FeH_xSeO_3^{x-1}\} / \{Fe\text{-oxide}\} [HSeO_3^-] \quad (5)$$

where { } and [] refer to concentrations in the fly ash (mol/kg) and leachate (mol/l), respectively. Taking the logarithm of equations 4 and 5 results in:

$$\text{Log } K_A = \text{Log}(N \cdot K_A) - x \cdot \text{pH} \quad (6)$$

{Fe-oxide} (mol/kg fly ash) is obtained from partial chemical extractions, whereas {=FeH_{x+1}AsO₄^{x-1}} and {=FeH_xSeO₃^{x-1}} (mol/kg fly ash) are estimated by both partial chemical extractions and isotopic exchange. Concentrations of the aqueous species H₂AsO₄⁻ and HSeO₃⁻ (mol/l) are calculated from the total leached As and Se concentrations using the chemical speciation model MINTEQA2 (FELMY *et al.*, 1984, updated for Se with data of COWAN, 1988).

Methods

Acidic fly ash composition and leaching

The acidic fly ash originated from the power plant 'Amer Centrale' in the Netherlands. The same fly ash was also used in an earlier study (VAN DER HOEK *et al.*, 1994). The composition of the fly ash is shown in Table 1.

Prior to the extraction of iron (hydr)oxides the acidic fly ash was leached in duplicate at

Table 1: Composition of the acidic fly ash

pH*	4.12	
total concentration	%	mg/kg
Si	31.8 ± 1.6	
Al	9.85 ± 5.5	
Fe	2.97 ± 0.11	
Mn	518 ± 0.5	
As	9.10 ± 0.59	
Se	3.70 ± 0.16	

*) Suspension of 100 g/l in deionized water

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different pH-values: 1 g of fly ash was leached for 24 hours in 10.1 ml of nanopure demineralized water at pre-determined pH-values in the range of 4 to 12.5, by adding 1 M NaOH. The pH was adjusted manually during the first few hours of equilibration. The solids for the extraction experiments were obtained by centrifugation at 20000 x g. Subsequently, the supernatant was removed from the tubes and filtered through 0.45 µm membrane filters. Removal of the fly ash from the centrifuge tubes was prevented by leaving the last 5 % of the supernatant in the tubes. Corrections were made for the amount of As, Se and Fe in the residual solution. The leached concentrations of As and Se (hydride-AAS) and Fe, Mn, Al and Si (ICP-AES) were measured in the filtrate (VAN DER HOEK *et al.*, 1994). Extractions of iron (hydr)oxides from the solids left in the centrifuge tubes were performed as described below.

Extraction tests

Many studies have shown undesired effects of partial chemical extractions (e.g. KHEBOA AND BAUER 1987; MARTIN *et al.*, 1987; GRUEBEL *et al.*, 1988), such as re-adsorption and poor selectivity. Therefore, we have tested a number of selected procedures for the extraction of iron (hydr)oxides from fly ash for re-adsorption of As and Se and for the selectivity of the extractions with respect to amorphous and crystalline iron (hydr)oxide.

Two methods to extract "amorphous" iron (hydr)oxide were tested: Method 1 originated from the sequential extraction scheme of TESSIER *et al.* (1979; 0.04 M NH₂OH.HCl in 25 % acetic acid, 6 hours at 96°C) and Method 2 was taken from Chao and Zhou (1983; 0.25 M NH₂OH.HCl in 0.25 M HCl, 30 minutes at 50°C). A commonly used method for extracting "amorphous + crystalline" iron (hydr)oxide is that using dithionite (CHAO, 1984, and references therein). We found this method inappropriate, because dithionite is generally contaminated with high concentrations of trace elements (CHAO, 1984). We observed high As and Se concentrations even after the purification step of MALO (1977). Another two extraction methods were tested to extract "amorphous + crystalline" iron (hydr)oxide: Method 3, based on oxalic acid exposed to ultra-violet light for 2 hours

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(SCHWERTMANN, 1964) and Method 4, based on 2 M HCl for 30 minutes at 96°C (CHAO AND ZHOU, 1983).

Table 2: Percentage readsorption of As and Se during different extractions of iron (hydr)oxide from fly ash

Method	As	Se
1. NH ₂ OH.HCl (TESSIER <i>et al.</i> , 1979)	15	30
2. NH ₂ OH.HCl (CHAO AND ZHOU, 1983)	0	0-5
3. Oxalic acid (SCHWERTMANN, 1964)	0-2	10-90
4. 2 M HCl (CHAO AND ZHOU, 1983)	0	0

Readsorption of the oxyanions was tested by adding ⁷³As/⁷⁵Se tracers (carrier-free) to the extraction agent prior to extraction of the fly ash. After extraction, the solid was removed and the remaining radioactivity in the solution measured relative to a standard containing 100 % of the initially added amount. Results are presented in Table 2. For those methods with acceptable levels of readsorption (see below), the selectivity for iron(hydr)oxides was tested by measuring the amounts of Si, Al and Mn that were co-extracted with Fe. These results are shown in Table 3, along with the co-extracted As and Se.

Table 2 shows that significant readsorption losses occurred when methods 1 or 3 were used. No readsorption was observed when using methods 2 or 4. Only when samples of method 2 were conserved for longer than one week, a minor loss of Se occurred. Experiments with single iron(hydr)oxide minerals have shown that method 2 is reasonably specific for "amorphous" iron(hydr)oxide (CHAO AND ZHOU, 1983; KOSTKA AND LUTHER, 1994). We found that method 4 extracts slightly more iron from the fly ash (16 ± 1 %) than the dithionite method (13 ± 1 %) which is well-accepted for the extraction of "amorphous + crystalline" iron(hydr)oxides (CHAO, 1984, and references therein). As is stated above, we were unable to use the latter method because of insufficient purity of the chemicals.

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Table 3 shows that, in addition to Fe, approximately equal percentages of Mn are extracted with either method 2 or 4. It is, therefore, not possible to differentiate between iron (hydr)oxide and manganese (hydr)oxide, but, as only minor absolute amounts of Mn are extracted, the importance of manganese (hydr)oxides as adsorbing surfaces is probably low. The relatively high amount of extracted Al in method 4 (Table 3) suggests that other mineral phases may be co-extracted with this method as well. Relatively low amounts of Si and Al are co-extracted when using method 2.

Table 3: Extracted amounts relative to total amounts of elements present in the fly ash after leaching, using different extraction methods for iron (hydr)oxide

	Method 2 NH ₂ OH.HCl (CHAO AND ZHOU, 1983)		Method 4 2 M HCl (CHAO AND ZHOU, 1983)	
	%	s	%	s
As	72	7	86	6
Se	51	4	65	7
Fe	1.6	0.1	16	1
Mn	2.2	0	19	1
Al	0.7	0	5.1	0.3
Si	0.1	0	0.8	0

Final Extractions Methods

Method 2 was selected to extract "amorphous" iron (hydr)oxide from fly ash, because of its reasonable selectivity and lack of readsorption. Although the selectivity of method 4 is not very high, this method was selected to extract "amorphous + crystalline" iron oxide because no readsorption losses were observed. The complete procedures were as follows: Prior to the extraction, duplicate samples of fly ash were leached at different pH values as described above. "Amorphous" iron (hydr)oxide was extracted from 1 g of the leached fly ash with 25 ml of 0.25 M NH₂OH.HCl in 0.25 M HCl for 30 minutes at 50°C. After cooling to room temperature the extracts were centrifuged for 30 minutes at 10000 x g. For this extraction centrifugation was used rather than filtration because cellulose nitrate membrane filters dissolved in the extract. The concentrations of As, Se and Fe were determined in the supernatant. Both "amorphous" and "crystalline" iron (hydr)oxide were extracted from 1 g of leached fly ash in 2 M HCl for 30 minutes at 96°C. After a short period of cooling the extracts

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were filtered and concentrations of As, Se and Fe determined in the filtrate. The extracts were stored at 4°C and analyses were carried out within 1 week for NH₂OH.HCl solutions and within 2 weeks for 2 M HCl solutions. The extracted amounts of As, Se and Fe were used in eqns. 4 and 5 for {≡FeH_{x+1}AsO₄^{x-1}}, {≡FeH_xSeO₃^{x-1}} and {Fe-oxide} (mol/kg fly ash), respectively.

Isotopic exchange

Prior to the isotopic exchange experiment, duplicate samples of fly ash were leached at different pH values as described above. The pH during the isotopic exchange experiment was controlled within ± 0.1 pH unit with a pH-stat at values in the range from 4 to 12. After 24 hours a subsample was taken and the concentration of As and Se in the filtrate measured. ⁷³As-tracer and ⁷⁵Se-tracer (carrier-free) were added to the fly ash suspensions and after another 24 hours of equilibration the suspensions were filtered through 0.45 µm membrane filters. The remaining radioactivity in the filtrate was measured. The solids, with adsorbed tracers, were extracted as described above and extracted amounts of ⁷³As and ⁷⁵Se-tracers measured.

Isotopic exchange was calculated as follows (COMANS, 1987):

$$E = \frac{(1-f)C_L}{f \cdot C_s \cdot m} \quad (7)$$

where

- E = isotopically exchangeable fraction of As or Se in the fly ash,
- f = fraction of aqueous As or Se radiotracer,
- C_L = aqueous As or Se concentration (µg/l),
- C_s = total concentration of As or Se remaining in the fly ash after leaching (µg/kg),
- m = particle (fly ash) concentration (kg/l).

As will be discussed below, the isotopically exchangeable fractions of As and Se are indicative for the amount associated with the iron (hydr)oxide surface, and are used in the surface complexation model as follows:

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$$\{=FeH_{x+1}AsO_4^{X-1}\} = E_{As} \cdot C_{S,As} \quad (8)$$

$$\{=FeH_xSeO_3^{X-1}\} = E_{Se} \cdot C_{S,Se} \quad (9)$$

Results and Discussion

Extraction of "amorphous" and "crystalline" iron (hydr)oxide

Table 3 shows the results of the extractions of iron (hydr)oxides, and co-extracted As, Se, Al, Si and Mn, from the fly ash. The relatively high amounts of As and Se co-extracted with iron (hydr)oxides (Table 3) confirm our earlier findings that iron(hydr)oxides are important in controlling the leaching process (VAN DER HOEK *et al.*, 1994). Already 70 % As and 50 % Se are extracted with hydroxylamine. While 16 times more iron is extracted using 2 M HCl, only an additional 15 % of As and Se is released. This demonstrates that hydroxylamine-extractable ("amorphous") iron (hydr)oxide is the more likely sorbent to control the leaching process. Therefore, we have used As, Se and Fe extracted with hydroxylamine as input parameters to the surface complexation model.

In the extractions, however, a high amount of aluminium is co-extracted as well (Table 3). The major species of As and Se in the fly ash leachates, arsenate and selenite (VAN DER HOEK *et al.*, 1995a), respectively, can both sorb on aluminium and iron (hydr)oxides (PARFITT, 1978). With most partial chemical extraction methods it is not possible to differentiate between iron and aluminium (hydr)oxides (TESSIER *et al.*, 1979). Many authors have shown, using different and often more direct methods, that arsenate in natural aquatic systems is generally associated with iron (hydr)oxides (KUNN AND SIGG, 1993; DE VITRE, *et al.*, 1991; FULLER AND DAVIS, 1986; AGGET AND ROBERTS, 1986; FARMER AND LOVELL, 1986; FORDHAM AND NORRISH *et al.*, 1979). It seems likely that this preference for iron (hydr)oxide is also existent in the fly ash/water environment. We did not find similar evidence in the literature for a predominant association of selenite with iron (hydr)oxide.

Modelling As and Se leaching from acidic fly ash

Surface complexation modelling

Tables 4 and 5 show the total amount of As and Se leached, the concentration of the aqueous species $H_2AsO_4^-$ and $HSeO_3^-$ in the leachates, as calculated with MINTEQA2, and the amount of As, Se and Fe extracted from the leached fly ash. These data were used to calculate values for K_A , according to equations 5 and 6, which are listed in the last column of each Table. At low pH almost no As and Se are leached, whereas high concentrations of As and Se are extracted from the fly ash. The reversed is observed at high pH.

Table 4: Arsenic concentrations in leachates and hydroxylamine extracts, isotopic exchangeability (E_{As}) and apparent adsorption constants (K_A) of As on "amorphous" iron (hydr)oxide calculated using extraction or isotopic exchange data.

pH	As _{TOT} leached µg/kg	H ₂ AsO ₄ ⁻ M x 10 ⁻⁸	extracted As mol/kg x 10 ⁻⁶	extracted Fe mol/kg x 10 ⁻³	E _{As} [#]	log(K _A) extr.	log(K _A) [#] isot.ex.
4.12	72.6	67.4±0.7	87.6±0.9	8.30	0.09±0.01	4.20±0.01	3.35±0.16
4.43	72.6	57.9±0.6	80.0±0.8	7.91	-	4.24±0.01	-
5.61	22.1	65.7±0.7	81.7±0.8	8.81	0.37±0.34	4.15±0.01	3.89±0.85
5.80	22.1	44.1±0.4	82.3±0.8	7.97	0.14±0.08	4.37±0.01	3.68±0.55
6.88	15.8	20.0±0.2	83.2±0.8	7.50	0.08±0.03	4.74±0.01	3.81±0.40
7.53	15.8	5.29±0.05	80.5±0.8	8.25	-	5.27±0.01	-
8.14	24.2	1.245±0.012	85.8±0.9	8.07	0.09±0.01	5.93±0.01	5.02±0.13
8.18	24.2	2.301±0.023	81.6±0.9	7.59	0.09±0.01	5.67±0.01	4.80±0.13
8.99	98.9	0.200±0.002	84.7±0.9	8.41	0.10±0.01	6.70±0.01	5.81±0.07
9.37	98.9	0.401±0.004	82.5±0.8	8.43	-	6.39±0.01	-
9.96	443	0.098±0.001	64.2±0.7	8.80	0.16±0.01	6.87±0.01	6.24±0.07
10.05	443	0.090±0.001	69.4±0.8	8.62	0.16±0.01	6.95±0.01	6.29±0.07
11.06	1868	7±0.07x10 ⁻³	56.5±2.1	8.72	-	7.98±0.04	-
11.07	1868	6±0.06x10 ⁻³	52.5±2.5	8.62	-	8.00±0.05	-
12.25	4142	7.4±0.07x10 ⁻⁵	28.2±3.5	9.41	0.19±0.01	9.61±0.12	9.26±0.07
12.44	4142	2.8±0.02x10 ⁻⁵	23.3±6.3	9.44	-	9.95±0.27	-

[#]radiotracer measurements were done in parallel experiments in which pH deviated on average by 0.18±0.14

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Table 5: Selenium concentrations in leachates and hydroxylamine extracts, isotopic exchangeability (E_{As}) and apparent adsorption constants (K_A) of As on "amorphous" iron (hydr)oxide calculated using extraction or isotopic exchange data.

pH	Se _{tot} leached µg/kg	HSeO3 ⁻ M x 10 ⁻⁹	extracted Se mol/kg x 10 ⁻⁶	extracted Fe mol/kg x 10 ⁻³	E_{As} [#]	log(K_A) extr.	log(K_A) [#] isot.ex.
4.12	117.9	93.0±0.9	26.7±0.3	8.30	0.16±0.01	4.54±0.02	3.97±0.09
4.43	117.9	48.5±0.5	23.0±0.2	7.91	-	4.78±0.01	-
5.61	80.0	34.7±0.3	24.8±0.3	8.81	0.20±0.03	4.91±0.01	4.47±0.13
5.80	80.0	55.4±0.6	25.6±0.3	7.97	0.17±0.02	4.76±0.01	4.25±0.09
6.88	113.7	96.8±1.0	22.9±0.3	7.50	0.15±0.01	4.50±0.02	3.97±0.07
7.53	113.7	58.8±0.6	23.0±0.3	8.25	-	4.68±0.02	-
8.14	196.8	9.0±0.1	24.2±0.4	8.07	0.11±0.01	5.52±0.02	4.78±0.05
8.18	196.8	88.6±0.9	21.5±0.7	7.59	0.11±0.01	4.50±0.03	3.79±0.05
8.99	394.7	42.0±0.4	18.1±1.3	8.41	0.06±0.00	4.71±0.07	3.78±0.06
9.37	394.7	63.7±0.6	14.7±0.3	8.43	-	4.44±0.02	-
9.96	1007	15.3±0.2	9.6±0.9	8.80	-	4.86±0.10	-
10.05	1007	12.2±0.1	9.6±0.7	8.62	-	4.96±0.07	-
11.06	2195	1.41±0.01	5.4±2.8	8.72	-	5.64±0.52	-
11.07	2195	1.34±0.01	5.5±3.9	8.62	-	5.68±0.70	-
12.25	2821	0.088±0.001	-	9.41	-	-	-
12.44	2821	0.058±0.001	-	9.44	-	-	-

[#]radiotracer measurements were done in parallel experiments in which pH deviated on average by 0.18±0.14

The distribution of As and Se among the leachate and extractable forms on the fly ash clearly follows the affinity of the oxyanions for sorption on iron(hydr)oxides (VAN DER HOEK *et al.*, 1994): strong retention on iron(hydr)oxides at low pH (i.e. small amounts leachable; large amounts extractable) and weak retention at high pH (i.e. large amounts leachable; small amounts extractable).

Figure 1 shows K_A , which is the apparent overall sorption constant modified for pH and the site density of the iron(hydr)oxide sorbent in the fly ash (equations 5-6), as a function of leachate pH. The K_A -values calculated from the hydroxylamine extractions of "amorphous" iron

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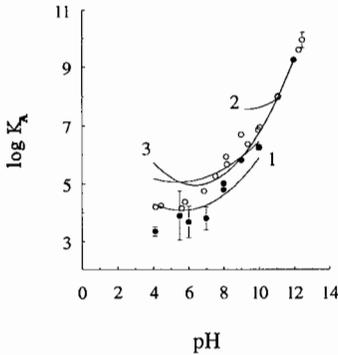


Fig. 1a: Apparent overall adsorption constant (K_A) of As on amorphous iron oxide as a function of pH. Leaching data were modelled by using As co-extracted with amorphous iron (hydr)oxides (●) and by using isotopically exchangeable As on fly ash (○). Curve 1, 2 and 3 are calculated from literature data: Curve 1 from PIERCE AND MOORE (1982; total-Fe 42 μ M, total-As 13.3 μ M). Curve 2 from LECKIE *et al.* (1980; total-Fe 1mM, total-As 5 μ M) and curve 3 from VAN DER HOEK *et al.* (1995b, total-Fe 0.1 mM, total-As 1.29 μ M).

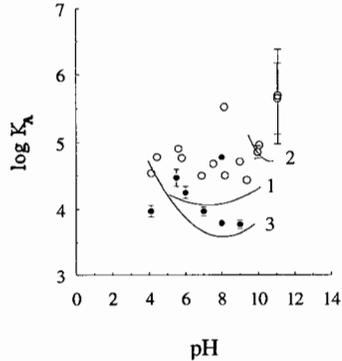


Fig. 1b: Apparent overall adsorption constant (K_A) of Se on amorphous iron oxide as a function of pH. Leaching data were modelled by using Se co-extracted with amorphous iron (hydr)oxides (●) and by using isotopically- exchangeable Se on fly ash (○). Curve 1, 2 and 3 are calculated from literature data: Curve 1 from BALISTRIERI AND CHAO (1990; total-Fe 148 μ M and total-Se 0.68 μ M). Curve 2 from LECKIE *et al.* (1980; total-Fe 1mM and total-Se 5 μ M) and curve 3 from VAN DER HOEK *et al.* (1995b, total-Fe 0.1 mM, total-Se 1.24 μ M).

(hydr)oxide in this study are compared with values calculated from published laboratory sorption data on amorphous iron (hydr)oxide. The values calculated for the acidic fly ash agree within one order of magnitude with the K_A -values derived from the literature data. The large analytical error associated with the small amount of Se extracted at pH values > 10 does not allow an accurate evaluation of Se sorption behaviour at strongly alkaline pH.

According to equation 6 the slope in Figure 1 represents the proton stoichiometry (-x). The values $x = -1, 0$ and $+1$ would indicate the arsenic

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surface species $\equiv\text{FeAsO}_4^{2-}$, $\equiv\text{FeHASO}_4^-$, and $\equiv\text{FeH}_2\text{AsO}_4$ (eqn. 4), respectively. For selenium, the values $x = 1$ and $x = 0$ would suggest the formation of $\equiv\text{FeHSeO}_3$ and $\equiv\text{FeSeO}_3^-$ (eqn. 5), respectively.

Table 6 summarizes the parameters obtained after linear regression of the data according to equation 6, and suggests that the surface species $\equiv\text{FeHASO}_4^-$ controls As leaching below, and $\equiv\text{FeAsO}_4^{2-}$ above pH 7. BELZILE AND TESSIER (1990) found the same species to control arsenate sorption as a function of pH in lacustrine sediments. The data in Table 6 suggest the leaching of Se at pH < 10 to be controlled by the surface species $\equiv\text{FeSeO}_3^-$.

Table 6: Linear regression of the apparent overall adsorption constant K_A as a function of pH, according to equation 6.

Method	As		Se	
	x	$N \cdot K_A$	x	$N \cdot K_A$
hydroxylamine extraction	-0.2 (pH < 7)	3.4 (pH < 7)	-0.02	4.6
	-0.9 (pH > 7)	-1.7 (pH > 7)		
isotopic exchange	-0.2 (pH < 7)	2.8 (pH < 7)	0.03	4.4
	-1.0 (pH > 7)	-3.5 (pH > 7)		

Isotopic exchange

In the above surface complexation modelling the amount of As and Se adsorbed on iron (hydr)oxide in the fly ash is obtained from hydroxylamine extractions of "amorphous" iron (hydr)oxide. These extractions are likely to dissolve not only the surface of the iron (hydr)oxide minerals but the deeper layers as well. Therefore, co-extracted As and Se do not necessarily originate from the mineral surface. The amount of As and Se at the surface, which is likely to be more representative for the rapid exchange (i.e. leaching) processes, was estimated by isotopic exchange.

In order to check whether the radiotracers exchange predominantly with "amorphous" iron (hydr)oxide, the fly ash was extracted with hydroxylamine after isotopic equilibration at each pH. Figure 2 shows the percentage of tracer in the leachate and extracted from the fly ash after

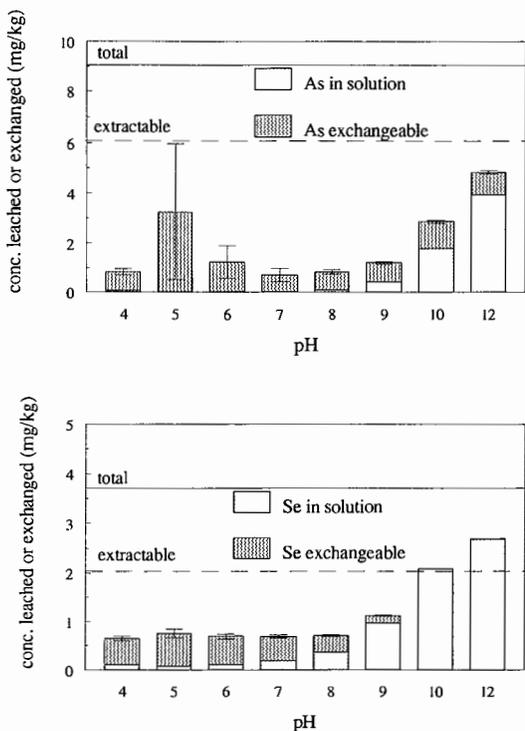


Fig. 2: Percentage ^{73}As - and ^{75}Se -tracer after isotopic exchange with fly ash, recovered in solution (leachate) and in hydroxylamine extracts of fly ash.

total amount available for leaching at a given pH, is the amount leached plus the amount which is isotopically exchangeable. At pH < 10, only small fractions of As and Se are available compared to the total amount present in the fly ash (Table 1) and the maximum amount available at pH 12. In view of the large analytical error, the apparent increase in the exchangeability of As at pH 5 is insignificant.

The relatively low availability at pH < 10 is remarkable. If the available (leachable) amount of As and Se would originate from reversible sorption

isotopic exchange. All As-tracer and almost all Se-tracer which had exchanged with the surface was recovered by the hydroxylamine extraction, suggesting that the radiotracers had exchanged almost entirely with the "amorphous" iron (hydr)oxide mineral phase. These results confirm at the same time that, within the 24-hour leaching period, crystalline iron oxide is not an important sorbent in the fly ash.

Figure 3 shows the isotopically exchangeable amount of As and Se on the fly ash surface, in addition to the amount leached, as a function of pH. The

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sites on the iron (hydr)oxide surface, we would expect no difference in availability between pH 4 and 12. The results indicate, however, that additional factors contribute to controlling As and Se availability in the fly ash. Following the above indications that iron (hydr)oxide controls the leaching of As and Se, the sequence of processes described below is consistent with both the leaching and isotopic exchange results:

Amorphous iron (hydr)oxide has been shown to be formed as a secondary mineral after reaction of fly ash with water (WARREN AND DUDAS, 1985). In the unweathered fly ash As and Se are likely to be present as oxides or salts (VAN DER HOEK *et al.*, 1995a), which dissolve upon first contact with water. During the initial stages of leaching (our experiments suggest within 24 hours), As and Se associate with the precipitating iron (hydr)oxide. This (coprecipitation) process may result in a low availability of the oxyanions for leaching, because As and Se are partly "buried" in the iron (hydr)oxide structure. At strongly alkaline conditions, however, coprecipitation of As and Se with iron (hydr)oxide is

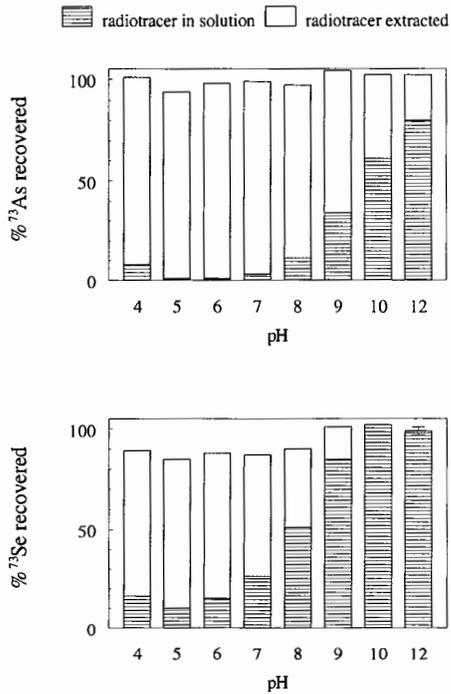


Fig. 3: Amount of As and Se leached from, and isotopically-exchanged with, fly ash as a function of pH. Solid lines indicate total As and Se concentrations in the fly ash (see Table 1). Broken lines indicate average extractable amounts (leached + extractable with hydroxylamine): 6.1 ± 0.3 mg kg for As and 2.1 ± 0.4 mg/kg for Se.

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insignificant because of the low affinity of the oxyanions for the mineral surface.

The data in Figs. 2 and 3 indicate that Se shows no isotopic exchange with the fly ash (i.e. iron (hydr)oxide) surface at $\text{pH} \geq 10$, whereas an additional amount of 0.5 mg/kg Se is leached from the ash between pH 10 and 12. A similar amount of 0.4 mg/kg (5.5×10^{-6} mol/kg; Table 5) is extractable with hydroxylamine at pH 11. It seems that about 0.5 mg/kg (i.e. 15 %) Se is not associated with the fly ash surface, yet available for leaching at strongly alkaline pH, possibly by partial dissolution of the fly ash matrix.

Summarizing the isotopic exchange results, we conclude that a substantial amount of the extracted As and Se is not likely to be sorbed at the iron (hydr)oxide surface. It is, therefore, more accurate to use isotopically exchangeable As and Se, indicative for the amount associated with the iron (hydr)oxide surface, in the surface complexation model.

K_A -values based on isotopically exchangeable As and Se, calculated using equations 8 and 9, are included in Tables 4 and 5 and in Figure 1, and are about one order of magnitude lower than those obtained from the hydroxylamine extractions of "amorphous" iron (hydr)oxide. Table 6 includes the parameters obtained after linear regression of these K_A -values, as a function of pH, according to equation 6. The N^*K_A values in Table 6 suggest that the number of surface sites (N) is indeed overestimated by the hydroxylamine extraction, the effect being more pronounced for As than for Se.

The K_A -values obtained after isotopic exchange are more realistic to compare with (short term) laboratory sorption experiments from the literature. The range in the available literature data does, however, not allow for a definite conclusion that the modelling approach using isotopically exchangeable As/Se on fly ash is better than the approach using As/Se co-extracted with "amorphous" iron (hydr)oxide. The less than one order of magnitude differences between the K_A -values calculated from the fly ash data, using either modelling approach, and the values based on literature sorption data is, however, satisfactory.

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Conclusions

We have shown that the partitioning of As and Se between acidic fly ash and leachate is controlled by sorption on iron (hydr)oxide. The contribution of crystalline iron oxides in controlling this process is low; the leaching of As and Se is mainly controlled by sorption on hydroxylamine extractable ("amorphous") iron (hydr)oxide. It is possible to describe the pH-dependent leaching of As and Se from acidic fly ash using a simplified model of oxyanion surface complexation on amorphous iron (hydr)oxide. Isotopic exchange experiments show a reduced availability of As and Se at pH < 10 and suggest that the oxyanions are partly coprecipitated with secondary-formed amorphous iron (hydr)oxide in this pH range. The surface complexation model was modified for this process by using the isotopically exchangeable fraction of As and Se at the fly ash surface. About 15% of Se is not associated with the fly ash surface, yet available for leaching at strongly alkaline pH, possibly by partial dissolution of the fly ash matrix. We believe that the simplified surface complexation approach described above constitutes a useful tool to model sorption-control of contaminant leaching from heterogeneous waste-material matrices. As the selectivity of extraction procedures for single mineral phases is limited, further and more direct evidence for sorption-control by specific sorbent minerals should come from surface spectroscopic analysis of the waste materials.

Acknowledgement

The authors thank Prof Dr. C.H. van der Weijden for carefully reading an earlier draft of the manuscript.

References

- AGGET, J. AND ROBERTS, L.S. (1986) Insight into the mechanism of accumulation of arsenate and phosphate in hydro lake sediments by measuring the rate of dissolution with ethylenediaminetetraacetic acid, *Environ. Sci. Technol.* **20**, 183-186.

Modelling As and Se leaching from acidic fly ash

- BALISTRERI, L.S. AND CHAO, T.T. (1990) Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide, *Geochim. Cosmochim. Acta* **54**, 739-751.
- BELZILE, N. AND TESSIER, A. (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments, *Geochim. Cosmochim. Acta* **54**, 103-109.
- BUFFLE, J. (1988) *Complexation reactions in aquatic systems: an analytical approach*, Ellis Horwood Limited publishers, Chichester.
- CHAO, T.T. AND ZHOU, L. (1983) Extractions techniques for selective dissolution of amorphous iron oxides from soils and sediments, *Soil Sci. Soc. Am. J.* **47**, 225-232.
- CHAO, T.T. (1984) Use of partial dissolution techniques in geochemical exploration, *J. Geochem. Exploration* **20**, , 101-135.
- COMANS, R.N.J. (1987) Adsorption, desorption and isotopic exchange of cadmium on illite: evidence for complete reversibility, *Wat. Res.* **21**, 1573-1576.
- COWAN, C.E. (1988) Review of selenium thermodynamic data. Electric Power Research Institute EA-5655.
- DE VITRE, R., BELZILE, N. AND TESSIER, A. (1991) Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides, *Limnol. Oceanogr.* **36**, 1480-1485.
- DZOMBAK, D.A. AND MOREL, F.M.M. (1990) *Surface complexation modeling: Hydrous ferric oxide*, John Wiley, New York.
- EARY, L.E., RAI, D., MATTIGOD, S.V. AND AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements, *J. Environ. Qual.* **19**, 202-214.
- FARMER, J. G. AND LOVELL, M.A. (1986) Natural enrichment of arsenic in Loch Lomond sediments, *Geochim. Cosmochim. Acta* **50**, 2059-2067.
- FELMY, A.R., GIRVIN, D.C. AND JENNE, E.A.(1984) *MINTEQA A computer program for calculating aqueous geochemical equilibria*. Environmental Protection Agency, Office of research and development, Rept. EPA 600/3/84/032.
- FORDHAM, A.W. AND NORRISH, K. (1979) Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention, *Aust. J. Soil Res.*, **17**, 307-316.

CHAPTER 4

- FRUCHTER, J.S., RAI, D. AND ZACHARA, J.M.(1990) Identification of solubility-controlling solid phases in a large fly ash field lysimeter, *Environ. Sci. Technol.* **24**, 1173-1179.
- FULLER, C.C. AND DAVIS, J.A. (1989) Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters, *Nature*, **340**, 52-54.
- GRUEBEL, K.A., DAVIS J.A. AND LECKIE, J.O. (1988) The feasibility of using extraction techniques for arsenic and selenium in soils and sediments, *Soil Sci. Soc. Am. J.* **52**, 390-397.
- HONEYMANN B.D. AND SANTSCHI, P.H. (1988) Metals in aquatic systems, *Environ. Sci. Technol.* **22**, 862-871.
- KHEBOA, C. AND BAUER, C.F. (1987) Accuracy of selective extraction procedures for metal speciation in model aquatic sediments, *Anal Chem.* **59**, 1417-1423.
- KOSTKA, J. E. AND LUTHER, III, G.W.(1994) Partitioning and speciation of solid phase iron in saltmarsh sediments, *Geochim. Cosmochim. Acta.* **58**, 1701-1710.
- KUNN, A. AND SIGG, L. (1993) Arsenic cycling eutrophic Lake Greifen, Switzerland: Influence of seasonal redox processes, *Limnol. Oceanogr.* **38**, 1052-1059.
- LECKIE, J.O., BENJAMIN, M.M., HAYES K., KAUFMAN G. AND ALTMANN S. (1980) Adsorption/Coprecipitation of trace elements from water with iron oxyhydroxide. Final Report EPRI CS-1513, Palo Alto, CA.
- MALO, B.A. (1977) Partial extraction of metals from aquatic sediments, *Environ. Sci. Technol.* **11**, 277-282.
- MARTIN, J.M., NIREL, P. AND THOMAS, A.J. (1987) Sequential extraction techniques: promises and problems, *Marine Chem.* **22**, 313-341.
- MATTIGOD, S.V., RAI, D., EARY, L.E. AND AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the mayor elements, *J. Environ. Qual.* **19**, 188-201.
- PARFITT, R.L. (1978) Anion adsorption by soils and soil materials, *Adv. Agron* **30**, 1-50.
- PIERCE, M.L. AND MOORE, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* **16**, 1247-1253.

Modelling As and Se leaching from acidic fly ash

- SCHWERTMANN, U. (1964) Differenzierrung der Eisenoxide des Bodems durch Extraktion mit ammoniumoxalat-lösung, *Z. Pflanzenern. Düng. Bodenkunde* **105**, 194-201.
- TESSIER, A., CAMPELL, P.G.C. AND BISSON, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844-851.
- VAN DER HOEK, E.E., BONOUVRIE, P.A. AND COMANS, R.N.J. (1994) Sorption of As and Se on mineral components of fly ash: relevance for leaching processe,s *Applied Geochem.* **9**, 403-412.
- VAN DER HOEK, E. E., VAN ELTEREN, J.T. AND COMANS, R.N.J. (1995a) Determination of As, Sb and Sb speciation during leaching from fly ash, submitted for publication.
- VAN DER HOEK, E. E., BOOTS, B.J. AND COMANS, R.N.J. (1995) Experimental observations on sorption reversibility of arsenate, selenite and molybdate on hematite and amorphous iron (hydr)oxide, to be published.
- WARREN, C.J. AND DUDAS, M.J. (1985) Formation of secondary minerals in artificially weathered fly ash, *J. Environ. Qual.* **14**, 405-410.

5

EXPERIMENTAL OBSERVATIONS ON SORPTION REVERSIBILITY OF ARSENATE, SELENITE AND MOLYBDATE ON HEMATITE AND AMORPHOUS IRON (HYDR)OXIDE

CHAPTER 5

EXPERIMENTAL OBSERVATIONS ON SORPTION REVERSIBILITY OF ARSENATE, SELENITE AND MOLYBDATE ON HEMATITE AND AMORPHOUS IRON (HYDR)OXIDE*

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Abstract

The reversibility of selenite, arsenate and molybdate sorption on amorphous iron (hydr)oxide and hematite was studied as a function of pH. It was observed that, within the time frame of the experiments selenite sorbs reversibly on both iron (hydr)oxides, whereas sorption of arsenate and molybdate appears to be irreversible, especially on hematite. The pH at which the oxyanion is adsorbed is crucial in controlling its sorption reversibility on iron (hydr)oxides. The pH at which the sorbent mineral is pre-equilibrated prior to the sorption experiment is also important.

Key words: sorption reversibility, arsenate, selenite, molybdate, hematite, amorphous iron (hydr)oxide, sorption experiments.

Introduction

Oxyanion sorption on oxides has been studied extensively in order to understand the mobility of these elements in the environment. Anion sorption is dependent on the nature of the anion, the pH, the type of adsorbing surface, and the presence of competing anions (HINGSTON, 1981). In a number of

*Submitted for publication

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studies in natural systems, such as sediments and soils, it has been shown that oxyanions are associated with iron oxide (BELZILE AND TESSIER, 1990; NEAL *et al.*, 1987; REYES AND JURINAK, 1967). Therefore, iron oxides play a prominent part in controlling the retention of oxyanions in the natural environment.

Knowledge of the reversibility of the sorption (on iron oxides) is needed to predict the availability of bound oxyanions for transport in the aqueous phase of the environment. For example, sorption of As and Se on iron oxides controls the leaching from acidic fly ash (VAN DER HOEK *et al.*, 1994).

Many researchers (PARFITT, 1978 and references therein) have studied oxyanion sorption on iron oxides, but only a few have studied the reversibility of the sorption process. In reversibility studies, desorption is measured either by changing the pH (e.g. BALISTRERI AND CHAO, 1987; TURNER AND KRAMER, 1992) or by resuspending the iron oxide with sorbed oxyanion in an oxyanion 'free' solution (e.g. HINGSTON *et al.*, 1974; TURNER AND KRAMER, 1992). In some cases, dilution and extraction methods have also been used (e.g. CABRERA *et al.*, 1981; ALYMORE, KARIM AND QUIRK, 1967).

Both reversible and less reversible behaviour has been observed in studies of oxyanions on iron oxides, in which desorption was studied by changing the pH: BALISTRERI AND CHAO (1987) found that selenite sorption on goethite is reversible with respect to changes in the pH after 24 hours of sorption. The sorption of arsenate on ferrihydrite was not found to be completely reversible after an increase of the pH (FULLER *et al.*, 1993). Also the sorption of other oxyanions such as sulphate and phosphate show a different reversibility behaviour. The sorption of sulphate on hematite was found to be reversible (TURNER AND KRAMER, 1992). MADRID AND POSNER (1979) observed slow desorption (> 1 week) of phosphate from goethite after changes in the pH and adsorption for < 1 day. From the extraction study of CABRERA *et al.* (1981), it was found that phosphate sorption on goethite is not completely reversible with respect to pH.

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In reversibility studies, where a desorption method at constant pH was used only (apparently) irreversible sorption of oxyanions was observed: HINGSTON *et al.* (1974) studied the reversibility of selenite on goethite and came to the conclusion that at a constant pH little of the adsorbed selenite could be desorbed. The sorption of other oxyanions such as sulphate and phosphate also seemed to be irreversible at constant pH (TURNER AND KRAMER, 1992; ALYMORE, KARIM AND QUIRK, 1967 ; HINGSTON *et al.*, 1974).

It seems that the reversibility of the sorption processes observed in the studies mentioned above differs according to the desorption method used and is also dependent on the oxyanion studied. In this study, the sorption reversibility of arsenate, selenite and molybdate on hematite and amorphous iron (hydr)oxide is investigated. This study was performed within the framework of a larger investigation concerning the leaching of oxyanions from coal fly ash. In acidic coal fly ash hematite and amorphous iron (hydr)oxides are the likely iron oxides which control selenite and arsenate leaching (VAN DER HOEK *et al.*, 1994). A change of pH is a commonly observed phenomenon in such systems. Therefore, changing the pH was chosen as the desorption method.

It is important to discuss sorption terminology in relation to reversibility processes. In the sorption literature the term 'adsorption' refers to a two-dimensional surface process but has also a more general meaning where it refers to a forward sorption process. In this study we imply a forward sorption process when using the term 'adsorption', rather than a two-dimensional surface process for the sake of convenience in discussing sorption reversibility.

Materials and Methods

Materials

Analytical grade iron(III)oxide (Baker) was used and identified by means of X-ray diffraction as hematite. A surface area of 9.18 m²/g was determined by N₂

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adsorption (BET). Amorphous iron (hydr)oxide was prepared according to DAVIS AND LECKIE (1978). An acidic solution (pH 2) of 0.04 M $\text{Fe}(\text{NO}_3)_3$ was titrated with 1 M NaOH until the pH was 7.8-8.0. The suspensions were then stored to pre-equilibrate for 17 hours.

Arsenate, selenite and molybdate stock-solutions (pH < 2) were prepared by diluting As_2O_5 (Baker), H_2SeO_3 (Merck) and $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ (Baker). A mixture of ^{74}As and ^{73}As was obtained from "Isotopen Dienst Benelux" as AsI_3 (40 MBq/mg As) in water. $^{74/73}\text{Arsenate}$ was prepared by oxidation of AsI_3 with H_2O_2 and concentrated HCl. $^{75}\text{Selenite}$ (188 MBq/mg Se) was purchased from Amersham. $^{99}\text{Molybdate}$ (carrier-free) was obtained from Mallinckrodt Medical. ^{99}Tc is the disintegration product of ^{99}Mo . The radioactivity of ^{99}Mo was measured by counting ^{99}Tc 48 hours after sampling. More than 99.5 % ^{99}Tc had disintegrated after 48 hours, therefore, more than 99.5 % of the radioactivity originated from the ^{99}Mo at the time of sampling. All other chemicals used were analytical-reagent grade. All suspensions and solutions were prepared with nanopure deionized water.

In this study, two methods have been used to examine the sorption envelopes

- 1) stepwise titration to decrease and increase the pH, a quick method to measure the relative sorption behaviour and the short term reversibility and;
- 2) adsorption at constant pH values and desorption at pH 12, in order to follow the sorption kinetics and reversibility in the long term.

Sorption titration (method 1)

Suspensions of 0.0625 mol/l hematite in 0.05 M NaOH (suspension pH of 12.5) were pre-equilibrated for at least 1 week in acid-cleaned 110-ml Teflon (PTFE) reaction vessels. Arsenate, selenite or molybdate stock-solution and the respective radiotracer were added to the pre-equilibrated hematite suspensions. The radioactivity in the suspensions was > 50 Bq/ml. The As, Se and Mo concentrations were approximately 1 μM after addition of stock and tracer

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solutions. At 30 minutes intervals a 2 ml subsample was taken. Subsequently, the pH of the suspensions was changed in stepwise order from ≈ 12.5 to 3 by adding HNO_3 solutions. Immediately after sampling, the subsample was centrifuged for 30 minutes at $20000 \times g$ and 1 ml supernatant was transferred to a polyethylene vial containing 10 μl of concentrated HNO_3 . The radioactivity was measured on a 3 inch NaI(Tl) well-type detector (LKB-wallac, 1282 compugamma) relative to a standard containing 100 % of the initially added radioactivity.

To study the desorption the suspensions of pH 3 were titrated with NaOH solutions in reversed order. Sampling was carried out in the same way as described above. During the titration experiment the suspensions were stirred by an electromagnetic stirrer at room temperature.

In the sorption titration experiments with amorphous iron (hydr)oxide, the pre-equilibrated solid was added to a solution of approximately 0.05 M NaOH (suspension pH was 12) in order to obtain a suspension of 10^{-4} M Fe. The above described procedure was followed thereafter to study adsorption and desorption.

Sorption at constant pH-values (method 2)

Arsenate, selenite or molybdate stock-solutions and their respective radiotracers were added to suspensions of 0.0625 M hematite in 80-ml acid cleaned Teflon (PFA) reaction vessels. Prior to the experiment, the hematite suspensions were pre-equilibrated for more than 2 weeks in NaNO_3 at pH values ranging from 3 to 12.5 and at a total ionic strength of 0.05 M. The total arsenate, selenite or molybdate concentration in the suspension was approximately 10 μM . During the equilibration and sorption experiment the suspensions were shaken in a reciprocating shaker at 22°C . Desorption was induced by changing the pH to 12 ± 0.3 in every vessel after 1 week of adsorption for molybdate or 2 weeks of adsorption for arsenate. Preliminary adsorption experiments showed no oxyanion uptake at this pH. Molybdate ad- and desorption was studied over a shorter equilibration time, because of the high decay rate of ^{99}Mo . At distinct

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times, subsamples were taken and handled as described in the previous section. Further information can be found in VAN DER HOEK *et al.* (1994)

Sorption isotherms

Arsenate, selenite or molybdate stock-solutions and their respective radiotracers were added to suspensions of 0.0625 M hematite, in order to obtain the sorption isotherms for hematite. Before adding the oxyanions, the hematite suspensions were pre-equilibrated at pH 4 in NaNO_3 for 2 weeks. In order to obtain the sorption isotherms for amorphous iron (hydr)oxide, the oxyanion stock-solution and the radiotracers were added to suspensions of amorphous iron (hydr)oxide containing 10^{-4} M Fe at pH 4. The final oxyanion concentration range was between 10^{-9} and 10^{-2} M. The suspensions were handled as described above and, during the experiments, the pH was measured periodically and adjusted to pH 4 when necessary. Subsamples were taken at intervals over a period of 4 weeks from the hematite suspensions and over a period of 2 days from the amorphous iron (hydr)oxide suspensions. After 4 weeks of adsorption in the hematite suspensions, desorption was induced as described under method 2.

At high concentrations oxyanion the difference between the concentration in solution at time zero and at the sampling time became smaller relative to the analytical error, so that the amount of oxyanion in solution could not be determined with sufficient accuracy. Therefore, at high concentrations the radioactivity remaining on the solid was also obtained: to this end the samples were recentrifuged and the supernatant was carefully removed. The radioactivity on the solid was measured by transferring the centrifuge tubes (Eppendorf cups) with the pellet into the counting vials. Standard solutions containing the radioactivity at time zero were also counted in a centrifuge tube and the geometric effects of the centrifuge tube were measured to be $< 2\%$.

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Results and Discussion

Sorption envelopes

Fig. 1 shows the sorption envelopes of arsenate, selenite and molybdate on hematite from experiments at constant pH. The position of the sorption edge indicates that the affinity order on hematite is as follows: arsenate > selenite > molybdate. BALISTRERI AND CHAO (1987) suggested the same affinity order on goethite on the basis of competition results. The affinity order in soil is: arsenate > selenite = molybdate (PARFITT, 1978).

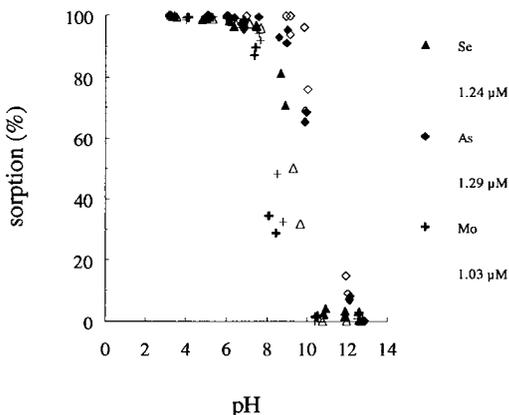


Fig. 1: Sorption envelopes of arsenate, selenite and molybdate on hematite after 1 d (closed symbols) and 1 w (open symbols) of sorption at constant pH.

In Fig. 2 the sorption envelopes of arsenate, selenite and molybdate on amorphous iron (hydr)oxide from titration experiments are shown. Again, the affinity order for the iron oxide was arsenate > selenite > molybdate. Both the shape of the sorption envelopes in Fig. 2 and the extent of sorption resemble the sorption envelopes of arsenate and selenite on amorphous iron (hydr)oxide measured by PIERCE AND MOORE (1982) and BALISTRERI AND CHAO (1990), respectively.

Kinetics

Figs. 3 and 4 show the arsenate and selenite sorption versus time at pH 4 and at

Sorption reversibility of As, Se and Mo on iron (hydr)oxides

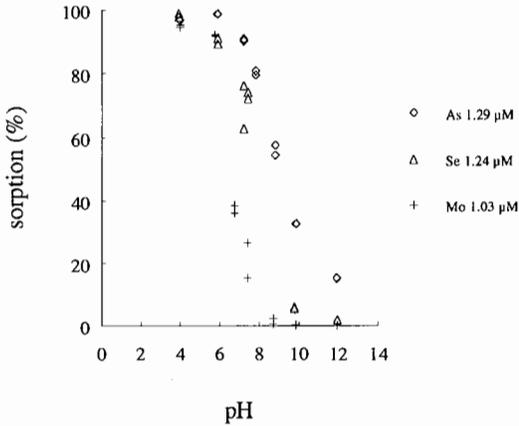


Fig. 2: Sorption envelopes of arsenate, selenite and molybdate on amorphous iron (hydr)oxide during titration from pH 12 to 3.

ferrihydrite within 5 minutes and a slow sorption step continuing for several days. They modelled this slow sorption by diffusion due to aggregation of the ferrihydrite.

Sorption isotherms

The sorption isotherms of arsenate and selenite on hematite after 24 hours of sorption are shown in Fig. 5. Maximum sorption seems to be reached at approximately 2 mmol/mol Fe (1.6 sites/nm²). This maximum is below the measured site-density range of 5-22 sites/nm² on hematite (DAVIS AND KENT, 1990). The isotherm increases again for selenite, at concentrations above 1 mmol/l in solution, which may indicate that surface precipitation occurs (FARLEY *et al.*, 1985). Due to increasing experimental errors at high concentrations, resulting from a low % adsorption, it is not possible to conclude whether the isotherm of arsenate reaches an absolute maximum or whether the

different concentrations. The sorption seems to be divided in two steps for both oxyanions. A fast initial uptake was observed within one day, followed by a slow sorption step which continued during the four weeks of the experiment. A number of mechanisms have been proposed to describe the slow sorption step (DAVIS AND KENT, 1990), for example, surface precipitation and diffusion. FULLER *et al.* (1993) observed an initial arsenate uptake on

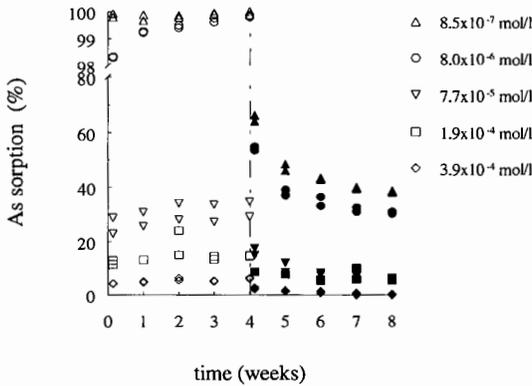


Fig. 3: Arsenate adsorption (open symbols) on hematite as a function of time at pH 4 and different concentrations arsenate. Desorption (closed symbols) was induced after 4 weeks (indicated by dotted line) by changing the pH to pH > 11.7.

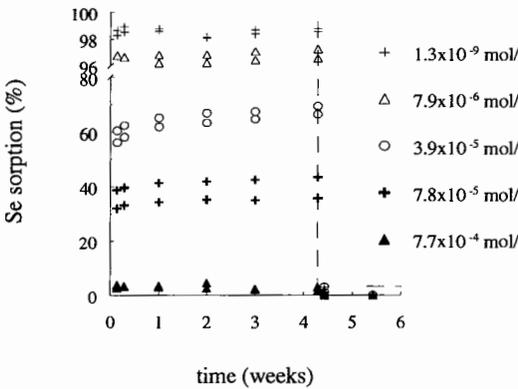


Fig. 4: Selenite adsorption on hematite as a function of time at pH 4 and different concentrations selenite. Desorption was induced after 4.2 weeks (indicated by dotted line) by changing the pH to pH > 11.7.

isotherm increases as well at concentrations above 1 mmol/l. We did not measure the sorption isotherm of molybdate on hematite, but REYES AND JURINAK (1967) found a sorption maximum of approximately 5 mmol molybdate/mol hematite. It is not possible to conclude from their results whether this is a true sorption maximum from their results. The solubility of iron arsenate and iron selenite in the hematite suspensions was calculated as not having been exceeded (using the geochemical speciation code MINTEQA2, FELMY *et al.*, 1984; updated for Se according to COWAN, 1988).

Fig. 6 illustrates the sorption isotherms of arsenate, selenite and molybdate on amorphous iron (hydr)oxide after 24 hours of sorption. A sorption maximum may be observed for the oxyanions

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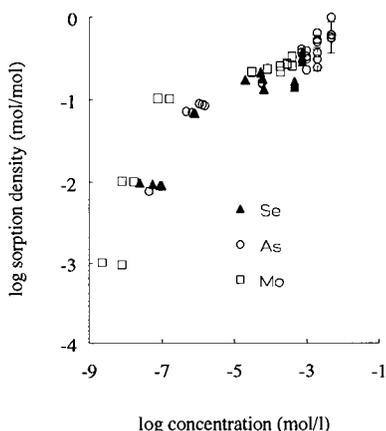


Fig. 5: Sorption isotherms of arsenate and selenite on hematite at pH 4.

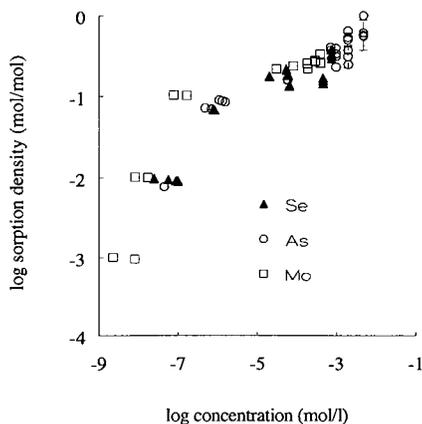


Fig. 6: Sorption isotherms of arsenate, selenite and molybdate on amorphous iron (hydr)oxide at pH 4.

at approximately 300 mmol/mol. This resembles the sorption maximum of 250 mmol/mol observed by FULLER *et al.* (1993) for arsenate on ferrihydrite at pH 8. The maximum is also within the range of the reported site densities of 100-900 mmol/mol for amorphous iron (hydr)oxide (DAVIS AND KENT, 1990). The sorption isotherms of arsenate and selenite seem to increase at concentrations above 1 mmol/l, but due to the occurrence of large experimental errors at these high concentrations it is again uncertain whether the further isotherm increase is significant. Molybdate sorption was not measured at high concentrations, because H_2MoO_4 was calculated to be oversaturated above 10 $\mu\text{mol/l}$.

It is possible that at high concentrations of arsenate and selenite in the experiments with amorphous iron (hydr)oxides (Fig. 6) the solubility of iron arsenates and iron selenites were exceeded. However, the reported solubility of amorphous iron (hydr)oxide varies over three orders of magnitude, which may have been caused by colloidal ferric complexation (FOX, 1988). Using the highest solubility of amorphous iron (hydr)oxide, the solubility of $Fe_2(OH)_4SeO_3$ was

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calculated to be oversaturated at Se concentrations higher than 5×10^{-5} M and the solubility of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ was calculated to be oversaturated at As concentrations higher than 10^{-3} M. Using the lowest solubility for amorphous iron (hydr)oxide in MINTEQA2, both solids (Fig. 6) were calculated to be undersaturated. The saturation indices are given in Table 1.

Table 1: Saturation indices (SI) of iron arsenate and iron selenite by different solubility of Ferrihydrite calculated in MINTEQA2

concentration oxyanion		Ferrihydrite solubility (log(k))	
		low (-1.557)	high (-4.996)
3×10^{-5} M of arsenate	SI of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	-3.270	0.221
5.5×10^{-5} M of selenite	SI of $\text{Fe}_2(\text{OH})_4\text{SeO}_3$	-6.862	0.016

Sorption after titration compared with sorption at constant pH

Two methods have been used to examine the sorption edge of the oxyanions on hematite; titration experiments and batch experiments at constant pH. In most sorption experiments reported in the literature (for example, HINGSTON *et al.*, 1974, FULLER *et al.*, 1993 and PIERCE AND MOORE, 1982) sorption is measured at constant pH, because the results are much easier to explain and to compare. Although it is more difficult to explain the results of titration experiments, this method is still being used in some studies (e.g. ZACHARA *et al.*, 1992). Abrupt pH changes can occur in natural systems, especially due to anthropogenic influences. For example, the pH in a disposal site for coal combustion residues may change after disposing a fly ash with an opposite pH. In those cases, titration experiments may provide a better reflection of reality. In order to investigate the differences between the two methods we used both methods and compared the results.

The sorption edge of arsenate on hematite observed after titration (Fig. 7) was shifted to a lower pH than the sorption edge observed at constant pH (Fig. 1).

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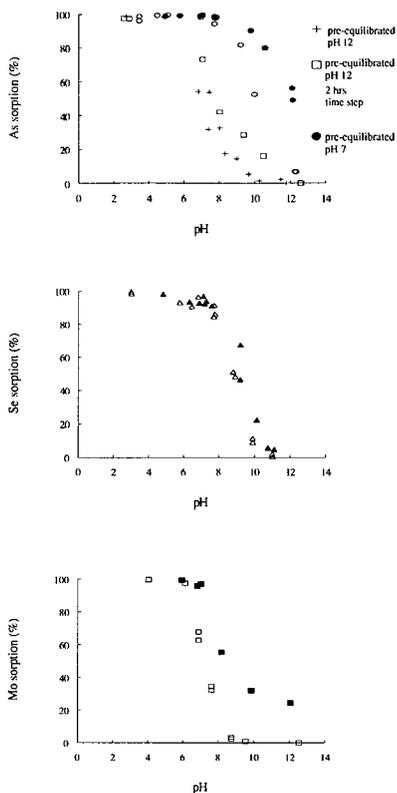


Fig. 7: Sorption envelopes of arsenate, selenite and molybdate on hematite during titration from pH 12 to 3 (adsorption = open symbols) and pH 3 to 12 (desorption = closed symbols). Hematite was pre-equilibrated for 2 weeks at pH 12 and for arsenate also at pH 7. The pH was changed every 30 minutes in the titration experiment and for arsenate also every 2 hours.

The sorption envelopes of selenite measured by the two methods are identical (Fig. 1 and Fig. 7). A small hysteresis is observed for molybdate (Fig. 1 and Fig. 7).

The kinetics of sorption may influence the position of the sorption edge, because there is a difference in sampling/equilibration time: during the titration experiment the pH was changed every 30 minutes and the whole sorption envelope (pH 12-3.5) was obtained in 3.5 hours. When measuring sorption at constant pH (method 2) the first sample was taken after 2 hours of sorption at each pH value. In order to investigate the effects of these differences in equilibration time, a sorption titration experiment with arsenate was carried out in which the pH was changed every 2 hours instead of every 30 minutes. The results were identical with the sorption titration envelope obtained after changing the pH every 30 minutes (Fig. 7). Therefore, it is not possible to explain the shift in the adsorption edge of arsenate in the two experiments by differences in equilibration time.

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Another possibility is that the position of the sorption edge was influenced by the difference in pre-equilibration pH. Prior to the sorption titration experiment, hematite was pre-equilibrated at pH 12 and prior to sorption at constant pH, the hematite was pre-equilibrated at the pH value at which sorption took place. In order to test the influence of pre-equilibration, a sorption titration experiment with arsenate was performed after a hematite suspension was pre-equilibrated without the addition of acid or base (pH \approx 7, for 2 weeks) and, only at the start of the experiment, was the pH adjusted to 12 (Fig. 7). This sorption envelope is identical to the sorption envelope observed at constant pH (Fig. 1). The hysteresis seems, thus, to be caused by the pH of the pre-equilibration of the hematite. XRD-analysis did not show a change of the solid after pre-equilibration at pH 12, but changes on the surface cannot be noticed with this technique. It seems that the hematite surface was changed during pre-equilibration in a way that affected arsenate sorption but did not affect selenite sorption. No sorption envelopes of amorphous iron (hydr)oxide were measured using batch experiments at constant pH. Amorphous iron (hydr)oxide was, however, pre-equilibrated (aged) at pH 8 for 17 hours prior to performing the titration experiments. Since the hysteresis in the hematite experiment was observed only after pre-equilibration at high pH we do not expect the above effect to appear in the amorphous iron (hydr)oxide sorption titration experiments.

Reversibility

The term sorption reversibility is generally used when the final distribution of a sorbing compound is the same after either adsorption or desorption. Sorption is said to be irreversible when some portion of a previously adsorbed compound is not available for desorption (COMANS, 1990). It is not generally possible to prove that a sorption process is truly irreversible, as sorption experiments have limited time frames and (de)sorption processes may be very slow (COMANS, 1990). Therefore, the term 'apparent irreversibility' is used below to indicate sorption processes which were not found to be reversible within the time scale of the experiment.

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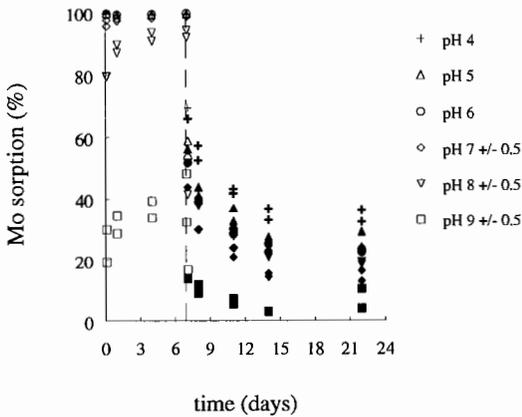


Fig. 8: Adsorption (open symbols) of molybdate on hematite in time at different pH values. Desorption (closed symbols) was induced after 4 weeks (indicated by dotted line) by changing the pH to $\text{pH} > 11.7$.

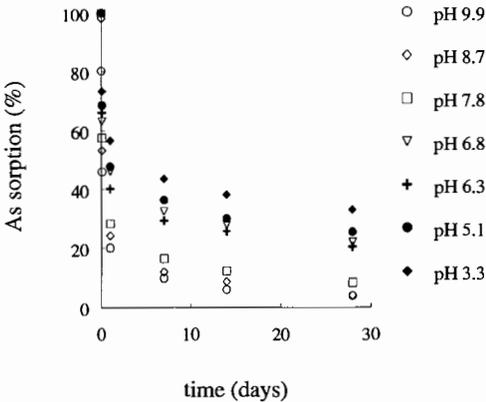


Fig. 9: Desorption of arsenate from hematite at $\text{pH} 12 \pm 0.3$. Prior to desorption, arsenate was adsorbed for 2 weeks at pH-values indicated in the legend.

At $\text{pH} 12 < 10\%$ arsenate, selenite and molybdate was bound to the iron oxides during the adsorption experiment (Figs. 1 and 2). Therefore, when sorption is reversible with respect to pH almost all arsenate, selenite and molybdate must be desorbed at this pH. Also, the ad- and desorption titration envelopes are expected to overlap when sorption is reversible. The sorption of selenite on hematite is reversible with respect to pH. All selenite is desorbed at $\text{pH} 12$ within 1 d (Fig. 4) and the desorption titration envelope overlaps the adsorption titration envelope (Fig. 7). Our observation that selenite sorbs reversibly, with respect to pH, on hematite corresponds with the observations of BALISTRERI AND CHAO (1987) on goethite, another crystalline iron oxide. Arsenate and molybdate show very slow desorption (Figs. 5, 8 and 9). After 4 weeks of arsenate

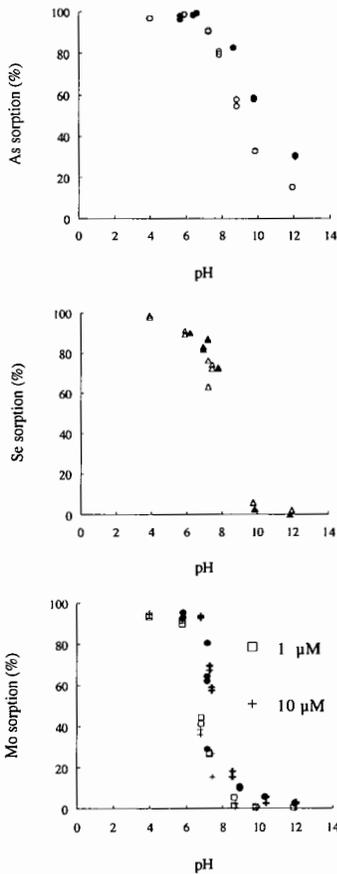


Fig. 10: Sorption envelopes of arsenate (1.29 μM), selenite (1.24 μM) and molybdate (1 and 10 μM) on amorphous iron (hydr)oxide during titration from pH 12 to 3 (adsorption = open symbols) and pH 3 to 12 (desorption = closed symbols).

adsorption (at pH < 7) and 4 weeks of desorption (at pH 12) more than 30 % still remains bound to hematite (Figs. 5 and 9). After 1 week of adsorption (at pH < 7) and 2 weeks desorption (at pH 12), molybdate remains bound to hematite for more than 20 % (Fig. 8). Furthermore, the arsenate and molybdate ad- and desorption titration envelopes show hysteresis (Figs. 7). No reversibility studies of arsenate and molybdate sorption on crystalline iron oxides were found in the literature.

The titration envelopes of selenite on amorphous iron (hydr)oxide overlap and, therefore, Se sorption on this solid was also found to be reversible (Fig. 10). A small hysteresis was observed in the ad- and desorption titration-envelopes of arsenate and molybdate on amorphous iron (hydr)oxide show (Fig. 10). The hysteresis for Mo is most pronounced at higher molybdate concentration. Thus, selenite sorbs reversibly on amorphous iron (hydr)oxides, whereas arsenate and molybdate show a partly irreversible behaviour. The observed hysteresis between ad- and desorption is, however, very small, especially for molybdate.

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FULLER *et al.* (1993) also found a small hysteresis for arsenate between adsorption on ferrihydrite at pH 8 and desorption at pH 9.

The formation of bidentate complexes has been proposed as one of the possible mechanisms which cause apparently irreversible behaviour (DAVIS AND KENT, 1990; HINGSTON *et al.*, 1974). HAYES *et al.* (1987) showed with a surface spectroscopic technique (EXAFS) that selenite forms bidentate surface complexes on goethite. WAYCHUNAS *et al.* (1993) showed with EXAFS that arsenate forms bidentate complexes on ferrihydrite, goethite, akagéinite and lepidocite. It is, therefore, not unlikely that both arsenate and selenite also form bidentate surface complexes on other iron oxides such as hematite and amorphous iron (hydr)oxide. Selenite shows reversible sorption behaviour with respect to pH on amorphous iron oxide (Fig. 10), hematite (Fig 4 and 7) and goethite (BALISTRIERI AND CHAO, 1987). The formation of bidentate surface complexes unlikely to have caused the hysteresis between adsorption and desorption in our experiments.

Another mechanism that may cause irreversible behaviour is the formation of surface precipitates (DAVIS AND KENT, 1990). Despite the high As/Fe ratio measured by WAYCHUNAS *et al.* (1993) on ferrihydrite, the authors did not observe surface precipitation using EXAFS. The EXAFS spectra of WAYCHUNAS *et al.* (1993) were measured on ferrihydrite with arsenate adsorbed at pH 8, but the authors indicated that it remains possible that As forms surface precipitates at low pH.

The apparently irreversible sorption behaviour of arsenate and molybdate in our experiments was mainly observed when adsorption occurred at low pH (Figs. 8 and 9). Although the sorption isotherms of As and Se at high sorption densities may be consistent with surface precipitation, the fact that As does and Se does not show apparently irreversible behaviour makes it unlikely that this mechanism causes the observed, hysteresis in As adsorption and desorption isotherms. Additionally, while arsenate and molybdate sorption on hematite were influenced by the pH of pre-equilibration prior to the sorption experiments,

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selenite sorption was not influenced. In any case, the pH is a crucial parameter in controlling sorption reversibility of oxyanions on iron (hydr)oxides.

An obvious difference between selenite, arsenate and molybdate is the difference in coordination. In the arsenate and molybdate ions, As and Mo are surrounded by 4 oxygen atoms, while with selenite Se is surrounded by only 3 oxygen atoms. It is possible that the different reversibility behaviour is related to these differences in coordination. Clearly, this issue cannot be resolved without a further surface spectroscopic investigation of the surface species.

Conclusion

In this study, it was observed that selenite sorbs reversibly with respect to pH on both amorphous iron (hydr)oxides and hematite. The sorption of arsenate and molybdate appears to be irreversible with respect to pH, especially on hematite. The reversibility of the oxyanions on iron oxides is very important for their mobility in natural and polluted environments. For example, the lower reversibility of arsenate sorption on iron oxide may explain the higher availability of Se, relative to As, in terms of leaching from coal fly ash (Van der Hoek et al, 1994). It is observed that the pH at which the oxyanion is adsorbed is a key parameter in controlling its sorption reversibility on iron (hydr)oxides. The pH at which the sorbent mineral is pre-equilibrated prior to the sorption experiment is also important. The sorption isotherms may indicate that surface precipitates occurs at high concentrations. These effects were observed for both arsenate and selenite and, therefore, do not seem to be the cause of the difference in sorption reversibility between the two oxyanions. Further study, in which careful sorption experiments are combined with surface spectroscopic investigation of the sorbent mineral, is required in order to reveal the mechanism underlying the observed differences in sorption reversibility.

Acknowledgement

The authors like to thank J.T. van Elteren for carefully reading an earlier draft of the manuscript.

References

- ALYMORE, L.A., KARIM, M., QUIRK, J.P. (1967) Adsorption and desorption of sulfate ions by soil constituents, *Soil Sci.* **103**, 10-15.
- BALISTRERI, L.S. AND CHAO, T.T. (1990) Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. *Geochim. Cosmochim. Acta* **54**, 739-751.
- BALISTRERI, L.S. AND CHAO, T.T. (1987) Selenium adsorption by goethite, *Soil. Sci. Soc. Am. J.* **51**, 1145-1151.
- BELZILE, N. AND TESSIER, A. (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments, *Geochim. Cosmochim. Acta* **54**, 103-109.
- CABRERA, F., DE ARAMBARRI, P., MADRID, L., TOCA, C.G. (1981) Desorption of phosphate from iron (hydr)oxides in relation to equilibrium pH and porosity, *Geoderma* **26**, 203-216.
- COWAN, C.E.(1988) *Review of selenium thermodynamic data*. Electric Power Research Institute EA-5655.
- COMANS R.N.J. (1990) *Sorption of cadmium and cesium at mineral water interfaces: reversibility and its implications for environmental mobility*. PhD-Thesis. University of Utrecht.
- DAVIS, J.A. AND KENT, D.B. (1990) Surface complexation modeling in aqueous geochemistry, *Reviews in mineralogy 23: Mineral-water interface geochemistry*, (edited by Hochella M.F., and White A.F.), 177-248, Mineralogical Society of America, Washington.
- DAVIS J.A. AND LECKIE J.O. (1978) Surface ionization and complexation at the oxide/water interface: II Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions, *J. Colloid Interface Sci.* **67**, 90-107.

CHAPTER 5

- FARLEY, K.J., DZOMBAK, D.A. AND MOREL F.M.M. (1985) A surface precipitation model for sorption of cations on metal oxides, *J. Colloid, Interface Sci.* **106**, 226-242.
- FELMY, A.R., GIRVIN, D.C., JENNE, E.A. (1984) *MINTEQA-A computer program for calculating aqueous geochemical equilibria*, EPA 600/3/84/032, U.S. environmental protection agency, Office of research and development, Athens, GA.
- FOX, L.E. (1988) Solubility of colloidal ferric hydroxide, *Nature* **333**, 442-444.
- FULLER, C.C., DAVIS, J.A AND WAYCHUNAS, G.A. (1993) Surface chemistry of ferrihydrite: part 2 Kinetics of arsenate adsorption and coprecipitation, *Geochim. Cosmochim. Acta* **57**, 2271-2282.
- HAYES, K.F., ROE, A.L., BROWN, JR., G.E., HODGSON, K.E., LECKIE, J.O., PARKS, G.A. (1987) In situ X-ray absorption study of surface complexes: selenium oxyanions on α -FeOOH, *Science* **238**, 783-786.
- HINGSTON, F.J., POSNER, A.M., QUIRK, J.P. (1974) Anion adsorption by goethite and gibbsite: II. Desorption of anions from hydrous oxide surfaces, *J. Soil Sci.* **25**, 16-26.
- HINGSTON, F.J. (1981) A review of anion adsorption. In *Adsorption of inorganics at solid-liquid interfaces*, (Edited by Anderson M.A. and Rubin A.L.), 51-91, Ann Arbor Sci. Publ., Michigan .
- MADRID, L. AND POSNER, A. M. (1979) Desorption of phosphate from goethite. *J. Soil Sci.* **30**, 697-707.
- NEAL, R.H., SPOSITO, G., HOLZCLAW, K.M., TRIANA, S.J. (1987) Selenite adsorption on alluvial soils: I. Soil composition and pH effects, *Soil Sci. Soc. Am. J.* **51**, 1161-1165.
- PARFITT, R.L. (1978) Anion adsorption by soils and soil materials *Adv. Agron.* **30**, 1-50.
- PIERCE, M.L. AND MOORE, C.B.(1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **16**, 1247-1253.
- REYES, E.D. AND JURINAK J.J. (1967) A mechanism of molybdate adsorption on α -Fe₂O₃ *Soil Sci. Soc Amer. Proc.* **31**, 637-641.
- TURNER, L.J. AND KRAMER, J.R. (1992) Irreversibility of sulfate sorption on goethite and hematite, *Water, Air Soil Pollut.* **63**, 23-32.

Sorption reversibility of As, Se and Mo on iron (hydr)oxides

- VAN DER HOEK, E.E., BONOUVRIE, P.A., COMANS, R.N.J. (1994) Sorption of As and Se on mineral components of fly ash: relevance for leaching processes *Applied Geochem.* **9**, 403-412.
- WAYCHUNAS, G.A., REA, B.A., FULLER, C.C. AND DAVIS, J.A. (1993) Surface chemistry of ferrihydrite: part 1 EXAFS studies of the geometry of coprecipitated and adsorbed arsenate *Geochim. Cosmochim. Acta* **57**, 2251-2269.
- ZACHARA, J.M., SMITH, S.C. RESCH, C.T. AND COWAN, C.E. (1992) Cadmium sorption to soil separates containing layer silicates and iron and aluminium oxides *Soil Sci. Soc. Am. J.* **56**, 1074-1084.

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INVESTIGATION OF PROCESSES CONTROLLING LEACHING OF AS AND SE FROM NATURALLY WEATHERED COAL FLY ASH IN A LYSIMETER

CHAPTER 6

INVESTIGATION OF PROCESSES CONTROLLING LEACHING OF AS AND SE FROM NATURALLY WEATHERED COAL FLY ASH IN A LYSIMETER*

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Abstract

The leaching of As and Se from fly ash under natural conditions was studied using solid and pore water profiles in fly ash, which had undergone weathering for 11 years in a lysimeter. In particular, it was investigated whether As and Se leaching from fly ash in the natural environment could be described by the processes which had been identified in earlier laboratory studies, i.e. by sorption on an iron (hydr)oxide or an alkaline Ca-phase in the fly ash matrix. Therefore, in addition to As and Se, the leaching of the relevant major ions was considered, using geochemical modelling of the pore water chemistry and XRD analyses of the fresh and weathered fly ash. The results showed that the potentially important sorbents for As and Se, amorphous iron (hydr)oxide and the alkaline Ca-mineral ettringite, were present and likely to be in equilibrium with the pore waters. The lysimeter profiles, the pH-dependency of As and Se leaching from the weathered fly ash and extractions of As, Se, and amorphous iron (hydr)oxide with hydroxylamine, were all consistent with leaching-control of As and Se by sorption on amorphous iron (hydr)oxide. Moreover, the partitioning of As and Se between fly ash and pore waters, especially in the upper section of the lysimeters, could be adequately described using a simplified model of surface complexation on amorphous iron (hydr)oxide. In the lower section of the

*Submitted for publication

lysimeter interaction with alkaline Ca-minerals such as ettringite may contribute in controlling the leaching process.

Introduction

Large quantities of coal fly ash are used in construction materials (MANZ *et al.*, 1995). However, fly ash is usually stored on disposal sites all over the world either temporarily or permanently (MANZ *et al.*, 1995; HJELMAR *et al.*, 1991). Fly ash contains high amounts of leachable and potentially hazardous elements (EARY *et al.*, 1990). Therefore, it is essential that the storage and use of fly ash be environmentally safe. Good environmental policy can be arrived at only when leaching under different storage conditions can be predicted.

Over the past decades much research was focused on the development of leaching tests (VAN DER SLOOT, 1991). However, a number of important processes occurring during weathering, such as carbonation, oxidation and reduction, were not included in these tests (VAN DER SLOOT, 1991; VAN DER HOEK AND COMANS, 1994). It is necessary to understand the underlying leaching mechanisms and the parameters controlling leaching, to enable translation of test results to leaching in the actual environment.

Leaching of major elements from coal fly ash (FRUCHTER *et al.*, 1990; GARAVAGLIA AND CARAMUSCIO, 1994) and MSWI (municipal solid waste incinerator) residues (COMANS *et al.*, 1993) can be described by precipitation/dissolution processes. Trace element leaching has sometimes been modelled on the basis of solubility-control (COMANS *et al.*, 1993; FRUCHTER *et al.*, 1990), but often no solubility relationships were found. Leaching of most trace elements is expected to be controlled by sorption processes (WARREN AND DUDAS, 1985; FRUCHTER *et al.*, 1990; VAN DER HOEK *et al.*, 1994).

Arsenic and selenium are generally leached from fly ash in large amounts and, therefore, considered as potentially hazardous (EARY *et al.*, 1990). In an earlier laboratory study we found that sorption controlled the leaching of As and Se from coal fly ash (VAN DER HOEK *et al.*, 1994). It was possible to model

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the leaching of As and Se from acidic fly ash by sorption on amorphous iron (hydr)oxide using a simplified model of surface complexation (VAN DER HOEK AND COMANS, 1995). In alkaline fly ash, leaching may be controlled by sorption on alkaline Ca-phases (VAN DER HOEK *et al.*, 1994).

In this study, we investigate whether As and Se leaching from fly ash in the natural environment can be described by the above processes we have identified earlier in the laboratory. Major element leaching has been considered in so far as it is important for the leaching of As and Se. Geochemical modelling, leaching experiments and chemical extractions are used to investigate the solid and pore water profiles in order to identify the exchange processes between the solid and aqueous phases.

Method

Description of the lysimeters

The lysimeter cells which have been studied were installed in Hørsholm (Denmark) and loaded with 10.5 tons of moisturized, neutral, coal fly ash (HJELMAR *et al.*, 1991; HF1) in June 1982. A schematic reproduction of the lysimeter cell is given in Fig. 1. A detailed description can be found in HJELMAR *et al.* (1991).

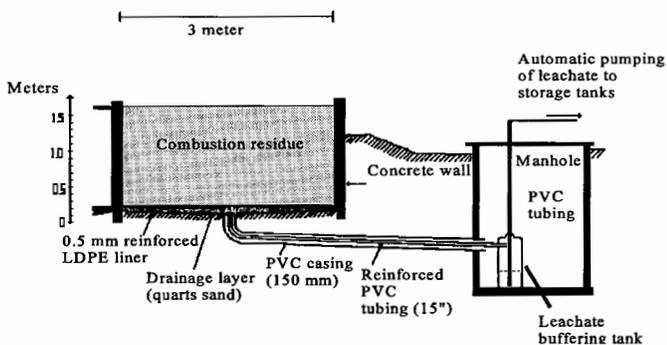


Fig. 1: Schematic reproduction of the studied lysimeter cell and leachate collection tank

Leaching of As and Se from naturally weathered coal fly ash

The composition of the original fly ash is presented in Table 1. The leachate resulting from natural precipitation and percolation through the lysimeter, was collected in storage tanks (Fig. 1). Samples were taken at different time intervals and analyzed (HJELMAR *et al.*, 1991). Nothing grew on the residue surfaces of the lysimeters during the first few years, but since then a substantial amount of self-sown plants, including moss, bushes and trees, has appeared. The leachate formation over time is shown in Fig 2. In November 1993, core samples were taken from one lysimeter cell as described below. Data of a parallel lysimeter cell of the same size and filled with the same fly ash is also shown in Fig 2, because more leachate samples have been analyzed for this cell (HJELMAR *et al.*, 1991).

Table 1: Composition of the original fly ash

major elements	concentration	trace elements	concentration
Si	221	As	130
Al	123	Cr	230
Fe	75	Mo	18
Ca	20	Se	22
K	16	Sr	400
Mg	8	V	230
Mn	2.9	Zn	450
Na	2.5		

Sampling of the cores

11 years after the installation of the lysimeters, 2 cores were taken from one lysimeter cell. The sampling device was a lined soil core sampler (Eijkelkamp Agrisearch Equipment, Giesbeek, NL), 30 cm long and with a $\varnothing = 7$ cm. The cores were split into 14 slices, resulting in samples from depths of respectively, 0-2.5, 2.5-5, 5-10, 10-15, 15-25, 25-36, 36-52, 52-68.5, 68.5-84.5, 84.5-101, 101-113.5, 113.5-126, 126-136 and 136-146 cm. The samples were stored in gas-tight glass bottles at 4-5°C, which was the temperature during sampling.

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Pore water and leachate

The pore water of the core slices was extracted (within 3 days of sampling) by means of centrifugation (10,000 x g, 30 min, 5°C) through a membrane filter (0.45 μm) using custom-made Teflon (PTFE) centrifuge tubes. After centrifugation, the pore water was refiltered (0.2 μm) under a nitrogen atmosphere. The pore

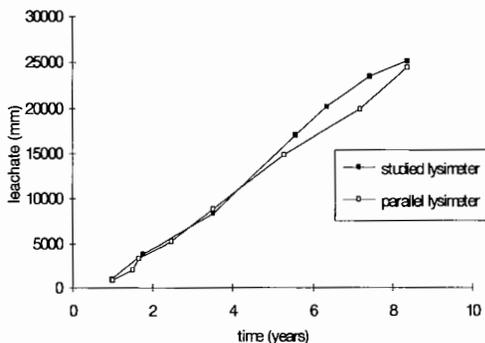


Fig. 2: Amount of leachate collected in the studied lysimeter and in a parallel lysimeter during 10 years

water samples from the same depths in parallel cores were combined. pH and Eh were measured in subsamples. Subsamples for ICP-AES and hydride-AAS analyses were acidified with suprapure HNO_3 to pH 2. As and Se were measured by hydride-AAS, Ca, Mg, Ba, Fe, Mn, Si, Al, Na, K, S by ICP-AES, and Cl and SO_4 by ion chromatography. Dissolved carbonate was determined by acidification of the pore water samples, collection of the liberated carbon dioxide in a $\text{Ba}(\text{ClO}_4)_2$ solution, followed by titration with NaOH.

Solid

After extraction of the pore water, the residual slices from each depth interval in parallel cores were combined and preserved at -20°C . For total element analysis, the solid samples were dried at 60°C . After destruction of the solids with HF/HNO_3 , or with Li-tetraborate, As, Se, Fe, Mn, Al, Ca and S were measured as described above for pore water.

X-ray diffraction (XRD)

The solids were dried under N_2 and ground in order to obtain solid samples for XRD analysis. The original fly ash was analyzed similarly. It had been

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moisturized before being used in the lysimeter and stored for 11 years in polyethylene bottles.

Extraction of amorphous iron (hydr)oxide

Amorphous iron (hydr)oxide was extracted from 1 g fly ash with 25 ml 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.25 M HCl at 50°C, as described by VAN DER HOEK AND COMANS (1995), and the extracted Fe, Mn, Ca, As and Se were measured as described above for pore water.

pH-stat experiments

pH-stat experiments were performed with two slices from the depth intervals 25-36 cm and 68.5-84.5 cm in the core. 100 ml nanopure water was added to 10 g (wet-weight, with 14.7% and 16.5% water, respectively) of the weathered fly ash and the suspension equilibrated for 24 hours at pre-determined pH values of 4, 7, 9 and 12. The pH was controlled within ± 0.05 pH unit using a computerized pH-stat system by addition of 1 M NaOH or 1 M HNO_3 . After 24 hours the suspensions were centrifuged for 30 minutes at 7500 rpm and subsequently filtered through 0.2 μm membrane filters. As and Se were measured in the filtrate using methods described above for pore water.

Geochemical modelling

The speciation and activity of the different elements in each individual pore water sample were calculated with the MINTEQA2 geochemical speciation model (FELMY *et al.*, 1984). The total concentrations of all measured major and trace elements in the pore water were used as input data. If pore waters are in equilibrium with a particular mineral, the calculated saturation index (SI) of that mineral should be ≈ 0 . A saturation index < 0 indicates that the solution is undersaturated with respect to that mineral and $\text{SI} > 0$ indicates oversaturation. MINTEQA2 is based on thermodynamic equilibrium calculations which may sometimes suggest minerals to be in equilibrium (or oversaturated) that cannot be formed under the ambient conditions (of low temperature and pressure) in the lysimeter. Therefore, the minerals

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considered in this study were selected on the basis of the results of the XRD analyses and on the basis of minerals expected and observed by WARREN AND DUDAS (1985), FRUCHTER *et al.* (1990), MATTIGOD *et al.* (1990) and COMANS *et al.* (1993). The MINTEQA2 database was updated for selenite with data from COWAN (1988). The solubility product of ettringite was taken from ATKINS *et al.* (1991). New data from ESSINGTON (1988) were used for Ba-arsenate. All other solubility data came from the MINTEQA2 (version 3.11) database.

Results and Discussion

High amounts of As and Se were leached during the first 2-3 years of weathering. Thereafter, concentrations in the leachate of the oxyanions decreased substantially (Fig. 3). The profiles of As, Se, and relevant major ions in both the solid and pore water, which were taken as the basic data to investigate the leaching processes, are discussed below. First, we discuss the profiles in general. Secondly, the most important parameters controlling leaching (pH, Eh and CO₂) are discussed, followed by a discussion of mineral phases controlling the leaching of relevant major ions. Finally, the leaching of As and Se is discussed on the basis of these measurements and knowledge obtained from previous laboratory studies on mechanisms of As and Se leaching.

Solid phase and pore water profiles

Solid phase and pore water profiles of the measured parameters in the lysimeter, after 11 years of weathering, are shown in Figs. 4 and 5, respectively. The composition of the samples below 140 cm in the profile corresponds with that of the original fly ash for most elements and, therefore, this section of the lysimeter seems to be relatively unweathered.

The pH in the pore waters (Fig. 5) increases with depth from 7.8 at the top of the profile to 9.8 at the bottom. The original pH of the fly ash was ≈ 10 at a liquid to solid ratio (L/S) of 20 (HJELMAR *et al.*, 1991). The pH in the leachate sampled in the storage tanks also decreased in time (Fig. 3). The total carbonate concentration in the pore waters (Fig. 5) first increases with depth

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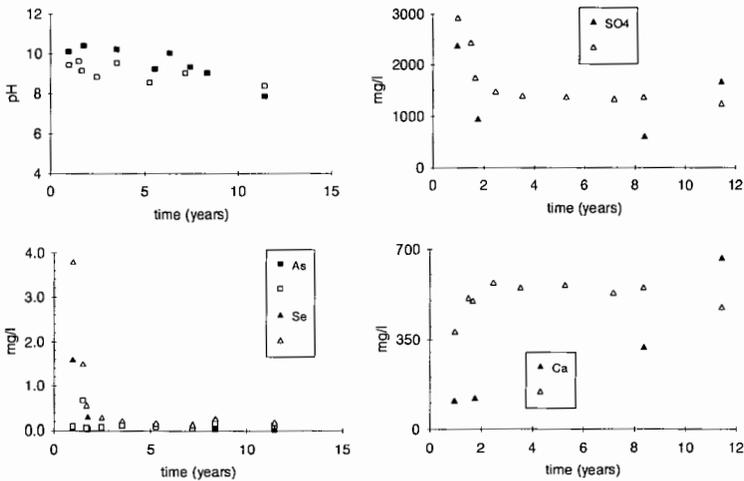


Fig. 3: Concentrations of different components and parameters in the leachate of the studied lysimeter (closed symbols) and of a parallel lysimeter (open symbols)

until about 20 cm, and then decreases. This decrease is possibly controlled by the formation of CaCO_3 as discussed below.

Although the Eh measurements (Fig. 5) indicate an oxic environment, irregular peaks are observed in the solid profiles of Fe and Mn (Fig. 4). The peaks suggest that Fe and Mn have been dissolved and reprecipitated lower down the profile. Only low concentrations of Fe and Mn are observed in the pore water samples at depths corresponding with these peaks in the solid profile (Fig. 5). The correspondence between the Fe and Mn profiles (Fig. 4) indicates that the same process is responsible for the peaks. The peaks may have been caused by temporarily low redox conditions during periods of saturation.

Extraction experiments on the different slices of the lysimeter with $\text{NH}_2\text{OH}\cdot\text{HCl}$ (discussed below) showed peaks in extractable Fe and Mn at the same depths (Table 3) as the peaks of total Fe and Mn in the solid profiles (Fig 4). This extraction does not attack the crystalline phases such as

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hematite and magnetite (CHAO AND ZHOU, 1983), confirming the above hypothesis that Fe and Mn have been dissolved and reprecipitated as amorphous phases during temporary saturation and low redox conditions.

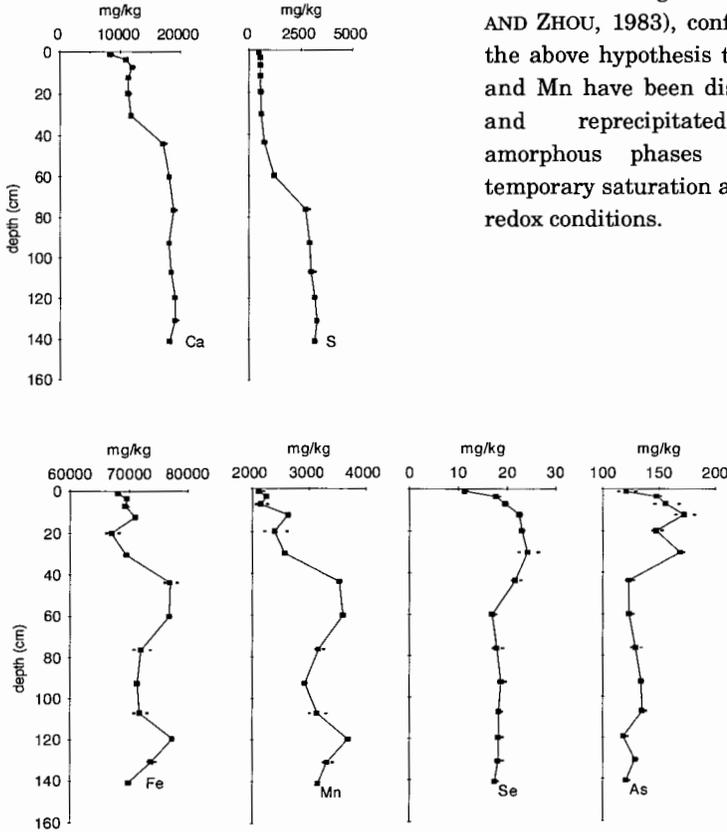


Fig. 4: Concentrations on the solid of different components as a function of depth

Controlling leaching processes

Coal fly ash consists predominantly of glass, quartz and mullite (MATTIGOD *et al.*, 1990). We have shown earlier that As and Se show only minor interactions with these minerals and that sorption on iron (hydr)oxides (in acidic fly ash) or alkaline Ca-phases (in alkaline fly ash) is likely to control

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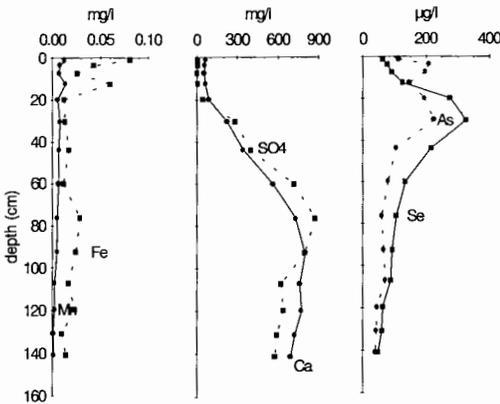
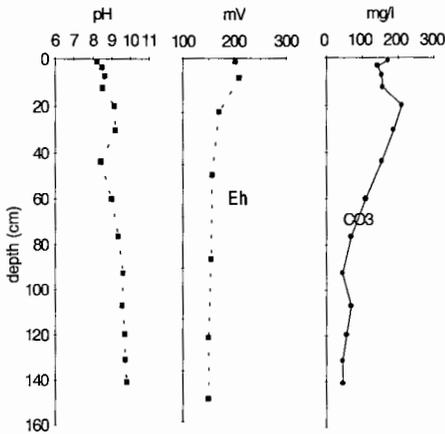


Fig. 5: Concentrations of different components in the pore water as function of depth

the partitioning of As and Se between fly ash and solution (VAN DER HOEK *et al.*, 1994). Therefore, prior to discussing the potential leaching mechanisms of As and Se, we first investigate the presence of these (secondary) Ca- and Fe-minerals and their stability in the weathered fly ash.

Ca- and Fe-minerals

Ca is leached in large amounts during the first few years (Fig. 3). After 2 years the concentration of Ca in the leachate became independent of time. Sulphate shows the opposite behaviour in the leachate and MINTEQA2 calculations suggest that the leachate after 2 years is in equilibrium with gypsum.

Both the solid and the pore water profile show that Ca and SO₄ are relatively low in the

upper part and high in the lower part of the lysimeter. Gypsum was identified in 8 of the 15 samples throughout the profile (Table 2). WARREN AND DUDAS (1985) found gypsum to be one of the minerals controlling Ca leaching.

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In another lysimeter study with coal fly ash (FRUCHTER *et al.*, 1990) geochemical modelling suggested gypsum to be the mineral controlling Ca and SO₄ leaching. In the present study lysimeter pore waters below 68.5 cm were also found to be close to saturation with respect to this mineral (Fig. 6).

Table 2: Minerals identified by XRD analysis in the original fly ash and in the profile of the lysimeter (i = identified mineral, p = possibly present in low concentrations, - = not identified)

Minerals	Sample code*														
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Quartz (SiO ₂)	i	i	i	i	i	i	i	i	i	i	i	i	i	i	i
Mullite (Al ₆ Si ₂ O ₁₃)	i	i	i	i	i	i	i	i	i	i	i	i	i	i	i
Hematite (Fe ₂ O ₃)	i	i	i	i	i	i	i	i	i	i	i	i	i	i	i
Magnetite (Fe ₃ O ₄)	p	i	p	-	p	p	i	-	-	-	p	-	-	-	-
Ferrispinel (MgFe ₂ O ₄)	p	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Calcite (CaCO ₃)	i	-	p	i	p	-	-	i	i	i	-	-	-	-	-
Dolomite (CaMg(CO ₃) ₂)	-	p	-	-	-	-	-	-	-	-	-	-	-	-	-
Gypsum (CaSO ₄ .2H ₂ O)	-	i	p	-	i	p	p	p	-	-	-	i	-	-	i
Anhydrite (CaSO ₄)	-	-	-	-	i	-	-	-	-	-	-	-	-	-	-
Chlorite (Mg ₅ Al ₂ Si ₃ O ₁₂ .6H ₂ O)	-	i	i	-	-	-	-	-	-	-	-	p	-	-	-
Ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ .26H ₂ O)	i	-	-	-	-	-	-	-	-	i	i	i	i	i	i

*Sample code: 0 = original fly ash, 1-14 = 0-2.5, 2.5-5, 5-10, 10-15, 15-25, 25-36, 36-52, 52-68.5, 68.5-84.5, 84.5-101, 101-113.5, 113.5-126, 126-136, 136-146, respectively.

Calcite has been identified by XRD analysis in most of the samples above 68.5 cm (Table 2) and, because of its lower solubility than gypsum, is expected to control the leaching of Ca in the upper part of the lysimeter. WARREN AND

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DUDAS (1985) have also identified calcite in leached coal fly ash. The activity product of Ca^{2+} and CO_3^{2-} in the pore water shows, however, oversaturation with respect to calcite (Fig. 6). SCHRAMKE (1992) showed oversaturation of fly ash leachates with respect to calcite to be caused by incorporation of SO_4 and Mg into the calcite lattice. In the lysimeter pore waters, oversaturation may also be due to complexation of Ca with dissolved organic material and/or higher partial pressures of CO_2 resulting from microbial degradation of organic material.

Ettringite has been identified in all samples below 68.5 cm (Table 2). Ettringite is unstable below a pH of 10 (COMANS AND MEIMA, 1994) and will probably decompose slowly at decreasing pH. The pore water Ca activities at depths below 68.5 cm are calculated to be close to those in equilibrium with ettringite (Fig. 6).

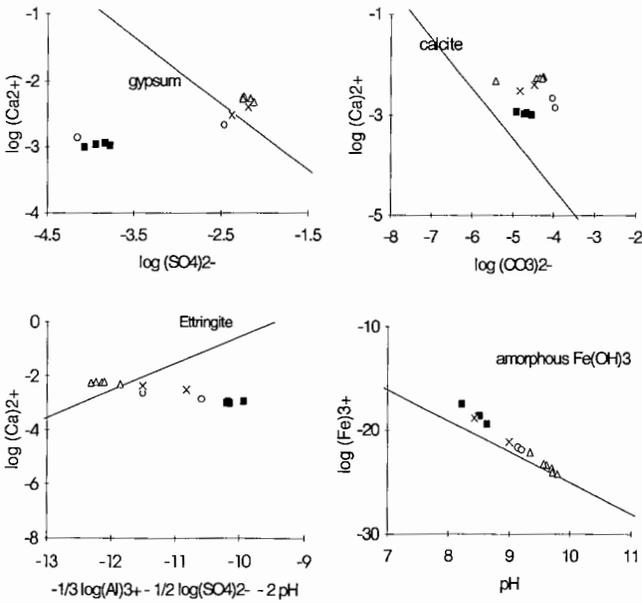


Fig. 6: The activity product calculated in MINTEQA2 compared with the solubility of different components

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The most important Fe phases which are generally identified in fly ash are magnetite and hematite (MATTIGOD *et al.*, 1990). We have also identified these minerals in the original and weathered fly ash (Table 2), but the Fe^{3+} activity in solution was calculated to be highly oversaturated with respect to these minerals. WARREN AND DUDAS (1985) found that amorphous iron (hydr)oxide is formed during artificial weathering of fly ash. The pore water concentrations of Fe can be reasonably well described by the solubility product of amorphous iron (hydr)oxide (Fig 6). In the upper part of the profile the ion activity product deviates from the solubility product for as yet unknown reasons

Processes controlling As and Se leaching

The oxidation state of As and Se influences the partitioning of their oxyanions between solid and solution (e.g. PIERCE AND MOORE, 1982; BALISTRIERI AND CHAO, 1990). We have found earlier that As is mainly present as arsenate and Se as selenite in fly ash leachates (VAN DER HOEK *et al.*, 1995a). Particularly these oxyanionic species are known to sorb strongly to mineral sorbents (PIERCE AND MOORE, 1982; BALISTRIERI AND CHAO, 1990). As was mentioned above, our laboratory studies have shown that As and Se leaching from acidic fly ash was controlled by sorption on amorphous iron (hydr)oxide and the leaching from alkaline fly ash by sorption on an alkaline Ca-phase, probably ettringite or portlandite (VAN DER HOEK *et al.*, 1994; VAN DER HOEK AND COMANS 1995). Both iron (hydr)oxide and ettringite are present in the lysimeter.

As and Se were enriched, relative to the composition of the original fly ash (Table 1), in the upper part of the profile (10-30 cm; Fig. 4). XRD analysis and geochemical modelling have shown that the major Ca-minerals in this section of the profile are calcite and gypsum. Both As and Se have a low sorption affinity for these minerals (VAN DER HOEK *et al.*, 1994). Ettringite is present only below 68.5 cm and, therefore, does not seem to be the principle sorbent mineral responsible for the retention of As and Se.

Hydroxylamine extractions of the solids from the different sections in the cores show that 90 % of As was extracted throughout the profile (Table 3). Se was extracted for approximately 40 %. This extraction has been shown to be

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reasonably specific for amorphous iron (hydr)oxides and suggests that As in the lysimeter is associated with this mineral phase. The limited percentage of extractable Se suggests that other mineral phases may contribute to the retention of this element. Due to the co-extraction of high concentrations of Ca (Table 3) we cannot rule out, however, that alkaline Ca-minerals such as ettringite (this mineral does dissolve in $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.25 M HCl) contribute to the binding of As and Se to the fly ash.

Table 3: Relative amount of As, Se, Mn, Fe and Ca extracted from different slices of the solid profile by 0.25 M hydroxylamine hydrochloride in 0.25 M HCL

depth cm	As		Se		Mn		Fe		Ca	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
0-2.5	110	91.3	4.28	38.9	1204	56.8	2812	4.1	3567	42.7
2.5-5	139	94.1	9.07	51.7	1252	55.6	2996	4.3	6400	58.5
5-10	150	95.9	11.04	57.0	1430	66.5	3033	4.4	8064	67.5
10-15	138	80.4	10.96	49.3	1482	56.5	2716	3.8	6106	53.9
15-25	136	92.3	9.50	42.9	1427	59.6	2922	4.4	6273	55.7
25-36	134	79.8	8.59	37.9	1433	55.8	3248	4.7	7458	63.5
36-52	119	96.7	7.07	33.2	2302	65.0	4568	5.9	11707	68.6
52-68.5	93	75.0	3.46	20.6	2275	63.2	4288	5.6	12840	70.8
68.5-84.5	110	85.0	7.71	44.2	1908	60.3	4304	6.0	13969	74.0
84.5-101	114	84.9	6.07	33.6	1764	60.4	4130	5.8	13819	76.4
101-113.5	92	68.3	5.81	32.4	1752	55.9	3568	5.0	12324	66.8
113.5-126	118	99.6	7.48	41.9	2164	58.6	3962	5.1	14815	77.6
126-136	127	98.3	7.27	41.6	2201	66.3	4258	5.8	15994	83.7
136-146	105	86.8	7.03	41.5	2368	75.3	3925	5.6	14810	81.5
Mean		87.7		40.5		61.1		5.0		67.2

pH-stat experiments were performed with the slices from depths of 25-36 cm and 68.5-84.5 cm to investigate the pH-dependency of the leaching process. We have observed As and Se leaching to increase with decreasing pH when these elements are associated with alkaline Ca-minerals, whereas the opposite behaviour was found when the elements were associated with iron (hydr)oxides (VAN DER HOEK *et al.*, 1994). Table 4 shows that, particularly in the upper slice where As and Se are strongly retained, these elements are clearly released when the pH in the pH-stat is increased. This pH-dependency confirms the above indications that the leaching of As and Se is controlled predominantly by sorption on iron (hydr) oxide. Although the leaching of As and Se from the lower slice shows a similar pH-pattern, the relative amount

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released at pH 12 is considerably less than in the upper slice. During the leaching experiment controlled at pH 12, As and Se in the lower slice may partly bind (by readsorption) to alkaline Ca-minerals such as ettringite, which is present in that section of the lysimeter.

Table 4: pH stat experiments from two slices of the solid profile
(m6 = 25-36 cm and m9= 68.5-84.5 cm)

	pH t =0	pH t =24 hrs	final volume ml	water in the solid %	As in leachate solution µg/l	As leached from the fly ash mg/kg %	Se in leachate solution µg/l	Se leached from the fly ash mg/kg %
m6-pH12	9.08	11.95	101	14.7	2219	25.94 15.35	673	7.49 30.92
m6-pH9	9.1	9.04	100		2071	24.12 14.27	198	2.00 8.27
m6-pH7	9.09	7.04	100.8		128	1.39 0.83	263	2.91 12.02
m6-pH4	9.03	4.09	102.3		43	0.43 0.25	19	0.07 0.30
m9-pH12	9.98	12.06	100.9	16.5	107	1.16 0.90	129	1.39 7.75
m9-pH9	9.96	9.1	100.5		36	0.36 0.28	163	1.82 10.18
m9-pH7	9.95	7.05	102.2		50	0.54 0.41	135	1.52 8.51
m9-pH4	9.93	4.09	105.5		36	0.39 0.30	11	0.06 0.30

Modelling As and Se leaching

We have shown that As and Se leaching from acidic fly ash in the laboratory can be described by a simplified model for the surface complexation of their oxyanions on amorphous iron (hydr)oxide (VAN DER HOEK AND COMANS, 1995). The same model is used here to investigate whether the partitioning of these elements between fly ash and pore water in the lysimeter can be described by the same process. The model is based on an apparent overall adsorption constant, $*K_A$, which is defined as follows (VAN DER HOEK AND COMANS, 1995):



where $=FeOH$ and $=FeH_{x+1}AsO_4^{x-1}$ indicate available and occupied adsorption sites on iron (hydr)oxide, and x is the proton stoichiometry in the overall reaction. At low surface coverage, the amount of iron (hydr)oxide in the fly ash, {Fe-oxide}, is used as a surrogate for the amount of available sorption

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sites in the fly ash ($=\text{FeOH}/N$), with N = the number of moles of adsorption sites per mole iron oxide. Therefore, the apparent overall adsorption constant is written as a function of pH and N :

$$K_A = N \cdot K_A [\text{H}^+]^x = \{ \equiv \text{FeH}_{x+1} \text{AsO}_4^{x-1} \} / \{ \text{Fe-oxide} \} [\text{H}_2\text{AsO}_4^-] \quad (3)$$

$$K_A = N \cdot K_A [\text{H}^+]^x = \{ \equiv \text{FeH}_x \text{SeO}_3^{x-1} \} / \{ \text{Fe-oxide} \} [\text{HSeO}_3^-] \quad (4)$$

where $\{ \}$ and $[\]$ refer to concentrations in the fly ash (mol/kg) and leachate (mol/l), respectively. $\{ \text{Fe-oxide} \}$ and the amount of associated As and Se were obtained from the hydroxylamine extractions.

Using equations (3) and (4), K_A values were calculated from the concentrations of Fe, As and Se in hydroxylamine extracts and the pore waters from individual slices in the cores. These values are compared in Fig. 7 with values derived, on the basis of the same model, from laboratory sorption experiments with pure amorphous iron (hydr)oxide (VAN DER HOEK *et al.*, 1995b).

The apparent overall adsorption constants calculated from the lysimeter data for As are within one order of magnitude from the values for pure iron (hydr)oxide, yet are always higher. The values also fall within the range of K_A 's calculated from laboratory leaching of acidic fly ash (VAN DER HOEK AND COMANS, 1995). The deviation of the lysimeter K_A -values from the iron (hydr)oxide data increases towards the bottom of the lysimeter, i.e. that section where As (and Se) may be partly associated with other minerals (see above). Similar to our observations for Se in that laboratory study, K_A values for this element show more scatter and deviate from the K_A -pH trend for amorphous iron (hydr)oxide at the more alkaline conditions lower down the profile.

Isotopic exchange experiments (VAN DER HOEK AND COMANS, 1995) have shown that the amount of both As and Se extracted with hydroxylamine is higher than the amount in fly ash which is in (isotopic) equilibrium with the leachate. These experiments have also shown that the isotopically

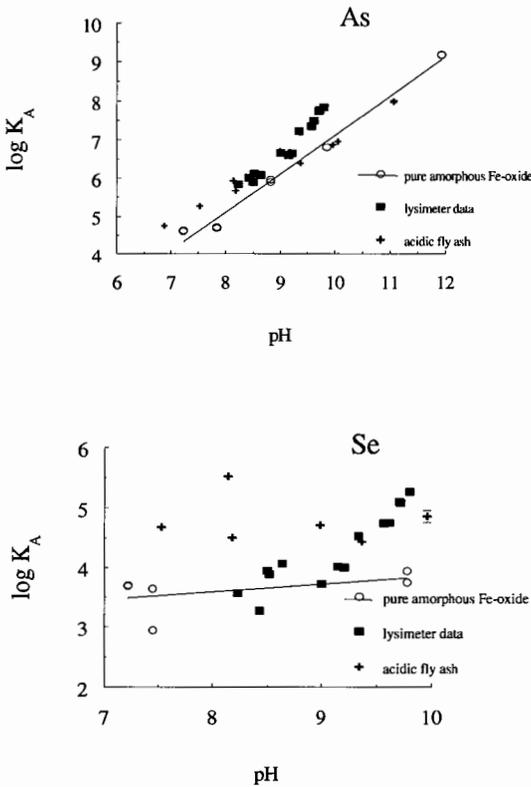


Fig. 7: Apparent overall sorption constants of As and Se on amorphous iron (hydr)oxide in the lysimeter compared to the constants measured in the laboratory on pure amorphous iron (hydr)oxide and on acidic fly ash

that of As (VAN DER HOEK *et al.*, 1995b). Although in the lower section of the lysimeter the difference between As extracted and leached at pH 12 is even greater, we cannot take the leached amount as the “exchangeable” fraction because of the possible interaction (by readsorption) with alkaline Ca-minerals such as ettringite (see discussion above).

exchangeable fraction of As and Se is comparable with the amount of As and Se leached at pH 12.

The amount of As leached at pH 12 in the pH-stat experiment with the fly ash sample from the upper part of the lysimeter (15% of the total amount in fly ash; Table 4) is indeed considerably smaller than the amount extracted with hydroxylamine (90%), whereas similar amounts of Se were leached and extracted (30 and 40%, respectively). This difference is consistent with our observations that the reversibility of Se sorption on amorphous iron (hydr)oxide is higher than

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Based on the above, the consistently higher K_A -values for the lysimeter fly ash, relative to those for (short-term) sorption of As on pure amorphous iron (hydr)oxide (Fig. 7) may, particularly for the upper part of the lysimeter, be explained by the fact that a proportion of the hydroxylamine-extractable As is not in equilibrium with the pore water. Hence, especially in the upper part of the lysimeter, leaching of As is likely to be controlled by sorption on amorphous iron (hydr)oxide. A substantial amount of Se is likely to be associated with mineral phases other than iron (hydr)oxide, but pore water concentrations in the neutral to slightly alkaline pH-range (i.e. the upper part of the lysimeter) may be predicted within an order of magnitude on the basis of sorption on amorphous iron (hydr)oxide.

Conclusions

The processes controlling As and Se leaching from a 11-year old, naturally weathered, fly ash have been investigated at different depths in a lysimeter by geochemical modelling of the partitioning of these elements between the solid phase and the pore waters.

The potentially important sorbents for As and Se, amorphous iron (hydr)oxide (down the entire profile) and the alkaline Ca-mineral ettringite (in the lower section of the profile), have been shown to be present and likely to be in equilibrium with the pore waters.

The lysimeter profiles, the pH-dependency of As and Se leaching from the weathered fly ash as well as extractions of As, Se, and amorphous iron (hydr)oxide with hydroxylamine, are all consistent with earlier laboratory observations that As and Se leaching from fly ash can be controlled by sorption on amorphous iron (hydr)oxide. This process seems to be particularly important in the upper section of the lysimeters. The partitioning of As and Se between fly ash and pore waters can be adequately described by using a simplified model for surface complexation of these elements on amorphous iron (hydr)oxide. In the lower section of the lysimeter interaction with alkaline Ca-minerals such as ettringite may contribute in controlling the leaching process.

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References

- ATKINS, M. MACPHEE, D., KINDNESS, A. AND GLASSER, F.P. (1991) Solubility properties of ternary and quaternary compounds in the $\text{CaO-Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ system, *Cem. Concr. Res.* **21**, 991-998.
- BALISTRIERI, L.S. AND CHAO, T.T. (1990) Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. *Geochim. Cosmochim. Acta* **54**, 739-751.
- CHAO, T.T. AND ZHOU, L. (1983) Extractions techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Sci. Soc. Am. J.* **47**, 225-232.
- COMANS R.N.J., VAN DER SLOOT, H.A., AND BONOUVRIE, P.A. (1993) Geochemical reactions controlling the solubility of major and trace elements during the leaching of municipal solid waste incinerator residues. In *VIP-32 Municipal Waste Combustion Proceedings of an international specialty conference*, Williamsburg, Virginia, 667-680.
- COMANS, R.N.J. AND MEIMA, J.A. (1994) Modelling Ca-Solubility in MSWI bottom ash leachates In: *Environmental aspects of construction with waste materials. Proceedings of the international conference on environmental implications of construction materials and technology developments*, Maastricht, Eds. Goumans J.J.J.M., van der Sloot, H.A., Aalbers, Th. G., Amsterdam, 467-477.
- COWAN, C.E. (1988) Review of selenium thermodynamic data. Electric Power Research Institute EA-5655.
- EARY, L.E., RAI, D., MATTIGOD, S.V. AND AINSWORTH C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements. *J. Environ. Qual.* **19**, 202-214.
- ESSINGTON, M.E. (1988) Solubility of Barium Arsenate, *Soil Sci. Soc Am. J.* **52**, 1566-1570.
- FELMY, A.R., GIRVIN, D.C. AND JENNE, E.A. (1984) MINTEQA A computer program for calculating aqueous geochemical equilibria. Environmental Protection Agency, Office of research and development, Rept. EPA 600/3/84/032.

Leaching of As and Se from naturally weathered coal fly ash

- FRUCHTER, J.S., RAI, D. AND ZACHARA, J.M.(1990) Identification of solubility-controlling solid phases in a large fly ash field lysimeter. *Environ. Sci. Technol.* **24**, 1173-1179.
- GARAVAGLIA, R. AND CARAMUSCIO, P. (1994) Coal fly-ash leaching behaviour and solubility controlling solids In: *Environmental aspects of construction with waste materials. Proceedings of the international conference on environmental implications of construction materials and technology developments*, Maastricht, Eds. Goumans J.J.J.M., van der Sloot, H.A., Aalbers, Th. G., Amsterdam, 87-102.
- HJELMAR, O. HANSEN, E.A., LARSEN, F. AND THOMASSEN H. (1991) Leaching and soil/groundwater transport of contaminants from coal combustion residues Water Quality Institute, Hørsholm, Denmark VKI-sagsnr.: 60.0010.
- MANZ, O.E. (1995) Worldwide production of fly ash and utilization in concrete and other productions. In *proceedings of the 5th CANMET/ACI international conference on fly ash, silica fume, slag & natural pozzolans in concrete*, (ed) Malhotra, V.M., Milwaukee, Wisconsin.
- MATTIGOD, S.V., RAI, D., EARY, L.E. AND AINSWORTH C.C.(1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the mayor elements. *J. Environ. Qual.* **19**, 188-201.
- PIERCE, M.L. AND MOORE, C.B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* **16**, 1247-1253.
- SCHRAMKE, J.A. (1992) Neutralization of alkaline coal fly ash leachates by CO₂(g) *Applied Geochem.* **7**, 481-492.
- VAN DER HOEK, E.E. AND COMANS, R.N.J. (1994) Speciation of As and Se during leaching of fly ash In: *Environmental aspects of construction with waste materials. Proceedings of the international conference on environmental implications of construction materials and technology developments*, Maastricht, Eds. Goumans J.J.J.M., van der Sloot, H.A., Aalbers, Th. G., Amsterdam, 467-477.
- VAN DER HOEK, E.E. AND COMANS, R.N.J. (1995) Modelling As and Se leaching from acidic fly ash by sorption on iron (hydr)oxide in the fly ash matrix, accepted for publication in *Environ. Sci. Technol.*

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- VAN DER HOEK, E.E., BONOUVRIE, P.A. AND COMANS, R.N.J. (1994) Sorption of As and Se on mineral components of fly ash: relevance for leaching processes, *Applied Geochem.* **9**, 403-412.
- VAN DER HOEK, VAN ELTEREN, J.T. AND COMANS, R.N.J. (1995a) Determination of As, Sb, and Se Speciation in fly ash leachates, submitted for publication.
- VAN DER HOEK, BOOTS, B.J. AND COMANS R.N.J. (1995b) Experimental observations on sorption reversibility of arsenate, selenite and molybdate on hematite and amorphous iron (hydr)oxide to be published.
- VAN DER SLOOT, H.A. (1991) Systematic leaching behaviour of trace elements from construction materials and waste materials. In *Waste materials in construction, Proceedings of the international conference on environmental implications of construction with waste materials*, Maastricht (eds) Goumans, J.J.J.M., van der Sloot, H.A., Aalbers, Th, G. Elsevier, Amsterdam, 19-37.
- WARREN, C.J. AND DUDAS, M.J. (1985) Formation of secondary minerals in artificially weathered fly ash. *J. Environ. Qual.* **14**, 405-410.

SUMMARY

The leaching (release) of large amounts of oxyanions, such as those of arsenic and selenium, is an major environmental problem when it comes to the disposal or use of coal fly ash. To predict environmentally safe conditions for the disposal or use of fly ash in, for example, construction materials, it is necessary to know the underlying leaching processes. The processes which cause leaching of arsenic and selenium from coal fly ash are studied in this thesis. Although combustion residues, such as coal fly ash, show a high variability in elemental composition, the residues show a systematic leaching behaviour. It is, therefore, also possible to use the results of this thesis to obtain a better understanding of the leaching of other combustion residues.

Arsenic and selenium can be present in different valency states in the environment. The valency state influences the toxicity and mobility of the oxyanions in the natural environment. Studies concerning the valency state of As and Se in fly ashes are reviewed in **Chapter 2**. After testing determination methods, the valency state was determined in leachates of five different coal fly ashes at different pH values. The results showed that As and Se leach preferentially as the oxyanions arsenate, As(V), and selenite, Se(IV). However, a relatively large amount of selenate, Se(VI), was found in the leachates of brown coal fly ash originating from a fluidized bed boiler.

The leaching process is not only is controlled by the speciation in solution, but also by the speciation on the solid (e.g. adsorbed species and minerals). The leaching of major elements can be generally described by precipitation/dissolution reactions. Trace element leaching is generally not controlled by these reactions but is expected to be controlled by sorption reactions. The possible controlling sorbents for As and Se are studied in **Chapter 3** by comparing the leaching of As and Se from an acidic fly ash and an alkaline fly ash with the sorption on their oxyanions the minerals hematite, mullite, portlandite and ettringite, which are generally present in the fly ash matrix. Hematite is one of the principal iron bearing minerals in fly ash. Mullite is an important crystalline aluminium silicate. Portlandite (calcium hydroxide) and ettringite (calcium-aluminium hydroxysulphate) may be formed during leaching of alkaline fly ashes. It

was shown that the leaching of As and Se from acidic fly ash can be described by sorption on an iron (hydr)oxide, such as hematite, and the leaching from a fly ash by sorption on an alkaline calcium phase.

Following the results of Chapter 3, an attempt is made to model the leaching of As and Se from acidic fly ash by sorption on iron (hydr)oxide in **Chapter 4**. Extractions of the crystalline and amorphous iron (hydr)oxide show that latter mineral is likely to dominate in controlling the leaching of As and Se. The amount of As, Se and Fe involved in the sorption process, are obtained from hydroxylamine extraction of amorphous iron (hydr)oxide and from isotopic exchange. It is shown that the leaching of As and Se can be described with an overall surface complexation model for the sorption of As and Se on amorphous iron (hydr)oxide.

When sorption on iron (hydr)oxides controls the leaching of As and Se from acidic fly ash the actual release of these elements is also dependent on the reversibility of the sorption process. The sorption reversibility is studied on different mineral phases in chapter 2. In **Chapter 5**, the reversibility of arsenate, selenite and molybdate on amorphous iron (hydr)oxide and hematite is investigated. Arsenate and molybdate sorb less reversibly on the iron (hydr)oxides while selenite sorbs reversibly with respect to changes in the pH. The pH at which the oxyanion is sorbed is crucial in controlling its sorption reversibility on iron (hydr)oxides. Arsenate is less reversibly sorbed than selenite on all the minerals studied. This behaviour may well be the reason for the general observation that the availability of As for leaching is less than that of Se.

Chapter 6 describes an investigation of the processes controlling As and Se leaching from fly ash under natural conditions using mechanistic insights developed in the earlier chapters of this thesis. For this purpose samples of solids and pore water were taken from an 11 year old, naturally weathered, fly ash at different depths in a lysimeter and were studied both experimentally and by geochemical modelling. The potentially important sorbents for As and Se, amorphous iron (hydr)oxide and alkaline Ca-mineral ettringite, are shown to be present and likely to be in equilibrium with the pore waters. Lysimeter profiles, pH dependent leaching

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experiments and extraction of As, Se, and Fe in the weathered fly ash, as well as the modelling results, confirm the findings in the earlier chapters; As and Se leaching from the fly ash, especially in the upper section of the lysimeters, is likely to be controlled by sorption on amorphous iron (hydr)oxide. In the lower section of the lysimeter interaction with alkaline Ca-minerals such as ettringite may contribute in controlling the leaching process.

SAMENVATTING

Een belangrijk milieuprobleem voor de opslag en het gebruik van poederkoolvliegias is het vrijkomen (uitloggen) van grote hoeveelheden oxyanionen na reactie met water. Oxyanionen zijn componenten van elementen die met zuurstof (oxy) negatief geladen verbindingen (anionen) vormen in water. Een aantal van deze oxyanionen, zoals de oxyanionen van arseen en seleen, kunnen al in kleine hoeveelheden gevaarlijk zijn voor het milieu. Een gedeelte van de oxyanionen zal na reactie met (regen)water in oplossing gaan en uitspoelen (uitloggen). De uitloging is afhankelijk van allerlei omstandigheden zoals de zuurgraad (pH) van het water, de reactie van de vliegias met de atmosfeer en de tijdsduur waarin de vliegias is opgeslagen. Om poederkoolvliegias op een veilige manier op te slaan of te gebruiken in bijvoorbeeld bouwmaterialen is het nodig te weten welke processen de uitloging tot stand brengen. In dit proefschrift zijn de processen onderzocht die de uitloging van arseen en seleen uit poederkoolvliegias bepalen.

Poederkoolvliegias is een reststof die wordt afgevangen bij de verbranding van steenkool. Een gedeelte van steenkool is niet brandbaar en blijft over als as (in Nederland is dit ongeveer 10 %). Het grootste gedeelte hiervan vliegt omhoog in de luchtstroom en wordt afgevangen als vliegias. Reststoffen die ontstaan bij verbrandingsprocessen zoals bij de verbranding van steenkool en huisvuil kunnen sterk verschillen in samenstelling. Ondanks de grote verschillen in samenstelling is gebleken dat al deze reststoffen een systematisch uitlooggedrag vertonen. De in dit proefschrift bestudeerde uitloogmechanismen van poederkoolvliegias kunnen daarom ook worden gebruikt om meer inzicht te krijgen in de uitloging van andere reststoffen van verbrandingsprocessen.

Vliegias kan worden beschouwd als een glasbolletje waaraan verschillende zouten en mineralen zijn gehecht. Na reactie met water gaan sommige van deze zouten in oplossing waarna weer andere zouten kunnen neerslaan. Voor hoofdelementen, stoffen die in grote hoeveelheden (in procenten) voorkomen in vliegias, is de uitloging te beschrijven met oplos- en neerslagreacties. Voor spoorelementen, stoffen die slechts in kleine hoeveelheden (in mg/kg) voorkomen, kan de uitloging meestal niet met

deze processen worden beschreven. Waarschijnlijk wordt de uitloging van spoorelementen, zoals arseen en seleen, gecontroleerd door binding (ad- en desorptiereacties) aan minerale fasen die aanwezig zijn in de vliegasmatrix.

Arseen en seleen kunnen in verschillende vormen (species) voorkomen in het milieu. De waardigheid (valentie) van arseen en seleen bepaalt onder andere de giftigheid en de mobiliteit van deze elementen. Het is daarom belangrijk te weten in welke waardigheid deze elementen uitlogen. In **hoofdstuk 2** zijn de verschillende studies uit de literatuur naar de waardigheid van arseen en seleen in vliegassamengevat. Een aantal methoden om de waardigheid van oxyanionen te bepalen is getest voor uitloogextracten uit vliegassamengevat. Vervolgens is in het extract van vijf verschillende vliegassen bij verschillende pH-waarden de waardigheid bepaald. Het blijkt dat arseen en seleen voornamelijk als het minder mobiele vijfwaardige arseen (arsenaat) en vierwaardige seleen (seleniet) uitlogen. In uitloogextracten van bruinkoolvliegassamengevat van een wervelbed-installatie is echter voornamelijk zeswaardig seleen (selenaat) gemeten.

Niet alleen de vorm van arseen en seleen in oplossing maar ook de bindingsvorm van de oxyanionen in de vaste stof (speciatie in zowel de oplossing als de vaste stof) is bepalend voor het uitloogproces. In **hoofdstuk 3** is onderzocht welke minerale fasen de arseen- en seleenuitloging kunnen controleren. Hiervoor is de uitloging van arseen en seleen uit een zure en basische vliegassamengevat vergeleken met de sorptie van de oxyanionen aan verschillende minerale fasen die in de vliegassamatrix kunnen voorkomen: hematiet, mulliet, portlandiet en ettringiet. Hematiet is één van de belangrijkste ijzerhoudende mineralen in vliegassamengevat en mulliet is een belangrijk aluminium-silicaat. Portlandiet (calciumhydroxide) en ettringiet (calcium-aluminiumhydroxysulfaat) zijn basische calcium fasen die kunnen worden gevormd na reactie van basische vliegassamengevat met water. Het blijkt dat de uitloging van arseen en seleen uit zure vliegassamengevat kan worden beschreven met sorptie aan ijzeroxide, zoals hematiet, en de uitloging uit basische vliegassamengevat door sorptie aan een basische calcium fase, zoals portlandiet of ettringiet.

SAMENVATTING

In **hoofdstuk 4** is getracht de uitloging van arseen en seleen te modelleren, door gebruik te maken van de observatie in hoofdstuk 3 dat ijzeroxiden een belangrijke rol spelen bij de uitloging uit zure vliegias. Hiervoor is de ijzeroxide fase van de zure vliegias na uitloging geëxtraheerd. Er is zowel een extractie van kristallijn ijzeroxide als amorf ijzeroxide uitgevoerd. De resultaten van de extracties tonen aan dat het waarschijnlijk is dat amorf ijzeroxide veel belangrijker is voor de binding van arseen en seleen aan vliegias dan kristallijn ijzeroxide. Uit de extractieresultaten zijn gegevens verkregen om de uitloging van arseen en seleen te modelleren, zoals de hoeveelheid ijzer, arseen en seleen gebonden aan de vaste stof. Hiernaast is de uitwisselbare fractie van arseen en seleen aan het oppervlak van de vliegias onderzocht met behulp van isotopische uitwisseling. Het is mogelijk gebleken de uitloging van arseen en seleen te beschrijven met een vereenvoudigd oppervlakte complexatie model voor de binding van arseen en seleen aan amorf ijzeroxide.

Om de hoeveelheid oxyanion die vrijkomt uit vliegias te voorspellen is het ook nodig te weten hoe omkeerbaar (reversibel) de controlerende sorptieprocessen zijn. In hoofdstuk 2 en 5 is de reversibiliteit bestudeerd van sorptieprocessen van arseen en seleen aan verschillende minerale fasen die kunnen voorkomen in de vliegasmatrix. Omdat sorptie aan ijzeroxide een belangrijke rol speelt in het uitloogproces is de omkeerbaarheid na adsorptie aan ijzeroxide in meer detail onderzocht. In **hoofdstuk 5** is daarom de reversibiliteit van de binding van arsenaat en seleniet aan hematiet en amorf ijzeroxide gemeten. Arsenaat adsorbeert minder reversibel aan deze ijzeroxiden dan seleniet na veranderingen in de pH. De pH waarbij het oxyanion is geadsorbeerd is de doorslaggevende factor voor de reversibiliteit van de sorptie. Arsenaat blijkt bij alle onderzochte mineralen minder reversibel te adsorberen dan seleniet. Dit gedrag kan de oorzaak zijn van de observatie dat arseen minder mobiel is en verhoudingsgewijs minder uitloogt dan seleen.

Hoofdstuk 6 beschrijft een onderzoek naar de uitloogprocessen van arseen en seleen onder natuurlijke condities gebruikmakend van de kennis over deze processen ontwikkeld in de eerdere hoofdstukken van dit proefschrift. Hiervoor zijn monsters genomen van de vaste fase en het poriënwater van

vliegias in een kunstmatige opslag (lysimeter) op verschillende dieptes. De vliegias in de lysimeter was vóór de bemonstering 11 jaar lang blootgesteld geweest aan regenwater en de atmosfeer. De monsters zijn bestudeerd met behulp van uitloogexperimenten en geochemische modellering. Het is aangetoond dat amorf ijzeroxide en het basische calcium-mineraal ettringiet aanwezig zijn in de vaste fase en waarschijnlijk in evenwicht zijn met het poriënwater. De concentratieprofielen in de lysimeter, de pH-afhankelijke uitloging van arseen en seleen in laboratorium experimenten en de extractie van arseen, seleen en ijzer uit de verweerde vliegias, in combinatie met modelleringsresultaten, bevestigen de resultaten uit de eerdere hoofdstukken: arseen- en seleen uitloging uit vliegias wordt waarschijnlijk gecontroleerd door sorptie aan amorf ijzeroxide. Deze sorptie-controle vindt vooral in de bovenste sectie van de lysimeter plaats. In het onderste gedeelte van de lysimeter kunnen interacties met basische calcium-mineralen zoals ettringiet bijdragen aan de controle van het uitloogproces.

DANKWOORD

Alhoewel een proefschrift slechts een auteur kent is het het produkt van samenwerking. Ik wil daarom iedereen bedanken die heeft bijgedragen aan dit proefschrift. Een aantal mensen wil ik in het bijzonder noemen. Als eerste wil ik het ECN bedanken voor de mogelijkheid die zij geboden heeft om dit promotie-onderzoek uit te voeren. Hierbij wil ik met name Henk Das bedanken voor het starten van dit onderzoek en Sjaak Slanina, Hans van der Sloot en Gerard de Groot voor de verdere voortzetting.

Ik wil Prof. van der Weijden bedanken voor de beschouwing van alle manuscripten en zijn kritische inbreng. Rob zonder jou had dit proefschrift er in deze vorm niet gekomen. Ik wil je bedanken voor de wetenschappelijke begeleiding en voor de lessen in het schrijven van Engelse manuscripten. Misschien was ik niet altijd de leerling die jij je wenste. Ik heb alle gezellige sessies die wij samen hebben gehad zeer gewaardeerd ook al duurde ze vaak langer dan ik graag wilde.

Twee stagiaires Maurice en Bram hebben veel werk verricht voor dit proefschrift. Een heleboel ECN collega's hebben aan dit proefschrift bijgedragen. Graag wil ik Petra, Dirk, Jan, Frits, Gerard en Dick bedanken. Alle collega's op het ECN en bij de KEMA die vooral bij alle lunches mijn frustraties hebben willen aanhoren wil ik bedanken voor alle steun en relativatie. Mijn kamergenoten, Hans, Renata en Jeanette hebben meegedacht, meegelezen en mij aangehoord. Alex wil ik bedanken voor het up to date houden van mijn computer.

Ik wil de KEMA bedanken voor de kans die zij mij geboden heeft dit proefschrift tot een einde te brengen. In het bijzonder wil ik Henk bedanken die mij maar bleef ondersteunen ondanks mijn chagrijnige kop. Wilna wil ik bedanken voor het na kijken van mijn manuscripten. Maire Bowmer, Ans Molenaars en W. de Kok wil ik bedanken voor het Engelse correctiewerk. Ook alle anderen die manuscripten hebben gecorrigeerd, onder andere Maria en Guido, wil ik bedanken.

Dankwoord

Verder wil ik alle vrienden en familie bedanken die mij hebben gesteund. Met name Jan Anne die mij geleerd heeft in mij zelf te geloven. Hans, Martijn, Arnout en Marianne wil ik vooral bedanken voor de steun bij de laatste loodjes.

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