

# Major Leaching Processes of Combustion Residues

Characterisation, modelling and experimental investigation

Jinying Yan



Department of Chemical Engineering and Technology

Division of Chemical Engineering

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parents

To Qin, Tao and my

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## ABSTRACT

Characterising leaching behaviour provides ample evidence to identify the major leaching processes of combustion residues. Neutralisation and chemical weathering govern the leaching reactions and control the release of major, minor and trace elements from combustion residues, and are thus considered to be the major leaching processes.

Several geochemical models are used to describe the neutralisation and chemical weathering processes based on leaching kinetics and the features of leaching systems. A reaction path model is used to evaluate the neutralising processes in a batch system. The neutralising processes in a flow-through system are assessed using an equilibrium reactive transport model which accounts for most neutralising reactions under the experimental conditions. A kinetic reactive transport model taking full kinetic consideration for heterogeneous reactions is used to simulate long-term chemical weathering.

According to experimental investigations and geochemical simulations, the leaching kinetics of buffering materials are key issues for the understanding of the neutralising processes. The acid neutralising capacity (ANC) at different pH levels depends mainly on the mineralogy of the combustion residues. The time-dependent and pH-dependent neutralising behaviours are determined by the matrix phases of a solid waste. In combustion residues, the dissolution of glass phases is expected to play an important role in a long-term neutralising process. The neutralising process in a flow system is significantly different from that in a batch system. In general, the information obtained from batch experiments cannot directly to be used in a flow system. The neutralising ability of a combustion residue may be strongly affected by solute transport and carbonation reactions in a natural leaching environment.

The chemical weathering mainly involves the matrix of combustion residues consisting mostly of glass phases. The dissolution kinetics of waste glass and other possible processes involved in the chemical weathering have been investigated and incorporated into a kinetic reactive transport model. Most important processes in the chemical weathering can be simulated simultaneously using this model. The results show that there is a complicated relationship between the factors controlling the long-term chemical weathering. The dissolution of the waste matrix is strongly affected by its dissolution kinetics and weathering environment. The environmental impact of the glass dissolution cannot be neglected. Although the glass dissolution provides considerable buffering capacity in long-term weathering, the carbonate is usually a dominant buffering mineral in actual weathering processes. The transformation of carbonate should be considered as an important process in the chemical weathering. The formation of secondary minerals, clay-like minerals (*e.g.* illite) and amorphous silica, may considerably alter the mineralogy of the waste, and thus change the leaching behaviours of the combustion residue during long-term chemical weathering.

**Keywords:** Leaching; neutralisation; chemical weathering; solid waste; combustion residues; long term; geochemical modelling; reaction path model; reactive transport model

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- II** Yan, J., Moreno, L., Neretnieks, I. 1998. Neutralising processes in leaching of solid wastes: Modelling of interactions between solid waste and strong acid. *J. Environ. Sci. Health (Part A), Toxic/Hazardous Substances & Environmental Engineering* A33 (6), 923-950.
- III** Yan, J., Bäverman, C., Moreno, L., Neretnieks, I. 1998. Neutralising processes of municipal solid waste incineration bottom ash in a flow-through system. *Sci. Total Environ.* (in press)
- IV** Yan, J., Neretnieks, I. 1995. Is the glass phase dissolution rate always a limiting factor in the leaching processes of combustion residues? *Sci. Total Environ.* 172, 95-118.
- V** Yan, J., Moreno, L., Neretnieks, I. 1998. Modelling long-term chemical weathering of combustion residues: 1. Development of a reactive transport model (submitted for publication)
- VI** Yan, J., Moreno, L., Neretnieks, I. 1998. Modelling long-term chemical weathering of combustion residues: 2. A case study for the chemical weathering of MSWI bottom ash. (submitted for publication)

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Yan, J. 1995. On leaching characteristics and dissolution kinetics of combustion residues. Licentiate treatise, TRITA-KET R27, Department of chemical Engineering and Technology, Royal Institute of Technology, Stockholm, Sweden.

Yan, J., Bäverman, C., Moreno, L., Neretnieks, I. 1997. The long-term acid neutralising capacity of steel slag. Studies in Environmental Science 71, Waste Materials in Construction: Putting Theory into Practice. J.J.J.M. Goumans, G.J. Senden and H.A. van der Sloot (eds), pp. 631-640, Elsevier Science B.V.

Yan, J., Moreno, L., Neretnieks, I. 1998. Characterising the neutralisation behaviour of MSWI bottom ash on different time scales and in different reaction systems. The 3rd Swedish Landfill Research Symposia, 6-8th of October, Luleå, Sweden.

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# 1 INTRODUCTION

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Combustion residues are the major sources of solid waste. They are primarily produced from the processes for power generation and waste reduction. The combustion residues include mainly coal ashes, municipal solid waste incineration (MSWI) ashes and some industrial slags. According to current estimation, coal combustion residues account for 90% of all fossil fuel combustion wastes, and more than 150 million tonnes of combustion residues will be produced in the United States each year by the year 2000 (Carlson and Adriano, 1993). On the basis of approximate data for some developed countries (United States, Canada, Japan, United Kingdom, Germany, France, the Netherlands, Sweden and Denmark), the combustion residues from municipal solid waste was about 37 million tonnes per year in the beginning of the 1990s (Chandler et al., 1997). Presently, some of the residues are utilised, but most of them are deposited in landfills or surface impoundments.

There are many similarities between different combustion residues, so that we can consider them as one type of solid waste, to study their common features in disposal or utilisation scenarios. The combustion residues undergo a high temperature combustion process, which means that the residues contain mainly inorganic substances and only small amounts of organic materials. The major components of the combustion residues are generally similar including constituents of Si, Al, Fe and Ca. These constituents usually account for over 80% of the weight of combustion residues. Most of them consist of a matrix of combustion residue, amorphous glasses (Fisher and Natusch, 1979; Roy et al., 1985; Hartlén and Lundgren, 1991; Kirby and Rimstidt, 1993; Zevenbergen et al., 1994; Eusden et al., 1994; Pfrang-Stotz and Schneider, 1995; Vassilev and Vassileva, 1997). The combustion residues are similar to igneous rocks, granite and basalt as well as some natural glasses in chemical composition and geochemical properties (Belevi et al., 1992; Kirby, 1993; Zevenbergen and Comans, 1994). From a geochemical point of view, the combustion residues can be defined as a rock-like material as far as their main elements are concerned. It should be possible to use geochemical knowledge to assess the environmental impact of combustion residues.

The combustion process results in a considerable reduction in weight of the original materials. This reduction concentrates some mineral and elements in the combustion residues. Compared to the original coal, most elements are enriched 10 to 20 times in the coal fly ash (Mukhopadhyay et al., 1996). The content of toxic metals (*e.g.* Cd, Zn, Pb, Hg, Cu, Cr and Ni) present in MSWI bottom ash is usually 10-100 times larger than in natural soils (Theis and Gardner, 1990). Therefore there is a growing concern for the

environmental impact of combustion residues in disposal and utilisation, especially for the release of toxic substances such as heavy metals, As, Cd, Cr, Cu, Hg, Mo, Ni, Pb and Zn, and soluble salts from the residues (Carlson and Adriano, 1993; Stegemann et al., 1995; Berenyi, 1996; Hartenstein and Horvay, 1996; Hunsicker et al., 1996).

The major potential hazard associated with the combustion residues in disposal or utilisation is the leaching of potentially toxic substances into the terrestrial ecosystem. The release of toxic substances directly influences adjacent aquatic ecosystems such as soils and groundwater. The leaching of combustion residues can also indirectly affect plant growth and increase the mobility and accumulation of potentially toxic elements through the food chain (Carlson and Adriano, 1993). In general, the major environmental impacts are usually associated with changes in water chemistry through interactions between a combustion residue and an aqueous solution. An understanding of these interactions become significantly important for leaching of combustion residues both in short- and long-term processes.

The leaching of combustion residues is like an acid titration process in a heterogeneous system. Combustion residues are not stable under natural conditions. This high-temperature product is active in the subsurface environment especially in an aquatic environment. When a residue is wetted with water, the various components start to dissolve. The dissolution rates for the soluble minerals are commonly faster than that for the matrix phase. The chemical environment initially provided by the soluble minerals will be gradually modified by the dissolution of matrix phase and by the chemical characteristics of the surrounding environment. With time, for example, the alkalinity of the residue will be neutralised by infiltrating acidic rain, carbon dioxide from the atmosphere or from the oxidation of organic carbon, or organic acids. Eventually, some elements will reach a saturation concentration with respect to some secondary minerals. Examples are  $\text{Al}(\text{OH})_3$  and amorphous  $\text{SiO}_2$ , but more complicated aluminium silicates can also form. The metastable phases in the residues will be altered to form the assemblages of thermodynamically stable minerals. The time frame for release of toxic elements from combustion residues is partly a function of the ability of the residue to resist such chemical alteration. To understand the changes in the combustion residue under different leaching conditions and on different time scales is therefore important for predicting its environmental impact.

Many reactions and processes are involved in the interactions between the combustion residue and an aqueous solution. It is necessary to distinguish the major processes from other leaching processes, because these processes control the leaching environment and strongly affect the release of minor or trace toxic elements. In most cases, several

reactions or processes may take place simultaneously and feed back to each other. Some of the reactions or processes are fast, and others are slow and time-dependent. A different approach may be required to describe different type of processes, *e.g.* a thermodynamic consideration for fast process, and a kinetic consideration for slow reactions. An integral understanding of the interactions between various processes is also critically important for a systematical assessment of the environmental impacts of combustion residues.

The emphasis of this study of combustion residues is on the major leaching processes which have been identified by experimental investigations. However, because most researchers pay more attention to the leaching of toxic elements which are directly related to the environmental impact of combustion residues, the major leaching processes have actually not been addressed very well. Even the acid-base reactions in the leaching of combustion residues have not been fully studied, especially with respect to their chemical kinetics and the influence of solute transport. Little is known so far about the long-term behaviour of combustion residues in utilisation and disposal. The major processes need to be understood first to provide insight into the leaching of trace elements. Moreover, there is a need to further develop quantitative models to describe the complicated leaching processes of combustion residues (van der Sloot et al., 1997). Experimental investigations combined with geochemical modelling to assess the major processes should be an important step towards this aim.

In this thesis, the leaching of combustion residues is characterised on the basis of experimental evidence. The emphasis of the characterisation has been to identify major leaching processes for further study. MSWI bottom ash and coal fly ash are taken as typical combustion residues to assess their leaching behaviours in different reaction systems and on different time scales. The studies focus on the neutralising and chemical weathering processes which have been shown to govern other leaching processes, and are considered to be the major leaching processes. On the basis of the interactions between a combustion residue and an aqueous solution, the leaching behaviour of various solid wastes can be described in a more scientific way. Both experimental investigation and geochemical modelling have been used in this study. Several geochemical and reactive transport models are proposed to describe the neutralising and chemical weathering processes according to the intrinsic characteristics of the combustion residue and the leaching scenarios.

## 2 LEACHING CHARACTERISTICS OF COMBUSTION RESIDUES

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The combustion residues are heterogeneous materials. The leaching characteristics therefore depend not only on the chemical composition of the combustion residue but largely on its mineralogy and morphology. Although leaching tests provide much experimental evidence concerning the leaching process, it is important to distinguish the difference between the leaching environment in a leaching test and that in a natural waste disposal. The critical evaluation of the information obtained from leaching tests aims to identify the major leaching mechanisms and processes.

### 2.1 Chemical composition, mineralogy and morphology

#### 2.1.1 *Chemical composition of combustion residues*

The bulk chemical compositions vary for different combustion residues. Although the variation in some trace species may be as high as several orders of magnitude, the contents of predominant components in the residues usually differ only in a limited range (Theis and Gardner, 1990; Murarka et al., 1991; Goldin et al., 1992; Meima, 1997). Four major elements, silicon, aluminium, iron and calcium, constitute the major part of the combustion residues. This feature indicates that the constituents of the four elements in the residues should play an important role in leaching chemistry. In addition, the major chemical compositions of the combustion residues are similar to those of some natural materials, *e.g.* basalt and basalt glass (Table 1).

It should be mentioned that some combustion residues contain non-combusted organic material, for example the organic carbon content of MSWI bottom ash is typically from 2 to 4% in well burned-out ashes (Chandler et al., 1997). It has been found that there is quite a good correlation between the organic content of the MSWI bottom ash and the reducing capacity measured by redox titration using Ce(IV) as the oxidant (Crawford et al., 1998). For this type of combustion residue, the organic content may be important for redox processes in leaching of the residues although the details of the processes in a natural system are largely unknown.

From an environmental point of view, the bulk composition of combustion residues can be compared with that of common soil. If we define the ratio of the abundance of a species in ash to that in soil as a so-called enrichment factor, there are two different

enrichment patterns for elements in combustion residues. The major elements appear to have no or little enrichment. However, many trace elements have strong enrichment in combustion residues, and show a different enrichment factor for different types of residues (Table 2). Because the toxic elements are concentrated in combustion residues, leaching of the toxic elements becomes a critical problem in the disposal and utilisation of the residues. The enrichment factors show the potential environmental impacts of combustion residues on adjacent aquatic ecosystems.

Table 1. The major compositions of combustion residues compared with natural materials (%)

	Combustion residues		Natural materials	
	coal fly ash <sup>[1]</sup>	MSWI bottom ash <sup>[2]</sup>	basalt glass <sup>[3]</sup>	alkali olivine basalt <sup>[4]</sup>
SiO <sub>2</sub>	45.20	50.96	46.70	50.48
Al <sub>2</sub> O <sub>3</sub>	21.82	9.31	14.60	18.31
CaO	2.20	11.73	17.90 (+MgO)	12.01 (+Na <sub>2</sub> O)
Fe <sub>2</sub> O <sub>3</sub>	16.48	11.52	12.00	9.24 (+FeO)
Total	85.70	83.52	91.20	90.04

Notes: [1] The mean values of four coal fly ashes (Murarka et al., 1991); [2] The mean values of four European MSWI bottom ashes (Hjelmar, 1987; Belevi et al., 1992; Fällman and Hartlén, 1994; Zevenbergen, 1994); [3] Cowan and Ewing, 1989; [4] Brownlow, 1996.

Table 2. Enrichment factor of minor and trace elements in combustion residues

Elements	Coal combustion		MSWI	
	bottom ash	fly ash	bottom ash	fly ash
As	4.20	157	7.50	3.00
Cd	1.41	5.66	18.8	1250
Cr	2.97	2.99	17.0	5.58
Cu	3.06	4.08	33.3	19.6
Mo	85.4	45.6	1.54	10.6
Ni	1.08	0.51	0.64	1.44
Pb	10.6	20.8	106	255
Se	6.40	61.0	2.27	7.31
V	1.77	3.85	0.23	0.89
Zn	5.81	11.3	77.4	407

Notes: 1. The enrichment factor = abundance of the species in ash / that in soil; 2. The abundances of species in ashes are the median values of the content ranges obtained from the references (Theis and Gardner, 1990; Murarka et al., 1991; EPRI, 1983) and the average values from Goldin et al., (1992); the abundances in soil are obtained from the median values of the data in Sharma et al., (1989)

### 2.1.2 Mineralogy of combustion residues

The mineralogy of a combustion residue refers to both amorphous and crystalline phases or other mineral fractions in the residue. The leaching behaviour of combustion residues can be related to their mineralogical characteristics. More attention should be paid to the major phases which may control leaching chemistry and the host phases of toxic elements which directly associate with the release of the elements, in order to understand the leaching processes.

Glass phases, ferrite spinel or other silicates are preferably formed in a high temperature combustion. Although this trend may not be exactly the same for various combustion residues, the major fraction of the residues is usually composed of amorphous phases of silicon, aluminium and iron such as the glasses, magnetic spinel and some aluminosilicates (Table 3). It is widely accepted that an impure aluminosilicate glass constitutes the bulk of the coal fly ash matrix (Fisher and Natusch, 1979; Roy et al., 1985). It has been found that the glass content in MSWI bottom ash varies between 40 and 75% (Hartlén and Lundgren, 1991; Kirby and Rimstidt, 1993; Zevenbergen et al., 1994; Eusden et al., 1994; Pfrang-Stotz and Schneider, 1995).

Table 3. The major mineral phases identified in combustion residues

Coal fly ashes	MSWI bottom ashes
aluminosilicate glasses	aluminosilicate glasses
magnetite	magnetite
quartz	quartz
melilite (gehlenite and akermanite, in high-Ca ash)	melilite (gehlenite and akermanite)
feldspar (in high-Ca ash)	feldspar
ferrite spinel (in high-Ca ash)	spinel-group minerals
mullite	calcite
anhydrite	
lime and periclase (in high-Ca ash)	
bredigite and larnite (in high-Ca ash)	

Notes: Data sources for coal fly ash (EPRI, 1983; Roy et al., 1985) and for MSWI bottom ash (Kirby and Rimstidt, 1993; Eighmy et al., 1994; Zevenbergen and Comans, 1994; Pfrang-Stotz and Schneider, 1995)

The release of species from solid wastes in an aqueous solution depends on the mineral patterns of the species existing in the solid wastes. Most trace elements exist as a solid solution in the combustion residues, especially in coal fly ash. The leaching behaviours of these elements are usually determined by their host phases. In most cases, the glass phases and magnetic fraction in the combustion residues contain most of the potentially toxic trace elements. The majority of trace elements in the aluminosilicate matrix of ashes are concentrated in the glass phases, while the crystalline phases have low concentrations. The mullite-quartz phase, for example, is relatively more pure than the glass phase. The glass phases and magnetic fraction are potentially the most important hosts for many toxic trace elements in the combustion residues (EPRI, 1983; Zevenbergen, 1994).

### 2.1.3 Morphology of combustion residues

The morphological appearance of a combustion residue can be related to the reactive properties of the solid wastes. Particle morphology is one of the most important morphological aspects of combustion residues. The particle size distribution together with the specific surface area provides quantitative information to evaluate the interaction between solid waste and aqueous solution. Fig. 1 shows typical ranges of particle size distribution for coal fly ash and MSWI bottom ash (Roy et al., 1985; Chandler et al., 1997).

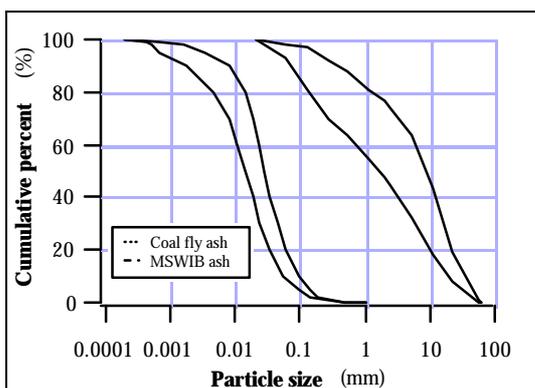


Fig. 1 Typical particle size distribution ranges of coal fly ash and MSWI bottom ash

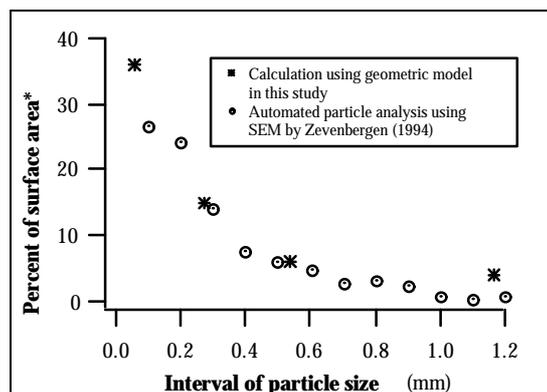


Fig. 2 The relationship between the initial surface area and particle size of MSWI bottom ash (\* the surface area (%) in the range between two sizes).

The specific surface area of combustion residues is determined by both particle size and particle morphology. The initial surface area of a solid can be estimated on the basis of either the macroscopic nature of the surface (geometric model) or the microscopic

nature, *i.e.* the areal extent of coverage by atoms or molecules (BET method). The relation between this kind of surface area and the reactive interface between a solid waste and an aqueous solution is, however, an open question so far. According to literature data, and the measurement and calculation for MSWI bottom ash in this study, the difference between the BET method and the geometric approach is estimated to be two orders of magnitude, which reflects the irregular particle shapes, the roughness of the particle surface and the inner porosity of the particles. The BET surface and geometric surface should represent the upper and lower limits for the reactive surface area respectively. Fig. 2 shows an example of the initial surface area of MSWI bottom ash estimated using the geometric model. It is found that small particles (less than 20% of the total weight of the ash) will provide most of the surface area (more than 80%) for leaching reactions. In addition to the initial surface area, the change in surface area as the reaction progresses is also important in a long-term leaching process.

## **2.2 General leaching characteristics (experimental evidence)**

Most experimental evidence relating to the leaching behaviour of combustion residues is obtained from leaching tests. Different types of leaching tests usually gives different results that reflect some aspects of the leaching behaviour. In the prediction of environmental impacts, the leaching characteristics of the residues in aqueous and weakly acidic solutions are most important although many leaching tests use more aggressive leaching media than those which occur in a natural environment. The leaching of combustion residues in an aqueous solution is similar to the situation during the early leaching of the waste. The weakly acidic solution is close to some natural leaching media, *e.g.* for example, acid rain. Because little information is available on field verifications of the results of the leaching tests (van der Sloot et al., 1997), most of the leaching tests provide a qualitative or semi-quantitative information relating to the relatively short-term leaching of combustion residues.

### *2.2.1 pH pattern in leaching process*

One of the major leaching effects in an aquatic environment is the acid-base properties of combustion residues. The pH value of the leachate is important for the environment and also for the dissolution of the combustion residues themselves. Figure 3 presents the pH-change patterns for different types of coal fly ashes when different amounts of ash are added to the aqueous solution and an equilibrium is reached.

In early or medium-term dissolution processes, the acid-base properties of a combustion residue are usually determined by the ratio between the acidic and alkaline components in a soluble fraction of the residue. For alkaline combustion residues, the high pH of the leachate is due to the dissolution and hydrolysis of alkali-earth and alkali metal oxides on the surface phases of the wastes. It has been found for various residues that a high concentration of calcium often occurs in the initial dissolution process (Theis and Wirth, 1977; Talbot et al., 1978; Warren and Dudas, 1984; Roy and Griffin, 1984; van der Sloot et al., 1985; Vogt et al., 1986; Dudas and Warren, 1988; Hjelmar, 1990; Kirby and Rimstidt, 1993, 1994; Johnson et al., 1995). The general pattern of pH changes in the leaching of alkaline combustion residues can be described as follows: the initial rise of pH is rapid and the value then reaches a relatively stable state when the combustion residue is dissolved in an aqueous solution. The pH buffering system is initially set up by the dissolution of soluble components of the solid waste. There are different buffering stages for various combustion residues, depending on the nature of the buffering component. These phenomena are also closely associated with the mineralogy of waste, the leaching kinetics of buffering components and the surrounding environment. It has been found that the acid neutralising capacity and carbonation reactions play important roles in the pH changes in the leaching process (Zevenbergen and Comans, 1994; Meima and Comans, 1997; Yan et al., 1998a, 1998b, 1998c). However, the general leaching characteristics obtained from the leaching tests provide experimental evidence to identify the major processes in the leaching of combustion residues.

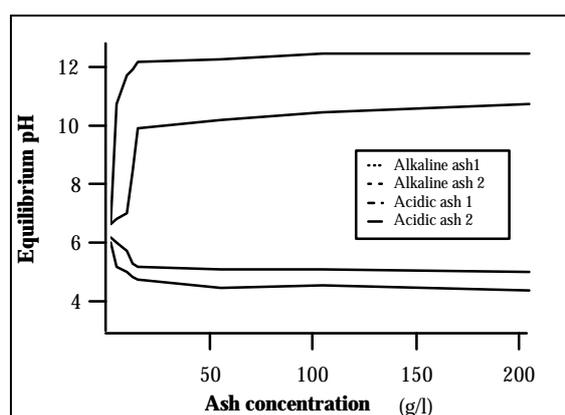


Fig. 3 Relationships between pH and the content of coal fly ashes (two alkaline ashes and two acidic ashes) in distilled water (data source: Theis and Wirth, 1977).

### 2.2.2 Initial leaching of surface and soluble phases

The initial leaching of the combustion residues can be characterised by surface hydrolysis and the dissolution of reactive phases formed under high temperature combustion (Dudas and Warren, 1988; Andrade et al., 1990). Many leaching experiments show a rapid early dissolution followed by a later, slower release of the elements (Harris and Silberman, 1983; Austin and Newland, 1985; Vogg et al., 1986; Wadge and Hutton, 1987). The water-soluble fraction of a combustion residue may reflect the early dissolution process in a natural environment. Table 4 shows the leachate composition of a field lysimeter test for a coal fly ash. It provides some information about major and minor components at an early stage of dissolution of the residues. It is obvious that the early dissolution mainly involves the soluble salts or oxides on the particle surface of the wastes and a buffering system is rapidly formed. Similar situations can be found for other kinds of combustion residues (Kirby and Rimstidt, 1993).

The dominant features of the initial dissolution stage are a high dissolution rate and the solution chemistry being controlled by buffering components of the residues themselves. At a high dissolution rate, it can be expected that there may be a release peak of the salts or heavy metals associated with surface phases in this stage. The high pH of leachate for the alkaline ashes will further affect the leaching of major or trace elements from the residues.

Table 4. The leachate composition of a coal fly ash in early natural leaching

Cations	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Li <sup>+</sup>	Mg <sup>2+</sup>	Others	Total
(meq/l)	26.90	10.35	8.06	3.75	1.46	0.20	50.72
(%)	53.00	20.40	15.90	7.40	2.90	0.40	
Anions	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>			Others	Total
(meq/l)	47.05	2.44	1.22				46.57
(%)	91.80	4.80	2.40				

Data source: Labuz et al., 1987. The leachate was obtained from the test cell six months after the leachate first appeared. The coal fly ash in the test cell was subjected to natural leaching processes by rainfall.

### 2.2.3 Leaching of the acid-soluble fraction

As combustion residues react with acidic solution (acid rain), the soluble surface phases are dissolved and the buffering capacity of the combustion residue is consumed by the neutralising reactions. A weakly acidic leaching environment (pH about 4 to 5) is probably reasonable for some waste disposal conditions. In this situation, the relatively

inactive phases of the residues in an alkaline environment, for example amorphous iron and aluminium oxides or some magnetic fractions, are able to dissolve into the acidic solution. The weakly acid-soluble fraction of combustion residues provides some information about the potential leachability of a given element. In many leaching assessments of solid wastes, the concept of "availability" of a constituent is used to describe the leaching ability with respect to a specific component or element of the solid waste (NNI, 1995; van der Sloot et al., 1997). According to the leaching pH of the availability test, the availability corresponds to the weakly acid-soluble fraction of a combustion residue. Table 5 shows the content of major elements in the acid-soluble fractions of combustion residues. These data reflect only the reactivities of the elements on a relatively short-time scale because the leaching (availability) tests are usually carried out for a short time in the laboratory. The difference between the acid-soluble fraction and the initial water-soluble fraction for a given waste may reflect its dissolution behaviour in different leaching stages.

Table 5. Acid-soluble fractions (availability) of combustion residues for major elements

Elements	Ca	Mg	K	Na	Al	Si	Total
Coal ashes							
(%)	15-72	1-5	0.5-3	1-5	0.05-0.5	0.05-0.1	
MSWI bottom ashes							
(%)	32-44	6-32	14-40	10-38	2-4	2	11

Data sources: the coal ashes (van der Sloot, 1984 and van der Sloot et al., 1985); the MSWI bottom ashes (Eighmy et al., 1994; Zevenbergen and Comans, 1994)

#### 2.2.4 Dissolution of matrix phases

The long-term leaching of the combustion residues occurs primarily in the aluminosilicate glass and some acid-insoluble magnetic spinel phases. These phases usually constitute the matrix of the residues. The dominant leaching features of the matrix phases are a low dissolution rate and phase alteration over long periods of time. Because of the low dissolution rate, it is difficult to investigate the leaching of matrix phases by laboratory leaching tests that are usually carried out for a relatively short time. Little information is available concerning the long-term chemical weathering of combustion residues, although it is believed that long-term chemical weathering may significantly alter their physical and chemical properties (Zevenbergen, 1994; Meima and Comans, 1997).

Besides of the influence of the matrix phases on the aqueous chemistry, the trace elements locked within the matrix phases are released only through the long-term chemical weathering (Theis and Wirth, 1977). Table 6 shows some potential release fractions of heavy metals of combustion residues in long-term leaching processes. The matrix phases of combustion residues are thought of as the host phases of the parts of these heavy metals (Querol et al., 1996; Vassilev and Vassileva, 1997). In this case, the chemical durability and dissolution kinetics of the matrix phases will determine the release of the heavy metals. A detailed discussion of the dissolution of matrix phases will be given in subsequent sections.

Table 6. Long-term potential leaching fractions of heavy metals in some combustion residues (%)

	As	Cd	Cr	Cu	Ni	Pb	Se	V	Zn
Coal ash	43	90	93	93		90	8	70	95
MSWI fly ash		15	98	85	99	92			50
MSWI bottom ash		93		93		90			81

Note: The data in the table are the remnant values on the basis of removing the maximum acid-soluble fraction from the data sources: van der Sloot, 1984; van der Sloot et al., 1985; Vogt et al., 1986; Sawell et al., 1988 and Cernuschi et al., 1990.

### 2.2.5 Release of trace elements

The release of trace elements is generally controlled by the dissolution of those major phases of combustion residues that control the bulk solution composition. The main influences of the bulk solution chemistry on the release of trace elements result from the pH and redox potential of the leaching system. Many heavy metals exhibit a markedly pH-dependent leaching (Buchholz and Landsberger, 1995; Eary et al., 1990; Mattigod et al., 1990). Typical examples are molybdenum, cadmium, copper, lead and zinc in MSWI ashes (van der Sloot et al., 1997). The redox potential in a leaching system is important as formation of phases results in different leachabilities for a given element in different valence states.

Adsorption reactions that take place on the surface of amorphous phases or secondary precipitates are important for many dissolved heavy metals. The combustion residues are made up mainly of amorphous phases that have large available surface areas and many reactive sites for the adsorption of trace metal ions. In view of the abundances of iron and aluminium associated with the combustion residues, iron and aluminium oxides or hydroxides are considered as major sinks for trace elements (Theis and Wirth, 1977;

Talbot et al., 1978; Chapelle, 1980). It has also been found that most combustion residues have certain cation exchange capacities (Kirby and Rimstidt, 1993; Amrhein et al., 1996). The cation exchange capacity will increase with the formation of clay-like minerals during the chemical weathering (Zevenbergen, 1994).

With dissolution or chemical weathering, secondary minerals are gradually developed and trapping or retention effects may occur for some heavy metals. Coprecipitation reactions play an important role in these processes. It has been found that some transition metal ions exhibit a high affinity for the hydrosilicate gel (Petit et al., 1990) which is formed in the long-term weathering of waste glass. The hydroxides of heavy metal precipitate on the waste glass phase may then be transferred into the hydrosilicates when solution conditions are favourable, to form a hydrosilicate gel. Other coprecipitation reactions associated with trace elements have also been found, for example, the release of Mo is controlled by  $\text{CaMoO}_4$ , the release of Cr(III) by  $(\text{Fe}, \text{Cr})(\text{OH})_3$ , and the release of Ba, Sr by  $(\text{Ba}, \text{Sr})(\text{SO}_4, \text{CrO}_4)$  in the dissolution of coal fly ash (Muraka et al., 1991). Coprecipitation and solid-solution formation with  $\text{BaSO}_4$  was also used to explain the low chromate concentrations in the leachates of a MSWI bottom ash landfill (Kersten et al., 1998).

Many of the particles of combustion residues may be not very permeable to gases or redox solutions. Thus the elements that are distributed between matrix and surface phases may exist in different oxidation states in various phases of the combustion residues. These elements may include Mn, Co, Cr, Cu, U, V and Mo (Hansen et al., 1984). Because of the differences in valence states and in chemical speciation in the aqueous phase, these elements exhibit very different release or retention mechanisms (Rai and Zachara, 1988). The influence of redox reactions depends on the properties of the element, on the phases present in the combustion residues and on the leaching conditions (pH and pE of solution).

Complexation reactions will change the speciation of a given element in an aqueous phase. This change may result in the mobilisation of the element in the combustion residues if the complexed species is in favour with the aqueous phase. A common example of inorganic complexation is the formation of mobile anionic  $\text{CdCl}_4^{2-}$  in the presence of chloride at high concentrations. The complexed metals with dissolved organic matter such as organic acids may increase the mobility of the metals by forming soluble complexes. It has been found that dissolved organic carbon (DOC) has a large influence on the leaching of Cu from MSWI bottom ash (van der Sloot et al., 1997).

## 2.3 Identification of major leaching processes

From the experimental evidence, the leaching of combustion residues depends strongly on the mineralogy, the morphology, the leaching environment and the time scale of the leaching reactions. The leaching characteristics of combustion residues related to a natural disposal environment are summarised in Table 7. It has been identified that the major leaching processes are neutralisation and chemical weathering. In addition, carbonation reactions must be taken into account in most natural leaching scenarios because carbonates are the dominant buffering minerals. The transformation of the carbonates should therefore be considered as an important process in long-term chemical weathering. For some kinds of combustion residues, for example MSWI bottom ash, the degradation of organic carbon in the residues provides the acidic sources that may be comparable with their acid neutralising capacity (Krebs et al., 1988). Although these biological processes in waste deposits are largely unknown so far, the degradation of the organic carbon is often related to the generation of CO<sub>2</sub>. Therefore the influence of these processes on the neutralisation of the residues can, at least in part, be considered in the carbonation reactions. The organic carbon of MSWI bottom ashes is also a major contributor to the redox capacity of the residues (Crawford et al., 1998). This should be an important factor in the redox reactions. For alkaline combustion residues, the redox reactions may mainly affect the release of trace elements from the residues. The redox processes are not considered in detail in this study.

Table 7. The leaching processes of combustion residues in natural disposal

Time scales	Initial or short-term	Medium-term	Long-term
Major processes	wash-off	neutralisation, carbonation, degradation of organic C	chemical weathering, carbonation
Leaching characteristics	Rapid wash-off,  first release peak occurs, pH buffering built-up	consumption of ANC  dissolving organic C	dissolution of matrix  phase, phase alteration  pH shift if any
Dissolved fraction	water-soluble	weak acid-soluble	the residues
Dissolved solid phases	soluble salts, species on the surface of particles	metal oxides, parts of amorphous phases and Ca-containing minerals	glass phases

Potential reactions related to trace elements	dissolution/precipitation complexation	dissolution/precipitation adsorption/desorption oxidation/reduction complexation	dissolution/precipitation adsorption/desorption co-crystallisation complexation
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The major leaching processes of combustion residues control the leaching chemistry, *i.e.* the pH of the leachate, the redox potential of the leaching system, sorption phases, and complex agents. The leaching chemistry in turn governs the release of minor or trace elements. Figure 4 shows the relationship between the major leaching processes and the release of trace elements.

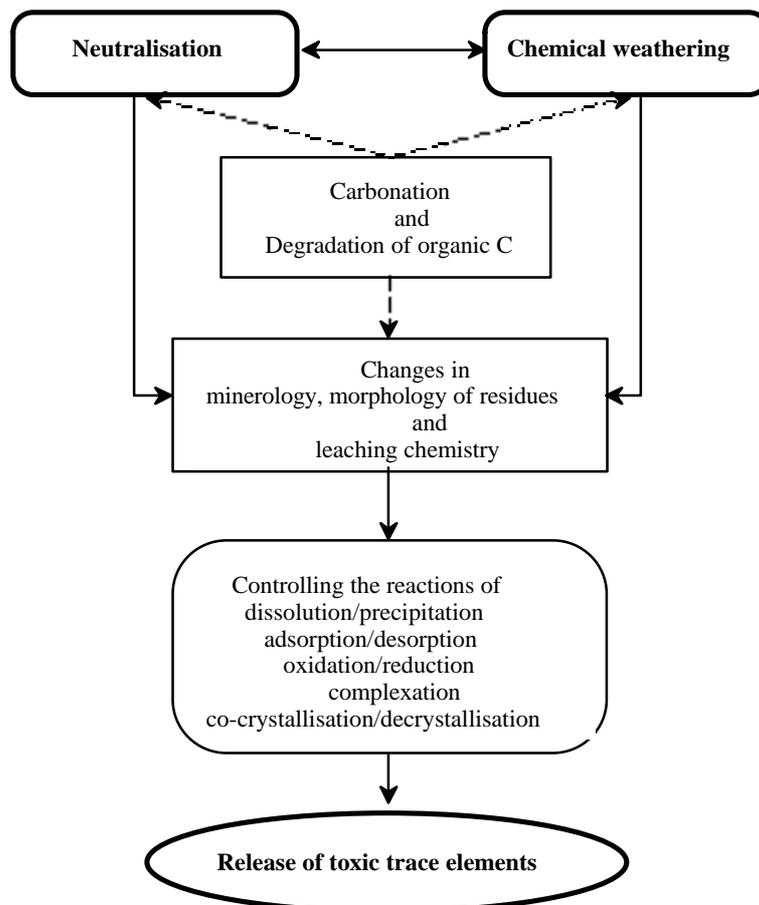


Fig. 4 The relationship between the major leaching processes and release of toxic elements

### **3 ASSESSING METHODS FOR MAJOR LEACHING PROCESSES**

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Several factors including the reaction type, the time scale of the leaching processes and the leaching environment must be considered in the assessment of major leaching processes. It is also necessary to use different approaches for different leaching scenarios. The methods used in this study are based on the interactions between the combustion residue and an aqueous solution, emphasising the leaching kinetics. Although experimental investigations provide important information on the leaching of combustion residues, geochemical modelling is essential to obtain an insight into the leaching processes. The experimental investigation combined with geochemical modelling is the basic method of assessing the leaching processes. It should be mentioned that geochemical models are often only tools to analyse the complicated processes and to predict their long-term behaviour when the processes involve times too long to perform laboratory experiments. Three kinds of models, a reaction path model, an equilibrium reactive transport model and a kinetic reactive transport model, are described in this chapter.

#### **3.1 General description of interaction between solid waste and aqueous solution**

The leaching of combustion residues results from the interactions between a solid waste and an aqueous solution. These interactions take place in a multi-component and multi-phase system. To analyse the features of the interactions and to understand the leaching characteristics, we mainly need to consider the reaction type and the nature of the reaction system. Different approaches are required to model different kinds of chemical reaction in different reaction systems.

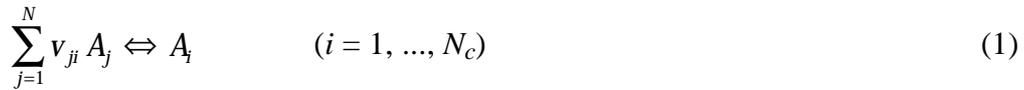
The mechanism of leaching reaction can be described by several elementary processes governing the interaction at the interface between the solid waste and the aqueous solution. The slowest of the successive processes is either the transport of aqueous species through a diffuse layer or the surface reaction on the interface. According to Madé's calculations (Madé et al., 1994), the dissolution of silicate minerals at geochemical surface [ $T < (25-100 \text{ }^\circ\text{C})$ ] is generally controlled by the surface reaction, because the dissolution rates controlled by diffusion are faster than those controlled by surface reaction. It is possible that the dissolution of very soluble minerals is controlled by the diffusion, especially when the particle size of the solid waste is rather large. Based on the reaction time scale in which we are interested and the experimental condition on the particle size of combustion residues, the very fast reactions are not considered in

detail in the reaction mechanism and they are simply referred to as fast reactions in this study.

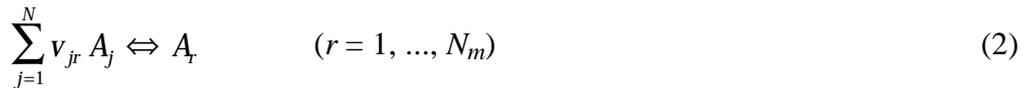
The chemical reactions in the leaching of combustion residues can be mainly divided into two groups based on their reaction rates. One group is "sufficiently fast" and reversible reactions, and the other is "insufficiently fast" and/or irreversible reactions. According to Rubin (1983), the "sufficiently fast" reversible reactions consist of reversible chemical changes with rates that are large in comparison with those of the system's other processes that change the species concentration. For this type of reaction, it is possible to use a local equilibrium assumption (LEA) to evaluate the effects of the reactions. On the other hand, the LEA is inapplicable for the other group of reaction. To assess the effects of the reactions which are "insufficiently fast" or irreversible, a reaction-rate relation must be taken into account. The two main groups of reactions can further be divided into two subdivisions, homogeneous reactions if the reaction takes place in one phase (*e.g.* the aqueous phase) and heterogeneous reactions involving more than one phase.

### 3.1.1 Description of chemical reactions (in a closed system)

For the purposes of illustration, a reaction system can be considered to consist of  $N$  primary species or components which are linearly independent and denoted by  $A_j$ . The  $N$  components are usually aqueous species that react with each other to form  $N_c$  complex species,  $A_i$ , and  $N_m$  precipitated solid species (minerals),  $A_r$  in the system. Homogeneous equilibrium reactions which take place in an aqueous phase are generally expressed in the form:



and heterogeneous reactions which take place between aqueous species and minerals take the form:



where  $v_{ji}$  is the stoichiometric coefficient of the component  $j$  in the complex  $i$ , and  $v_{jr}$  the stoichiometric coefficient of the component  $j$  in the mineral  $r$ .

The homogeneous equilibrium reactions, for example the aqueous complexation reactions, are assumed to be sufficiently fast to maintain local equilibrium in the aqueous phase. The total concentration of component  $j$  in an aqueous phase,  $Y_j$ , is expressed by

$$Y_j = C_j + \sum_{i=1}^{N_c} \nu_{ji} C_i \quad (j = 1, \dots, N) \quad (3)$$

where  $C_i$  is the concentration of the  $i$ th complexed species. The complexation reactions are described by a set of non-linear algebraic equations on the basis of the law of mass action for each complexation reaction.

$$C_i = K_i \prod_{j=1}^N C_j^{\nu_{ji}} \quad (i = 1, \dots, N_c) \quad (4)$$

where  $K_i$  is the equilibrium constant of the  $i$ th complexed species.

For heterogeneous reactions, two approaches have been used in different cases. For a fast heterogeneous reaction, for example the dissolution/precipitation of minerals under the local equilibrium assumption (LEA), the mass-action equations can be used to express the heterogeneous reactions as follows:

$$I = K_r \prod_{j=1}^N C_j^{\nu_{jr}} \quad (r = 1, \dots, N_m) \quad (5)$$

where  $K_r$  is the solubility constant for the  $r$ th mineral.

However, rate-reaction equations should be used instead of the mass-action equations if the rates of the heterogeneous reactions are insufficiently fast or the reactions are irreversible.

$$\frac{dX_r}{dt} = R_r \quad (r = 1, \dots, N_m) \quad (6)$$

where  $X_r$  is the concentration of mineral  $r$ ,  $t$  the time, and  $R_r$  the dissolution/precipitation rate of the  $r$ th mineral. A reaction-rate relation (a so-called reaction rate law) is determined by reaction mechanisms which are dependent on the particular form of the reaction. For common minerals,  $R_r$  may be expressed as

$$R_r = (k_r K_r) a_r \left( 1 - \frac{Q_r}{K_r} \right) \quad (r = 1, \dots, N_m) \quad (7)$$

where  $k_r$  is the reaction rate constant of the  $r$ th mineral,  $a_r$  the specific surface area of the  $r$ th mineral, the term  $(k_r K_r)$  is the so-called initial rate constant, which can be measured as the reaction is far from equilibrium, and  $Q_r$  denotes the activity product defined by

$$Q_r = \prod_{j=1}^N c_j^{v_{jr}} \quad (r = 1, \dots, N_m) \quad (8)$$

It is noted that most of the rate laws devised for mineral dissolution and precipitation are more empirical than theoretical, but the above expression is commonly used when the detailed mechanism of the reaction is not available.

As the reaction rate is sufficiently fast it can be assumed that there is local equilibrium between the mineral and the corresponding aqueous species, so that it is possible using the rate-relation equations to describe a "sufficiently fast" reaction.

### 3.1.2 Taking in account solute transport (in an open system)

If there is an interaction between a combustion residue and an aqueous solution, for example in a one-dimensional open system, the effects of solute transport must be taken into account. Transport with chemical reactions in a one-dimensional system can generally be expressed by mass-balance equations as follows:

$$\mathbf{q} \frac{\partial Y_j}{\partial t} = D \frac{\partial^2 Y_j}{\partial x^2} - V \frac{\partial Y_j}{\partial x} + S_j \quad (j = 1, \dots, N) \quad (9)$$

where  $\mathbf{q}$  is the porosity,  $Y_j$  the total concentration of component  $j$ ,  $D$  the dispersion coefficient,  $x$  the distance along the flow direction,  $V$  the water flux, and  $S_j$  the source/sink term due to the chemical reaction. If only advective transport is considered, equation 9 is then simplified to

$$\mathbf{q} \frac{\partial Y_j}{\partial t} = -V \frac{\partial Y_j}{\partial x} + S_j \quad (j = 1, \dots, N) \quad (10)$$

If reactions are sufficiently fast and reversible, a system of algebraic equations expresses chemical equilibrium relations between concentrations of reaction species. For homogeneous reactions,

$$Y_j(x, t) = C_j(x, t) + \sum_{i=1}^{N_c} v_{ji} C_i(x, t) \quad (j = 1, \dots, N) \quad (11)$$

$$C_i(x, t) = K_i \sum_{j=1}^N C_j^{v_{ji}}(x, t) \quad (i = 1, \dots, N_c) \quad (12)$$

and for heterogeneous reactions,

$$I = K_r \prod_{j=1}^N C_j^{v_{jr}}(x, t) \quad (r = 1, \dots, N_m) \quad (13)$$

The chemical-reaction equations (algebraic equations) combined with the transport equations and neglecting the source/sink term  $S_j$  of equation 10 (partial differential equations) can be used to describe the equilibrium reaction system.

If reactions are insufficiently fast and/or irreversible, the effects of the chemical reactions should be taken into account through the source/sink term  $S_j$  of equation 10. For mineral reactions, the chemical-reaction equations are written as

$$S_j = \sum_{r=1}^{N_m} v_{jr} R_r(x, t) = \sum_{r=1}^{N_m} v_{jr} \frac{\partial X_r(x, t)}{\partial t} \quad (j = 1, \dots, N) \quad (14)$$

Two groups of partial differential equations, in which one group is for transport and the other for slow or irreversible reactions, are used to describe the kinetic reactive transport system. Equation 14 is similar to equation 6, except for the additional dimension  $x$  needed for the reactive transport, so that the chemical-reaction equations 7 and 8 can be used for the open system.

### 3.2 A reaction path model for the leaching processes in a batch system

The interaction between a combustion residue and an aqueous solution involves all of the reaction types and reaction systems that have been described above. Because many leaching tests are carried out in a batch system and some solid wastes are deposited

under conditions where water flow can be neglected, a reaction path model presented here is used to evaluate the leaching processes in a batch (closed) system.

The model follows the principles discussed in section 3.1.1, but a special concept, the reaction path, is used to handle the irreversible chemical reactions for reactants or primary minerals. The reaction path usually represents a process in which one or more irreversible reactions proceed to a series of successive local equilibrium states for a reaction system. The interactions between solid waste and aqueous solution can be described using the reaction path model. The dissolution of combustion residue is considered to be an irreversible process in which the solid waste cannot be re-formed. As the combustion residue is dissolved, secondary minerals may precipitate. Equilibrium is assumed between the secondary solids and the aqueous solution when the original waste continues to react with the solution. The irreversible reaction is then evaluated by the sequential states of partial equilibrium between the aqueous solution and the successive phases produced along the reaction path. The physical concept of the reaction path model is very similar to a multiphase titration process, such as the pH titration of solid waste in a batch experiment.

A theoretical approach to the reaction path calculation was first introduced by Helgeson (Helgeson, 1968; Helgeson et al., 1969, 1970). The important aspects of the evaluation of the interaction between a solid and an aqueous phase using the reaction path model are: (1) defining irreversible reaction progress, (2) setting constraints imposed implicitly by partial equilibrium or explicitly by reaction kinetics to determine the reaction coefficients, and (3) providing a sub-model for the distribution of species in the aqueous solution. The first two items are used to handle heterogeneous irreversible reactions either by a local equilibrium consideration or by a kinetic consideration. The last item is used to handle the "sufficiently fast" homogeneous reactions in an aqueous phase. Wolery and Daveler (1992) further developed the concept of reaction path and applied the concept to a geochemical program.

In a reaction path model, the extent of irreversible reaction is described in terms of a reaction progress variable  $\xi$ . The effects of the irreversible reactions on component  $j$  in a closed system are given by

$$\frac{dY_j}{dt} = \sum_{i=1}^{N_{ir}} v_{jr} R_i \quad (j = 1, \dots, N) \quad (15)$$

where  $N_{ir}$  is the number of irreversible reactions, and  $R_i$  is here defined by the progress of the  $i$ th irreversible reaction,  $x_i$ ,

$$R_i = \frac{dx_i}{dt} \quad (i = 1, \dots, N_{ir}) \quad (16)$$

An irreversible process can be defined by an array of simple irreversible reactions that have their own progress variables (Wolery and Daveler, 1992). The relation between an overall process and the simple irreversible reactions is expressed by the relative rate of the  $i$ th irreversible reaction,  $dx_i / dx$ . Using the relative rate function, the reaction path calculations can be performed without reference to any time frame. A detailed discussion about the reaction path model can be found in a previous paper (Yan et al., 1995).

The reaction path modelling is used to simulate the neutralisation of combustion residues in a batch system (Paper I and II). In most cases, the assumption of partial equilibrium between secondary minerals and an aqueous solution is imposed to fix the values of the reaction coefficients at a given stage of the reaction progress, and a sub-model is included to account for complex reactions, redox reactions (if necessary) and the interactions among aqueous species (ionic strength) in a aqueous phase. The irreversible reaction progress can be handled in different ways using either the relative rate ( $dx_i / dx$ ) or the absolute rate ( $dx_i / dt$ ). In this study only a relative rate function is specified for the neutralisation of combustion residues. In the reaction path calculations, solid waste can be treated as a special reactant which is defined by its elementary composition instead of its mineralogical composition. In this way, the poorly characterised combustion residues in mineralogy are easily handled in the calculations.

### **3.3 Reactive transport models for the leaching processes in a flow system**

#### *3.3.1 An equilibrium reactive transport model for short-term leaching processes*

The leaching of combustion residues is strongly affected by solute transport in a natural environment. In an open system with water flow, the leaching of combustion residues should be described by a coupled solute transport and chemical reaction model. As has been discussed in section 3.1, the form of the model depends mainly on the type of reactions involved, *i.e.* whether the reaction rates are sufficiently fast. Comparing the rates of leaching reactions with the rate of water flow can be used to define whether a reaction is "sufficiently fast" or not. For most column leaching tests used for combustion residues, the water flow rate is usually large and this results in a short residence time for the water in the system. In this case, only relatively fast reactions may be evaluated by

the tests. It is possible to use an equilibrium transport model to simulate the short-term leaching phenomena in a column leaching test.

An equilibrium reactive transport model is used to simulate the neutralising processes in a flow-through system. The model assumes that the neutralising reactions taking place in the system are sufficiently fast, so that these reactions can be expressed by equations 11, 12 and 13. One-dimensional advective transport is included in the model and the transport equations are similar to equation 10. Moreover, a mixing cell concept (Appelo and Willemssen, 1987; Appelo et al., 1990; Appelo and Postma, 1994) is used to couple the solute transport with the chemical reactions.

Using the mixing cell concept, a reactive transport in a flow-through column can be simulated by serial batch reactors (cells). A one-dimensional column is divided into several cells. Aqueous solutions in the cells react with minerals. The reactive transport by water flow is defined in shifts, which mean that all solutions in the column move down or up, react with minerals in each cell, and mix with their new neighbour cells. Equation 10 is discretised to apply to the serial batch system

$$q \left( \frac{dY_j}{dt} \right)_l = V (Y_{j(in)} - Y_{j(out)})_l + \sum_{r=1}^{N_m} v_{jr} \left( \frac{dX_r}{dt} \right)_l \quad (l = 1, \dots, N_{cell}) \quad (17)$$

where  $V$  is the water flux from one cell to another,  $Y_{j(in)}$  the in-flow concentration of component  $j$  to a cell and  $Y_{j(out), l} = Y_{j(in), l+1}$ ,  $l$  the order of a cell in a column, and  $N_{cell}$  the number of cells in a column. With this concept, the contents in the aqueous phase of each cell are shifted into the next, and the remaining minerals in each cell then react with the aqueous phase in the next time step. The solute transport is in fact calculated separately from the chemical reactions.

The equilibrium transport model has been used to simulate the neutralisation of MSWI bottom ash in a flow-through system (paper III). The simulating results are compared with the model assumption to confirm the kinetic features of the neutralisation reactions.

### 3.3.2 A kinetic reactive transport model for long-term chemical weathering

For long-term leaching processes, both sufficiently and insufficiently fast reactions, and homogeneous and heterogeneous reactions must be considered. A kinetic reactive transport model has been developed to model the long-term chemical weathering of combustion residues in a natural environment. The model accounts for advective transport in one-dimensional system. The model gives full-kinetic consideration to

heterogeneous reactions, so that these reactions are represented by the reaction-rate relations instead of the mass-action relations. The main governing equations of the model are equations 10 - 12 and 14. Equation 10 can be written here as

$$q \frac{\partial Y_j}{\partial t} + \sum_{r=1}^{N_m} v_{jr} \frac{\partial X_r}{\partial t} = -V \frac{\partial Y_j}{\partial x} \quad (j = 1, \dots, N) \quad (18)$$

For general mineral reactions,

$$\frac{\partial X_r(x,t)}{\partial t} = R_r(x,t) = (k_r K_r) a_r(x,t) \left( 1 - \frac{Q_r(x,t)}{K_r} \right) \quad (r = 1, \dots, N_m) \quad (19)$$

where  $k_r$  is the reaction rate constant of the  $r$ th mineral, and  $a_r$  the specific surface area of the  $r$ th mineral. The term  $(k_r K_r)$  is the initial rate constant, and  $Q_r$  the activity product defined here by

$$Q_r(x,t) = \prod_{j=1}^N C_j^{v_{jr}}(x,t) \quad (r = 1, \dots, N_m) \quad (20)$$

As the reaction rate is sufficiently fast, it is assumed that there is local equilibrium between the mineral and the corresponding aqueous species. In this way, it is possible to treat "sufficiently fast" reactions by this full-kinetic approach. In general, if the rate constants are chosen so that they are sufficiently but not excessively large, a local equilibrium can be obtained for the reaction (Steefel and MacQuarrie, 1996).

Several special approaches have been applied to the model. The quasi-stationary state approximation (Lichtner, 1988; 1992) is used to simplify the reactive transport model. The basic idea of the approach is that, when the rate of change in the system is dominated by the mineral reactions, the local concentration change with time in the aqueous phase will contribute little to the total mass in the system. The term  $\partial Y_j / \partial t$  can then be neglected compared to the term  $\sum v_{jr} \partial X_r / \partial t$  in equation 18. The time evolution of a chemical system with this quasi-stationary state approximation is represented by a sequence of stationary states. Each stationary state describes the aqueous composition and rates of reacting minerals as a function of distance corresponding to a particular state of the alteration of mineral assemblage (Lichtner, 1988). Using the quasi-stationary state approximation, the system of partial differential equations is reduced to a system of ordinary differential equations in  $Y_j$ . Equation 18 then becomes:

$$\sum_{r=1}^{N_m} v_{jr} \frac{dX_r}{dt} = -V \frac{dY_j}{dx} \quad (21)$$

In addition, moving boundaries associated with mineral alteration zones can easily be taken into account during the calculations.

For special heterogeneous reactions, for example the dissolution of the glass phase in combustion residues, the reaction rate  $R_r$  can be specified by a sub-model to account for its kinetic rate law. A detailed description of the leaching kinetics of the glass phase and a general kinetic rate law is given in paper V.

### 3.4 Experimental investigations

Two types of pH titration experiments have been used to investigate the neutralising processes of combustion residues. One was carried out in a batch system, in which the time-dependent neutralising behaviour of MSWI bottom ash and steel slag, acid neutralising capacity (ACN), and the interactions between major buffering components have been studied. A reaction path model was then used to simulate the neutralising processes to establish a better understanding of the complicated processes involved.

Another type of experiment was performed in a serial batch system. This column-like experiment can be used to investigate the effects of water flow on the neutralising processes, by which the experimental conditions are believed to be close to a natural leaching environment of solid waste. An equilibrium reactive transport model is then used to simulate both solute transport and chemical reactions in the neutralising processes.

It should nevertheless be mentioned that these types of experiments provide limited information on the long-term chemical weathering of combustion residues, even when the experiments are carried out for a long period of time.

#### 3.4.1 Long time pH titration—a batch experiment

Long time static batch pH titration experiments was performed using an automatic titration system (Metrohm 719S Titrino). The experiments were carried out at several pH levels, for example, pH=6, 7, 8, 9 and so on. At each pH level, the waste sample was mixed with pure water in a liquid-to-solid ratio of 5:1 (40 g ground solid waste and 200

ml of water) in a plastic bottle. The acid solution (1M HNO<sub>3</sub> solution) was automatically added to the plastic bottle to maintain a constant pH value (a given pH ± 0.02). The acid neutralising capacities of the solid wastes were then determined at this given pH level for different titration times. The titration experiments were run for about 1200 or 6000 hours depending on the waste type. Finally, the acid neutralising capacities of the solid wastes were given as a function of pH level and titration time. The leachates were periodically analysed for the main cations (*e.g.* Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) using the DIONEX DX-300 Series Ion Chromatography System with suppressed conductivity detection. In order to minimise the diffusion resistance in the particles, all the samples used in the experiments were ground to particle sizes less than 0.160 mm.

This pH titration method is different from ordinary pH titration in which a solid sample is continuously titrated by acid solution in a single batch reactor (Johnson et. al., 1995). The ordinary pH titration method cannot generally provide time-dependent information for the neutralising processes. Because neutralising reactions in the batch reactor depend on both the rate of solid reaction and the rate of acid addition, it is important to control the relative rate between solid reaction and acid addition in order to obtain a valuable result from the experiment.

#### *3.4.2 Serial batch pH titration—a column-like experiment*

The serial batch system was set up using 10 polypropylene bottles (this is similar to dividing a column into 10 cells), with 100 grams of solid sample in each of the 10 bottles. At the beginning of the pH titration experiment, 100 grams of 0.104 M nitric acid was added to the first bottle (cell). After a certain time, the reacted solution in the first bottle was moved to the second bottle, and 100 grams of fresh acid solution was again added to the first bottle. In the same way, the acid solution was shifted from the first bottle to the second, to the third and so on. The bottles were open to the atmosphere. The pH was measured in each bottle periodically, and in the last bottle each time the water was shifted. The experiment was carried out continuously for about 5 months.

This system is used to simulate a flow-through system, in which the column is divided into 10 cells, as shown in Figure 5. This type of experiment may provide more information than a conventional column test. For example, it is possible not only to determine the behaviour of breakthrough curves for species leaving the system but also to observe the evolution of the pH fronts in different parts of the system. This is an advantage over a column experiment in which it is difficult to follow the processes within the column.

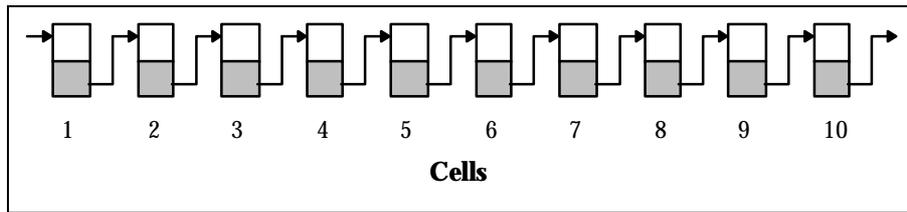


Fig. 5 A serial batch system was used to simulate the neutralising process in a flow-through system.

## 4 NEUTRALISING PROCESSES IN LEACHING OF MSWI BOTTOM ASH

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The neutralising processes in the leaching of combustion residues are not simple acid-base reactions. Because many heterogeneous reactions are involved in the processes, leaching kinetics are important for understanding their mechanisms. In contrast to the traditional way, the neutralising process is here studied not only with regard to the acid neutralising capacity (ANC) of a solid waste but also on a more detailed basis. More aspects of the neutralising process have been investigated including the time-dependent behaviour in the neutralisation, the distribution of ANC at different pH levels, and the reactivity of the buffering component in different types of system. All the information is necessary to obtain an insight into the neutralising process and especially to fill a gap in knowledge between a leaching test and its application to a certain leaching environment. It is clear that an experimental investigation alone is not enough to evaluate the complicated processes. Geochemical modelling is used to reveal more information from the experiment, and to simulate the interaction of several complicated processes simultaneously. The detailed descriptions are presented in papers I to III.

In this chapter, the neutralising processes of MSWI bottom ash are evaluated for both batch and flow-through reaction systems. In a batch reaction system, the neutralising processes are characterised on the basis of time- and pH-dependent behaviour and the interactions between the buffering components of combustion residues. In addition, the geochemical simulations show the importance of titration kinetics on the measurement of the ANC. In a flow-through system, the neutralising processes are assessed under water transport. Comparing the neutralising characteristics of MSWI bottom ash in the flow-through system with those in the batch system, it is found that the neutralising ability of the MSWI bottom ash in an open reaction system is very different from that in a closed system.

### 4.1 Neutralising processes in a batch system

#### 4.1.1 ANC as a function of time and pH

The ANC of a combustion residues depend on both reference pH value and reaction time. The ANC was here measured using the batch titration experiments as a function of titration time and pH. Figures 6 and 7 show the distributions of ANC for a MSWI bottom ash and for a steel slag respectively. The distribution of ANC indicates how

much the ANC will be available when the neutralising processes reach different pH values. As shown in these figures, there are differences between the two waste materials regarding the distribution of ANC. For the MSWI bottom ash, most of the ANC is available in the pH range below 8.5, whereas for the steel slag, the ANC can be consumed mainly above pH 8.5. This means that the neutralising mechanisms of two solid wastes should be different in different pH ranges. Moreover, the time dependence of ANC becomes small only after approximately 200 hours. This suggests that short-time experiments may lead to a considerable underestimation of the ANC.

From the pH-dependent behaviour of two solid wastes, the heterogeneous reactions may be related to the mineralogy of the waste materials. Figures 8 and 9 show the time required to reach a given ANC at different pH levels. These results provide information about the neutralising rates of the wastes in different pH ranges. In the MSWI bottom ash (Fig. 8), the neutralising reactions are fast in both high and low pH ranges but slow in a middle range. In the steel slag (Fig. 9), however, the neutralising reactions are slower only in the high pH range. This pH-dependent behaviour is more obvious when more ANC is consumed. Since a pH-dependent behaviour similar to that in the MSWI bottom ash has been found in many normal silicate minerals and glasses (Sverdrup and Warfvinge, 1988; Madé et al., 1994; Nagy, 1995), the pH-dependent behaviour of the MSWI bottom ash may be related to its matrix phases, for example glass phases. Although the reaction kinetics of major mineral phases in the steel slag have not yet been greatly studied, it is possible to explain the pH-dependent behaviour if there are some similarities between the steel slag and some inosilicates whose dissolution rates were observed to decrease steadily from pH 2 to 12, with none of the alkaline acceleration of dissolution which is a characteristic of aluminosilicates (Brantely and Chen, 1995).

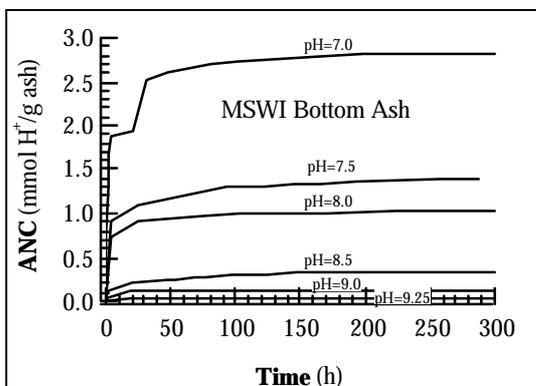


Fig. 6 The ANC of MSWI bottom ash for different pH values and different reaction times

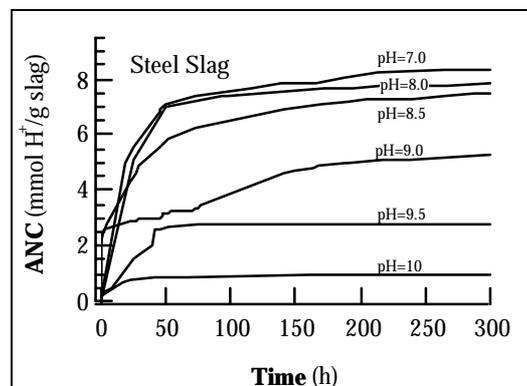


Fig. 7 The ANC of the steel slag for different pH values and different reaction times

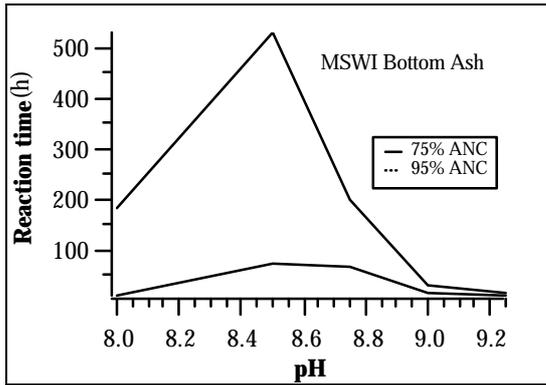


Fig. 8 The reaction time versus pH for different amounts of the ANC reacted in the neutralisation of the MSWI bottom ash.

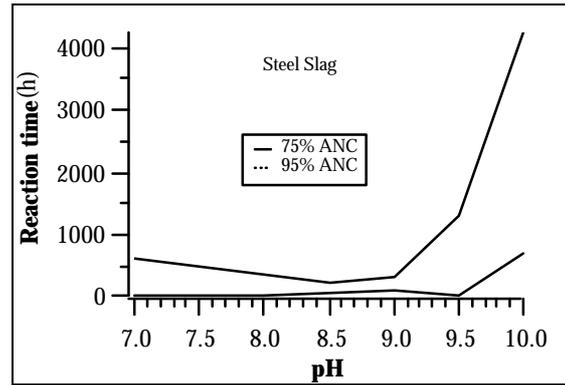


Fig. 9 The reaction time versus pH for different amounts of the ANC reacted in the neutralisation of the steel slag.

#### 4.1.2 Geochemical simulation and reactivity of buffering component

A reaction path model has been used to simulate the neutralising processes in the pH titrations. The geochemical calculations were performed using the geochemical computer program EQ3/6 (Wolery and Johnson, 1995). The purpose of the geochemical simulations is to assess the reactivities of buffering components in the neutralising reactions, and to analyse the major controlling factors for the neutralising processes over different pH ranges. The titration kinetics of the experiments were also evaluated during the simulations. This information cannot in general be obtained directly from the leaching experiments.

The concept of the model and the simulations are described in detail in papers I and II. As shown in Figures 10 and 11, the reaction path simulations can reproduce the neutralising processes both for the short and long time experiments. Independent comparisons with experimental results for major species in an aqueous phase are shown in Figures 12 and 13, which indicate that the distribution of main aqueous species obtained in the simulations is very similar to the experimental data. These comparisons confirm the applicability of the reaction path model in simulating the neutralising processes.

The geochemical simulations provide quantitative information about the reactivities of major constituents of solid wastes in the neutralising reactions. As shown in Table 8, the reacted fractions of major elements indicate their reactivities and contributions in the neutralising processes. It is obvious that Ca-, Mg-, and Si-containing constituents of the solid wastes play an important role in the neutralising reactions. Of these constituents, the calcium component provides the largest amount of ANC. The influence of the silicon

component may be complicated because the interactions between silicon and other components are significant in the neutralising processes.

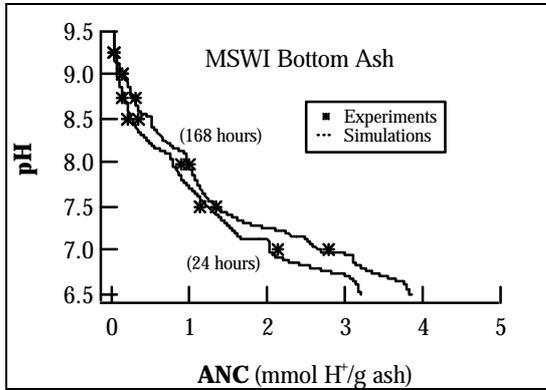


Fig. 10 Geochemical simulations of the neutralising processes for the MSWI bottom ash.

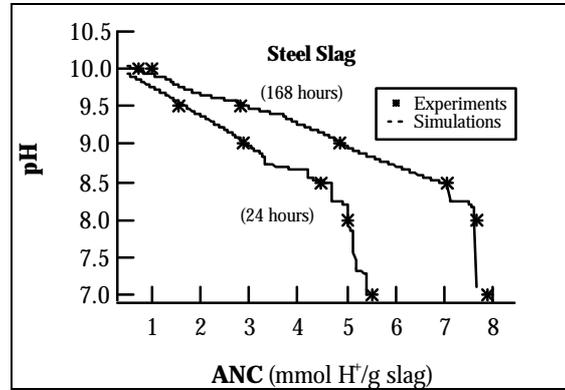


Fig. 11 Geochemical simulations of the neutralising processes for the steel slag.

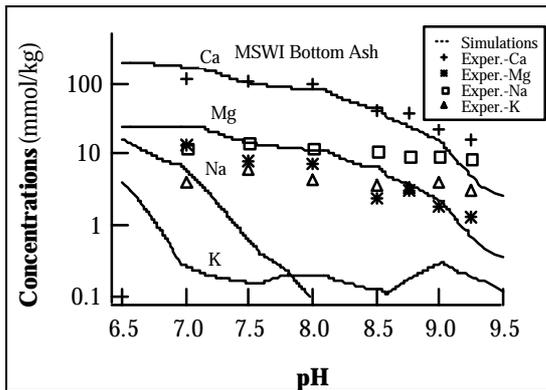


Fig. 12 Comparison of simulation with experiments for dissolved species in the aqueous phase in the pH titration of the MSWI bottom ash.

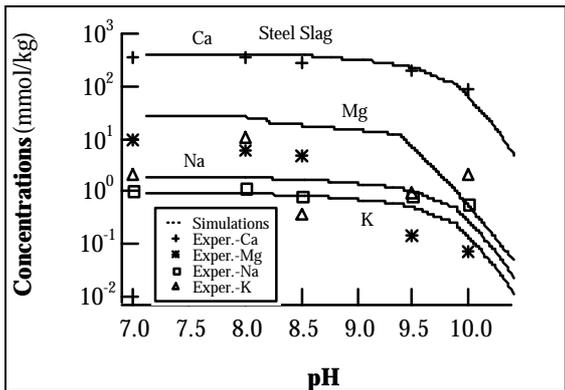


Fig. 13 Comparison of simulation with experiments for dissolved species in the aqueous phase in the pH titration of the steel slag.

Table 8. Reacted fractions of main elements in the neutralising processes

	Ca	Mg	Na	K	Al	Si	S
Case 1	0.70	0.67	0.15	0.15	0.04	0.06	0.43
Case 2	0.84	0.76	0.22	0.20	0.06	0.10	0.61
Case 3	0.50	0.03	0.30	0.20	0.01	0.01	0.10
Case 4	0.65	0.18	0.80	0.80	0.03	0.05	0.30

Notes: Case 1 means the 24-hour batch titration experiment and case 2 the 168-hour experiment for the MSWI bottom ash; case 3 means the 24-hour batch titration experiment and case 4 the 168-hour experiment for the steel slag.

## 4.2 Interactions between buffering components and an acid solution

### 4.2.1 Sensitivity analysis for neutralising reaction system

A geochemical simulation combined with a sensitivity analysis for a neutralising reaction system is used to study the interactions between buffering components and an acid solution. The sensitivity analysis is performed by a statistical approach, a full factorial design at two levels (Box et al., 1978; Box and Draper, 1987). The main effects of the different factors on the neutralising processes are shown in Figure 14 for a fresh water-quenched MSWI bottom ash, and in Figure 15 for a 10-year weathered MSWI bottom ash. The main factors used in the analysis are the same as the major components of the solid wastes except for an additional factor, the rate constant, used for the weathered sample. The responses shown in the figures mean that the change in the ANC of the system as a corresponding factor (component) changes from a low level to a high level. In spite of the difference in coverage of pH in the neutralising processes of the two samples, a general discussion of the effects of the factors for acid neutralising capacities is possible. The calcium-containing constituents (F-CaO and F-CaCO<sub>3</sub>) were found to give a large contribution to the ANC over a wide pH range. Calcium is the most important element in the neutralising reactions even for a weathered sample. In neutral and weakly acidic environments, carbonates have a large effect on the neutralising processes. The effects of silicon components seem to be complicated in the neutralising processes. They generally made a negative contribution to the ANC. As the pH decreases, the contribution of the silicon component becomes less negative. This phenomenon is probably the consequence of precipitation of Ca-silicates that leads to a decrease in the calcium concentration in the aqueous phase. The effect of the silicon component on the ANC should then be negative. The aluminium component gave a positive contribution to the ANC in the high pH range. Interactions among these three factors, F-CaO, F-SiO<sub>2</sub> and F-Al<sub>2</sub>O<sub>3</sub>, may explain this behaviour. The net effect on the ANC seems to be due to competition between Ca-SiO<sub>2</sub> and Al-SiO<sub>2</sub> interactions. If the Al-SiO<sub>2</sub> interaction inhibits Ca-SiO<sub>2</sub> interaction, a net effect may be a positive contribution to the ANC given by the aluminium component. For the weathered sample, the influence of the dissolution rate of the solid waste is different in different pH ranges (see Fig. 15). The dissolution rate has a positive effect on the ANC and this effect becomes less important at lower pH. This means that the dissolution kinetics should control the neutralising reactions of the weathered sample at least in a high pH range.

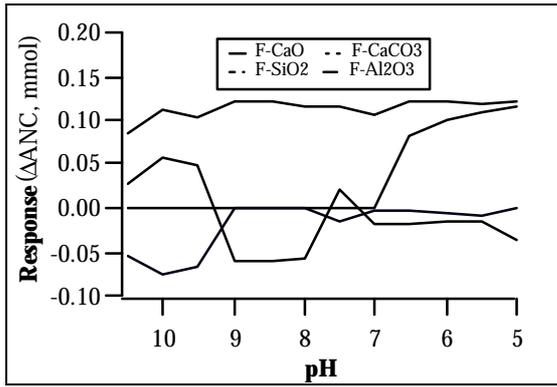


Fig. 14 Main effect analysis of full factorial design for neutralising process of a new MSWI ash

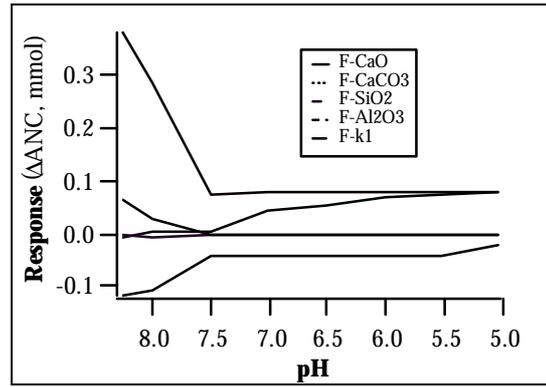


Fig. 15 Main effect analysis of full factorial for neutralising process of a weathered MSWI ash

#### 4.2.2 Impact of titration kinetics

The simulation results also provide information regarding the titration kinetics of the experiments. In the pH titration of solid waste, the ratio of the rate of waste dissolution to the rate of acid addition determines the titration kinetics of the experiment. Using a geochemical simulation, it is possible to evaluate the ratio of the rates of the two processes which take place simultaneously in a heterogeneous pH titration. This ratio shows whether the rate of acid addition balances the dissolving buffer components from the solid waste in a titration experiment. The long time static pH titration method used in this study has been compared with a conventional continuous pH titration method (Johnson et al., 1995), as shown in Table 9. The long time static pH titration is different from the conventional titration in several ways. First, the long time static titration is carried out in several batch reactors in which the reference pH value is fixed. The pH value is kept constant in each reactor during the titration so that it is called the static pH titration. Second, the criterion of the static pH titration is only the reference pH and no criterion is set up on any time interval. This feature makes it possible to evaluate a time-dependent neutralising behaviour. It is clear that the static pH titration keeps a good balance between the dissolution of waste and the acid addition. The continuous pH titration may mainly take fast neutralising reactions into account because of the relatively short time for the titration criterion. It is obvious that there is also a difference between the two methods in the titration kinetics.

Table 9. The comparison of titration kinetics for two type of pH titration methods

	static pH titration				continuous pH titration		
	MSWIB 1	MSWIB 2	SSL 1	SSL 2	f-MSWIB 1	f-MSWIB 2	w-MSWIB
Ratios	0.86 - 1.36	0.88 - 1.37	0.93 - 1.01	0.98 - 1.08	> 100	> 100	1.88

Notes: The ratio is the rate of dissolution of waste divided by the rate of acid addition. MSWIB is the MSWI bottom ash, SSL the steel slag, f-MSWIB the fresh sample of MSWI bottom ash and w-MSWIB the weathered sample of MSWI bottom ash.

### 4.3 Neutralising processes in a flow-through system

To investigate the neutralising processes of MSWI bottom ash in a flow system (paper III), a serial batch experiment was performed to simulate a flow-through system. This type of experiment provides more information than a conventional column test where it is difficult to follow the processes within the column. A coupled one-dimensional transport (advection) and geochemical reaction model was used to assess the neutralising reactions to gain an insight into the neutralising processes in an open system. The model used an equilibrium assumption for the neutralising reactions in the pH titration. The assumption was inspected in the simulations in order to confirm the reaction type in the pH titration. A geochemical program, PHREEQC (Parkhurst, 1995), was used for the geochemical calculations.

#### 4.3.1 Characteristics of neutralising processes in a flow-through system

The experimental results presented in Figure 16 show the pH changes in the flow system with an increase in the pore volumes of the acid solution that flowed into the system. It is obvious that the chromatographic phenomenon is developed in the flow-through system and that a pH jump (called a front) forms between the reacted and unreacted solid waste. As the acid solution continuously flows into the system, the pH front moves downstream in the system accompanied by the neutralising processes. The pH changes at the front were significant in the experiments. Some distance into the system, the pH became nearly constant. The form is more pronounced in the simulations as will be shown later. A similar chromatographic phenomenon has also been observed in natural soil systems (Reuss and Johnson, 1986; Schnoor, 1996).

The pH-front movement is significant for the release of some toxic species, *e.g.* Cd, Cu, Pb and Zn. As shown in Figure 16, the pH increases through the front. Some species in the waste, which have higher solubilities under low pH conditions, may dissolve

upstream of the pH front and then reprecipitate downstream. As the pH front moves downstream, these species will also be transferred downstream and the concentrations of these species should increase more and more at the front. When the pH front reaches the end of the system, these species may suddenly be released to the environment in potentially very high concentrations. This phenomenon has been observed in the experiments. It was found that the leachates were clear on both sides of the pH front, but that there were rust brown precipitates, probably ferric hydroxides, at the front.

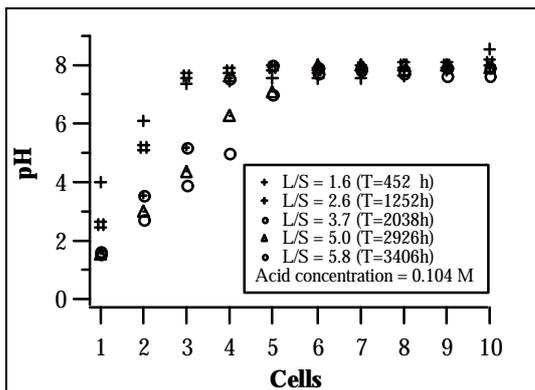


Fig. 16 pH titration experiments performed in a serial batch (column-like) system. The movement of the pH front occurred in the first cells of the system.

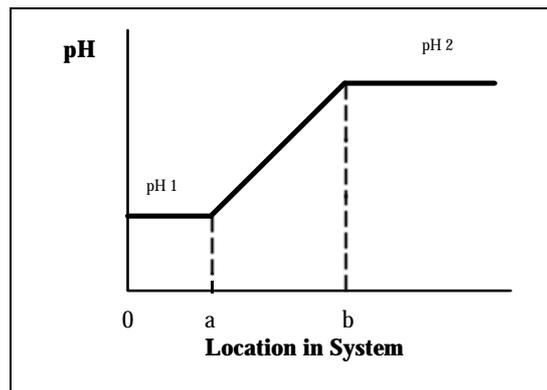


Fig. 17 Description of neutralised status of solid waste in flow-through system by a simplified situation.

The neutralising ability of solid waste will be affected by solute transport in the flow system. It remains to be seen whether the ANC can be directly used to predict conditions in a flow-through system. The experimental results indicate that the neutralised extent of MSWI bottom ash differs in different locations of a flow-through system. Figure 17 shows a simplification of the neutralisation of solid waste in a flow-through system. As neutralisation proceeds, the pH front divides the system into three parts according to the neutralised status of the solid waste. Upstream of the pH front (location from 0 to  $a$  in the system), the neutralising capacity of the waste has been completely been consumed and the pH corresponds to the acid solution ( $\text{pH}_1$ ), and the pH of the leachate is very close to that of the leachant. In the pH front (from  $a$  to  $b$ ), there is a pH gradient, so that the consumption of the neutralising capacity of the solid waste should vary from location  $a$  to  $b$  in the system. Downstream of the pH front, where there is a buffer pH ( $\text{pH}_2$ ), most of protons have been neutralised by the waste material, and the pH of the leachate will be constant. The neutralising capacity of the solid waste in this part will not be consumed by reactions, but some soluble minerals may wash out, and they will then later not be able to act as buffering materials. It is obvious that the neutralising ability of solid waste in a flow-through system is affected by the pH gradient in the pH front and by the

washing-out effect of the water flow. Therefore, the ANC of MSWI bottom ash measured by a batch titration cannot, in general, be directly used to estimate the neutralising ability of the waste in a flow-through system. A quantitative estimation of the neutralising ability can be obtained from experimental results and calculations which take into account the neutralising features in a flow-through system.

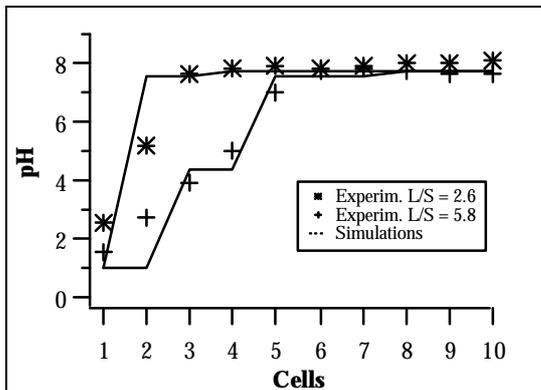


Fig. 18 The movement of the pH front in the flow-through system simulated using the identified primary minerals and secondary minerals  $\text{SiO}_2(\text{am})$  and  $\text{Al}(\text{OH})_3(\text{am})$ .

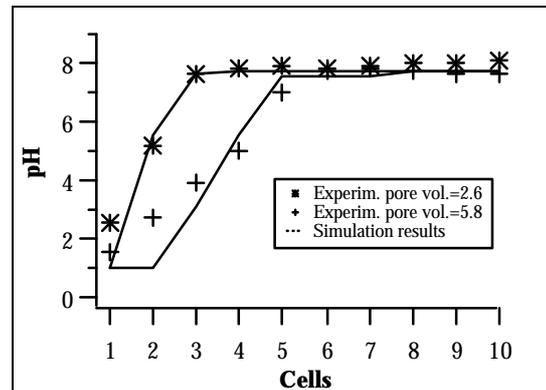


Fig. 19 The movement of the pH front in the flow-through system simulated using the same minerals as in Fig. 18, but adding the secondary minerals, anorthite and K-mica.

Two kinds of geochemical simulation results are presented here, Figure 18 describes a simulation that used only the minerals identified in some experimental investigations. The second simulation, shown in Figure 19, includes extra secondary minerals, such as anorthite and K-mica, to provide a better fit of the experimental data. A rough agreement between simulation and experiment has been obtained, especially in the high pH range. This range is of most interest for the neutralising processes of the MSWI bottom ash. The results indicate that the equilibrium assumption is reasonable for the neutralising reactions under these experimental conditions, and thus confirm that most of the neutralising reactions are rapid under the experimental conditions. The mineral reactions included in the model can be used to simulate the neutralising reactions, at least over a high pH range. However, a comparison of Figure 18 with Figure 19, for which the extra minerals anorthite and K-mica are included, shows that a better fit is obtained for the experimental data when these secondary minerals are included. It should be noted that these minerals have not been identified. They are as yet unknown and probably amorphous. They may not be formed in the relatively short-term experiments, but other minerals of similar composition may be formed. This model did not represent the experiment results very well in the low pH range, for two reasons. One is that chemical kinetics are not considered in the model. According to the leaching behaviour of the

MSWI bottom ash, the dissolution of matrix phases, for example glass phases may influence the neutralising process in the low pH range. The dissolution rate of glass phases will increase under acidic conditions, but the dissolution rate is very slow under a neutral condition. Another possibility is that some mineral reactions taking place in the low pH range have not been identified. So far, little information is available regarding the minerals that affect the neutralisation of the MSWI bottom ash over a very low pH range.

The geochemical simulations also provide the reactivity of major buffering components in the flow-through system (Table 10). The results indicate that Ca- and Mg-containing constituents make a large contribution to the neutralising reactions in such a system. A comparison with batch titration will be given later.

Table 10. The reactive concentration of the MSWI bottom ash for main components in neutralising processes obtained from the geochemical simulations.

	CaO	MgO	CaCO <sub>3</sub>	MgCO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>
(mmol/g ash)	0.490	0.100	0.165	0.080	0.175	0.750	0.100	0.050

The mineral changes and the influence of carbonation in the neutralising process have been evaluated by geochemical simulations. The results indicate that the carbonates are important buffer minerals. These minerals determined the front pH and the movement of the front. We should understand the importance of the carbonation reactions in two aspects. From a mass transformation point of view, the carbonation reactions may change the soluble minerals, *e.g.* lime to the less soluble carbonate, calcite. The carbonation process will thus increase the usable neutralising capacity of the solid waste in a flow system. From the dissolution kinetics of solid waste, on the other hand, the leachability of waste components will limit the carbonation reactions. It has been found that only 18 per cent of the total non-carbonate minerals of alkaline-earth metals was transformed into carbonates in the present titration experiment.

#### 4.3.2 Comparison of the neutralising characteristics in two reaction systems

Compared with the neutralising processes in a batch system, the major features of the neutralising process in a flow-through system are the formation and movement of a pH front and the washing-out effect of the water flow. These features mean that the available neutralising capacity of MSWI bottom ash is considerably reduced in the flow-through system. Table 11 provides a comparison of the reactivity of major components

of a MSWI bottom ash in a batch with that in a flow-through system. The reactive compositions of calcium and magnesium in the flow-through system are only about one third of those in the batch system. This is due mainly to the washing-out effect. In a flow system, readily soluble components of the waste will be washed out of the system and cannot take part in the neutralising reactions. The simulation results confirmed that the soluble part of the MSWI bottom ash involves mainly Ca- and Mg-containing constituents. This is consistent with the results of the availability tests for these elements (Eighmy et al., 1994; Zevenbergen and Comans, 1994). Because the Ca and Mg-containing constituents provide most of the acid neutralising capacity of the MSWI bottom ash, a rough estimate is that only a third of the ANC measured from a batch pH titration may be used for the neutralising reactions in a flow-through system. Moreover, the concept of the ANC for a batch reaction system is not suitable for a flow-through system in which the pH front forms and moves, and no single pH level can be given. The neutralising capacity of a solid waste may represent only an average effect which will depend strongly on the features of a flow-through system.

It is clear that, in principal, the ANC obtained from batch experiments cannot directly be used to assess the neutralising conditions in a flow-through system. The knowledge of neutralising mechanisms may help to establish a relation between different reaction systems.

Table 11. Comparison of the reactive composition of the MSWI bottom ash for major elements in the flow-through system with that in the batch system (mmol/g ash)

	Ca	Mg	Al	Na	K	Si	S
In flow-through system	0.655	0.180	0.250	0.200	0.100	0.750	0.150
In batch system	1.850	0.308	0.128	0.254	0.074	0.743	0.164
Ratio (flow-through/batch)	0.354	0.584	1.950	0.787	1.350	1.010	0.915

## **5 LONG-TERM CHEMICAL WEATHERING OF COMBUSTION RESIDUES**

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The leaching of combustion residues involves different time scales. The chemical weathering of combustion residues is dominant in the leaching processes for long-term environmental impacts. Chemical weathering alters the matrix phases of combustion residues in mineralogy, which in turn governs the leaching processes of combustion residues during long periods of time. In this chapter, the time scales of the leaching processes are first discussed. The importance of the chemical weathering on the environmental impact is then shown by a case study for coal fly ash. The dissolution kinetics of the matrix phase, the glass phase, are studied in theoretical and practical aspects. The long-term chemical weathering of MSWI bottom ash under natural disposal conditions has been simulated using a reactive transport model that takes into account major factors for influencing the long-term leaching processes. The main content of this chapter is based on papers IV, V and VI.

### **5.1 Time scales of leaching processes**

The time scale of a leaching process depends on the physical and chemical properties of the solid waste, and on the leaching conditions. Combustion residues are materials in which the mineral distribution is highly heterogeneous, so that the time scale for different leaching processes or for the release of different species may be significantly different in a certain leaching condition. On the other hand, a leaching process may be accelerated or retarded under different leaching conditions, so that the time scale for a certain process can be changed by the leaching environment. The time scale is also important in the evaluation of environmental risk when a toxic element is released from a combustion residue. In most cases, the release rate is considered to be more important for an environmental concern than the absolute quantity.

In most laboratory leaching tests, an aggressive leachant or a high ratio of the solution volume to solid volume (or weight) is often used to accelerate a leaching process. The test results are usually used to predict the leaching behaviour of solid waste over a much longer actual time scale. The questions are whether there is a relation between the two time scales for a leaching process, and how to relate the information obtained from the short-term leaching tests to an actual long-term leaching situation. This is a challenge for the prediction of the long-term leaching behaviour of combustion residues in a natural leaching environment.

In general, it is possible to relate the information from two different time scales if the leaching mechanisms are the same or quite similar. The leaching mechanisms are thus the basis for establishing a relationship between a leaching test and its applications. This is one of the major reasons for studying the neutralising processes in more detail, because we need to know about the neutralising mechanisms. For most homogeneous neutralising processes, the reaction mechanism does not change with time. Heterogeneous neutralising processes are more complicated due to the variety of leaching kinetics in a solid waste. In most situations, the leaching processes which have fast reaction kinetics may be easily investigated by leaching tests. The experimental results can possibly be used to predict the leaching behaviour on a longer time scale. For example, the neutralising processes involved in soluble parts of combustion residues can be evaluated by laboratory experiments. The information about this kind of neutralising reaction can be used to assess similar processes taking place in a natural leaching environment.

Even when a reaction mechanism is the same on different time scales, the interactions between various processes must be considered. Most leaching tests involve several processes and there are the interactions between these processes. It is important to realise that it is impossible to assess a single process without taking into account all other significant processes. With geochemical models, the interaction between several simultaneous processes on different time scales can be studied.

Unfortunately not all leaching processes can be reproduced by a laboratory experiment. For example, although it has been found that the matrix phase of combustion residues affects neutralising processes over longer times, it is impossible to reproduce the chemical weathering processes in a laboratory experiment, due to the huge difference in time scales.

The chemical weathering of a combustion residue mainly involves its matrix phase, which is mostly an amorphous glass phase. There is no doubt that the glass phase has a potential environmental impact because it makes up a major part of the residue, and many toxic metals are concentrated in the glass phase. However, there is a limited understanding of the long-term leaching behaviour of combustion residues especially for the glass phase, so that the major part of the residues, which cannot be easily tested by conventional leaching tests, are often considered to be an inert phase. In fact, the impact of long-term chemical weathering is still an open question. To solve this kind of problem, we must find a way to relate a laboratory time scale to a geochemical time scale. One suitable approach is using a geochemical model to simulate a long-term chemical process

based on the reaction kinetics and the features of reaction system. This approach has been used to study the chemical weathering of combustion residues in a natural environment (papers IV, V and VI).

## 5.2 Dissolution kinetics of waste glass

### 5.2.1 Reaction rate law of glass phase

In the long-term leaching of a combustion residue, the primary concern is the reactivity of the glass phase with an aqueous solution. The interaction of a multi-component waste glass phase with an aqueous solution is very complicated. Several rate-controlling processes are involved in the dissolution of complex waste glasses. An approach based on the transition state theory (TST) has been applied to evaluate and interpret the hydrolysis of silicate minerals, including aluminosilicate glasses (Aagaard and Helgeson, 1982; Helgeson et al., 1984; Murphy and Helgeson 1987, 1989). The main point of applying the TST is to obtain an insight into the mechanisms of the interaction between mineral (glass) and aqueous solution. On the basis of the TST and recent experimental studies, a general rate law (Lasaga et al., 1994) for mineral (glass) dissolution and mineral precipitation can be expressed as:

$$R_m = k e^{-E_a/RT} A_s f_a(\mathbf{x}) a_{H^+}^{n_{H^+}} g(I) \prod_i a_i^{n_i} f(\Delta G_r) \quad (22)$$

where  $R_m$  is mineral reaction rate,  $k$  is a rate constant which incorporates all the pre-exponential factors involving the surface reaction,  $e^{-E_a/RT}$  designates the temperature effect on the overall reaction (Arrhenius law),  $E_a$  is an apparent activation energy of the overall reaction;  $A_s$  is the specific surface area,  $f_a(\mathbf{x})$  is a function representing the change of reactive surface area with reaction progress  $\xi$ ;  $a_{H^+}^{n_{H^+}}$  refers to the pH dependence of the reaction,  $g(I)$  represents the influence of the ionic strength of solution on the reaction,  $a_i^{n_i}$  denotes the catalytic or inhibitory effects of the species  $a_i$  other than  $H^+$ ,  $f(\Delta G_r)$  accounts for the variation in the reaction rate with the deviation from equilibrium, and  $G_r$  is the Gibbs free energy of the overall reaction. The general rate law provides a comprehensive structure to understand the reaction kinetics of the silicate minerals and glasses. In addition, although studies of various glass phases have shown that the dissolution of a glass phase in an aqueous solution is very similar to the hydrolysis of some silicate minerals, a glass phase is naturally a metastable phase in aqueous solution. Therefore, we need to take into account its metastable property.

The major factors which affect the dissolution kinetics of waste glass include temperature, reactive surface area, the pH of the leachate and the reaction affinity that corresponds to the term  $f(\mathbf{DG})$  in the general rate law. To account for the metastable property of a glass phase in aqueous solution, further consideration must be given to the term  $f(\Delta G_r)$ . A reaction rate law for the dissolution of waste glass can be expressed as:

$$R_g = k' f_{T_0}(T) A_s f_a(\mathbf{x}) f_{H_0^+}(H) f_{glass}(\Delta G_r) \quad (23)$$

where  $R_g$  is the dissolution rate of the waste glass,  $k'$  is the initial dissolution rate constant at temperature  $T_0$  and hydrogen ion activity  $H_0^+$ ,  $f_{T_0}(T)$  accounts for the influence of temperature change from  $T_0$  to  $T$ ,  $f_{H_0^+}(H)$  represents the pH effect on the reaction rate, and  $f_{glass}(\Delta G_r)$  includes the metastable property of the glass phase. The items  $g(I)$  and  $\prod_i a_i^{n_i}$  in equation 22 are here assumed to be constant and are incorporated into the species activity and the rate constant respectively.

The form of the function  $f(\Delta G_r)$  depends on the reaction mechanism. When the overall mechanism consists of an elementary reaction,  $f(\Delta G_r)$  can be derived from transition state theory. For the dissolution of waste glass, based on the knowledge of rock/water interactions, and assuming that there is one irreversible reaction (the dissolution of glass) in the reaction process, the function  $f_{glass}(\Delta G_r)$  can be expressed as a function of chemical affinity (A):

$$f_{glass}(\Delta G_r) = \left( 1 - \exp\left(-\frac{A}{RT}\right) \right) \quad (24)$$

where A is the reaction affinity for the dissolution of glass and is related to the Gibbs free energy (G) and reaction progress ( $\xi$ ) according to:

$$A = -\left(\frac{\mathcal{J}G}{\mathcal{J}x}\right)_{P,T} = \sum \mathbf{m}_i \mathbf{n}_i = RT \ln\left(\frac{K}{Q}\right) \quad (25)$$

where  $\mathbf{m}_i$  is the chemical potential of the  $i$ th component in the reaction,  $\mathbf{n}_i$  the stoichiometric coefficient (positive for products, and negative for reactants),  $K$  the equilibrium constant for the reaction, and  $Q$  the reaction quotient.

A simplified treatment of the chemical affinity for the dissolution of waste glass was given by Grambow (1985; 1987), based on the influence of aqueous species on the reaction rates. The saturation of species in the aqueous phase was understood to be a

local surface equilibrium, *i.e.* the rate of desorption of a surface complex is equal to the rate of adsorption of the surface complex. It has been found that the saturation of silica in aqueous solution has a major effect on the reaction rate (Berger et al., 1994). The desorption of silica tetrahedron (silicic acid) from the glass surface limits the rate of release of glass constituents. At silica saturation, the condensation of silanol groups stabilises the glass network. Silica is thus the dominant constituent that may form the activated complex. In the simplest case, and considering a unit of glass network, the rate-limiting reaction is expressed as:



For this reaction,

$$A = RT \ln \left( \frac{K}{a_{\text{H}_4\text{SiO}_4}} \right) \quad (27)$$

where  $K$  stands for the equilibrium constant of the rate-limiting reaction, and  $a_{\text{H}_4\text{SiO}_4}$  the activity of silica in aqueous solution.

The term equilibrium is ambiguous for the reaction between glass and aqueous solution because glass is usually thermodynamically unstable with respect to an assemblage of its alteration products. The chemical weathering of glass in an aquatic environment will never stop even if the solution has reached a "saturation" condition (Grambow B. and Strachan, 1984; Conradt et al., 1985; and Freude et al., 1985). The "saturation" may only involve the reacting surface, and the weathering reactions may still take place in a region adjacent to the bulk glass phase. A final rate of dissolution of glass under the silicon-saturation condition has been observed in experiments (Grambow et al., 1985; Conradt et al., 1985; Freude et al., 1985; Grambow et al., 1986; Iseghem and Grambow 1988). If we suppose that the saturation concentration of silicon in aqueous solution is determined by the solubility of a common silica—amorphous silica, a fictitious equilibrium constant  $K_{\text{glass}}$  can be calculated using the final dissolution rate.

According to equation 27, the final affinity  $A_{\text{final}}$  for the reaction (26) should be

$$A_{\text{final}} = RT \ln \left( \frac{K_{\text{glass}}}{a_{\text{H}_4\text{SiO}_4 \cdot \text{sat}}} \right) \quad (28)$$

where  $a_{H_4SiO_4, \text{sat.}}$  is the "saturated" activity of silica in the bulk solution, which is determined by the solubility of the amorphous silica.

### 5.2.2 Estimate of dissolution rates of glass phases

According to the dissolution rate law, an important kinetic parameter, the dissolution rate constant must be determined in order to evaluate the chemical weathering of a combustion residue. Because the glass phases in combustion residues are usually mixed with other constituents, it is difficult to separate the glass phases from the solid waste in order to measure their kinetic properties even when the composition, structure and fractions of the glass phases have been determined by various methods. Reasonable theoretical prediction and estimation may, however, provide a way to study the dissolution rates of the waste glass phases.

A thermodynamic approach has been successfully proposed for the prediction of the chemical durability of various glasses. This approach is based on the hydration theory of glass (Paul, 1977, 1990). The glass phase is assumed to be a mechanical mixture of orthosilicate and oxide components. The long-term chemical resistance of a glass is determined mainly by the thermodynamic activity and stability of its component oxides in an aqueous solution. This approach assumes that the calculated free energy of hydration of the glass is the chemical driving force for glass alteration or dissolution. The chemical potential,  $m_i$ , of component  $i$  in the glass is the free energy of formation of the component. The chemical potential of the hydrated form of component  $i$  is assumed to be the free energy of formation of the hydrated species.

$$m_{i, \text{glass}} = \Delta G_{f, i, \text{glass}} \quad (29)$$

$$m_{i, \text{hydrated}} = \Delta G_{f, i, \text{hydrated}} \quad (30)$$

The chemical driving force for glass hydration,  $\Delta m_{\text{hydration}}$ , is given by:

$$\Delta m_{\text{hydration}} = \sum_{i=1}^N (m_{i, \text{glass}} - m_{i, \text{hydrated}}) \quad (31)$$

$$\Delta m_{\text{hydration}} = \sum_{i=1}^N \Delta G_{i, \text{hydration}} \quad (32)$$

The calculated free energy of hydration of the glass is related to the free energies of hydration of its component oxides by the following equation:

$$\Delta G_{glass, hydration} = \sum_{i=1}^N (\Delta G_{i, hydration} \cdot X_i) \quad (33)$$

where  $\Delta G_{glass, hydration}$  is the free energy of the glass,  $\Delta G_{i, hydration}$  the free energy of component  $i$  in the glass, and  $X_i$  the mole fraction of component  $i$  in the glass.

This approach has been applied to predict the chemical durability of various types of glasses covering a broad range of compositions (Plodinec et al. 1984a; 1984b). The linear relationships between the free energy of hydration of a given glass and the logarithm of the normalised mass loss of component  $i$  (usually SiO<sub>2</sub>),  $L_i$ , under a standard leaching testing condition have been determined:

$$\Delta G_{glass, hydration} = C \cdot \text{Log } L_i \quad (34)$$

where  $C$  is the constant of proportionality. This empirical relationship connects the intrinsic chemical durability of a glass phase with its chemical composition. There is experimental evidence that a constant and maximal dissolution rate may be obtained at infinite dilution or at a high flow rate and constant temperature and pH (Lutze, 1988). The rate is dependent only on glass composition and structure. It can therefore be considered to be one of the intrinsic kinetic properties of a glass. According to the standard leaching test condition (Strachan et al., 1981), the property of normalised mass loss,  $L_i$ , reflects the initial dissolution behaviour (dissolution rate far from equilibrium) of the glass phase in pure water. This approach can provide a simple way to take into account the intrinsic kinetics of the glass phase as a function of the chemical composition of glass phase under certain conditions.

Table 12. The initial and final dissolution rates of the glass phases in MSWI bottom ashes and coal fly ashes calculated by the free-hydration-energy approach (mol Si/m<sup>2</sup> s)

Samples	1	2	3	4	5	6	7
Glass phases of MSWI bottom ash							
$k_{initial}$	5.74x10 <sup>-9</sup>	3.01x10 <sup>-9</sup>	2.64x10 <sup>-9</sup>	1.96x10 <sup>-9</sup>	7.81x10 <sup>-10</sup>	7.22x10 <sup>-11</sup>	3.97x10 <sup>-11</sup>
$k_{final}$	1.82x10 <sup>-11</sup>	9.52x10 <sup>-12</sup>	8.35x10 <sup>-12</sup>	6.20x10 <sup>-12</sup>	2.47x10 <sup>-12</sup>	2.28x10 <sup>-13</sup>	1.26x10 <sup>-13</sup>
Glass phases of coal fly ashes							
$k_{initial}$	2.97x10 <sup>-10</sup>	1.33x10 <sup>-10</sup>	1.10x10 <sup>-10</sup>	6.13x10 <sup>-11</sup>	1.64x10 <sup>-11</sup>	6.63x10 <sup>-12</sup>	
$k_{final}$	9.40x10 <sup>-13</sup>	3.57x10 <sup>-13</sup>	3.48x10 <sup>-13</sup>	1.94x10 <sup>-13</sup>	5.19x10 <sup>-14</sup>	2.10x10 <sup>-14</sup>	

Note:  $k_{initial}$  is initial dissolution rate and  $k_{final}$  is final dissolution rate.

The dissolution rates of glass phases in coal fly ash and MSWI bottom ash have been studied using this method. Six samples of coal fly ash and seven samples of MSWI bottom ash represent various types of ashes and various chemical compositions. The chemical composition of the samples was obtained on the basis of individual particles in the ashes. The initial dissolution rates of the glass phases calculated according to the hydration-free-energy approach are given in Table 12. According to the dissolution kinetics of glass phase, another important kinetic parameter is the final dissolution rate. This parameter reflects the metastable property of the glass phase when the aqueous phase reaches saturation with respect to the major component (usually Si) of the glass phase. On the basis of the similarity of multi-component silicate glass phases in dissolution kinetics, we compare the final dissolution rates with corresponding initial rates for some multi-component silicate glasses and assume that the final dissolution rate is lower by 2.5 orders of magnitude than the initial dissolution rate for the glass phase of the ashes. The final dissolution rates of the glass phases are also included in Table 12.

### **5.3 Simulating the long-term leaching of coal fly ash**

In order to assess the chemical weathering of a combustion residue in a possible disposal environment, particularly for long-term dissolution of the glass phase, geochemical simulations of the dissolution of glass phases of coal fly ashes have been performed. The simulation is on the basis of the dissolution kinetics of waste glass. The leaching of coal fly ash in a simple flow-through system is studied. Heavy metals, Zn, Cu, Pb and Cr, are assumed to be incorporated with the glass phase to examine the release of the trace elements during the dissolution of the glass phase. The content of each heavy metal in the glass phases is about 0.1% (weight percentage), close to the higher content of the elements in coal fly ash. A landfill is considered to be the disposal environment of solid waste. About 10% of the average precipitation (0.5 - 0.8 m<sup>3</sup>/m<sup>2</sup> year in Sweden) is assumed to flow through the waste deposit site in the simulation.

A volume unit (1 m<sup>3</sup>) in a combustion residue monofill is considered to be a well mixed flow-through reactor. Glass phase dissolution takes place together with the release of other components of solid waste in the reactor. The dissolution process of waste glass is evaluated by the aqueous phase composition of the system outflow when the system reaches a steady state. The simulation system is shown in Figure 20.

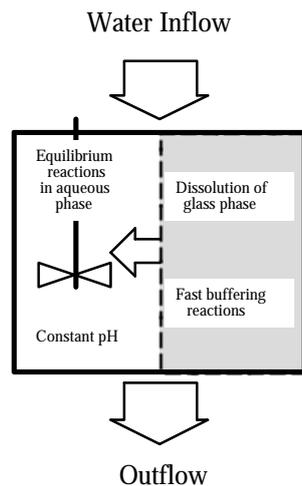


Fig. 20 A well mixed bed flow-through reactor system used to simulate the long-term leaching of coal fly ash in which the dissolution of the glass phase is considered to be one of major processes.

In the model, fast reversible processes are described in terms of chemical equilibria, and the slow dissolution of the glass phase is described by a kinetic rate law which takes mainly the reaction rate and the reactive surface area of the glass phase into account. A simplified treatment for the reactive transport is evaluating its steady-state solution. A geochemical computer program, STEADYQL (Furrer et al., 1989, 1990), is used to simulate the dissolution of waste glass phase in the fixed bed flow-through system. This geochemical simulation focuses, in fact, on the assessment of the environmental impact of the dissolution of waste glass to address the important issue of whether the glass phases could significantly contribute to the release of toxic metals under landfill conditions, instead of providing an accurate description of the evolution of chemical weathering.

The simulation results show the potential contribution of the dissolution of waste glass to the concentrations of dissolved species in the outflow of the system (Table 13). The potential concentration is here the available concentration of a species dissolved due to glass dissolution if other reactions do not affect the concentration of the species in the aqueous phase. It is obvious that some of the heavy metals may be released in millimolar to ten millimolar concentrations from the glass phases if other retention processes such as adsorption, precipitation or co-precipitation can be neglected. This means that the primary release of toxic metals from the glass phases cannot be neglected. The glass phases cannot be considered as inert materials in the long-term leaching of combustion residues. The reactivity of waste glass must be accounted for in the long-term chemical weathering of combustion residues.

Table 13. Simulation results for the glass phase dissolution under initial dissolution rates (potential concentrations of the heavy metals in an aqueous phase (mol/l))

Samples	Zn	Cu	Pb	Cr
1	$3.02 \times 10^{-2}$	$3.22 \times 10^{-2}$	$1.01 \times 10^{-2}$	$3.83 \times 10^{-2}$
2	$1.66 \times 10^{-2}$	$1.77 \times 10^{-2}$	$5.53 \times 10^{-3}$	$2.10 \times 10^{-2}$
3	$6.32 \times 10^{-2}$	$6.74 \times 10^{-2}$	$2.11 \times 10^{-2}$	$8.00 \times 10^{-2}$
4	$2.80 \times 10^{-2}$	$2.98 \times 10^{-2}$	$9.33 \times 10^{-3}$	$3.54 \times 10^{-2}$
5	$1.88 \times 10^{-3}$	$2.01 \times 10^{-3}$	$6.28 \times 10^{-4}$	$2.39 \times 10^{-3}$
6	$4.58 \times 10^{-3}$	$4.89 \times 10^{-3}$	$1.53 \times 10^{-4}$	$5.80 \times 10^{-3}$

Note: The potential concentration is 316 times lower for the corresponding final dissolution rate.

The simulations also indicate that the dissolution of the glass phase depends not only on the chemical kinetics of the glass phase but also on the morphology of the waste particles and the properties of the reaction system. The most important factors which have been identified here are the reactive surface area and the water flow. The small particles of coal fly ash make a large surface area available for glass dissolution. A slow water flow provides a relatively long reaction time in the system. The reactivity of waste glass is a consequence of the interaction of many factors in a given system. A detailed study is necessary to further identify the controlling factors and their interactions. An understanding of the main mechanisms and a more accurate description of the chemical weathering have a direct utility for the prediction of the long-term leaching behaviour of combustion residues in subsurface aquifers.

## 5.4 Modelling the long-term chemical weathering of MSWI bottom ash

### 5.4.1 A conceptual model for long-term chemical weathering

For a long-term consideration, we pay attention to the chemical weathering of the matrix glass phase in combustion residues. In addition to the essential properties of the glass phase, the chemical weathering of the glass phase is affected by the weathering environment. Because waste landfills exhibit a typical chemical weathering condition for combustion residues, this type of system has been simulated in this study. A landfill of solid waste may be thought of as a column reactor, as shown in Figure 21.

When acidic water (acidic rain) percolates through a combustion residue, carbon dioxide or other reactants react with the residues, and the chemical weathering of the glass phase takes place in this system. Neutralising reactions control the pH environment and thus

affect the chemical weathering. Meanwhile, the chemical weathering of a glass phase consumes protons, and it should be closely related to the neutralising processes in the reaction system. According to their leaching characteristics, the combustion residues may be assumed to consist simply of glass phases and other buffering components if the neutralising reactions are mainly considered to control the weathering environment. These buffering components in a combustion residue represent a small fraction of the total potential neutralising capacity, but they usually have relatively fast reaction rates compared with the glass phases. The pH environment of the system is thus initially controlled by the fast neutralising reactions. In this reaction system, the major acid sources should be the acidic input water (acidic rain) and carbon dioxide that either comes from the atmosphere or is produced by the degradation of organic carbon or biochemical activities in the landfill. As the acidic water flows into the column-like system, the neutralising reactions start at the inlet of the column, and carbonation reactions may take place. After a certain time, different reaction zones may form in the system as shown in Figure 21.

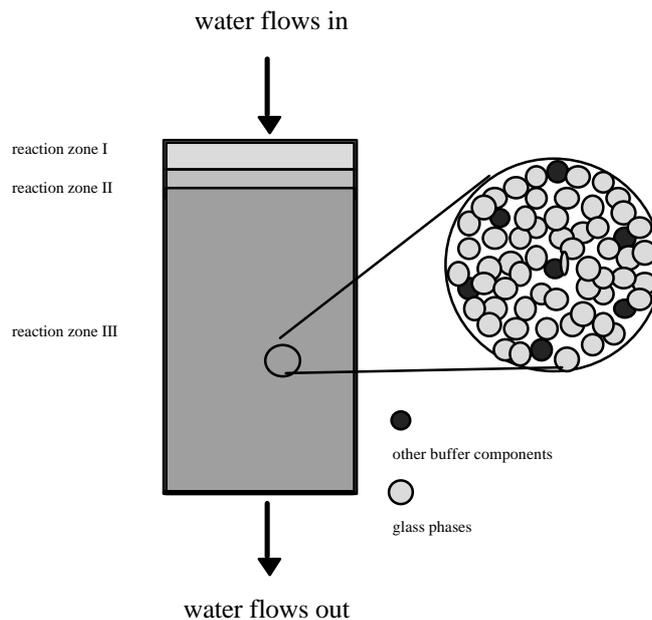


Fig. 21. Schematic representation of the reaction system for the chemical weathering of combustion residues in the residue deposit

To model the long-term chemical weathering of combustion residues in a flow-through system, we must consider several aspects, which include: the chemical kinetics of the glass dissolution, the particle size that relates to the reactive surface area of the glass phase or residues, the precipitation of secondary minerals when the aqueous solution

becomes saturated to the corresponding minerals, the solute transport that results in mass transfer by the flowing water, carbonation reactions that are the most important buffering mechanisms, and the interaction among the aquatic species, i.e. complexing reactions. The conceptual structure of the reactive kinetic transport model is shown in Figure 22.

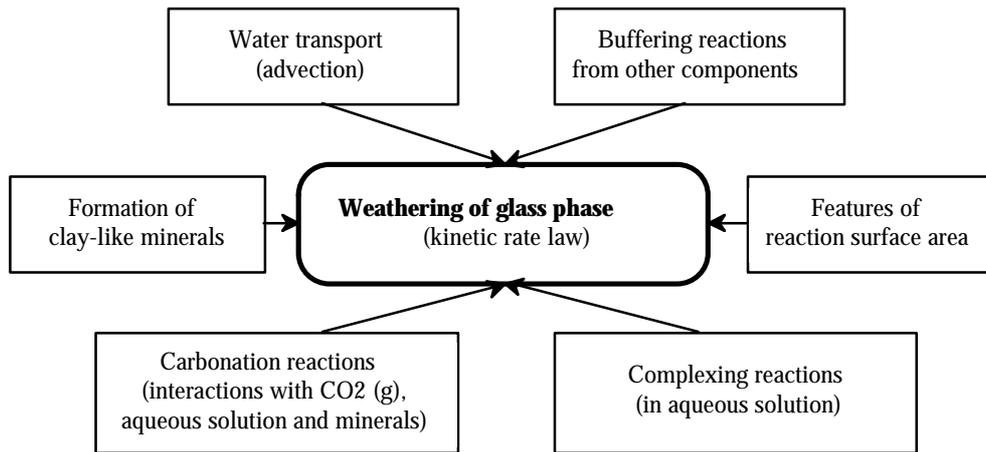


Fig. 22. The conceptual structure of the reactive transport model for long-term chemical weathering of combustion residues.

#### 5.4.2 Major factors influencing chemical weathering

Solute transport, surface reactions and the precipitation of secondary minerals are considered to be fundamental processes in the chemical weathering of combustion residues. A comprehensive description of the chemical weathering should account for the most important factors which may affect the fundamental processes. Although the general reaction rate law for the dissolution of waste glass (equation 23) shows in principally the influences of these factors, a detailed description is usually needed for each individual factor. Sub-models included in the reactive transport model incorporate the most important factors simultaneously:

- A special consideration for the reaction affinity of glass phase has been included in the rate law, which represents the irreversible properties of glass phase and the influence of aqueous chemistry.

- The temperature effect on the weathering reaction is represented by the Arrhenius law. The apparent activation energy, which is used in the Arrhenius law, is estimated on the basis of the dissolution reactions for many waste glasses and natural glasses.
- A geometric model has been used to calculate the initial surface area of solid particles, the relation between the surface area and the particle size distribution, and the surface area change as a result of weathering reaction.
- A simplified approach is used to simulate the carbonation process. It is assumed that equilibrium is rapidly reached between an aqueous phase and the gas phase, and that the partial pressure of CO<sub>2</sub> in the gas phase can be kept at a constant value according to the requirement of modelling.
- Information obtained from experimental observations and from geochemical principles can be used to select the potential weathering products according to the solid waste and leaching environment.

One-dimensional advective transport is coupled with weathering reactions using the quasi-stationary state approach, by which the pH front and the movement of the reaction region are easily handled during the simulation. The homogenous reactions in the aqueous phase are defined by chemical equilibrium, and the heterogeneous reactions between solid phase and aqueous phase are treated by a full kinetic consideration, the reaction rate law. A modified version of the computer program CHEMFRONTS (Bäverman, 1993) has been used to model the long-term chemical weathering. All the submodels which are specified for the chemical weathering of a combustion residue are included in the modified version.

#### *5.4.3 Simulation of chemical weathering processes*

A case study has been performed to model the long-term chemical weathering of MSWI bottom ash. The important factors related to the long-term chemical weathering were identified according to a critical evaluation of the current knowledge of leaching characteristics of MSWI bottom ash. On the basis of this information, a reactive kinetic transport model has been set up to integrate all the important factors and to specify the submodel for the MSWI bottom ash. All the parameters or information required by the modelling have been critically reviewed with regard to experimental evidence and geochemical principles ( the details can be found in paper VI). The major concerns of the modelling are listed in Table 14.

The dissolution of glass phases is a major process in the long-term chemical weathering of MSWI bottom ash. The results indicate that the dissolution of the glass phase (Figures 23 and 24) takes place mainly in the top layer of the column reactor and that the reaction depth in the column is small even after more than one hundred years. The dissolution rate of glass phase is reduced with time and the average dissolution rate is much lower than the initial rate. These phenomena can be explained both by the dissolution kinetics of the glass phase and by the change in surface area with weathering. Because the glass dissolution is strongly affected by the chemical affinity, especially the activity of silica in the aqueous solution, the dissolution rate of the glass phase is reduced to a very low level compared with its initial rate when the activity of silica is high in the solution. From the simulations, it was found that the silica could easily reach a saturated concentration with respect to amorphous silica in the aqueous phase under such a low water flux. This is the major reason for the relatively narrow reaction region in the column reactor. The aqueous chemistry controls the dissolution of the glass phase in this situation.

Table 14. The main considerations for simulating chemical weathering of MSWI bottom ash

1	The features of simulating systems
	1.1 the length of column reactor
	1.2 physical properties of MSWI bottom ash and the content of glass phases
	1.3 initial surface area of the waste particles
	1.4 pH buffer (ANC) excluding the glass phase
	1.5 partial pressure of CO <sub>2</sub> in the system
	1.6 water flux and the chemical composition of input water
	1.7 temperature
2	The chemical kinetics of waste glass phase
	2.1 stoichiometry of the dissolution reaction
	2.2 reaction rates
	2.3 the irreversible properties of glass phase dissolution
	2.4 the surface area change as a function of the weathering reaction
3	Other chemical reactions in the system
	3.1 heterogeneous reactions:
	primary and secondary mineral reactions
	the transfer between gas (CO <sub>2</sub> ) phase and aqueous phase
	3.2 homogeneous reactions
	complexing reactions in aqueous phase

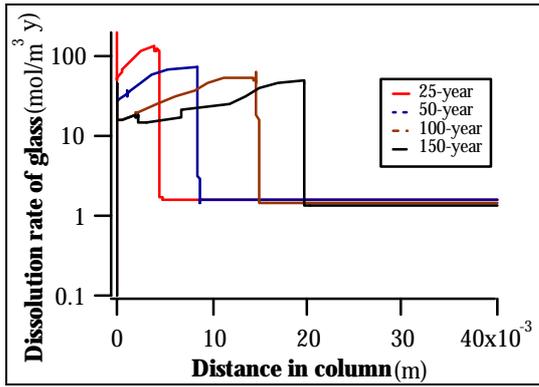


Fig. 23 The dissolution rates of the glass phase at different different times (the main weathering conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm)

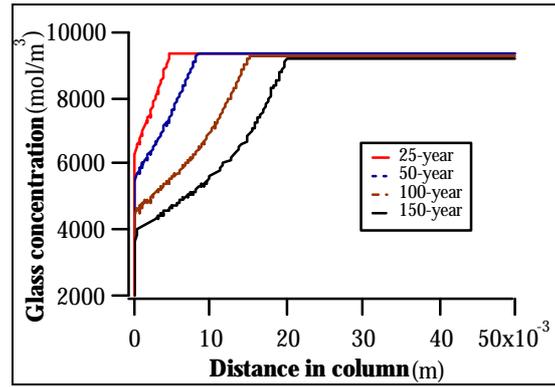


Fig. 24 Remaining glass in the system after reaction times (the main weathering conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm)

The influences on the dissolution of the glass phase of other factors such as water transport and the initial rate product (the product of the initial rate constant and initial reaction surface area) of the glass phase have also been assessed in the simulations. The simulation results are shown in Figures 25 and 26. In Figure 25, it is clear that increasing water flux results in a deeper reaction region. Water transport not only removes the dissolved species but also increases the reaction affinity for the dissolution of glass phase. The influence of the initial reaction rate (Figure 26) is complicated due to two opposite effects. The higher the initial reaction rate, the more glass dissolution is dissolved. However, if the dissolved species is not removed from the reaction region, the chemical affinity of the reaction is quickly reduced, and the dissolution rate of the glass phase is, in turn, reduced. Under a slow water flow, the latter effect becomes dominant, as shown in Figure 26. In this situation, the initial dissolution rate (rate constant times reaction surface area, *i.e.* rate product) has only a limited influence on the dissolution of the glass phase.

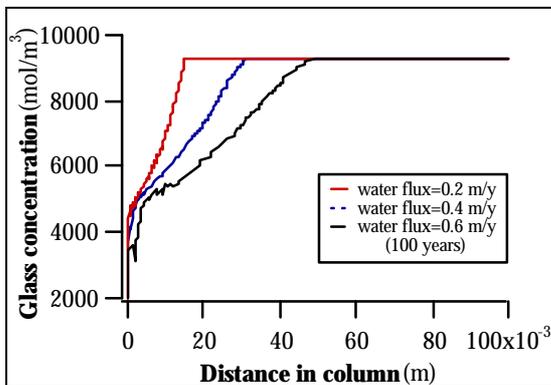


Fig. 25 The influence of water transport on the dissolution of glass phase (main weathering cond-

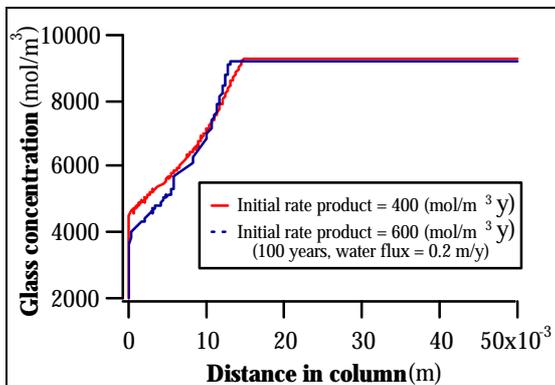


Fig. 26 The influence of the initial rate production on the dissolution of glass phase (main weathering

itions:  $P_{CO_2}=10^{-4.5}$  atm; Time=100 year)

conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm;  
Time=100 year)

The evolution of pH in long-term chemical weathering is shown in Figure 27. The movement of the pH fronts corresponds to the change in the calcite front (Figure 28), and is not directly related to the dissolution of the glass phase (Figure 24). This means that carbonation reactions play an important role in controlling the aqueous chemistry during the long-term chemical weathering of MSWI bottom ash. Although dissolution of the glass phase affects the solution pH in the reaction region, as shown in Figure 27, the major effect of glass dissolution is to provide a source of alkaline cations to form the buffering minerals, for example calcite. The simulation results are consistent with the field studies of leachate from a more than 20-year old MSWI ash monofill (Hjelmar, 1991). According to the field study, without any topsoil layer covering the landfill, the leachate pH was between 8.7 and 9.3. The pH value is very close to the simulation results. When the ashes were covered by a topsoil layer, the leachate pH increased to about 10. We believe that this is due to a decrease in the partial pressure of  $CO_2$  in the landfill after the top-cover was provided.

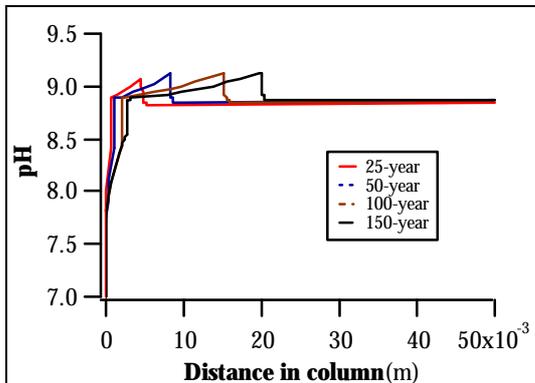


Fig. 27 The evolution of pH along the column reactor during chemical weathering (main weathering conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm)

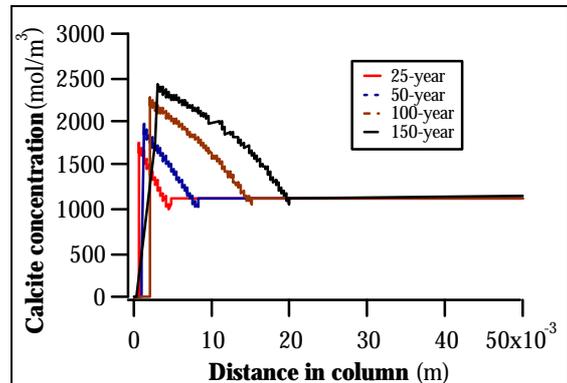


Fig. 28 The distribution of calcite in the column reactor during chemical weathering (main weathering conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm)

The contribution of glass dissolution to the pH environment is shown in Figure 29. This simulation provides a comparison between glass dissolution and other buffering reactions. The inclusion or exclusion of other pH-buffering minerals had no great effect on the pH-buffering pattern in the leaching solution. This means that the dissolution of the glass phase can provide considerable acid neutralising capacity (ANC) in the long-term chemical weathering of MSWI bottom ash. The contribution of glass dissolution to the ANC is also seen in Figure 28. If we consider the calcite as, in fact, controlling the

pH buffering mineral in the chemical weathering processes, the glass dissolution will provide a larger amount of calcium for calcite formation than other mineral transformations which can be found in the reaction front in Figure 28.

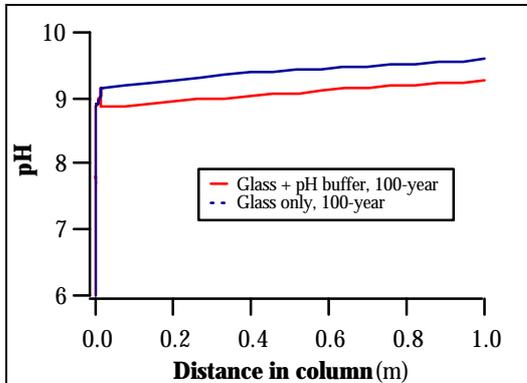


Fig. 29 The contribution of glass dissolution to the pH environment in long-term chemical weathering (main weathering conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm)

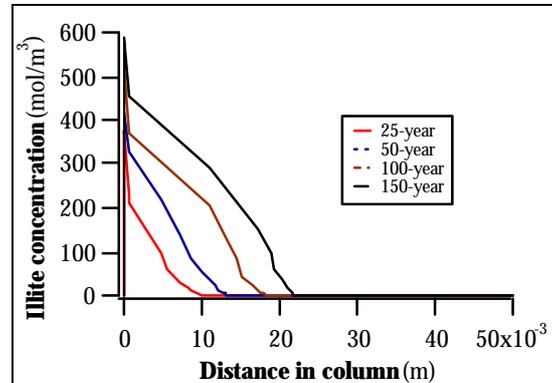


Fig. 30 Formation of the clay mineral, illite, in the long-term chemical weathering of MSWI bottom ash (main weathering conditions: water flux=0.2 m/y;  $P_{CO_2}=10^{-4.5}$  atm)

The formation of secondary minerals is critical for evaluating the leaching characteristics of MSWI bottom ash. In addition to the formation of carbonates, the dominant secondary minerals which form during the long-term weathering are the clay-like mineral, illite, and amorphous silica. The formation of illite is shown in Figure 30. This is consistent with the investigation of weathered MSWI bottom ash (Zevenbergen, 1994) and the geochemical principles for the chemical weathering of natural aluminosilicate minerals in soil environments (Brownlow, 1996; Langmuir, 1997). The simulations reproduced well the weathering products in an intermediate weathering and weak alkaline environment. The formation of the clay mineral indicates that the adsorption ability of the MSWI bottom ash will increase with the chemical weathering particularly after a long period of time. This is significant for considering the long-term leaching behaviour of heavy metals.

In summary, the simulation results show that the dissolution of the waste matrix, the glass phase, is a complicated function of the initial reaction rate, the surface area and the change in surface area during the chemical weathering. The aqueous chemistry strongly affects the dissolution of the glass phase when the water flow rate is low. Although the chemical weathering of the glass phase provides considerable buffering capacity for neutralising reactions, carbonate is the dominant buffering mineral in the long-term chemical weathering, and the leaching pH may be controlled by carbonation reactions under these conditions. Besides the dissolution of the glass phase, the transformation of

carbonates is another key process in the chemical weathering of MSWI bottom ash. The simulations show that the dominant secondary minerals, illite and amorphous silica, form in the long-term chemical weathering. This is consistent with the investigation of weathered MSWI bottom ash and the geochemical principles for chemical weathering of some natural minerals in a similar soil environment. The reactive transport model is a useful tool to describe the non-linear relationship among the important factors that are involved in the long-term chemical weathering of combustion residues.

## 6 CONCLUDING REMARKS

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Studies of the leaching of combustion residue provide ample evidence to identify the major leaching processes of combustion residues. It has been found that neutralisation and chemical weathering govern other leaching processes, and thus control the release of minor and trace elements from combustion residues. Although attempts have been made to determine the acid neutralising capacity of combustion residues in a batch system, little is known about the neutralising mechanisms, *i.e.* the interaction between buffering components in a heterogeneous reaction system, the reactivity of buffering materials under different leaching conditions and different time scales, and the titration kinetics of the experiments. Because of the time limits of the experiments, few systematic studies have been performed relating to long-term chemical weathering.

It is important to distinguish between the time scale of a leaching process in a laboratory experiment and that in a natural leaching environment. The major aim of leaching tests is to predict the leaching behaviour of combustion residues under actual conditions. However the information obtained from a leaching experiment cannot be directly transferred to a natural leaching process because of the difference in time scale. It is a challenge to establish the relationship between the laboratory experiment and an actual long-term leaching process. A correct geochemical model based on a full understanding of the leaching mechanisms can provide an opportunity to build a bridge between the different time scales.

Both the neutralising process and chemical weathering are complicated by heterogeneous reactions and solute transport which simultaneously take place in the reaction system. It is necessary to use geochemical modelling to evaluate the complicated leaching processes, and to simulate a long-term leaching process which cannot be reproduced in a laboratory experiment. On the basis of reaction kinetics and the features of the reaction system, different models have been applied to describe various leaching processes in different reaction systems. A reaction path model is used to evaluate the neutralising processes in a batch system. Using this model, the reactivity of solid waste and the interaction between major buffering components in a neutralising process have been investigated. It is possible to evaluate the titration kinetics using the reaction path simulation. The neutralising processes in a flow-through system have been assessed using an equilibrium reactive transport model which can account for most of the neutralising reactions under the test conditions. A kinetic transport model giving full kinetic consideration to heterogeneous reactions has been used to simulate long-term chemical weathering. All the models are closely related in the descriptions of chemical reactions

and solute transport for the leaching processes. The different models emphasise different aspects.

Heterogeneous neutralising reactions take place in the leaching of combustion residues, so that the interactions between buffering components are complicated. The dissolution kinetics of buffering materials is central to an understanding of the neutralising processes. The ANC at different pH levels depends mainly on the mineralogy of the combustion residue. The time-dependent and pH-dependent neutralising behaviours are determined by the matrix phases of a solid waste. For most combustion residues, the dissolution of glass phases is expected to play an important role in a long-term neutralising process.

The neutralising process in a flow system is significantly different from that in a batch system. The information obtained from batch experiments, *e.g.* the ANC, cannot be used directly in a flow reaction system. The neutralising ability of a combustion residue is strongly affected by solute transport and carbonation reactions in a natural leaching environment.

The chemical weathering of a combustion residue mainly involves the matrix phases, waste glasses. The importance of the chemical weathering is mainly due to two aspects. First, the reactivity of the glass phases cannot be neglected in long-term leaching processes, as has been shown in this study. Second, the chemical weathering changes the mineralogy of the combustion residue. This influences its leaching characteristics in a long-term disposal or utilisation.

To address the long-term chemical weathering of combustion residues, the dissolution kinetics of waste glass phases must first be studied because glass dissolution is one of the key mechanisms in the long-term chemical weathering. A reaction rate law has been used to describe the general kinetic properties of the glass phase and its metastable features. Other possible processes involved in the chemical weathering have been investigated and incorporated in a geochemical model. All the important processes can be simulated simultaneously. The simulation results for MSWI bottom ash show that there is a complicated relationship between the factors controlling the long-term chemical weathering. The dissolution of the waste matrix, the glass phase, is strongly affected by its kinetic properties and by the weathering environment. Although the glass dissolution can provide considerable buffering capacity, the carbonate is a dominant buffering mineral in a natural weathering environment. The transformation of carbonate should be considered as an important process in long-term chemical weathering. The simulations indicate that the formation of secondary minerals, illite and amorphous silica, may

considerably change the leaching behaviour of the combustion residue during the long-term chemical weathering.

There is still a gap in knowledge between leaching tests and their applications. There are several uncertainties both in the experimental investigation and in the geochemical simulations. These uncertainties mainly result from the limited knowledge of the long-term leaching processes. The influence of these uncertainties can be estimated by geochemical simulation. The geochemical modelling provides an efficient way to analyse these uncertainties and their importance for long-term leaching processes.

## NOTATION

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$a_i$	activity of the $i$ th component	$\text{mol m}^{-3}$
$a_r$	specific surface area of the $r$ th mineral	$\text{m}^2 \text{m}^{-3}$
$A$	reaction affinity	$\text{J mol}^{-1}$
$A_i$	complex species in a reaction system	
$A_j$	primary species in a reaction system	
$A_s$	specific surface area of mineral (glass)	$\text{m}^2 \text{m}^{-3}$
$C$	constant of proportionality	
$C_i$	concentration of the $i$ th complexed species	$\text{mol m}^{-3}$
$E_a$	apparent activation energy of the overall reaction	$\text{J mol}^{-1}$
$f(\Delta G_r)$	a function accounting for the variation in the reaction rate with the deviation from equilibrium	
$f_{\text{glass}}(\Delta G_r)$	a function accounting for the variation in the glass dissolution rate with the deviation from equilibrium	
$f_a(\mathbf{x})$	a function relating surface change to reaction progress	
$f_{H_0^+}(H)$	a function for the influence of pH change on the reaction rate constant;	
$f_{T_0}(T)$	a function accounting for the temperature influence on reaction rate constant for a temperature change from $T_0$ to $T$	
$g(I)$	a function for the influence of ionic strength of solution on the reaction	
$G_r$	Gibbs free energy of overall reaction	$\text{J mol}^{-1}$
$H^+$	hydrogen ion activity	$\text{mol m}^{-3}$
$I$	ionic strength of solution	$\text{mol m}^{-3}$
$k$	rate constant defined by equation 22	
$k'$	the initial dissolution rate constant at constant temperature and constant hydrogen ion activity	
$k_{\text{final}}$	final dissolution rate (constant)	$\text{mol m}^{-2} \text{s}^{-1}$
$k_{\text{initial}}$	initial dissolution rate (constant)	$\text{mol m}^{-2} \text{s}^{-1}$
$k_r$	reaction rate constant of the $r$ th mineral	
$K_i$	equilibrium constant of the $i$ th complexed species	
$K_r$	solubility constant of mineral $r$	
$l$	order of a cell in a column	
$L_i$	logarithm of the normalised mass loss of component $i$	
$n$	reaction order	
$N$	number of components in a reaction system	
$N_c$	number of complex species in a reaction system	

$N_{cell}$	number of cells in a column	
$N_{ir}$	number of irreversible reactions	
$N_m$	number of solid species (minerals) in a reaction system	
$Q_r$	activity product of mineral reaction	
$R$	gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
$R_g$	dissolution rate of glass	$\text{mol m}^{-3} \text{s}^{-1}$
$R_i$	reaction rate of the $i$ th irreversible reaction	
$R_m$	mineral reaction rate	$\text{mol m}^{-3} \text{s}^{-1}$
$R_r$	reaction rate of the $r$ th mineral	
$S_j$	source/sink term caused by chemical reaction	
$t$	time	s
$T$	temperature on Kelvin scale	K
$n_i$	stoichiometric coefficient of the species $i$	
$v_{ji}$	stoichiometric coefficient of component $j$ in complex $i$	
$v_{jr}$	stoichiometric coefficient of component $j$ in mineral $r$	
$V$	water flux	$\text{m}^3 \text{m}^{-2} \text{s}^{-1}$
$X_i$	mole fraction of component $i$ in the glass	
$X_r$	concentration of mineral $r$	$\text{mol m}^{-3}$
$Y_j$	total concentration of component $j$	$\text{mol m}^{-3}$
$Y_{j(in)}$	in-flow concentration of component $j$ to a cell	$\text{mol m}^{-3}$
$Y_{j(out)}$	out-flow concentration of component $j$ from a cell	$\text{mol m}^{-3}$
$q$	porosity	
$\mu_i$	chemical potential of the $i$ th component	J
$x$	overall reaction progress variable	
$x_r$	reaction progress of the $r$ -th irreversible reaction	

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## APPENDIXES

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### PAPERS

- I** Yan, J., Bäverman, C., Moreno, L., Neretnieks, I. 1998. Evaluation of the time-dependent neutralising behaviours of MSWI bottom ash and steel slag. *Sci. Total Environ.* 216, 41-54.
- II** Yan, J., Moreno, L., Neretnieks, I. 1998. Neutralising processes in leaching of solid wastes: Modelling of interactions between solid waste and strong acid. *J. Environ. Sci. Health (Part A), Toxic/Hazardous Substances & Environmental Engineering* A33 (6), 923-950.
- III** Yan, J., Bäverman, C., Moreno, L., Neretnieks, I. 1998. Neutralising processes of municipal solid waste incineration bottom ash in a flow-through system. *Sci. Total Environ.* (in press)
- IV** Yan, J., Neretnieks, I. 1995. Is the glass phase dissolution rate always a limiting factor in the leaching processes of combustion residues? *Sci. Total Environ.* 172, 95-118.
- V** Yan, J., Moreno, L., Neretnieks, I. 1998. Modelling long-term chemical weathering of combustion residues: 1. Development of a reactive transport model (submitted for publication)
- VI** Yan, J., Moreno, L., Neretnieks, I. 1998. Modelling long-term chemical weathering of combustion residues: 2. A case study for the chemical weathering of MSWI bottom ash. (submitted for publication)