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Chemical Modelling of Pore Water Composition from PFBC Residues

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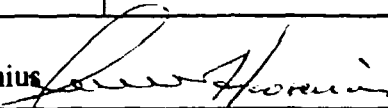
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Title

Chemical Modelling of Pore Water Composition from PFBC Residues

Summary

Combustion of coal in fluidised beds is today considered to be an established and commercially available technique for heat and power production. Large amounts of residues from these processes have to be disposed over the coming years. One potential problem with the disposal is contamination of surface waters and ground water by hazardous elements present in trace quantities as a result of leaching from the residues.

The concentration of trace elements varies depending on the source of the coal and also due to the combustion process being used. Mercury is one important element among the trace elements in the coal residues, generally recognised as potentially harmful to the biological system. To predict the pore water concentrations of mercury and other important constituents leached from coal combustion residues disposal sites, mechanistic data on chemical reactions are required.

The present study is an application of a basically thermodynamical approach using the geochemical code EQ3NR. The presence of discrete solid phases that control the aqueous concentrations of major elements such as aluminum, calcium and silicon are identified. Solid phases are modelled in equilibrium with a hypothetical pore water at a pH range of 7-11. In this study the thermodynamic database of EQ3NR has been complemented with data for cadmium, mercury and lead taken from the OECD/NEA Thermodynamic Database and from a compilation made by Lindsay (1979).

Possible solubility limiting phases for the important trace elements arsenic, cadmium, chromium, copper, mercury, nickel and lead have been identified. Concentrations of these trace elements as a function of pH in the hypothetical pore water were calculated using mechanistic thermodynamical data.

The thermodynamical approach in this study seems justified because most solid residues that are either present or expected to form during weathering have relatively fast precipitation/dissolution kinetics.

Chemical Modelling of Pore Water Composition from PFBC Residues

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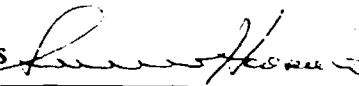
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Chemical Modelling of Pore Water Composition from PFBC Residues

Sammanfattning

Förbränning av kol i fluidiserade bäddar är numera en kommersiellt tillämpbar teknik för produktion av värme och elektrisk kraft. Dessa processer genererar stora mängder restprodukter som kommer att behöva deponeras. Vid deponering av restprodukterna finns det risk för att spårelement lakas ut och förorenar ytvatten och grundvatten.

Koncentrationen av spårelement i restprodukterna är beroende av vilken typ av kol som förbränns samt vilken typ av förbränningsprocess som används. Ett av de viktigaste spårelementen är kvicksilver på grund av dess giftighet och negativa påverkan på ekosystemet. Halter av kvicksilver och andra spårämnen i lakvatten från deponerade restprodukter kan beräknas genom termodynamisk jämviktsmodellering av de kemiska reaktionerna.

I detta arbete har de termodynamiska jämvikterna beräknats med geokemikoden EQ3NR. Fasta faser av huvudkomponenterna i restprodukten från PFBC, aluminium, kalcium och kisel har identifierats. Jämviktskoncentrationerna av dessa ämnen i ett hypotetiskt porvatten har beräknats i pH-intervallet 7-11. Den termodynamiska databasen till programmet EQ3NR har kompletterats med data för kadmium, kvicksilver och bly. Dessa data har hämtats från OECD/NEA:s termodynamiska databas samt från en sammanställning av Lindsay (1979).

Löslighetsbegränsande fasta faser för de viktiga spårelementen arsenik, kadmium, krom, koppar, kvicksilver, nickel och bly har också identifierats. Koncentrationerna av dessa ämnen i ett hypotetiskt porvatten har sedan beräknats som funktion av pH vid oxiderande och reducerande förhållanden.

Den termodynamiska metod som har använts i detta arbete är berättigad eftersom upplösning och utfällning av de fasta faser som antingen finns i restprodukterna initialt eller bildas i samband med vittring, har en relativt snabb kinetik.

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**Chemical Modelling of Pore Water Composition
from PFBC Residues**

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January

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1 BACKGROUND

Combustion of coal in fluidised beds is today considered to be an established and commercially available technique for power and heat production. In comparison with conventional combustion of coal, fluidised bed combustion (e.g. PFBC, Pressurised Fluidised Bed Combustion) has the advantage of reducing emission of sulphur dioxide and nitrogen oxides. The combustion process takes place in a fluidised bed consisting of coal and limestone.

Due to the introduction of a sulphur sorbent, the amount of solid residuals from a fluidised bed exceeds the amount from e.g. pulverised combustion. Furthermore have the residuals different physical and chemical properties. At present, little is known of the extent of contamination of surface water and groundwater originating from land disposal of e.g. PFBC residues. The electricity producer is interested in knowing how and when leachates from the residues will affect the environment and how it if necessary, can be controlled.

Laboratory studies have shown that under certain solution conditions many toxic elements are leached in amounts exceeding recommended drinking water standards.

Existing methods of studying the leaching behaviour of fossil fuel residues identify elements empirically as either readily soluble or rather insoluble. One disadvantage of empirical methods is the inability to make reliable predictions of the leaching behaviour for environmental conditions other than those used in the experiments. An additional disadvantage is the lack of knowledge of the chemical reactions that control the observed concentrations.

The amounts leached from solid residues are dependent on the chemical form in which the residues are present and the composition of the aqueous medium. The two main processes that control the geochemical behaviour of elements are precipitation/dissolution and adsorption/desorption.

The possibility to give answer to the questions on leaching depends on our ability to understand the hydrologic processes and the geochemical reactions that result in chemical migration. Movement of water through a disposal of coal residues lead to dissolution of trace elements. Contamination of surface waters and groundwater by trace elements depends on the distribution of the trace elements between the mobile aqueous phase and the immobile solid phase.

To accurately and quantitatively describe the leaching behaviour of elements in residues from PFBC and their subsequent interactions with geologic media, a mechanistic approach and thermodynamic data are required. One tool which can be used to assess the geochemical interactions of elements from deposited residues with soil matrix and ambient groundwater is a geochemical code like EQ3NR.

2 PFBC RESIDUES

2.1 Introduction

Fossil fuel residues contain many chemical constituents, some of which may become mobile and adversely affect groundwater. A large volume of empirical data on the chemical characterisation of fossil fuel residues is available, e.g. Ainsworth (1987) and Nilsson (1987). These data pertain primarily to the total elemental content of the residues and the distribution of the elements in different particle size fractions or within a given particle.

The chemical characterisation of the collected residue samples consists primarily of the total elemental composition determined by energy dispersive x-ray fluorescence analysis and analysis of solutions from different leaching experiments. The chemical composition of coal ashes depends primarily on the composition of the coal and the applied technique for the coal combustion.

2.2 Total Concentrations of Major Elements in PFBC Residues

Coal ash from pulverised coal combustion consists of a mixture of amorphous glass and crystalline phases and some unburnt material.

The main components are:

- Aluminium silicate glass SiO_2
- Mullite $3\text{Al}_2\text{O}_3-2\text{SiO}_2$
- Hematite Fe_2O_3

From materials introduced in the PFBC combustion come:

- Calcium sulphate CaSO_4
- Calcite CaCO_3

In the case of PFBC a mixture of pulverised coal and lime (calcite) forms a bed that is fluidised in a gas stream. The amount of calcite fed to the combustion depends on the sulphur content in the unburnt coal, and the calcite-coal ratio is usually in the range of 5-15%.

For optional sulphur capture, pressurised fluidised bed combustion is conducted at a temperature of about 850 °C. This temperature is much below the temperatures reached during conventional combustion of coal. Therefore, melting of most inorganic constituents does not occur and formation of glasses is reduced. On the other hand, PFBC combustion can contribute to the formation of calcium compounds in the ash.

Chemical analyses of residues from combustion of coal from two different sources are given in Table 2.1 (Nilsson 1987).

Table 2.1 Chemical analyses (wt.%) of PFBC residues.

Major oxides	Polish coal		American coal	
	Bottom ash	Fly ash	Bottom ash	Fly ash
CaO	18.8	19.9	35.3	25.3
SiO ₂	36.2	33.8	15.0	29.4
Al ₂ O ₃	15.6	13.7	5.7	15.6
Fe ₂ O ₃	4.8	6.5	2.6	7.6
K ₂ O	1.9	1.5	0.7	1.5
Na ₂ O	0.4	0.4	0.2	0.4
SO ₃	8.0	9.4	14.6	9.8
CaO (free)	0.5	1.3	0.4	2.3

2.3 Total Concentration of Some Trace Elements in PFBC Residues

The concentration of trace elements in the coal combustion residues is primarily dependent on the source of the coal, the type of combustion process and the combustion parameters.

The trace elements in the coal can be classified into four classes based on their affinities and tendencies to occur in minerals (Wu 1987).

Class 1

Litophile elements associated with aluminosilicate minerals in coal

Class 2

Calcophile elements generally present in coal as sulphide minerals

Class 3

Volatile elements

Class 4

Unclassified elements exhibiting properties of either Class 1 or Class 2

Most trace elements in coal are present as aluminosilicates, inorganic sulphides or organic complexes. The aluminosilicates are not decomposed during combustion but rather melt and coalesce to form slag and fly ash. During the initial state of combustion, a reducing environment probably exists within the coal particles and their surrounding environment. The chemical bonds between the metallic elements and the sulphur (in sulphide mineral inclusions) as well as the organic matrix are broken. These elements can then form volatile species which may condense or be adsorbed on fly ash particles when the temperature drops or be oxidised in the gas stream from the combustion process and form less volatile species.

The number of trace elements in coal/coal ash is quite large. This study, however, has concentrated on some of the most important: arsenic, cadmium, chromium, copper, lead,

mercury and nickel. Of these arsenic, cadmium, copper, mercury and lead can be classified as Class 2 elements while chromium and nickel occur in the coal as sulphides or as silicates.

Because of the dilution effect of sorbent added in the PFBC process, the concentrations of metals, are usually smaller (except for calcium) in PFBC residues than in residues from conventional combustion. Generally, most trace elements are found in the fly ash due to the vaporisation-condensation mechanisms.

Chemical analysis of trace metals from two different coal sources are given in Table 2.2 (Nilsson 1987).

Table 2.2 Metal concentrations (mg/kg) in bottom ash and fly ash

Metal	Polish coal		American coal	
	Bottom ash	Fly ash	Bottom ash	Fly ash
As	48	129	186	85
Cr	159	163	50	139
Cu	105	195	143	293
Ni	119	168	108	403
Pb	173	267	65	337

2.4 Chemical Properties of PFBC Solid Residues

Many residue characteristics, such as the pH, Eh, solid phase composition, complexing ligands, competing ions and gaseous phase, influence both precipitation/dissolution and adsorption/desorption reactions. These reactions in turn influence the pore water composition.

The composition of the solid phase is the most important residue property, because it controls, through the solubility, the aqueous concentration of inorganic elements and the precipitation of secondary solid phases.

Elements, present in major amounts in the solid residue, such as iron oxides, silicon-aluminium oxides, provide large reactive surface on which adsorption/desorption of aqueous species can occur.

The concentrations of major elements in PFBC residues (e.g. aluminium, calcium, iron, sulphur and silicon) are likely controlled by precipitation/dissolution reactions. As the kinetics of these reactions are rapid (Rai 1988), concentrations of these elements can be evaluated using thermodynamic data.

The major elements are mainly present in unweathered residues in the form given below (Nilsson 1987 and Rai 1987b):

Al as Al_2O_3 and Al-silicates
 Ca as CaSO_4 , CaO and CaCO_3
 Fe as Fe_2O_3

S as Sulphates

Si as SiO₂ and silicates

These compounds determine the chemical environment in the residue.

Precipitation and dissolution of the trace elements are the primary chemical processes that must be understood in order to predict their mobility from a disposal of residues. Based on the mode of dissolution, the trace elements in coal ash can be divided into four categories (Wu 1987):

- The by pH controlled group. This group consists of residue elements that form compounds with hydroxides, oxides or anions of weak acids.
- The oxidisable group. Elements in this group can be further oxidised because of incomplete combustion.
- The reducible group. To this group belong metals in higher oxidation states which are soluble only under reducing conditions.
- The residual group. Metals in this group are associated with the aluminosilicate lattice and are not "leachable".

In addition to these primary processes there are also secondary processes such as speciation of elements into several aqueous forms, of which some are in different oxidation states. The problem rapidly becomes complex enough to require a computer code to evaluate the speciation and mobility.

3 CHEMICAL MODELLING OF AQUEOUS SOLUTIONS

3.1 Types of Chemical Models for Aqueous Systems

Computerised chemical models are today almost necessary tools for the interpretation of chemical processes in aqueous systems and the interaction between water and solid materials. Such models can help in identifying geochemical processes that control the concentration of dissolved constituents and may also assist in quantifying the effects of temperature, speciation, sorption and solubility on the concentrations of dissolved constituents. An understanding of these phenomena, when applied to the issues of the disposal of coal residues, can also be of importance in the evaluation and the analysis of impact on the environment.

Two types of geochemical models exist; *the speciation-solubility models* and *the reaction path models*. The speciation-solubility model calculates the distribution and activities of species on the assumption that equilibrium exists throughout the aqueous phase. The model also tests the hypothesis that certain of the dissolved constituents in the water are in equilibrium with particular solid phases. The model then solves directly for the final equilibrium state from the initial, specified conditions, i.e. the mass is transferred from an initial state to a final equilibrium state. Finally, the models compute an estimate of the closeness to equilibrium of dissolved constituents and solid phases.

Reaction path models attempt to predict the resulting composition of a system when a quantity of water of given chemical composition reacts with a given quantity of a particular mineral or mineral assemblage. A reaction path model solves for the final equilibrium state by working through the entire reaction process in iterative steps. It transfers mass between one or more solids of a stated chemical composition and the aqueous phase as a function of the progress of the reaction.

3.2 The EQ3NR Computer Code

EQ3NR (Wolery 1983) is a speciation-solubility code, whose function is to compute a model of the thermodynamic state of an aqueous solution. The distribution of aqueous species in the solution is calculated by solving the equilibrium equations for a set of master aqueous species. This code is very flexible in terms of the input that it will accept.

The speciation calculation is based on thermodynamic equilibrium constraints. The thermodynamic data are read by EQ3NR from a supporting data file DATA1 and alteration or suppression of these data can be selected by the user on the input file for EQ3NR. EQ3NR uses the B-dot equation for electrically charged species to approximate the activity coefficients of aqueous species and an expression suggested by Helgesson (1969) for neutral aqueous species to estimate the activity of water.

Input may consist of analytical measurements, assumptions (such as that the fluid is in equilibrium with specified minerals), or some mixture of measurements and assumptions. The output contains the distribution of aqueous species, their thermodynamic activities and saturation indices for various solids. If the input contains the assumption that the fluid is saturated with a certain mineral, the output also gives the total concentration of an element

that forms part of that mineral. The output also normally includes a calculation of the electrical balance of the fluid, which is a useful indicator of the quality and completeness of aqueous solution analyses.

The EQ3NR computer code is capable of calculating, on the basis of thermodynamics, possible types of minerals that will be formed, causing their constituent elements to be immobile, or dissolve and thus being mobile. To determine which solids are most likely to form, the most possible stable solids can be selected from the data base by comparing saturation indices predicted by the code.

4 THERMODYNAMIC DATA

4.1 Introduction

Equilibrium constants for chemical equilibria are the bases for calculating chemical equilibria. There are several important factors to consider for the thermodynamic data that support geochemical modelling calculations pertaining to aqueous solutions. The most important is the number of species represented. The greater number, the more likely that all the important species will be represented in a given application. Another important factor is that any set of supporting data would be both accurate and internally (i.e. thermodynamically) consistent. The data in the database should also be well documented internally or externally. The database should allow modelling over a useful range of temperature.

The original database of EQ3NR contains 670 aqueous species and 650 minerals, including 50 elements, and it supports calculations over the temperature range 0-300 °C. The consistency of most of the important data are well documented. The database is also documented internally by the inclusion of references in the related data file package MCRT.

4.2 KEMAKTA EQ3/6 Thermodynamic Database

The KEMAKTA EQ3/6 Thermodynamic Database for the EQ3NR geochemical code was mainly obtained from the EQ3/6 program package (Wolery 1983). Most of the thermodynamic data in the database for aqueous redox reactions, involving the major geochemical elements Na, K, Ca, Mg, Al, Fe, Si, O and H, are generated from the SUPCRT program/database (Helgeson and Kirkham 1974, a, b, 1976). A significant number of log K values for aqueous complex dissociation involving these and other elements are taken from Helgeson (1969).

The internal database of EQ3/6 is regularly updated. The KEMAKTA version of the EQ3/6 Thermodynamic Database is based on DATA0 3245R48 in MCRT.

The KEMAKTA EQ3/6 Thermodynamic Database includes those aqueous species, redox couples, solids and gases that contain elements that are present in residues from coal combustion and which are of environmental concern. In Table 4.1 a number of elements have been selected from the complete KEMAKTA database on the basis of their presence in residues from coal combustion and of their environmental importance. The table also includes elements, though not present in the ashes, that are present in geochemical systems and may therefore affect the composition of natural waters or leachates from land disposed coal residues. The table also lists the formula for the basic species of each element in the thermodynamic database.

Table 4.1 Elements and basic species in the KEMAKTA EQ3/6 thermodynamic database

Element	Master Basic Species, and Auxiliary Basic Species:	
Ag	Ag^+	
Al	Al^{3+}	
As	$\text{As}(\text{OH})_4^-$	AsO_4^{3-}
Au	Au^+	
B	$\text{B}(\text{OH})_3$	
Ba	Ba^{2+}	
Br	Br^-	
C	HCO_3^-	$\text{CH}_4(\text{aq}), \text{CO}_2(\text{aq}), \text{CO}_3^{2-}, \text{CH}_3\text{COO}^-$
Ca	Ca^{2+}	
Cd	Cd^{2+}	
Cl	Cl^-	
Co	Co^{2+}	Co^{3+}
Cr	Cr^{3+}	$\text{Cr}^{2+}, \text{CrO}_4^{3-}, \text{CrO}_4^{2-}$
Cs	Cs^+	
Cu	Cu^+	Cu^{2+}
F	F^-	
Fe	Fe^{2+}	Fe^{3+}
H	H^+	$\text{H}_2(\text{aq})$
Hg	Hg^{2+}	Hg_2^{2+}
I	I^-	
K	K^+	
Li	Li^+	
Mg	Mg^{2+}	
Mn	Mn^{2+}	
N	NO_3^-	$\text{NO}_2^-, \text{NH}_4^+$
Na	Na^+	
Ni	Ni^{2+}	
O	$\text{O}_2(\text{g})$	$\text{O}_2(\text{aq})$
P	HPO_4^{2-}	
Pb	Pb^{2+}	Pb^{3+}
Ra	Ra^{2+}	
Rb	Rb^+	
S	SO_4^{2-}	HS^-
Se	SeO_3^{2-}	$\text{Se}^{2-}, \text{SeO}_4^{2-}$
Si	$\text{SiO}_2(\text{aq})$	
Sn	Sn^{3+}	Sn^{2+}
Sr	Sr^{2+}	
U	U^{4+}	$\text{U}^{3+}, \text{UO}_2^+, \text{UO}_2^{2+}$
V	V^{3+}	$\text{VO}^{2+}, \text{VO}_4^{3-}$
Zn	Zn^{2+}	

The thermodynamic database includes chemical speciation reactions and precipitation reactions for the trace elements of interest and also other major elements whose chemical properties affects the behaviour of the trace elements.

In the work of improving the KEMAKTA EQ3/6 Thermodynamic Database described in Appendix 1, cadmium and mercury have been included as new elements. 45 aqueous cadmium species and 19 aqueous mercury species were added together with 33 mineral cadmium species and 12 mineral mercury species.

Additional data for lead minerals and aqueous species were also added to the already existing lead species and the database now contain 38 aqueous and 71 mineral lead species. Some of the already existing species in the database with doubtful data e.g. $\text{Pb}_3(\text{OH})_5^+$ are either excluded from the database or have had their data exchanged for more recent data.

The thermodynamic data for aqueous species, redox couples and solids, except those that contain cadmium, have been taken from the Thermodynamic Database of OECD/NEA. The NEA database does not contain a critical review of the original references describing the experimental measurements from which the data were derived. The NEA compilation lists the fundamental thermodynamic constants measured for different compounds: i.e. Gibbs energy of formation, enthalpy of formation, entropy and heat capacity. The data represents a wide compilation based on individual results extracted from the literature. Several sets of values are listed for the same compounds or reaction but single recommended values are not given. The thermodynamic data extracted from the database were from commonly accepted and well known sources, primarily from the 1982 National Bureau of Standards compilation (Wagman 1982). The thermodynamic data for cadmium species were taken from a compilation made by Lindsay (1979).

A complete set of all aqueous species, minerals and gases included in the KEMAKTA EQ3/6 Thermodynamic database is found in Appendix 2.

5 CALCULATIONS

5.1 Chemical Modelling of the Main Components in PFBC Residues

The characteristics of the solids present in the PFBC residues depend primarily on the nature of the inorganic compounds in the source materials, coal and lime, and the transformations that take place during the combustion process. Due to relative low combustion temperature in the PFBC-process, the noncombustible portion of the coal will be less affected than is the case in conventional combustion processes. The existing process temperature in a PFBC unit will, however, cause a series of reactions involving the minerals in the coal. Of the major mineral groups, only quartz is not altered (Wu 1987).

Clay minerals:

The water is lost during combustion.

Sulphide minerals:

The sulphide minerals are oxidised to metal oxides and sulphur dioxide.

Carbonate minerals:

The carbonate minerals are converted mainly to oxides and carbon dioxide, except for CaCO_3 .

The major solids formed containing aluminum, are expected to be glass and mullite. Iron is primarily present in the coal as sulphide and is converted to ferric oxide and sulphur dioxide. Trace of calcium carbonate is converted to CaO which in a second step reacts with sulphur dioxide to form calcium sulphate (Rai 1987a, 1988). As the coal ash consists of hollow spheres with very thin walls and vesicles, this results in large surface areas. Hence the major elements in PFBC residues should easily be accessible to leaching. The general equilibrium approach should then be applicable in describing the behaviour to leaching of most elements in PFBC residues.

The main purpose with the study was to model leaching of PFBC residues consisting of a mixture of pure solids including the major elements produced as result of the coal-burning process and to identify the solubility controlling minerals in the pH-range 7-11. This pH interval was chosen because it is believed that after disposal of PFBC residues, the presence of alkali oxides and calcium carbonate will for a very long period of time buffer the infiltrating leachate and thus stabilise the pH within that interval.

In order to perform the modelling a hypothetical pore water was selected from empirical leaching studies (Liem 1983). Only the major elements (Al, Ca, Fe, Si), alkali metals (Na, K, Mg) and anions like chloride, sulphate and carbonate were included in this hypothetical pore water. No trace element were contained in this part of the modelling due to the fact that they are present in low concentrations in the residue and will therefore not influence the chemical environment.

The composition of the pore water is given in Table 5.1

Table 5.1 Composition of hypothetical pore water used in the modelling of major elements.

Element	Concentration (mol/l)
Al	$6.3 \cdot 10^{-6}$
Ca	$2.2 \cdot 10^{-2}$
Mg	$8.0 \cdot 10^{-7}$
Fe	$2.1 \cdot 10^{-6}$
Na	$4.2 \cdot 10^{-4}$
K	$1.2 \cdot 10^{-4}$
Si	$1.6 \cdot 10^{-5}$
S	$1.0 \cdot 10^{-2}$
C	$1.7 \cdot 10^{-2}$
Cl	$2.2 \cdot 10^{-3}$

5.2 Chemical Modelling of Trace Elements in PFBC Residues

Trace elements or chemical compounds containing trace elements in the coal entering the PFBC process may be transformed in two ways at the combustion. They may be vaporised or oxidised. The vaporised elements will either condense on existing particle surfaces or escape into the air. Some trace elements may also pass through the combustion process without any transformation.

As sulphates do not originally exist in coal but are formed during the combustion, they can deposit on the outer layer of coal ash particles and thus become more readily soluble. Trace metals deposited on the coal ash particles may also be combined with sulphite, carbonate, halides and oxides. It can therefore be assumed that many trace elements in the PFBC residue are readily accessible to a leaching solution and will rapidly reach steady state concentrations. If the solubility-controlling solid of an element is present in the residue or if such a solid can precipitate when the leaching water get in contact with the waste, the aqueous concentrations of the element can be predicted from the precipitation or dissolution reactions and the associated thermochemical data. This thermodynamical approach is therefore made assuming that the kinetic effects are negligible and that the chemical equilibrium primarily control the aqueous concentrations of the elements.

Knowledge of the redox conditions in disposed PFBC residues is essential in order to make a proper characterisation of the chemical environment. Both oxidising and reducing zones can occur in the various micro-environments in the residue, due to the mixture of oxidised elements from the combustion and unburnt coal particles. It has also been stated that the assumption that all redox reactions in an aqueous system are in a state of thermodynamic equilibrium is inaccurate for real systems, including all natural systems (Stumm 1981). Consequently there are many parameters determining the redox state inside a repository

containing PFBC residues. The most important parameter is the design of the soil cover, which will control the access of oxygen to the residues.

The redox transformations among the trace elements can be evaluated by the EQ3NR code. Because of lack of information on the redox potential in the present system, we have arbitrarily used the approach that the system is either at a reducing state or at an oxidising state. The reducing state is given by the normal potential of the redox pair $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ at 25°C.

$$\text{Eh} = 0.2 - 0.059 \text{ pH}$$

The oxidising state is calculated for a system in equilibrium with oxygen. The redox potential is then given by:

$$\text{Eh} = 0.8 - 0.059 \text{ pH}$$

When modelling the trace elements, the hypothetical pore water according to Table 4.1 has been used with the exception that the concentrations of magnesium and calcium were assumed to be equal, $5 \cdot 10^{-3}$ mol/l. The reason for this was the wish to make a comparison between the solubilities of the calcium and magnesium arsenates. The solubility limiting phases and the dominating species for the trace elements arsenic, cadmium, chromium, copper, lead, mercury and nickel hypothetical pore water were then identified.

ARSENIC

Arsenic is in the coal primarily associated with metals in the form MAs or MAs_2 ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ etc) or is present as As_2S_3 and As_4S_4 . The valences +3 and +5 are the only important valence states in aqueous solution (Rai 1986).

The content of arsenic reported for bulk samples of coal ash residues varies considerably. Generally, fly ash contains more arsenic than other combustion residues because volatilisation of arsenic during combustion results in condensation of arsenic solids, primarily on the fly ash particles.

Arsenic in the leaching water from PFBC residues indicates the presence of As_2O_3 or soluble arsenates in the coal ash (Wu 1987). These solid phases has melting points in the range of 200 to 300°C and they are therefore probably produced after the combustion and are not primary solid phases.

Secondary As-containing solids that might be produced during the weathering of residues are expected to be in the form of metal arsenates such as $\text{Ca}_3(\text{AsO}_4)_2$ and $\text{Mg}_3(\text{AsO}_4)_2$.

CADMIUM

Cadmium is mainly associated with sulphide in the coal, while a small fraction is organically bound (Rai 1987a). Organically bound cadmium is reported to be volatilised during combustion (Smith 1980).

As elements that are vaporised during combustion condense on particle surfaces when the temperature has decreased in the flue gas dust before the baghouse filter, this implies that the cadmium content in the fly ash is higher than in the bottom ash. The surface deposit of cadmium on the fly ash particles is supposed to be primarily CdO (Rai 1987).

Most of the cadmium in PFBC residues is found in the residual fraction after leaching because of the connection of cadmium to the glassy matrix. This has been confirmed by leaching of coal ash in columns where the concentration of cadmium in the leachate after an initial flush decreases until a constant low level is reached (Liskowitz et al 1983).

CHROMIUM

Chromium exists initially in the coal in the +2 and +3 oxidation states, probably as the sulphides CrS and Cr₂S₃. At the combustion it is possible that an oxidation up to the +6 valence state occurs. Under moderately oxidising to reducing conditions Cr(III) minerals are expected to be less soluble than Cr(VI) minerals (Rai 1986). In general, the chromium existing in mineral form is not expected to be significantly volatilized during combustion and the chromium content reported for fly ash is much lower than that reported for bottom ash (Rai 1987). The concentration of chromium in leachates from a coal ash repository is governed primarily by the oxidation state of the chromium and the pH. Most of the chromium in residues from coal combustion is expected to be present as Cr(III) compounds, which forms low-solubility solids in aqueous environments. It has been reported that most chromium solid phases in PFBC residues are highly insoluble and can only be dissolved with strong acids (Wu 1987).

COPPER

Copper has a great affinity to sulphur and sulphidic minerals, Cu₂S, CuFeS₂, etc. (Hägg 1979). Copper in coal occurs principally as CuFeS₂. Smaller fractions of copper may also occur as other sulphidic solids and as oxides and carbonates (Rai 1987a).

Copper is not a volatile element and is thus not expected to be enriched on fly ash particles. In solution, copper exists in two oxidation states +1 and +2, dominating in reducing and oxidising conditions respectively. The solubility of the Cu(I) and Cu(II) solid phases depends upon the redox potential. The high percentage of copper in the leachate from PFBC residues with ammoniumacetate and acetic acid indicate that CuO is a possible solid phase (Wu 1987).

LEAD

Lead in coal occurs principally as PbS or in sulphide-poor coal as sulphate, carbonate and silicate. During combustion, lead tends to be volatilised to some extent, resulting in an enrichment on fly ash particles. Lead has also been reported to be associated with the glassy phases and metal oxides in the fly ash (Rai 1987).

The nature of Pb-solid phases in unweathered residue is not known and the existence of the expected solid PbO has not been confirmed by extraction studies due to the high solubility of this phase. Secondary solid phases will therefore probably limit the solubility.

When leaching PFBC residues with different leachants, according to the Successive Geochemical Fraction Scheme, up to 95% of the lead is found in the residual fraction (Wu 1987).

MERCURY

Mercury is also mainly linked to the sulphide content in coal. The high volatility of mercury at combustion temperatures causes much of the mercury originally present in the coal to leave the power plant stacks in the gaseous phase. Due to the high volatility and the resulting very low content of mercury in the residues essentially no quantitative data on the solid forms of mercury or the rates of mercury in the leachate from the residues are available in the literature.

With the introduction of the PFBC combustion technique with systems operating at low temperatures for cleaning the flue gases, the content of mercury in the residue is supposed to increase. Further knowledge is therefore needed regarding the chemical behaviour of mercury during natural weathering of especially PFBC residues.

The high volatility of mercury and mercury compounds imply that most of the mercury would be found on the particle surfaces in the fly ash fraction, due to condensing mechanisms. Small amounts of mercury have however been reported in bottom ash fraction (Rai 1987a). This is probably a result of residual concentrations that have passed through unaltered, perhaps as inclusions in other minerals.

NICKEL

Nickel is found in nature as sulphides and arsenides and in aqueous environments in +2 valence state. In coal nickel is linked to both the organic and the inorganic part of the coal. Inorganically bound nickel appears to be mainly in sulphide form (Rai 1987a).

During combustion, fractions of nickel may be partially volatilised, but the main part of the nickel is expected to be present as oxides and combined with the magnetic fraction. This is also confirmed by leaching experiments where the nickel concentration in extracts from coal combustion residues were found to be a function of pH, with lower pH values associated with higher nickel concentration (Ainsworth 1987).

Thermodynamic and solubility data indicate that the residual fraction from leaching of PFBC residues retains a very high portion of nickel, 98%, probably in the form as NiS, Ni₃S₄ and NiO (Wu 1987).

6 RESULTS

6.1 Major Elements

The primary solid phases for aluminium and silicon in unweathered coal ashes are reported to be aluminosilicate glasses (e.g. albite, $\text{NaAlSi}_3\text{O}_8$, and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$) and mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$, (Warren 1986). Upon weathering there is a possibility that secondary solid phases such as gibbsite, $\text{Al}(\text{OH})_3$, and quartz, SiO_2 , are produced. Results from the calculations, as given in Figure 6.1 and 6.2, show that the primary compounds, aluminosilicate glasses and mullite, of aluminium and silicon, in contact with the hypothetical pore water, would lead to higher solubilities than the secondary solid phases. Consequently the primary solid phases of aluminium and silicon in the residues are unstable and will, therefore dissolve to form secondary minerals, such as gibbsite and quartz.

As can be seen from Figure 6.1 the solubility of aluminium increases with increasing pH above pH 6 due to hydrolysis of aluminium. The calculated distribution of Al- and Si-species in the hypothetical pore water in equilibrium with $\text{Al}(\text{OH})_3$ and SiO_2 are shown in Figure 6.3 and Figure 6.4.

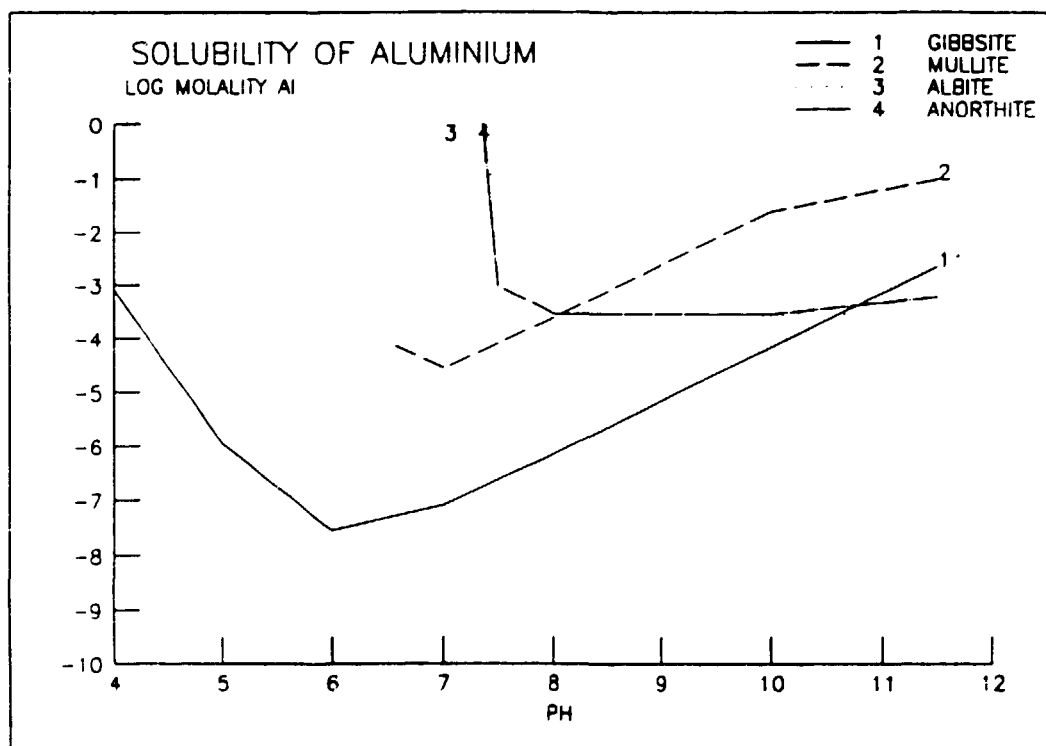


Figure 6.1 Solubility of primary and secondary Al-solid phases in a hypothetical porewater in PFBC residues.

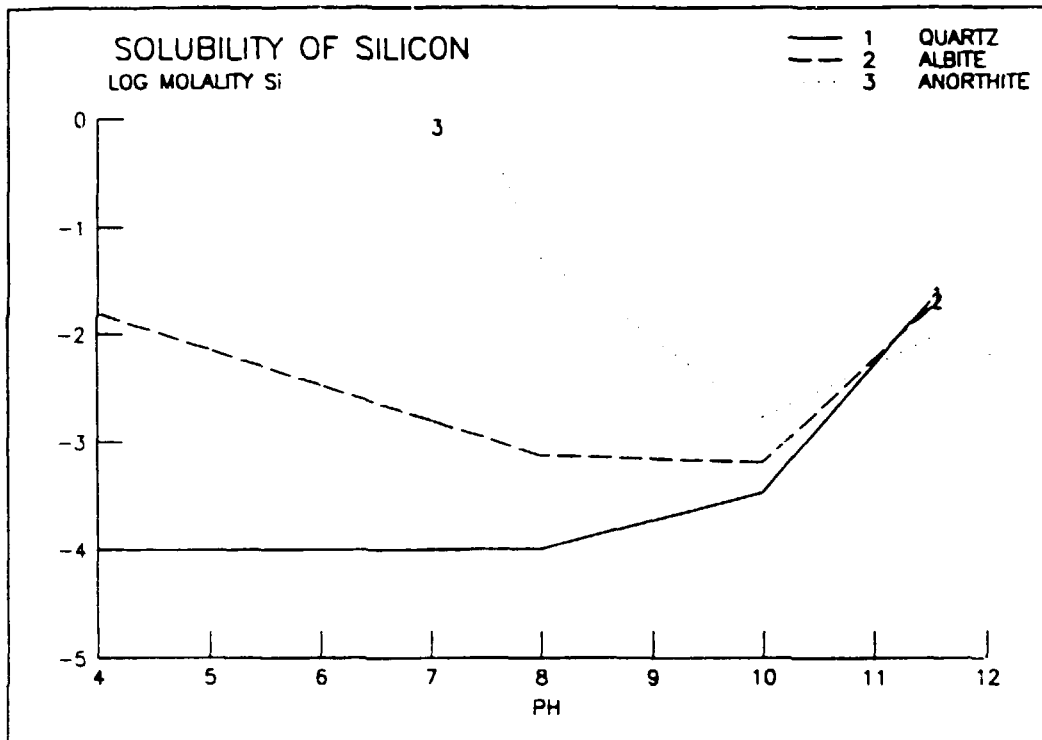


Figure 6.2 Solubility of primary and secondary Si-solid phases in a hypothetical porewater in PFBC residues.

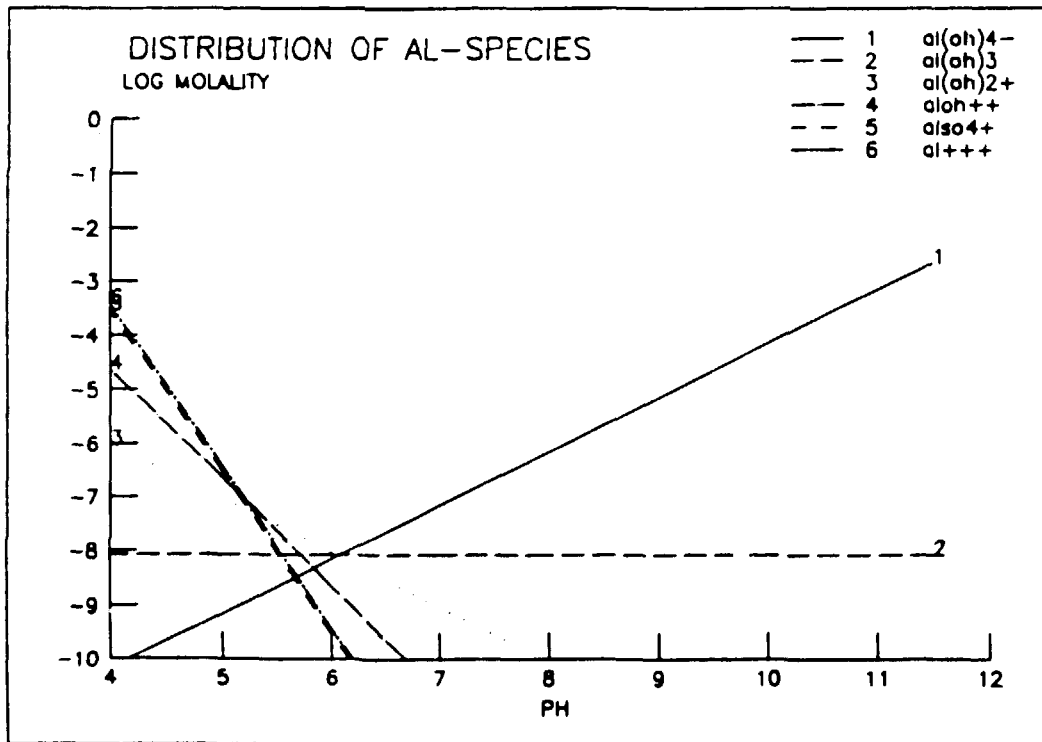


Figure 6.3 Distribution of major Al-species in a hypothetic pore water in PFBC residues.

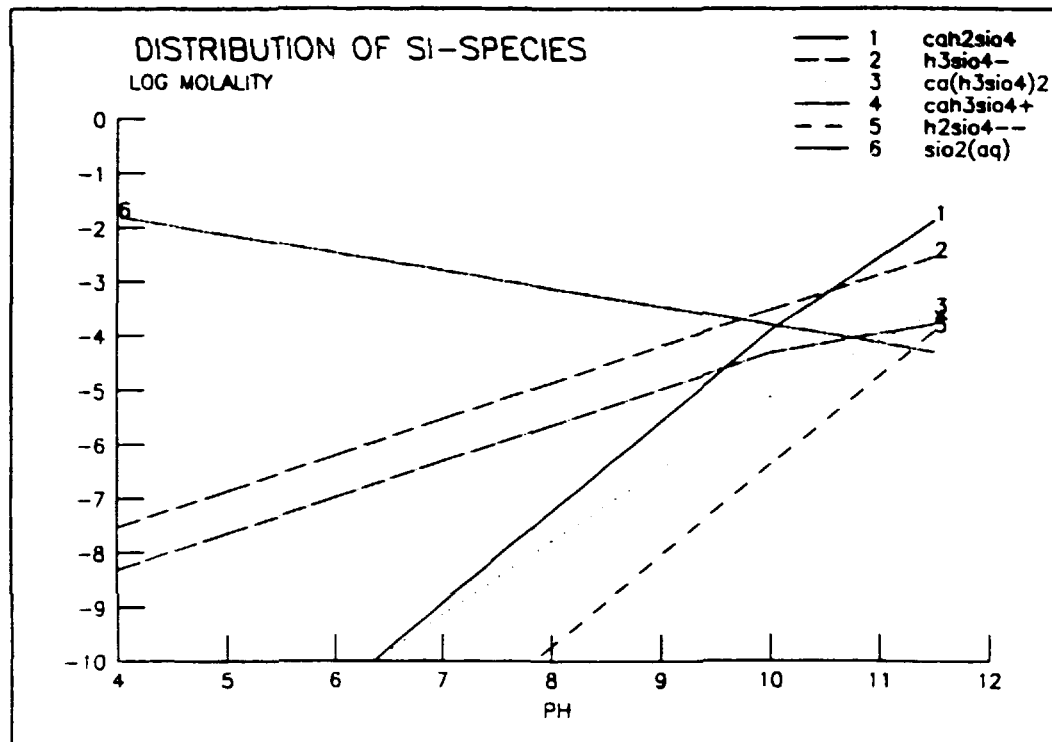


Figure 6.4 Distribution of major Si-species in a hypothetical pore water in PFBC residues.

The dominating primary Ca-solid phases in PFBC residues are probably CaSO_4 and unaffected CaCO_3 from the sorbent. Also some CaO may be present.

CaO and CaSO_4 are not stable in coal residues and secondary phases like portlandite, $\text{Ca}(\text{OH})_2$ and gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, are formed because of weathering (Rai 1987b).

The results from the solubility calculations of Ca-solids show, according to Figure 6.5, that calcite, CaCO_3 , limits Ca-concentration to approximately 10^{-4} M at pH greater than 9, and at pH 7-9 to less than 10^{-2} M. The calculations also show that portlandite has higher solubility than gypsum and is therefore not solubility limiting for calcium at pH 7-11.

The interpretation of the solubility calculations for calcium is that, due to hydrolysis, the primary solid Ca-phases are converted to portlandite and gypsum resulting in rather high calcium concentrations in the pore water. With the intrusion of CO_2 from the air, these high calcium concentrations will be lowered by the precipitation of calcite.

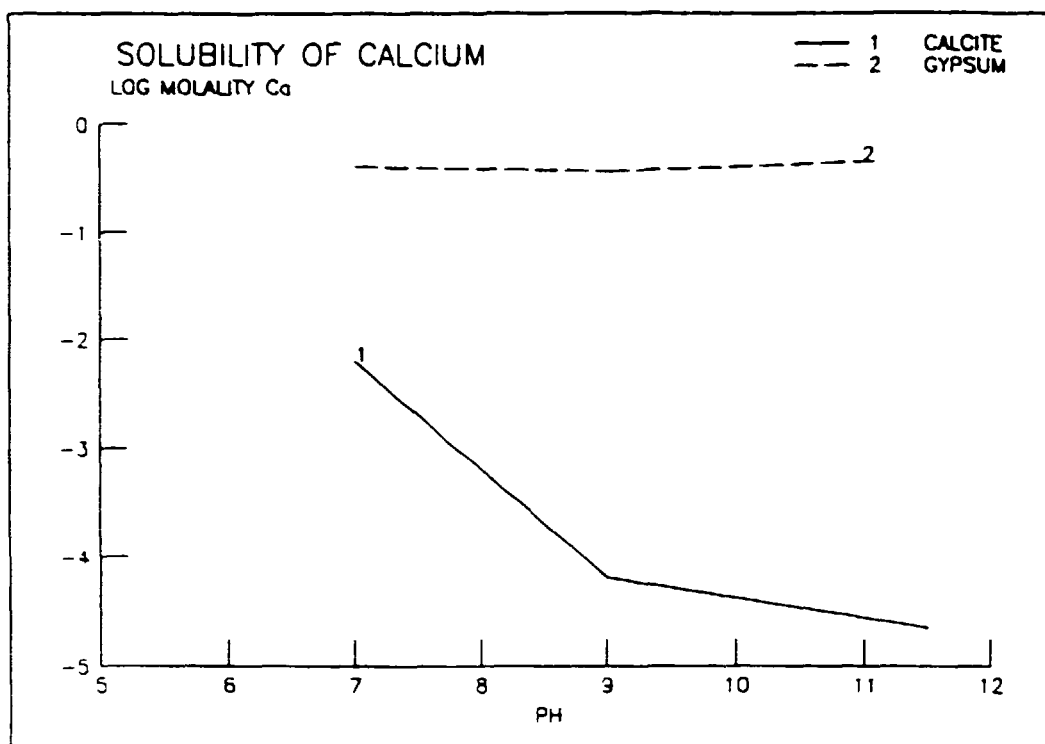


Figure 6.5 Solubility of Ca-solid phases in a hypothetical pore water in PFBC residues.

6.2 Trace Elements

The release of trace elements from PFBC residues depends on their chemical form in the primary solid phases in the unweathered residues and on their chemical speciation in the pore water. The trace elements may either precipitate as secondary solid phases or be present in the pore water.

The modelling of trace elements has been an attempt to identify possible solubility limiting phases for arsenic, cadmium, chromium, copper, mercury, lead and nickel in PFBC residues.

6.2.1 Arsenic

The solid phases for arsenic and their solubility are shown in Figures 6.6 and 6.7 at oxidising and reducing conditions. As can be seen from Figure 6.7, sulphide phases are almost completely soluble at high pH with decreasing solubility at decreasing pH. The arsenates, $\text{Ca}_3(\text{AsO}_4)_2$ and $\text{Mg}_3(\text{AsO}_4)_2$, show an opposite tendency. Initially the pH is high in the residues. As the arsenic sulphides will dissolve, it is possible that the arsenates will precipitate and limit the concentration of arsenic to 10^{-4} M (8 mg/l). With decreasing pH the concentration of arsenic will increase with increasing solubility of the arsenates.

At oxidising conditions the arsenates will constitute the primary solid phases and $\text{Ca}_3(\text{AsO}_4)_2$ or $\text{Mg}_3(\text{AsO}_4)_2$ will limit the concentration of arsenic to 10^{-3} - 10^{-4} M (8-80 mg/l) at high pH (Figure 6.6). With decreasing pH the concentration of arsenic will increase due to the dissolution of the arsenate-phases.

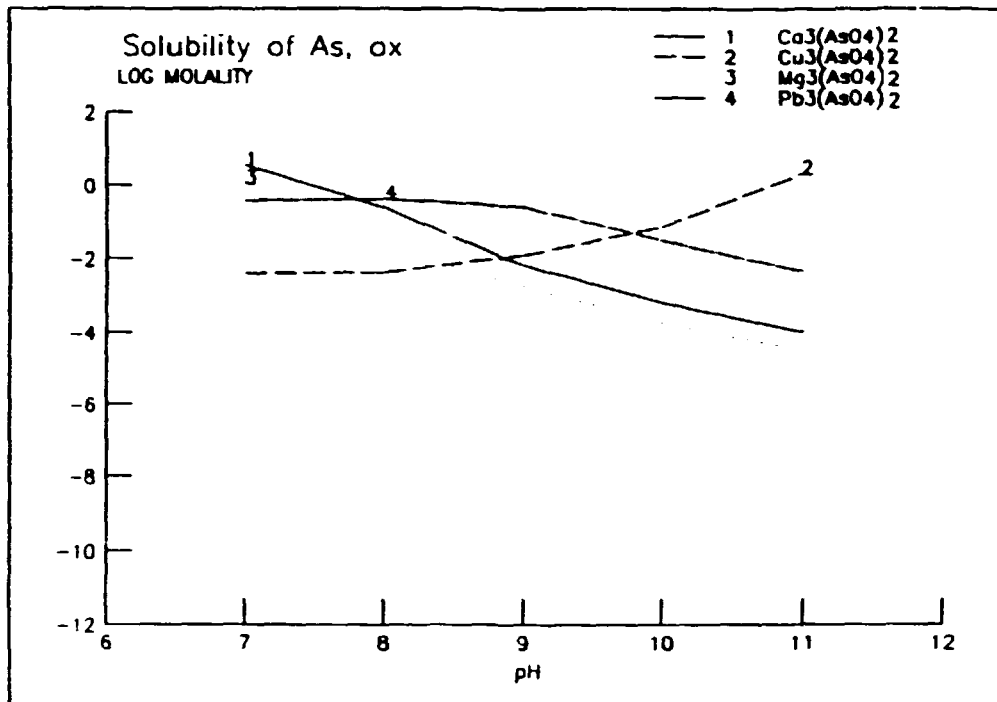


Figure 6.6 Solubility of As-solid phases at oxidising conditions in pore water from PFBC residues.

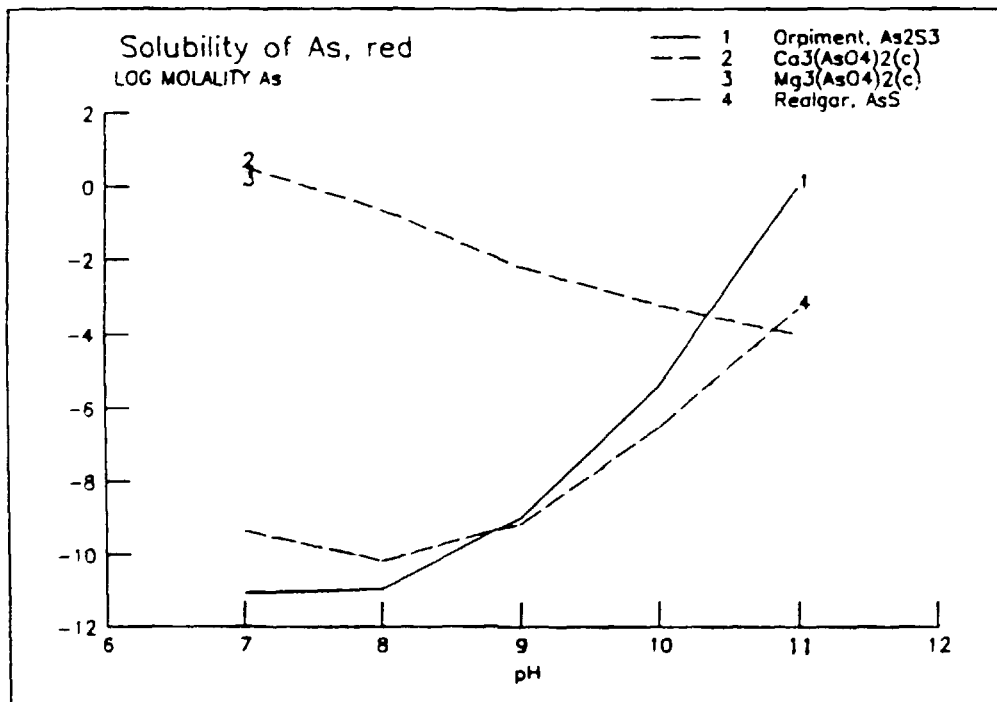


Figure 6.7 Solubility of As-solid phases at reducing conditions in pore water from PFBC residues.

6.2.2 Cadmium

The predicted solid cadmium species in unweathered residues is probably CdO, which, however, is highly soluble. This has been confirmed at the calculations. Due to hydrolysis and carbonisation reactions CdO may be converted to the possible solubility limiting phases Cd(OH)₂ and CdCO₃.

According to Lindsay (1979) the solubility of CdCO₃ (octavite) controls the concentration of dissolved Cd during neutral and basic conditions. If CdCO₃ is assumed to be the solubility limiting phase, the concentration of Cd will be less than 10⁻⁶ M (10⁻¹ mg/l) in the pH range 7-11 (Figure 6.8). A possible primary solubility limiting phase can also be CdSiO₃ according to Figure 6.8. Due to weathering reactions CdSiO₃ is probably converted to CdCO₃.

The increasing solubility of CdCO₃ at high pH depends upon hydrolysis reactions.

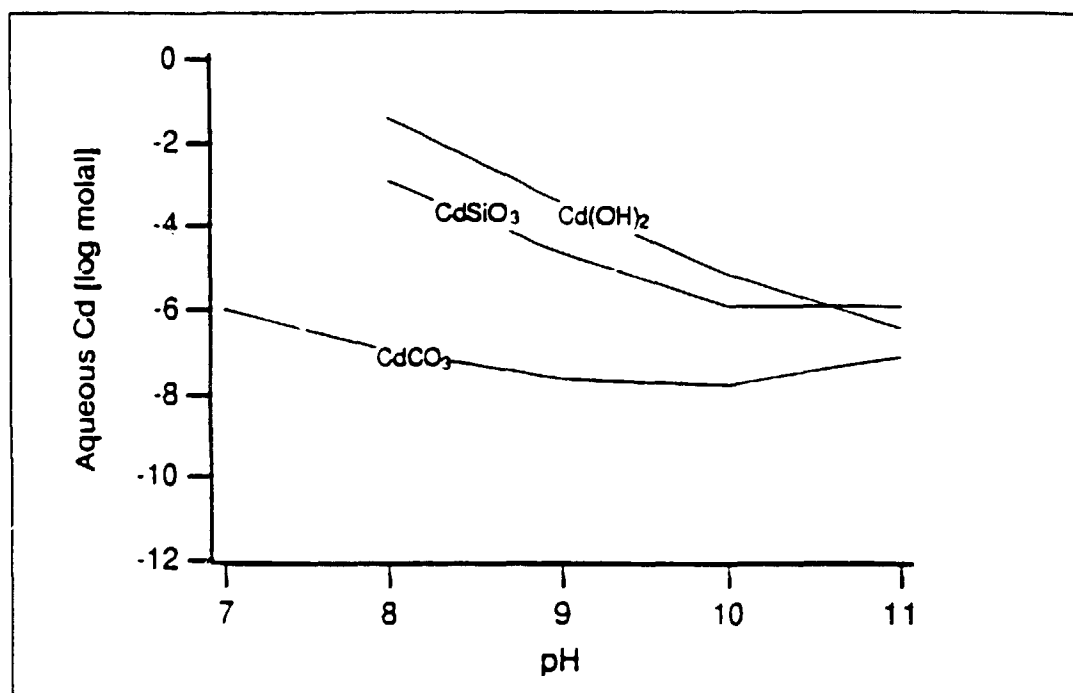


Figure 6.8 Solubility of Cd-solid phases at oxidising conditions in pore water from PFBC residues.

Solubility calculations at reducing conditions indicate that CdS can be expected to limit aqueous concentration of cadmium to 10⁻¹⁶ M at high pH (Figure 6.9) With decreasing pH the solubility will increase due to the formation of an Cd(HS)₂-complex.

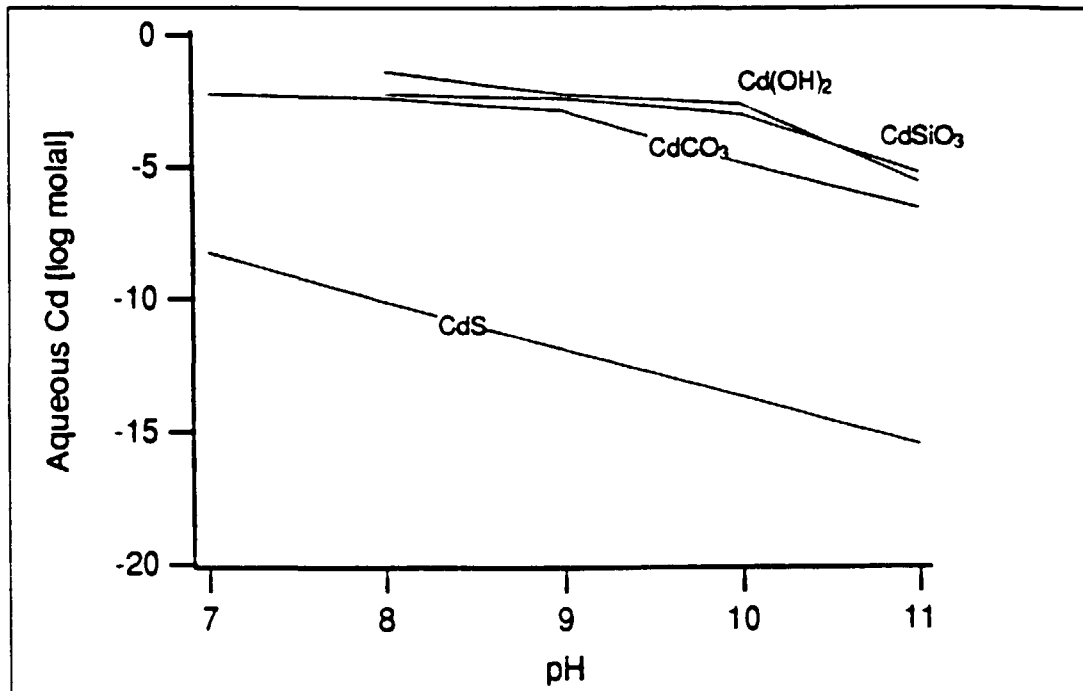


Figure 6.9 Solubility of Cd-solid phases at reducing conditions in pore water from PFBC residues.

6.2.3 Chromium

Chromium in coal is mainly associated with the mineral fraction and only a minor part is present in the organic fraction. The content of chromium in fossil fuel residue have been found to be enriched in the bottom ash fraction and is not expected to be significantly volatilised during combustion (Smith 1980).

The leaching behaviour of chromium depends primarily on pH and the oxidation state because of the vastly different solubilities of solids containing Cr(III) versus Cr(VI). Leaching studies from fossil fuel residues indicate that solubilities of Cr(III) solids will limit the total chromium concentration (Rai 1987a).

The solubility of Cr(III)-solid phases at reducing conditions are shown in Figure 6.10. At oxidising conditions no solid phases for chromium were identified. The solubility of chromium at reducing conditions is limited by oxide-phases like Cr_2O_3 , MgCr_2O_4 and CuCr_2O_4 . The concentration of chromium will be less than 10^{-12} M (10^{-4} $\mu\text{g/l}$) in the pH range 7-11.

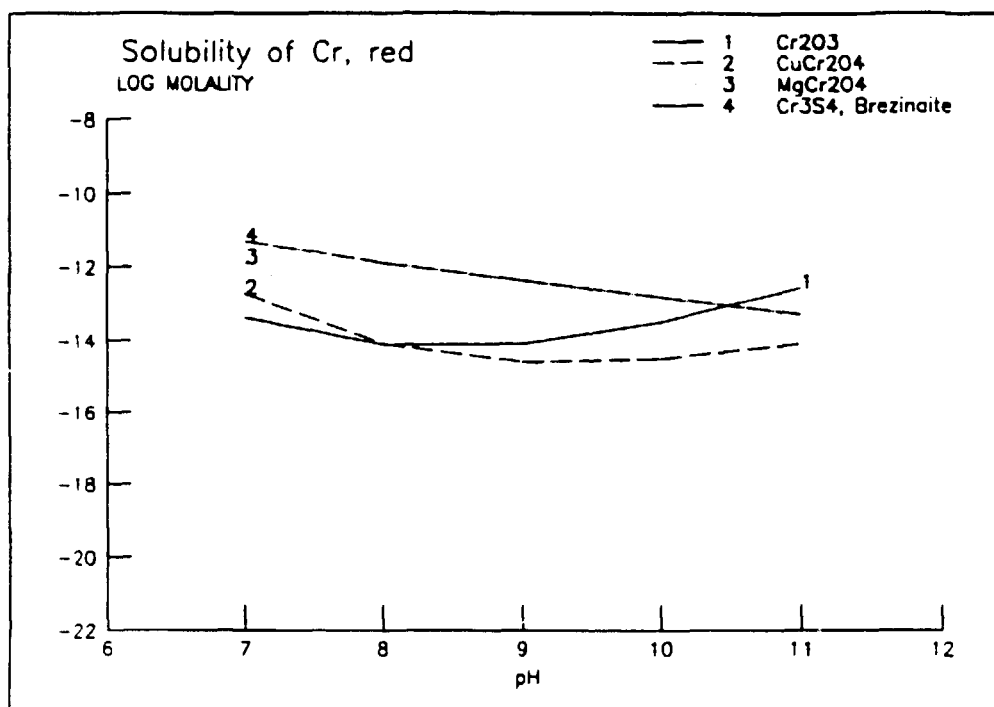


Figure 6.10 Solubility of Cr-solid phases at reducing conditions in pore water from PFBC residues.

6.2.4 Copper

In Figure 6.11 and 6.12 the Cu-solid phases are plotted at oxidising and reducing conditions, respectively. Under oxidising conditions, CuO would be the solubility controlling solid (Figure 6.11).

Copper sulphides present in the residues (Figure 6.12) as primary solid phases will be almost insoluble at reducing conditions. The major solubility limiting phases for copper will, however, probably be CuO/Cu₂O at reducing conditions, since only minor fractions of unaltered sulphide phases are expected in the residues.

The aqueous concentration of Cu due to dissolution of CuO will increase from 10^{-10} M ($6 \cdot 10^{-3}$ $\mu\text{g/l}$) at pH 11 to 10^{-6} M (60 $\mu\text{g/l}$) at pH 7 for both redox cases.

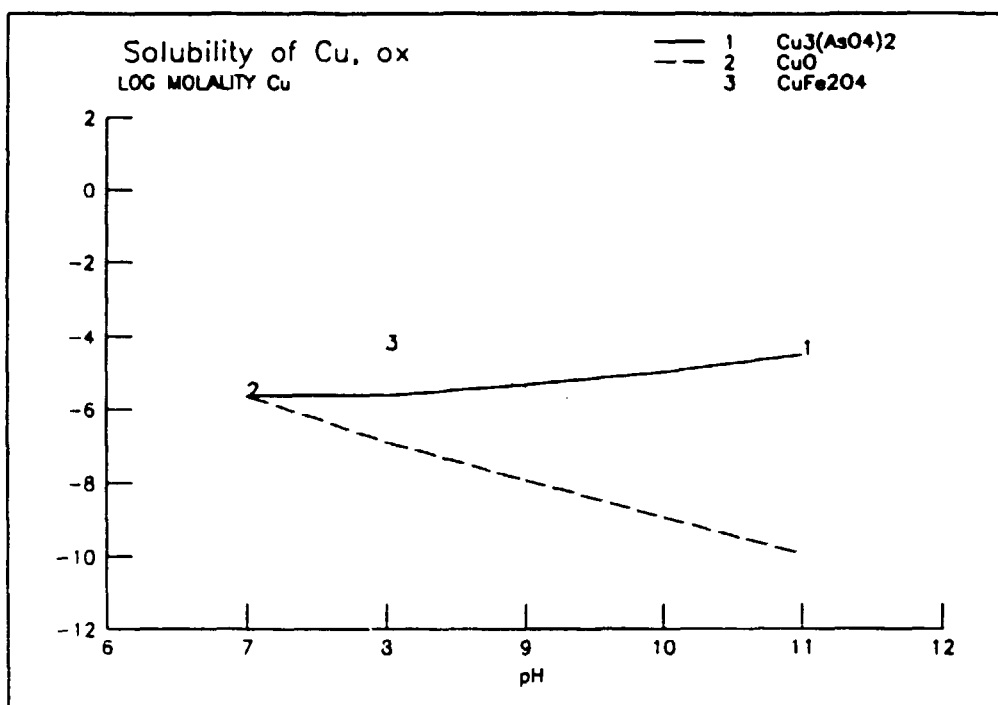


Figure 6.11 Solubility of Cu-solid phases at oxidising conditions in pore water from PFBC residues.

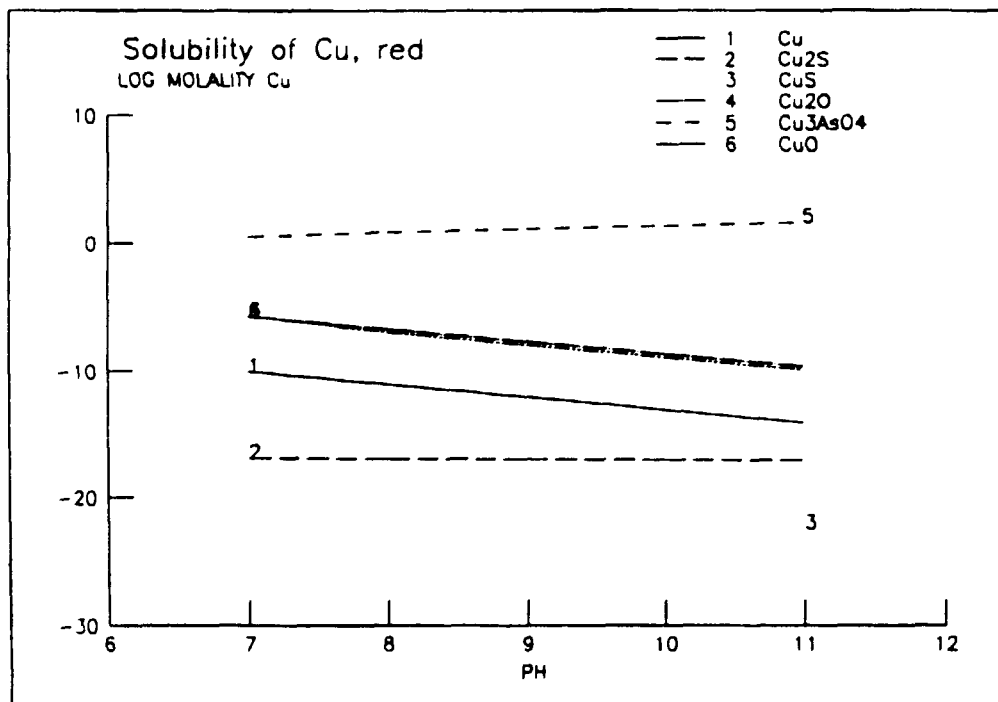


Figure 6.12 Solubility of Cu-solid phases at reducing conditions in pore water from PFBC residues.

6.2.5 Lead

The primary solid of lead that are formed during combustion and deposited on particle surfaces are too soluble to limit the concentration of lead in the pore water. The secondary phases that probably are formed due to weathering processes are $\text{Pb}(\text{OH})_2$ and PbCO_3 . Lead is also to a large extent associated with the interior of the glassy matrix of the residue and is therefore not accessible to the pore water.

The solubility limiting solid of the accessible phases at oxidising conditions will probably be $\text{Pb}(\text{OH})_2$ at high pH. The solubility will be limited to 10^{-6} M (0.2 mg/l) at pH 11. The solubility increases with decreasing pH to approximately 10^{-3} M (0.2 g/l) at pH 9 and the solubility limiting solid is probably then PbCO_3 (Figure 6.13).

Possible solubility limiting phases and their solubility at reducing conditions are shown in Figure 6.14. It is apparent that PbS has the lowest solubility in the considered pH range. The solubility of lead will be limited to 10^{-11} M (10^{-6} mg/l) at pH 11. With decreasing pH the solubility will increase to 10^{-5} M (1 mg/l) due the formation of sulphide complexes.

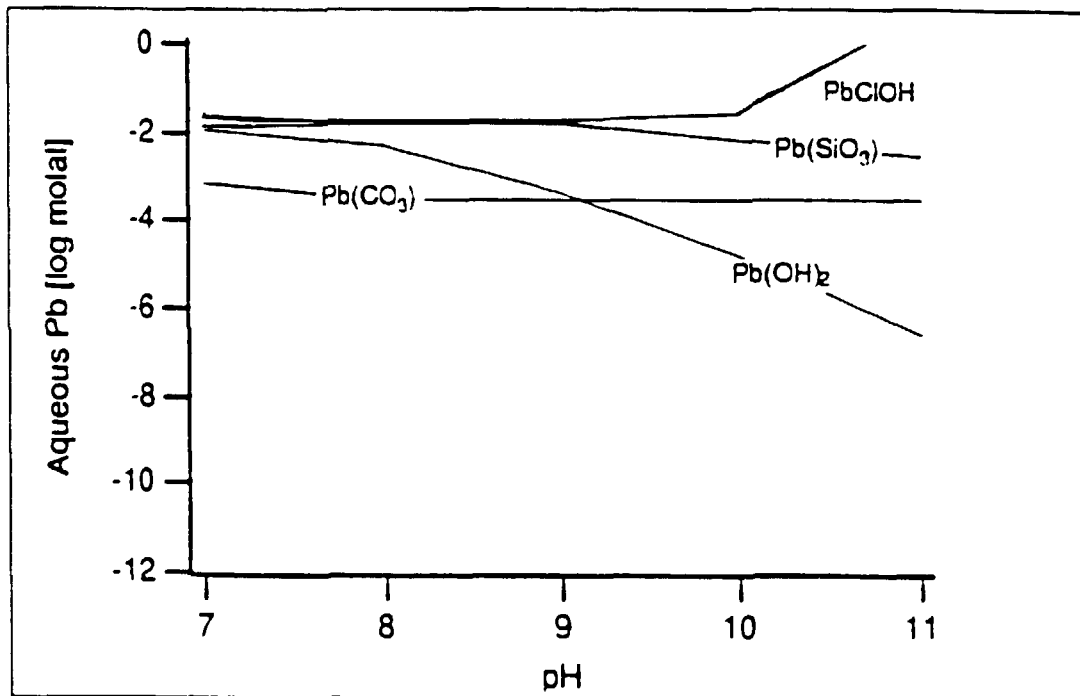


Figure 6.13 Solubility of Pb-solid phases at oxidising conditions in pore water from PFBC residues.

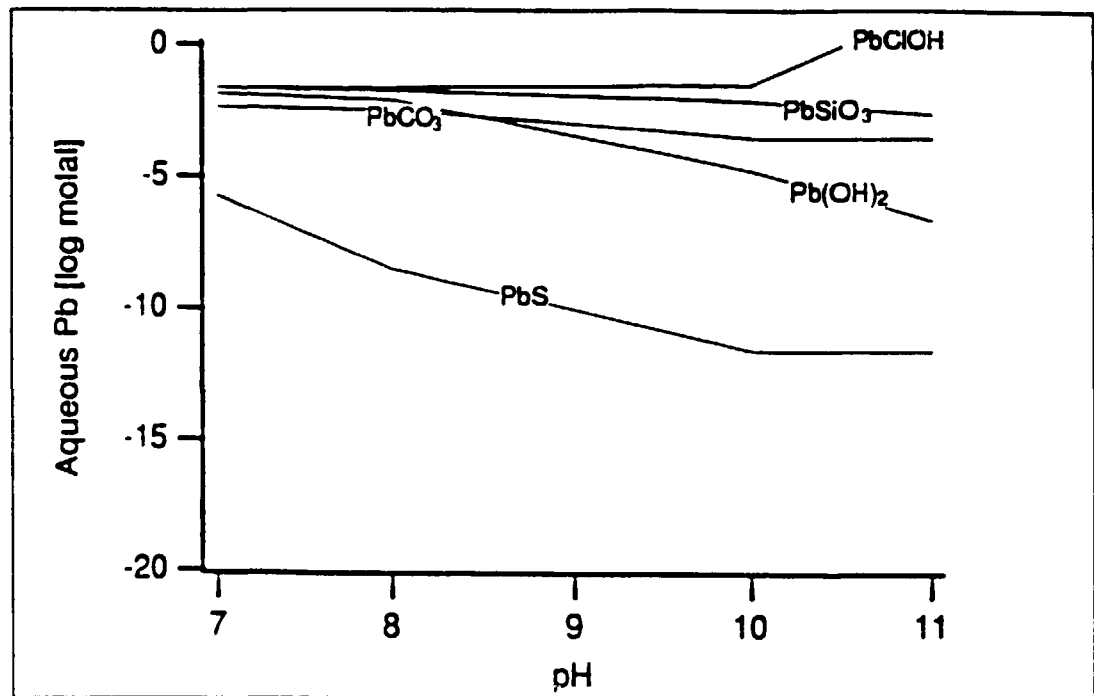


Figure 6.14 Solubility of Pb-solid phases at reducing conditions in pore water from PFBC residues.

6.2.6 Mercury

As the information of mercury in the solid phases in fossil fuel residue is very limited, possible solubility controlling phases had to be acquired from available thermodynamic data. One of the least soluble solid mercury species under oxidising conditions is HgO. This solid is not likely to set an upper limit on the aqueous mercury concentration in the pore water, however. The high solubility, 10^{-4} M (20 mg/l), is due to the hydrolysis of mercury (Figure 6.15).

Hg₂Cl₂ is, according to the calculations, less soluble but the existence of this solid in PFBC-residue have to be verified by experiments. No solid compound with mercury and selenium have been found under oxidising conditions that could limit the solubility of mercury.

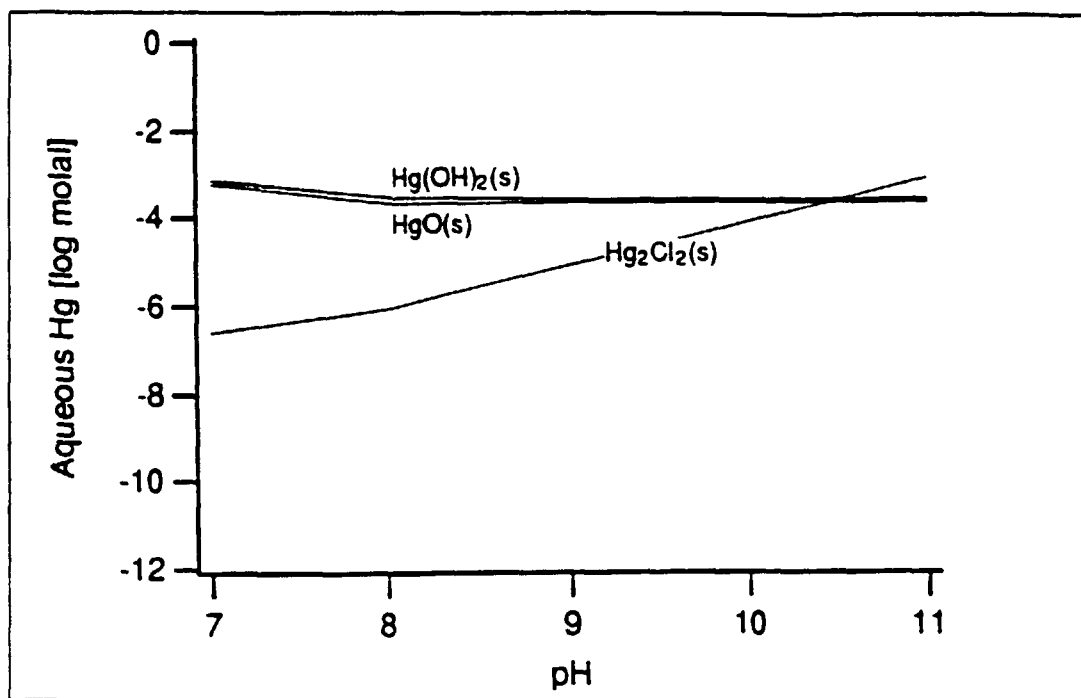


Figure 6.15 Solubility of Hg-solid phases at oxidising conditions in pore water from PFBC residues.

Experimental studies of mercury leached from coal ashes containing unburnt coal, have indicated that the solubility of mercury in that kind of material is controlled by HgS or HgSe.

In reducing environments, HgS is probably the solubility controlling solid and will limit the Hg concentration to a very low level, 10^{-10} M ($2 \cdot 10^{-5}$ mg/l), according to Figure 6.16. It is also possible, if Se is present in the residue, that HgSe will be formed and therefore be the solubility limiting phase. A scenario may be that at the beginning HgSe is formed, when pH is high. When pH decreases the HgSe will dissolve and HgS is formed as a new secondary limiting phase in the presence of sulphide ions.

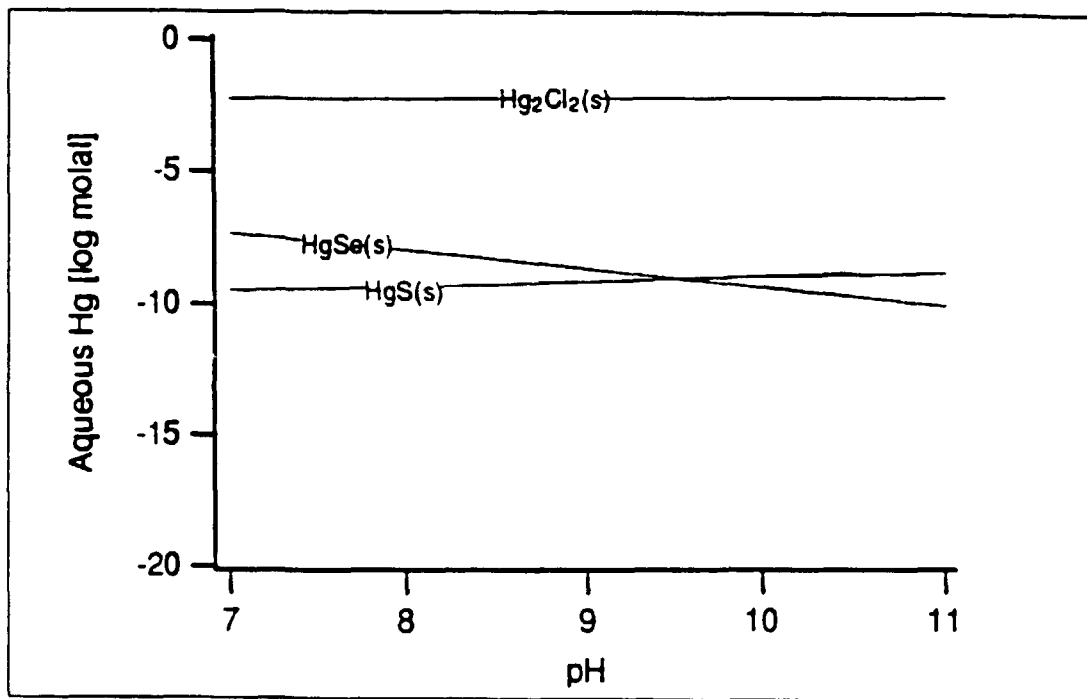


Figure 6.16 Solubility of Hg-solid phases at reducing conditions in pore water from PFBC residues.

6.2.7 Nickel

At present, there is no information about extraction data that can be related to specific solid forms of Ni. Therefore thermodynamic data must be used to identify possible solubility limiting solids.

Possible solid Ni-phases and their solubility under oxidising and reducing conditions are given in Figures 6.17 and 6.18.

The sulphide and the oxide phases are the important solubility-controlling solids at reducing conditions. According to Figure 6.18 the solubility of the most important sulphide, NiS, is less than 10^{-9} M ($6 \cdot 10^{-3}$ $\mu\text{g/l}$) at pH 7-11. The concentration of Ni in the pore water will probably be determined by the dissolution of primary phase NiO or the secondary phase Ni(OH)₂ at both reducing and oxidising conditions. Both these phases show an increasing solubility when pH decreases, from 10^{-7} M (6 $\mu\text{g/l}$) at pH 11 to an almost complete solubility at pH 7. A possible solubility-controlling solid under oxidised condition is NiFe₂O₄ which could limit the Ni-concentration about three orders of magnitude in comparison with the NiO/Ni(OH)₂ phases. This has also been suggested elsewhere (Rai 1986).

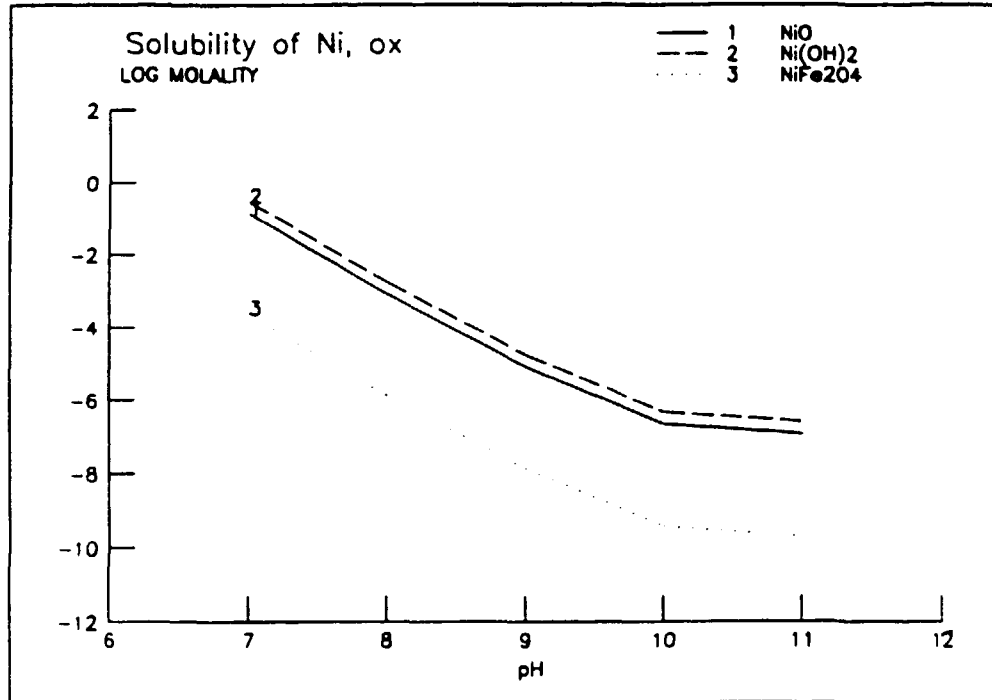


Figure 6.17 Solubility of Ni-solid phases at oxidising conditions in pore water from PFBC residues.

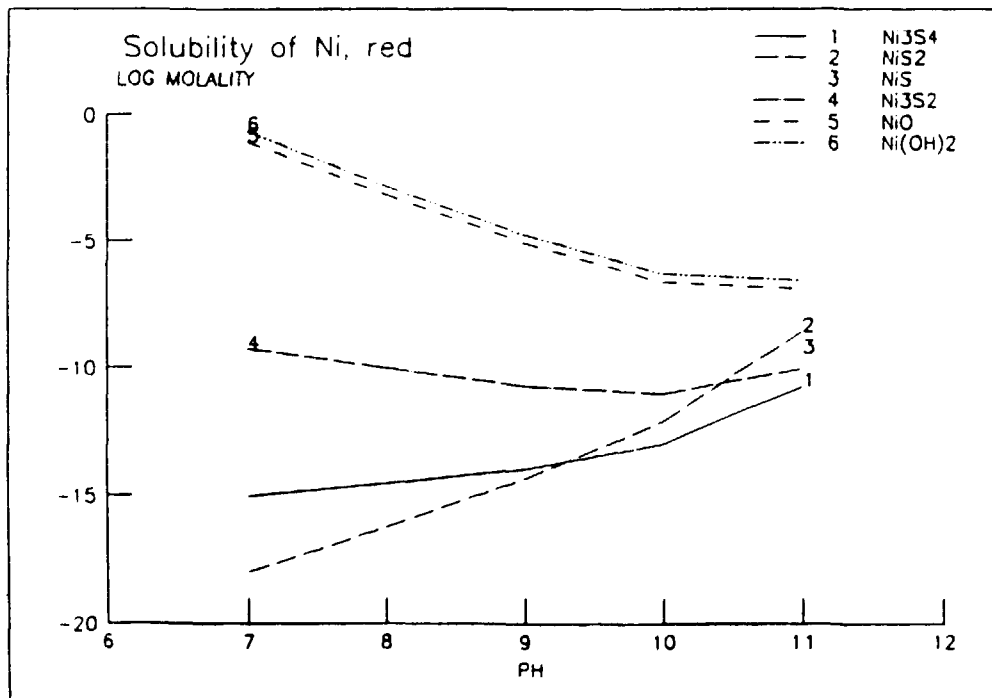


Figure 6.18 Solubility of Ni-solid phases at reducing conditions in pore water from PFBC residues.

7 DISCUSSION

Release of constituents in deposited PFBC residues depends on their chemical form and distribution within the particles. The chemical reactions occurring between the residues and the infiltrating water can be grouped under two headings: precipitation/dissolution and adsorption/desorption.

These processes are affected by many factors, such as pH, Eh, aqueous ion composition, gaseous atmosphere, and the nature of adsorbents and of solid phases containing specific elements. To develop the ability to predict aqueous concentrations of important constituents, quantitative mechanistic data for precipitation/dissolution and adsorption/desorption are needed.

It can be stated however, that if the solubility-controlling solid of an element is present in the residues or if such a solid can precipitate when water contacts the residues, then the adsorption reactions for that element can be ignored. The aqueous concentration of the element can therefore be predicted from the precipitation/dissolution reactions and the associated thermochemical data. In the absence of a solubility-controlling solid, the aqueous concentration is expected to be controlled by adsorption/desorption reactions.

This study shows that the primary compounds of aluminium and silicon in the residues are unstable and that secondary minerals will be formed which will control the aqueous concentrations of these elements. Solid phases of these major elements provide large reactive surface areas on which the adsorption/desorption of aqueous trace elements can occur. Also the formation of iron oxyhydroxides can contribute to the adsorption and retention of several trace constituents.

The preliminary set of equilibrium constants included in the database coupled to the geochemical code EQ3NR have been complemented with thermodynamic data for inorganic aqueous species and solids that contain cadmium, lead and mercury. Potential solubility-controlling solids for the trace elements arsenic, cadmium, chromium, copper, lead, mercury and nickel have been identified. To accurately predict the concentrations of trace elements in the residue leachates, thermodynamic data for the elements need to be developed. The predicted concentrations in this study should only be used as a guide and the predictions have to be validated by experiments.

Generally it can be stated, however, that the solubility of trace elements increase when the redox potential in the system is high. This is a result of a leaking soil cover, where oxygen from the air reacts with the PFBC residues. Oxidation of sulphides, especially $\text{FeS}_2(\text{s})$ is one of the most important redox reactions, since this process leads to the formation of acidic pore water with increasing solubility of trace elements.

The calculations have showed that especially Hg in the residues can be a problem at oxidising conditions. As the potential solubility limiting phase, HgO , is very soluble, there will be no limitation of the solubility in the leaching pore water. The information of the redox potential in the PFBC residues is very limited and there is a need for further investigation of this important parameter, since it has a great influence on the solubility of the trace elements. In the further chemical modelling with EQ3NR, the redox potential can be varied to describe the possible chemical reactions in detail.

The nature of the aqueous species is also important in understanding both precipitation/dissolution and adsorption/desorption reactions, since complexed species increase the solubility of solid phases.

In this work only inorganic species and reactions have been considered but it is known that many organic compounds are present in residues from coal burning. It is also well known that many metal cations are subject to complexation with organic compounds that contain functional groups, such as -OH or -COOH. These oxygenated compounds are unlikely to occur in the residues, however, due to the high temperatures that occur during combustion. There are, on the other hand several other types of organic compounds that are more likely to be found in PFBC residues which can be of potential interest for metal complexation.

Another potential problem that has turned up is the content of ammonia and ammonium salts in the PFBC residues. Ammonia is added to the PFBC process with the purpose to reduce the emissions of NO_x . Some of this ammonia will probably react with elements in the solid residue, especially silver, cadmium, mercury, copper and nickel, resulting in an increased solubility for these elements. These circumstances ought to be considered in further work.

The calculations made so far have been performed without modelling any chemical reactions. The solubility of various chemical elements have been determined at discrete values of Eh, pH, etc. Further work should deal with these parameters in a more realistic way by modelling continuous chemical changes in the PFBC residues caused by (acid) water, dissolved oxygen and carbon dioxide infiltrating through the soil cover.

In conclusion it can be stated that a comprehensive approach that strives to relate solution concentrations to specific solubility-controlling or adsorption-controlling solids is desirable and necessary to accurately predict the leaching behaviour of PFBC residues. This approach is relevant to both major and minor elements in the residues and requires a verified database on the chemical attenuation mechanisms that affect aqueous concentrations of elements. Thus, residue characterisation must include the data needed for implementing a mechanistic approach, that is, the identity of elements and compounds, the mass and surface area of important solids and the valence states of redox sensitive elements.

ACKNOWLEDGEMENT

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Appendix 1: Upgrading of the KEMAKTA EQ3/6 Thermodynamic Database

The database is an integral part of the EQ3/6 program package. This package is a group of programs for geochemical aqueous speciation – solubility calculations and reaction path modelling. The package includes two programs for geochemical calculations (EQ3 and EQ6), and six programs for data processing to provide the EQ3/6 programs with the thermodynamic data needed to perform the calculations.

The present size of the KEMAKTA EQ3/6 Database is 1508 chemical species of 47 elements. The defined species are aqueous species, solid species, gases, and solid solutions. The 47 elements of the KEMAKTA EQ3/6 Thermodynamic Database are present as:

- 755 aqueous species
- 736 minerals
- 10 gases
- 7 solid solutions

98 of these species are defined as master species. All other species (aqueous, mineral, or gas) is associated to respective master specie with a reaction. An aqueous complex is defined with its dissociation reaction, and a mineral with its dissolution reaction. For each of the defined reactions, thermodynamic data are provided to the calculating programs.

The data are grouped into blocks for each defined chemical specie (Figure 1). The data provided are the name of the species, chemical formula, a dissociation/dissolution reaction for the species, and a grid of calculated equilibria constants for the reaction at different temperatures.

Recent Upgrading of the KEMAKTA EQ3/6 Thermodynamic Database

The KEMAKTA EQ3/6 Thermodynamic Database has been upgraded concerning three elements, cadmium, mercury, and lead. A number of minerals and aqueous species have been added to the database and some of the already existing species have had their data exchanged for more recent data where such have been found.

Cadmium: Cadmium has been added as a new element to the database. The "basis species" was chosen to be Cd^{2+} , also added were 45 aqueous species and 33 mineral cadmium species.

Lead: Additional mineral and aqueous species have been added to the already existing lead-species. The database now contains 38 aqueous and 71 mineral lead species.

Mercury: Mercury has been added as a new element to the database. The "basis species" was chosen to be Hg^{2+} . Also 19 aqueous and 12 mineral mercury species have been added to the database.

```

+-----+
cd(oh)2(aq)
  entered by= mcrt (see below)          date= 5Dec86
          source= mcrt.3245R65          quality= unspecified
          charge= .0                    titr. factor= .0 eq/mol
          ion size= 4.0 a                hydr. number= .0
  3 chemical elements=
    1.000 cd          2.000 o          2.000 h
  4 species in reaction=
    -1.000 cd(oh)2(aq)  -2.000 h+          1.000 cd++
    2.000 h2o
*   log k grid (0-25-60-100/150-200-250-300
    19.2398  19.2398  500.0000  500.0000
    500.0000  500.0000  500.0000  500.0000
*   delvr grid (0-25-60-100/150-200-250-300
    500.0000  36.1364  500.0000  500.0000
    500.0000  500.0000  500.0000  500.0000
*   mcrt file mdas.3245r98, rev. 5Dec86, insufficient data
*   (quality of cd(oh)2(aq)          data = unspecified )
+-----+

```

Figure 1: An example of a datablock from: DATA0:

Adding New Elements and Species

The program package contains six programs to aid in adding new elements and species (Figure 2). The process is initiated at the "START" location, and the new data to be added should be specified in a text file named "input" (Figure 2). The data processing programs produce the databases DATA1, DATA2, and DATA3 that are formatted for direct access by the chemistry equilibria programs EQ3 and EQ6.

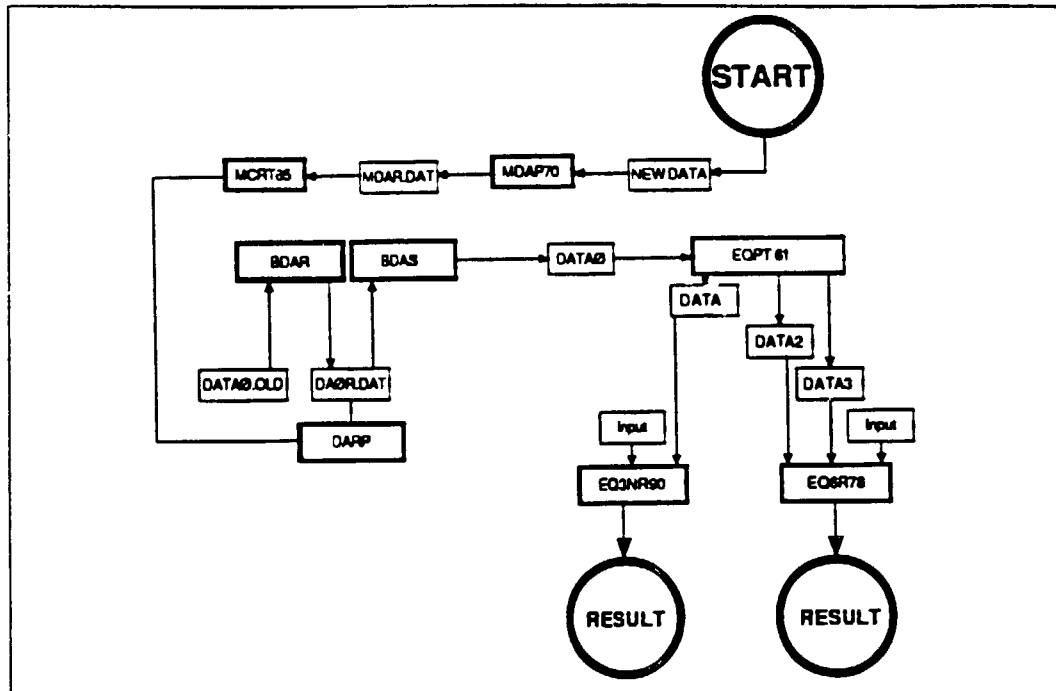


Figure 2: The EQ3/6 Program Package and the flow of data from basic thermodynamic data to processed geochemical modelling results.

The data to be defined in the input file are the name of the species, the chemical formulae of the species, the physical state (i.e. mineral, aqueous, etc.), a dissociation reaction (not for "basis species"), charge, Gibbs' free energy of reaction, ΔG^0 , the heat of formation, ΔH_f , and the entropy, S^0 .

MDAP 70

MDAP 70 is an interactive program to modify the original database MDAS. This program is used for modifying data of already existing species. The modified MDAS is named MDAR and includes the basic thermodynamic data of the original database along with the modifications.

MCRT 65

MCRT 65 is a program for calculation of the equilibrium constant, $\log K$, for reactions at temperatures between 0 to 300°C. The input to this program consist of MDAR, from the program MDAP 70, and the file INPUT. The file INPUT includes data blocks for each new

specie that should be added to the database. Also needed is the file GMI.DAT which includes status information regarding different ion-equations.

The INPUT file should be carefully assembled because any fault in positioning of text, or other errors may cause the chain of programs to malfunction.

```

+-----+
pboh+                                     date= 210590
entered by= ld                           quality=
keys =
subsets= pb
  charge= 1.0          titr. factor= 0.0 eq,mol
  ion type= 1        ion size= 0.0 a      hydr. no.= 0.0
3 chemical elements
  1.000 pb          1.000 o          1.000 h
  temp= 298.150 k      press= 1.013 bars
  delg0= -54.100 kcal/mol  delh0= 500.000 kcal/mol
  s0= 500.000 cal/mol/k      se= 0.000 cal/mol/k
  v0= 0.000 cc/mol          cp= 500.000 cal/mol/k
0 species in reference reaction
4 species in data0 reaction
-1.000 pboh+          -1.000 h+
1.000 pb++          1.000 h2o          t-p
data grid is absent
source= [82WAG/EVA] from nEA-TDB
+-----+

```

Figure 3: An example of a data block in the INPUT file.

The equilibrium constant for the reaction, $\log K$, is calculated from the values of Gibbs' free energy of formation, ΔG_f^0 , for the products and reactants or from the changes of the heat of formation, ΔH_f^0 , and the entropy, ΔS^0 :

$$\Delta G_f^0 = \Delta H_f^0 - T\Delta S^0$$

$$\ln K = \Delta G^0/RT$$

The program also checks for discrepancies between the calculated ΔG_f^0 (if ΔH_f^0 , and S^0 are given) and ΔG^0 if defined in the input to the program. Inconsistencies are noted in the file OUTPUT.MCR. It should be noted that the program uses an S^0 for H^+ which is not zero, this is contrary to common convention.

The file DFILE is created including all species of the input files along with their calculated equilibria constants. This file will be compared to the large database DATA0 which includes all existing species and their data in the database. To avoid error messages, the DFILE

should be edited to include only the data blocks with new data.

BDAR 52

This program converts the format of the large database DATA0 to a direct access format, for fast processing by following programs. The input apart from DATA0 is DA0H.DAT which includes data needed for producing the output file DA0R.DAT.

DARP 53

This is an interactive program where the file DA0R.DAT is modified to include the additions/alterations specified in the edited DFILE.

BDAS 51

This program converts the format of the modified DA0R.DAT back to a sequential file that is more easily read. This file is called DATA0 and includes all data available to the programs for geochemical calculations.

EQPT 61

At this stage the large database DATA0 is divided into the smaller databases DATA1, DATA2, and DATA3. These are formatted for direct access by the programs for geochemical calculations.

Selection of Data

Data has been selected from the thermodynamic database of OECD/NEA. This database contains several references of ΔG_f^0 , ΔH_f^0 , and S^0 , as well as values of $\log K$. The OECD/NEA thermodynamic database is not a selection of data, instead a wide variety of references are cited for each chemical specie. This enables the user to choose his own criteria for selection of data.

**Appendix 2: All Elements and Species in the KEMAKTA EQ3/6
Thermodynamic Database**

Copy of the datafile SLIST, of the EQ3/6 program package:

aqueous species

1	h2o	ag+	al+++
4	am+++	as(oh)4-	au+
7	b(oh)3	ba++	br-
10	ca++	cd++	cl-
13	co++	cr+++	cs+
16	cu+	eu+++	f-
19	fe++	h+	hco3-
22	hg++	hpo4--	i-
25	k+	li+	mg++
28	mn++	na+	np++++
31	ni++	no3-	pb++
34	puo2++	ra++	rb+
37	ru+++	sio2 (aq)	seo3--
40	sn++++	so4--	sr++
43	th++++	tco4-	u++++
46	v+++	zn++	o2 (g)
49	o2 (aq)	h2 (aq)	ch4 (aq)
52	co2 (aq)	au+++	am++++
55	amo2+	amo2++	aso4---
58	ch3coo-	clo4-	co+++
61	co3--	cr++	cro4--
64	cro4---	cu++	eu++
67	fe+++	hg2++	hs-
70	nh4+	no2-	np+++
73	(c-phth)--	io3-	pu+++
76	pu++++	puo2+	ru++
79	ruo4	ruo4-	ruo4--
82	ru(oh)2++	se--	seo4--
85	sn++	tc++	tc+++
88	tco+	tco++	tco4--
91	tco4---	vo++	vo4---
94	u+++	uo2+	uo2++
97	pb++++	oh-	(npo2)2(oh)2++
100	(npo2)3(oh)5+	(puo2)2(oh)2++	(puo2)3(oh)5+
103	(uo2)2(oh)2++	(uo2)2oh+++	(uo2)3(co3)(oh)3+
106	(uo2)3(co3)6(6-)	(uo2)3(oh)4++	(uo2)3(oh)5+
109	(uo2)3(oh)7-	(uo2)4(oh)7+	(vo)2(oh)2++

112	(vo) 2 (oh) 5-	[tco (oh) 2] 2	ag (so4) 2---
115	agcl	agcl2-	agcl3--
118	agcl4---	agf	agso4-
121	al (o-phth) +	al (o-phth) 2-	al (oh) 2+
124	al (oh) 3	al (oh) 4-	al (so4) 2-
127	al13o4 (oh) 24 (7+)	al2 (oh) 2++++	al3 (oh) 4 (5+)
130	alch3coo++	alf++	alf2+
133	alf3	alf4-	alf5--
136	alf6---	alh2po4++	alhpo4+
139	aloh++	also4+	am (co3) 2-
142	am (co3) 3---	am (h2po4) 2+	am (h2po4) 3
145	am (h2po4) 4-	am (no3) 2+	am (oh) 2+
148	am (oh) 3	am (so4) 2-	amcl++
151	amcl2+	amco3+	amf++
154	amf2+	amf3	amh2po4++
157	amno3++	amo2hco3	amoh++
160	amso4+	as (oh) 3	ash3 (aq)
163	aso2oh--	aso3f--	ass2-
166	aucl++	aucl2+	aucl2-
169	aucl3	aucl4-	b (oh) 4-
172	b2o (oh) 5-	b3o3 (oh) 4-	b4o5 (oh) 4--
175	ba (o-phth)	bab (oh) 4+	bach3coo+
178	bacl+	baco3	baf+
181	bahco3+	bano3+	baoh+
184	baso4	bf2 (oh) 2-	bf3oh-
187	bf4-	bh4-	ca (h3sio4) 2
190	ca (o-phth)	cab (oh) 4+	cach3coo+
193	cacl+	caco3	caf+
196	cah2sio4	cah3sio4+	cahco3+
199	cahpo4	cano3+	caoh+
202	capo4-	caso4	cd (hs) 2 (aq)
205	cd (nh3) 2++	cd (nh3) 3++	cd (nh3) 4++
208	cd (no3) 2 (aq)	cd (oh) 2 (aq)	cd (oh) 3-
211	cd (oh) 4--	cd (oh) 5---	cd (oh) 6----
214	cd2oh+++	cd4 (oh) 4++++	cdbr+
217	cdbr2 (aq)	cdbr2i-	cdbr2i2--
220	cdbr3-	cdbr3i--	cdbr4--
223	cdbri (aq)	cdbri2-	cdbri3--
226	cdcl+	cdcl2 (aq)	cdcl2br-
229	cdcl2br2--	cdcl2i-	cdcl2i2--
232	cdcl3-	cdcl4--	cdclbr (aq)
235	cdclbr2-	cdclbr3--	cdcli (aq)
238	cdcli2-	cdcli3--	cdco3 (aq)
241	cdf+	cdhco3+	cdhpo4 (aq)
244	cdi+	cdi2 (aq)	cdi3-
247	cdi4--	cdi5---	cdn2h4++
250	cdnh3++	cdno2+	cdno3+
253	cdo2--	cdoh+	cdohcl (aq)
256	cdp2o7--	cdso4 (aq)	co (hs) 2
259	co (no3) 2	co (oh) 2	co (oh) 3-
262	co (oh) 4--	co2 (oh) 3+	co4 (oh) 4++++
265	cobr2	cocl+	cocl2

268	cohs+	cohso4+	coi2
271	cono3+	cooh+	coseo4
274	coso4	cr (oh) 2+	cr (oh) 3
277	cr (oh) 4-	cr2 (oh) 2++++	cr2o7--
280	cr3 (oh) 4 (5+)	crbr++	crcl++
283	crcl2+	cro3cl-	croh++
286	cscl	csf	cu (nh3) 2+
289	cu (nh3) 2++	cu (nh3) 3++	cu (no2) 2
292	cucl	cucl+	cucl2
295	cucl2-	cucl3-	cucl3--
298	cucl4--	cuf+	cuh2po4+
301	cuhpo4	cunh3+	cunh3++
304	cuno2+	cuoh+	cupo4-
307	cuso4	eu (co3) 2-	eu (oh) 2+
310	eu (so4) 2-	eubr++	eubr2+
313	eubro3++	eucl++	eucl2+
316	euco3+	euf++	euf2+
319	euio3++	euno3++	euoh++
322	euo4+	fe (b (oh) 4) 2+	fe (ch3coo) 2+
325	fe (ch3coo) 3	fe (oh) 2	fe (oh) 2+
328	fe (oh) 3	fe (oh) 3-	fe (oh) 4-
331	fe (so4) 2-	fe2 (oh) 2++++	fe3 (oh) 4 (5+)
334	feb (oh) 4++	fech3coo+	fech3coo++
337	fecl+	fecl++	fecl2
340	fecl2+	fecl3	fecl4-
343	feco3	feco3+	fef+
346	fef++	fef2+	fef3
349	feh2po4+	feh2po4++	feh3sio4++
352	fehco3+	fehpo4	fehpo4+
355	fehseo3	fehso4++	feno2++
358	feno3++	feoh+	feoh++
361	fepo4-	feso4	feso4+
364	h (o-phth) -	h2 (o-phth)	h2aso4-
367	h2cro4	h2f2	h2p2o7--
370	h2pbo2 (aq)	h2po4-	h2ruo5
373	h2s (aq)	h2se	h2seo3
376	h2sio4--	h2so4	h3aso4
379	h3p2o7-	h3po4	h3sio4-
382	h4 (h2sio4) 4----	h4p2o7	h6 (h2sio4) 4--
385	haso3f-	haso4--	hass2
388	hcdo2-	hch3coo	hcl
391	hcoo2-	hcro4-	hf
394	hf2-	hg (hs) 2 (aq)	hg (oh) +
397	hg (oh) 2 (aq)	hg (oh) cl (aq)	hg (so4) 2--
400	hg2 (so4) 2--	hg2so4	hgcl+
403	hgcl2	hgcl2 (aq)	hgcl3-
406	hgcl4--	hgf+	hgo (oh) -
409	hgs2--	hgso4	hgso4 (aq)
412	hno2	hp2o7---	hpbo2-
415	hruo5-	hse-	hseo3-
418	hseo4-	hso4-	htco4-
421	kcl	kco3-	khpo4-

424	koh	kso4-	lioh
427	liso4-	mg(h3sio4)2	mg2co3++
430	mg2oh+++	mg4(oh)4++++	mgb(oh)4+
433	mgch3coo+	mgcl+	mgco3
436	mgf+	mgh2po4+	mgh2sio4
439	mgh3sio4+	mghco3+	mghpo4
442	mgoh+	mgpo4-	mgso4
445	mn(nh3)2++	mn(nh3)3++	mn(no3)2
448	mn(oh)2	mn(oh)3-	mn(oh)4--
451	mn2(oh)3+	mn2oh+++	mncl+
454	mncl2	mncl3-	mnco3
457	mnf+	mnh2po4+	mnhco3+
460	mnhpo4	mnnh3++	mnnco3+
463	mno4-	mno4--	mnoh+
466	mnp4-	mseo4	mns4
469	na(o-phth)-	nab(oh)4	nach3coo
472	nacl	naco3-	naf
475	nah3sio4	nahco3	nahpo4-
478	naoh	nas4-	nh3
481	nh4so4-	ni(nh3)2++	ni(nh3)6++
484	ni(no3)2	ni(oh)2	ni(oh)3-
487	ni(oh)4--	ni2oh+++	ni4(oh)4++++
490	nibr+	nihp2o7-	nino3+
493	nioh+	nip2o7--	niseo4
496	niso4	np(co3)5(6-)	np(h2po4)2+
499	np(h2po4)3	np(hpo4)2	np(hpo4)3--
502	np(hpo4)4----	np(hpo4)5(6-)	np(oh)2++
505	np(oh)3+	np(oh)4	np(oh)5-
508	np(so4)2	npcl+++	npcl2++
511	npf+++	npf2++	nph2po4++
514	nphpo4++	npo2(co3)2--	npo2(co3)2---
517	npo2(co3)3(5-)	npo2(co3)3----	npo2+
520	npo2++	npo2cl	npo2cl+
523	npo2co3-	npo2f	npo2f+
526	npo2f2	npo2h2po4	npo2h2po4+
529	npo2hpo4	npo2hpo4-	npo2oh
532	npo2oh+	npo2so4	npo2so4-
535	npoh++	npoh+++	npso4++
538	p2o7----	pb(clo3)2(aq)	pb(co3)2--
541	pb(hco3)2(aq)	pb(hco3)3-	pb(hs)2(aq)
544	pb(hs)3-	pb(no3)2(aq)	pb(oh)2(aq)
547	pb(oh)3-	pb(so4)2--	pb2oh+++
550	pb3(oh)4++	pb3(oh)5+	pb4(oh)4++++
553	pb6(oh)8++++	pbcl+	pbcl2
556	pbcl3-	pbcl4--	pbclo3+
559	pbco3	pbf+	pbf2
562	pbf3-	pbf4--	pbh2po4+
565	pbhpo4	pbhs3-	pbno3+
568	pbo3--	pbo4----	pboh+
571	pbpo4-	pbso4	po4---
574	pu(hpo4)2	pu(hpo4)3--	pu(hpo4)4----
577	pu(oh)2++	pu(oh)3(aq)	pu(oh)3+

580	pu (oh) 4	pu (oh) 4-	pu (oh) 4co3--
583	pu (oh) 5-	pu (so4) 2	pucl+++
586	puco3+	puco3++	puf+++
589	puf2++	puf3+	puf4
592	puh2po4++	puhpo4++	puo2 (co3) 2--
595	puo2 (oh) 2hco3-	puo2cl+	puo2co3
598	puo2f+	puo2f2	puo2f3-
601	puo2f4--	puo2h2po4+	puo2oh
604	puo2oh+	puo2so4	puoh++
607	puoh+++	puso4+	puso4++
610	puso4hso4+	ru (cl) 2+	ru (cl) 3
613	ru (oh) 2+	ru (oh) 2cl+	ru (oh) 2cl2
616	ru (oh) 2cl3-	ru (oh) 2cl4--	ru (oh) 2so4
619	ru (so4) 2-	ru4 (oh) 12++++	rucl+
622	rucl++	rucl4-	rucl5--
625	rucl6---	ruoh++	ruso4
628	ruso4+	s--	s2--
631	s3--	s4--	s5--
634	s6--	sif6--	sn (oh) 2
637	sn (oh) 2++	sn (oh) 3+	sn (oh) 3-
640	sn (oh) 4	snbr+	snbr2
643	snbr3-	sncl+	sncl2
646	sncl3-	snf+	snf+++
649	snf2	snf2++	snf3+
652	snf3-	snf4	snoh+
655	snoh+++	snso4++	srch3coo+
658	srco3	srf+	srh2po4+
661	srhco3+	srhpo4	srno3+
664	sroh+	srpo4-	srso4
667	tco (oh) 2	tco2	tcooh+
670	th (h2po4) 2++	th (hpo4) 2	th (hpo4) 3--
673	th (oh) 2++	th (oh) 3+	th (oh) 4
676	th (so4) 2	th (so4) 3--	th (so4) 4----
679	th2 (oh) 2 (6+)	th4 (oh) 8 (8+)	th6 (oh) 15 (9+)
682	thcl+++	thcl2++	thcl3+
685	thcl4	thf+++	thf2++
688	thf3+	thf4	thh2po4+++
691	thh3po4++++	thhpo4++	thoh+++
694	thso4++	u (co3) 5 (6-)	u (hpo4) 2
697	u (hpo4) 3--	u (hpo4) 4----	u (oh) 2++
700	u (oh) 3+	u (oh) 4	u (oh) 5-
703	u (so4) 2	u6 (oh) 15 (9+)	ucl+++
706	ucl4	uf+++	uf2++
709	uf3+	uf4	uf5-
712	uf6--	uhpo4++	uo2 (co3) 2--
715	uo2 (co3) 3----	uo2 (h2po4) 2	uo2 (h2po4) h3po4+
718	uo2 (no3) 2	uo2 (oh) 2	uo2 (oh) 3-
721	uo2 (oh) 4--	uo2 (so4) 2--	uo2cl+
724	uo2co3	uo2f+	uo2f2
727	uo2f3-	uo2f4--	uo2h2po4+
730	uo2h3po4++	uo2oh+	uo2sio (oh) 3+
733	uo2so4	uoh+++	uso4++

736	v (oh) 2+	v2 (oh) 2++++	vo (oh) 3
739	vo2 (hpo4) 2---	vo2 (oh) 2-	vo2+
742	vo2f	vo2f2-	vo2f3--
745	vo2h2po4	vo2hpo4-	vo2so4-
748	vo3oh--	vof+	vof2
751	vof3-	vof4--	voh++
754	vooh+	voso4	vso4+
757	zncl+	zncl2	zncl3-
760	zncl4--	znf+	znh2po4+
763	znhpo4	znpo4-	znseo4
766	znso4		

minerals

1	(bao) 2. (sio2) 3 (c)	(bao) 2. sio2 (c)	(cdso4) 2cd (oh) 2 (cr)
4	(pb (oh) 2) 3pbcl2	(pbcl2) 2nh4cl	(pbo) 2pbco3 (cr)
7	(pbo) 2sio2 (cr)	(uo2) 3 (po4) 2 (c)	(vo) 3 (po4) 2 (c)
10	acanthite	ag2se	ag3po4 (c)
13	akermanite	al (aso4) (c)	al2 (so4) 3
16	al2 (so4) 3. 6h2o	alabandite	albite
19	albite high	albite low	alstonite
22	alunite	am (oh) 3 (am)	am (oh) 3 (c)
25	am2 (co3) 3 (c)	amesite-14a	amohco3 (c)
28	amrph. silica	analc-dehydr	analcime
31	andalusite	andradite	anglesite
34	anhydrite	annite	anorthite
37	antarcticite	anthophyllite	antigorite
40	aragonite	arcanite	arsenolite
43	arsenopyrite	artinite	as2o5 (c)
46	autunite-h	autunite-na	azurite
49	ba (no3) 2 (c)	ba (oh) 2. 8h2o	ba2pb (cr)
52	ba3 (aso4) 2 (c)	babr2 (c)	babr2. 2h2o
55	bacl2 (c)	bacl2. 2h2o	bacl2. h2o
58	bacro4	baf2 (c)	bahpo4 (c)
61	bai2 (c)	bamno4 (c)	bao (c)
64	bao. (sio2) 2 (c)	bao. sio2 (c)	bapb3 (cr)
67	barite	barytocalcite	bas (c)
70	baseo3	baseo4	basif6 (c)
73	bassanite	bassetite	beidellit-ca
76	beidellit-h	beidellit-k	beidellit-mg
79	beidellit-na	berlinite	bieberite
82	birnessite	bischofite	bixbyite
85	bloedite	boehmite	boltwood-na
88	boltwoodite	borax	boric acid
91	bornite	brezinaite	brucite
94	burkeite	ca (oh) 2 (c)	ca-al pyroxene
97	ca2cl2 (oh) 2. h2o	ca2si3o8. 5/2h2o	ca2sio4 (gamma)
100	ca2sio4. 7/6h2o	ca2v2o7 (c)	ca3 (aso4) 2 (c)
103	ca3si2o7. 3h2o	ca3sio5	ca3v2o8 (c)
106	ca4cl2 (oh) 6. 13h2o	ca4si3o10. 2h2o	ca5si6o17. 11/2h2o
109	ca5si6o17. 21/2h2o	ca5si6o17. 3h2o	ca6si6o18. h2o
112	cacl2. 2h2o	cacl2. 4h2o	cacl2. h2o

115	cahpo4.2h2o	calcite	carnallite
118	carnotite	caseo3.2h2o	caseo4
121	casi2o5.2h2o	caso4.1/2h2o	cattierite
124	cav2o6(c)	cd(no3)2(cr)	cd(oh)2(cr)
127	cd(oh)cl(cr)	cd3(po4)2(cr)	cd3as2(cr)
130	cdal2o4(cr)	cdbr2(cr)	cdbr2.4h2o(cr)
133	cdcl2(cr)	cdcl2(nh3)2(cr)	cdcl2(nh3)4(cr)
136	cdcl2(nh3)6(cr)	cdcl2.2.5h2o(c)	cdcl2.h2o(cr)
139	cdco3(cr)	cdf2(cr)	cdi2(cr)
142	cdk2i4.2h2o(cr)	cdki3.h2o(cr)	cdo(cr)
145	cds(cr)	cdse(cr)	cdseo3(cr)
148	cdseo4(cr)	cdsio3(cr)	cdso4(cd(oh)2)2(cr)
151	cdso4(cr)	cdso4.2.667h2o	cdso4.h2o(cr)
154	celestite	cerussite	chalcedony
157	chalcocite	chalcopyrite	chamosite-7a
160	chloromagnesite	chloropyromorph	chrysotile
163	cinnabar	claudetite	clinocl-14a
166	clinocl-7a	clinoptil-ca	clinoptil-k
169	clinoptil-mg	clinoptil-na	clinozoisite
172	co(feo2)2	co(no3)2(s)	co(oh)2(s)
175	co2sio4	co3(aso4)2	co3(aso4)2.8h2o
178	co3(po4)2	co3o4	cobr2(c)
181	cocl2(s)	cocl2.2h2o	cocl2.6h2o
184	coco3	cof2	cof3
187	coffinite	cohpo4	colemanite
190	coo	copper	cordier.anhy
193	cordier.hydr	corundum	cos
196	cose	coseo3	coso4(s)
199	coso4.3co(oh)2	coso4.6h2o	coso4.h2o
202	covellite	cr2o3	crcl3
205	crf3	crf4	cri3
208	cristobalite	cro2	cro3
211	cronstedt.-7a	crs	cu3(aso4)2(c)
214	cu3(po4)2(c)	cu3(po4)2.3h2o	cu3se2
217	cucr2o4	cuf(c)	cuf2(c)
220	cuf2.2h2o	cufeo2(c)	cuprite
223	cuse	cuse2	cuseo3
226	cuseo3.2h2o	daphnite-14a	daphnite-7a
229	dawsonite	diaspore	diopside
232	dolomite	dolomite-dis	dolomite-ord
235	enstatite	epidote	epidote-ord
238	epsomite	ettringite	eu
241	eu(io3)3.2h2o	eu(no3)3.6h2o	eu(oh)2.5cl.5
244	eu(oh)2cl	eu(oh)3	eu2(co3)3.3h2o
247	eu2(so4)3.8h2o	eu2o3(cubic)	eu2o3(monoclinic)
250	eu3o4	eubr3	eucl2
253	eucl3	eucl3.6h2o	eucryptite
256	euf3.0.5h2o	euo	euocl
259	eus	euso4	fayalite
262	fe(oh)2(ppd)	fe(oh)3(ppd)	fe2(so4)3(c)
265	fecr2o4	fef2(c)	fef3(c)
268	feo(c)	ferrite-2-ca	ferrite-ca

271	ferrite-cu	ferrite-mg	ferrite-zn
274	ferrosilite	fese	fese2
277	feso4 (c)	fev2o4 (c)	fluorapatite
280	fluorite	forsterite	galena
283	gaylussite	gehlenite	gibbsite
286	goethite	gold	graphite
289	greenalite	grossular	gummite
292	gypsum	haiweeite	halite
295	hausmannite	hedenbergite	hematite
298	hercynite	heulandite	hexahydrite
301	hg (oh) 2 (s)	hg2cl2 (s)	hg2seo3
304	ng2so4 (s)	hgcl2 (s)	hgo (s)
307	hgse	hgseo3	hgso4 (s)
310	hinsdalite	htco4 (s)	huntite
313	hydroboracite	hydromagnesite	hydrophilite
316	hydroxyapatite	hydroxypyromor	illite
319	jadeite	jarosite-k	jarosite-na
322	k (uo2) (aso4) (c)	k-feldspar	k2co3.3/2h2o
325	k2cr2o7	k2cro4	k2pb (so4) 2 (cr)
328	k2se	k4cdcl6 (cr)	k8h4 (co3) 6.3h2o
331	kainite	kalicinite	kalsilite
334	kaolinite	kasolite	kbr
337	kbr (cdbr2) 3.h2o	kcdbr3.h2o (cr)	kcdcl3.h2o (cr)
340	kcl (cdcl2) 3.4h2o	kcl (pbcl2) 2 (cr)	kieserite
343	kmgcl3	kmgcl3.2h2o	knaco3.6h2o
346	kpbcl3.0.33h2o	ktco4 (s)	kyanite
349	larnite	laumontite	lawrencite
352	lawsonite	leonhardite	leonhardtite
355	li (uo2) (aso4) (c)	li2se	lime
358	linnaeite	magnesite	magnetite
361	malachite	manganite	manganosite
364	margarite	matlockite	maximum microcli
367	melanterite	mercallite	merwinite
370	metacinnabar	mg2cl (oh) 3.4h2o	mg2pb (cr)
373	mg3 (aso4) 2 (c)	mgbr2	mgbr2.6h2o
376	mgcl2.2h2o	mgcl2.4h2o	mgcl2.h2o
379	mgcr2o4	mgf2 (c)	mgohcl
382	mgseo3	mgseo3.6h2o	mgso4 (c)
385	mgv2o6 (c)	mhsh (mg1.5)	minnesotaite
388	mirabilite	misenite	mn (oh) 2 (am)
391	mn (oh) 3 (c)	mn3 (aso4) 2 (c)	mn3 (po4) 2 (c)
394	mncl2.2h2o	mncl2.4h2o	mncl2.h2o
397	mnhpo4 (c)	mnse	mnseo3
400	mnseo3.2h2o	mnso4 (c)	mnv2o6 (c)
403	moderite	molysite	monohydrocalcite
406	monosulfate	monticellite	mordenite-k
409	mordenite-na	mullite	muscovite
412	na2cr2o7	na2cro4	na2pbo3 (cr)
415	na2se	na2se2	na2si2o5
418	na2sio3	na2so4	na2u2o7 (c)
421	na2uo4 (c)	na3h (so4) 2	na3uo4 (c)
424	na4sio4	na6si2o7	nabr

427	nafeo2 (c)	nanpo2co3.3h2o	natco4 (s)
430	nepheline	nesquehonite	nh4hse
433	ni(oh) 2 (s)	ni2p2o7	ni2sio4
436	ni3(po4) 2	ni3s2	ni3s4
439	ni3se4	nicl2	nicl2.2h2o
442	nicl2.4h2o	nicl2.6h2o	nico3
445	nif2	nif2.4h2o	nife2o4
448	ningyoite	nio	nis
451	nis2	nise2	niseo3.2h2o
454	niso4 (s)	niso4.6h2o	niso4.7h2o
457	nitratite	nontronit-ca	nontronit-k
460	nontronit-mg	nontronit-na	np
463	np(hpo4) 2 (s)	np(oh) 4 (s)	np2o5
466	npo2	npo2(oh) (am)	npo2(oh) 2
469	o-phth acid(c)	orpiment	paragonite
472	pargasite	pb(h2po4) 2 (cr)	pb(mno4) 2 (pbo) 3 (cr)
475	pb(oh) 2 (cr)	pb(oh) 4 (cr)	pb10(co3) 6 (oh) 6o (c)
478	pb2(co3) cl2 (cr)	pb2(oh) 3cl (cr)	pb2co3cl2 (cr)
481	pb2cupo4(oh) 3	pb2oso4 (cr)	pb2sio4 (am)
484	pb2sio4 (cr)	pb3(aso4) 2 (c)	pb3(co3) 2 (oh) 2 (cr)
487	pb3(po4) 2 (c)	pb3o2co3 (cr)	pb3o2so4 (cr)
490	pb3o4 (cr)	pb4o(po4) 2 (c)	pb4o3so4 (cr)
493	pb4sio6 (am)	pb4sio6 (cr)	pb5(po4) 3cl (cr)
496	pb5(po4) 3oh (cr)	pb5o4so4 (cr)	pbcl2.pbco3 (cr)
499	pbcloh (laur)	pbcloh (para)	pbco3pbo (cr)
502	pbcro4	pbcro4 (cr)	pbf2 (c)
505	pbfe3po4so4(oh) 6	pbhpo3 (cr)	pbhpo4 (c)
508	pbo (c)	pbo.0.33h2o (cr)	pbo.0.3h2o (cr)
511	pbo.pbso4 (cr)	pbo2 (cr)	pbohno3 (cr)
514	pbse	pbseo3	pbseo4
517	pbsio3 (am)	pbsio3 (cr)	pbso4 (nh3) 2 (cr)
520	pbso4 (nh3) 4 (cr)	pbso4 (pbo) 3 (cr)	pd-oxyannite
523	pentahydrate	petalite	phengite
526	phlogopite	pirssonite	plumbogummite
529	portlandite	prehnite	przhevalskite
532	pseudowollastoni	pu(hpo4) 2 (c)	pu(oh) 3
535	pu(oh) 3 (c)	pu(oh) 3 (s)	pu(oh) 4 (am)
538	pu(oh) 4 (s)	pu2(co3) 3 (c)	pu2o3 (c, beta)
541	puf3 (c)	puf4 (c)	puo2
544	puo2 (c)	puo2(co3)	puo2(oh) 2
547	puo2(oh) 2 (c)	puo2hpo4 (c)	puo2oh (am)
550	pyrite	pyrolusite	pyrophyllite
553	pyrrhotite	quartz	quicksilver
556	ra (c)	ra(no3) 2 (c)	rac12.2h2o
559	rankinite	raso4	realgar
562	rhodochrosite	rhodonite	ripidolit-14a
565	ripidolit-7a	ru (c)	ru(oh) 3.h2o (am)
568	rubr3 (s)	rucl3 (s)	rui3 (s)
571	ruo2 (s)	ruo2.2h2o (am)	ruo4 (s)
574	rus2 (s)	rutherfordine	safflorite
577	saleeite	sanidine high	saponite-ca
580	saponite-h	saponite-k	saponite-mg

583	saponite-na	scacchite	schoepite
586	scorodite	se(black)	se2o5
589	secl4	seo2	seo3
592	sepiolite	siderite	sillimanite
595	silver	sklodowskite	smectite-high-fe-m
598	smectite-low-fe	smectite-reykja	smithsonite
601	sn(oh)2(s)	sn(so4)2(c)	sn2s3
604	sn3s4	snbr2(s)	snbr4
607	sncl2(s)	sno	sno2
610	sns	sNSE	sNSE2
613	snsO4	soddyite	sphalerite
616	spinel	spodumene-a	sr(no3)2(c)
619	sr(no3)2.4h2o	sr(oh)2(c)	sr-autunite
622	sr2sio4(c)	sr3(aso4)2(c)	sr3(po4)2(c)
625	srbr2(c)	srbr2.6h2o	srbr2.h2o
628	srcl2(c)	srcl2.2h2o	srcl2.6h2o
631	srcl2.h2o	srcro4	srf2(c)
634	srhpo4(c)	sro(c)	srs(c)
637	srse	srseo3	srseo4
640	s-sio3(c)	strengite	strontianite
643	sulfur-rhmb	sylvite	tachyhydrite
646	talC	tc(c)	tc(oh)2(s)
649	tc(oh)3(s)	tc2o7(s)	tc2s7(s)
652	tc3o4(s)	tc4o7(s)	tco2(c)
655	tco2.2h2o(am)	tco3(s)	tcoh(s)
658	tcs2(s)	tcs3(s)	tenorite
661	tephroite	th(no3)4.5h2o	th(oh)4(c)
664	th(so4)2(c)	th2s3	th2se3
667	th7s12	thbr4	thcl4(c)
670	thenardite	thf4(c)	thf4.2.5h2o
673	thi4	tho2	thorianite
676	ths2	todorokite	torbernite
679	tremolite	tricalciumalu	tridymite
682	troilite	tsumebite	tyuyamunite
685	u(c,alph)	u(hpo4)2.4h2o	u(so4)2(c)
688	u(so4)2.4h2o	u(so4)2.8h2o	u3o7(c)
691	u3o8(c,alph)	u3se4	u4o9(c)
694	ucl4(c)	uf4(c)	uf4.2.5h2o
697	uo2(am)	uo2(fuel)	uo2(no3)2(c)
700	uo2(no3)2.2h2o	uo2(no3)2.3h2o	uo2(no3)2.6h2o
703	uo2(oh)2(c,bet)	uo2cl2(c)	uo2f2(c)
706	uo2hpo4(c)	uo2so4(c)	uo2so4.(2.5h2o)
709	uo2so4.(3.5h2o)	uo2so4.3h2o	uo2so4.h2o
712	uo3(c,gamma)	uof2.h2o	uramphite
715	uraninite	uranocircite	uranophane
718	use2	v2o3(c)	v2o4(c)
721	v2o5(c)	v3o5(c)	v4o7(c)
724	vivianite	wairakite	weeksite
727	whitlockite	witherite	wollastonite
730	wurtzite	wustite	zn3(aso4)2(c)
733	zn3(po4)2.4h2o	zncr2o4	znf2(c)
736	znse	znseo3.h2o	zoisite

gases

1	ch4(g)	co2(g)	h2(g)
4	h2s(g)	n2(g)	o2(g)
7	ru(g)	ruo4(g)	s2(g)
10	steam		

solid solutions

1	(na,k)-sanidine	biotite	ca-smectite
4	na-smectite	olivine	orthopyroxene
7	plagioclase		