Quantitative geochemical modelling using leaching tests: Application for coal ashes produced by two South African thermal processes

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ABSTRACT

The present work focuses on the reactivity of coal fly ash in aqueous solutions studied through geochemical modelling. The studied coal fly ashes originate from South African industrial sites. The adopted methodology is based on mineralogical analysis, laboratory leaching tests and geochemical modelling. A quantitative modelling approach is developed here in order to determine the quantities of different solid phases composing the coal fly ash. It employs a geochemical code (PHREEQC) and a numerical optimisation tool developed under MATLAB, by the intermediate of a coupling program. The experimental conditions are those of the laboratory leaching test, i.e. liquid/solid ratio of 10 L/kg and 48 h contact time. The simulation results compared with the experimental data demonstrate the feasibility of such approach, which is the scope of the present work. The perspective of the quantitative geochemical modelling is the waste reactivity prediction in different leaching conditions and time frames. This work is part of a largest research project initiated by Sasol and Eskom companies, the largest South African coal consumers, aiming to address the issue of waste management of coal combustion residues and the environmental impact assessment of coal ash disposal on land.

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1. Introduction

South Africa produces large quantities of coal combustion residues from different thermal processes. The countries largest coal consumers, Sasol and Eskom are confronted with waste management and environmental impacts. Both these companies are committed to a reduction in their environmental footprint, and are faced with similar environmental concerns and challenges. In order to address these concerns, both companies embarked on a cooperative research initiative with participation from industry and academia to address the sustainability of coal ash disposal in inland ash dams and heaps [1].

This paper presents one aspect of the research work dealing with the geochemical modelling of the fly ash reactivity in water, using fly ash produced by the industrial sites of Secunda (Sasol) and Tutuka (Eskom). The objective of the modelling approach adopted is to build a solid phase mineralogical assemblage of fly ash which would enable description of the material and prediction of its reactivity in water at a laboratory scale. The ash

leaching behaviour was studied experimentally and by geochemical modelling, based on a methodology previously described [2]. The steps of this methodology used in the present work are: (1) material intrinsic characterisation i.e. elemental total content and mineralogy; (2) leaching study in batch system for dissolution kinetics and equilibrium assessment in different pH conditions; (3) geochemical modelling of the material and its reaction path in water.

The methodology of jointly using leaching tests and geochemical modelling for understanding the leaching behaviour of mineral wastes is not new, and has been used by the scientific community (mainly in Europe and USA) for finding the most appropriate tools and methodologies for leaching behaviour assessment. The literature survey shows that, in the field of mineral wastes, geochemical modelling was used at different levels.

(1) A qualitative approach consisting on the proposition of a solid phase controlling the release of a given element in the system waste/water by using the ANC eluates composition. The method is based on calculation of saturation indexes of the eluates and consideration of the identified equilibrium phases. Another way to identify the equilibrium phases is the comparison of the experimental curve concentration vs. pH for a given element

with calculated curves solubility vs. pH for different phases containing this element. The phase exhibiting the best agreement is selected for representing the given element in the mineralogical model. In the literature one can find examples of the qualitative approach application for different wastes like fly ash [3], municipal solid waste incineration ash [4] or solidified/stabilized air pollution control residues [5].

(2) Qualitative model of the solid waste: a phase assemblage (and the corresponding water/solid reactions) is proposed in order to simulate the eluates composition. The quantities of the different phases are not specified, or are evaluated only for a specific phase of interest (e.g. surface complexation sites). The focus is mainly on the representation of the eluate composition not on the quantitative modelling of the solid material. This approach was used for example by [6] (slags), [7] (mortars containing wastes) and [8] (mortars containing municipal solid waste incineration ash).

The qualitative approaches do not estimate the quantity of different phases and, as a result, they have two major limitations: (1) they do not allow the calculation of all chemical properties of the waste e.g. the acid/base neutralisation capacity; (2) the leaching processes encountered in reality take place in open systems, in which some phases and elements can disappear by dissolution and transport. Thus the elements' depletion in time depends on the phase quantities and cannot be calculated by these approaches.

(3) Quantitative modelling approaches of leaching processes in ANC tests have been published, tending to evaluate the quantities of different reactive phases, particularly those containing pollutants. In addition to eluates' composition, knowledge about the elemental composition and mineralogy of the waste is required. There are fewer examples in the literature on quantitative modelling applied to wastes: chromite ore processing residue [9], municipal solid waste incineration ash [10], coal fly ash [2].

This detailed approach allows the distinction between the initial phases contained in the waste before the solubilisation process and the neo-formed phases in contact with the leachate. Quantitative geochemical modelling then promises to provide a realistic representation of the leaching process at laboratory and field scales, for different time frames. However, in the literature there are no clearly defined methodologies and tools for performing quantitative modelling using leaching tests (like ANC test).

The main objectives of this work can be summarised as follows:

(1) To propose an improved methodology for quantitative geochemical modelling using laboratory leaching tests results. The original aspect introduced by this work (in our knowledge never published for similar research studies) is a numerical method and tool for phase quantities calculation. The numerical tool is an optimisation algorithm developed in MATLAB and coupled with the geochemical code PHREEQC.

(2) To apply this modelling methodology to South African coal fly ashes experimentally studied by leaching tests and advanced mineralogical investigation methods.

2. Experimental

2.1. Waste characterisation

Samples of fresh fly ash from Secunda and Tutuka plants were used in this study. Both samples were analysed, in order to determine total elemental content and mineralogy of the ash samples.

The total content of the elements present in the fly ash samples was determined by total acid digestion ($HF + aqua\ regia + H_3BO_3$) of the samples and analysis of the eluates [11]. Spectrometric analyses of the fly ash samples were also done, using X-ray diffraction in order to determine the major mineralogical composition [11]. In addition results from an earlier study of fresh fly ash from Secunda and Tutuka were also used. In this study an advanced mineralogical characterisation technique known as the Computer Controlled Scanning Electron Microscopy (CCSEM) technique was used so as to improve mineralogical characterisation of those minerals present in fly ash, which other techniques would otherwise fail to identify [12].

2.2. pH dependent solubility and acid neutralisation capacity (ANC test)

The assay is based on the methodology of the European standard TS14429 [13] named here ANC test. It is carried out by mixing 150 ml of water containing various amounts of HNO_3 with 15 g of ash in order to obtain a series of 6 batches with pH values ranging from natural pH to about pH 4. After equilibration and stirring for 2 days at room temperature, the solid residue is separated by filtration using a membrane filter of 0.45 μm. The pH and the concentrations of the leached components were then measured in the eluates.

2.3. Analytical methods

The eluates obtained in ANC test were analysed by ion-chromatography (IC) for anions. Eluate samples acidified to pH 2 with dilute HNO_3 (65%) were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) for cations [11].

3. Geochemical modelling

The coupling of a geochemical model and leach test results was based on a methodology developed by [2]. Literature information about the fly ash mineralogical composition, the elemental total content, mineralogical investigations and the experimental results obtained in the ANC test were used to build a solid phase model of the fly ashes involved in this study. The geochemical modelling code chosen was PHREEQC (v 2.12, developed by the United States Geological Survey). PHREEQC is capable of undertaking speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations, both in natural and polluted water. It is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchange phases and sorption surfaces in which minerals and soluble species are equilibrated simultaneously [14]. PHREEQC was used with the Lawrence Livermore National Laboratory (LLNL) thermodynamic database, with the original equilibrium constant values.

3.1. Modelling methodology

The reactivity of different ash phases in contact with water is very different and has an impact on the pollutant release on different time scales. The main reactivity typologies are:

- Phases having very slow dissolution kinetics or being quasi insoluble can be considered as inert in laboratory conditions and for short time frames (e.g. a large variety of silicates, oxides – spinels). They constitute the solid matrix determining the main mechanical and physical properties of the material. For short time leaching
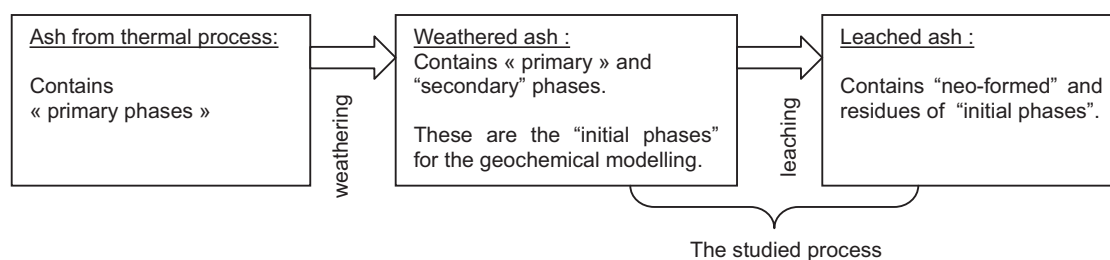
Fig. 1. Transformation pathway of fly ashes.

processes and specific leaching conditions (non aggressive pH, closed system) their presence can be neglected.

- Phases having a very important solubility and rapid (modelled as instantaneous) dissolution kinetics (e.g. soluble salts containing Na^+, Cl^-, SO_4^{2-}, etc.).
- Between these two extremes, a large variety of phases have limited solubility and different dissolution kinetics; and they represent the core of the mineral assemblage used for the model.

The waste used for the leaching studies contains a mixture of primary and secondary phases depending on the state of maturation of the material. The primary phases formed by the thermal processing of coal undergone processes of hydration and even dissolution followed by precipitation, the consequence of which can result in the secondary phases being amorphous or crystalline with precipitation being total or partial depending on the weathering conditions. These primary and secondary phases will be further modified by water contact during leaching test, by dissolution and neo-formations. Material transformation path is presented in Fig. 1.

The modelling methodology adopted may be described in several steps:

(1) An analysis of the ANC test results in terms of dissolved element concentrations vs. pH and the neutralisation curve (pH vs. H^+ added) gives the first piece of important information on the behavioural typology of the phases controlling elemental concentrations (i.e. amphoteric nature, surface complexation, non reactive elements) and the buffering properties of the material's behaviour towards acid or base.

For each ANC eluate composition, the calculation of the saturation index allows the identification of phases close to equilibrium and the possibility of their existence under the conditions of the test. It includes initial and neo-formed phases.

(2) A first phase assemblage is proposed synthesising the elemental content data; the mineralogical investigation data, literature information, and qualitative information extracted from the ANC test results. The mineralogical information on the initial material is qualitative and not exhaustive. Depending on the investigation technique used, it often concerns only the major phases and possibly may include some minor species. This information is directly used, and the identified (reactive) phases are selected for the model. Besides the solubility constant, knowledge of the dissolution kinetics of the identified phases is essential for evaluation of the reactivity character. The literature information on similar materials allows one to validate the chosen phases, or to complete the model for specific phases especially in the case of minor elements. Finally, the ANC results allow one to consider those phases (initial or neo-formed) being in equilibrium with the liquid phase in different operating conditions, as explained above. The selection of the neo-formed phases in the system waste/water/operation

conditions is a difficult task which has to obey several rules.

The precipitation priority rule of Ostwald states that the precipitate with highest solubility is kinetically favoured, and will form first in consecutive precipitation reactions [15]. In the case of metals susceptible to precipitate as different hydroxide forms, the most soluble "active" form (microcrystalline, amorphous, disordered lattice) is obtained in laboratory conditions (short-term), and in strong oversaturated solution. Some solid phases like high temperature silicates and oxides can dissolve but not precipitate in the experimental conditions because of different kinetic laws of dissolution and precipitation processes. Finally, the phase rule must be respected for the number of phases considered at equilibrium with the eluate (i.e. at constant T and P the maximum number of solid phases equals the number of chemical elements except H and O).

(3) The model is adjusted for phase quantities. The experimental data for elemental total content and the ANC eluates composition are used to determine the quantities of the initial phases considered in the geochemical model. Concerning the initial phases, one distinguishes several cases:
   • total dissolution at particular pH conditions of the ANC test: the phase quantity has to be evaluated by model fitting on specific chemical parameters experimentally measured in eluates, like (H^+ added, pH) and (pH, concentration). The problem is particularly difficult when a given element is present in many solid phases.
   • total dissolution independent of the pH or other chemical conditions—the simplest case. The phase quantity can be directly evaluated from the eluate concentration of the respective element.
   • partial dissolution in any pH conditions. For a given contact time (as chosen in the ANC test), a phase quantity can be considered solubilised and evaluated by fitting the model for respective element concentrations. If the dissolution rate is a function of pH, a kinetic law is necessary to be introduced in the model.

The quantities of the neo-formed phases will result from the model application and numerical simulation of the leaching test samples. The geochemical model represents the initial phase assemblage with their phase quantities defined. The model must be able to simulate the acid-base properties of the material (e.g. the neutralisation curve pH vs. H^+) and the eluate concentrations for the constitution elements in different pH conditions (e.g. concentration vs. pH). Finally, the elemental total content is used for the adjustment validation by verifying that the calculated total content is less than or equal to the experimental one.

3.2. Solid phase calculation

Quantitative calculation of ash formulation consists of adjusting the proportions of the initial phases to give the best fit between the measured and simulated solution values for the ANC

tests. These measured values were the pH and ion concentrations from each eluate solution. The geochemical modelling program PHREEQC does not provide a regression or optimisation facility, however its C source code is made available so that users can customise it for special purposes. In this case, the PHREEQC code was interfaced with the computational package MATLAB, which provides general purpose optimisation routines. The optimisation routines minimise an *objective function* by varying a set of *parameter values*.

In its standard form, PHREEQC uses an input file which specifies the structure of the modelling problem, the input data, and the required computed results. In a modelling run it reads the input file, constructs a set of data structures in memory which correspond to the system being modelled, populates them with the required parameter values, carries out the specified computations, and sends these results to output files. It then clears the memory structures and exits.

For optimisation, the same model structure needs to be run hundreds of times with different values of a certain set of parameters, and a selected set of output values needs to be passed to the optimisation routine in order to construct the objective function which evaluates how well the simulated results match the measured data. Consequently, for computational efficiency, the interface was set up to have three calling modes:

(1) a *setup* mode which reads the input file and sets up the data structures and computational procedures to represent the model system;
(2) an *iteration* mode which accepts the adjusted parameter values from the optimisation routine and inserts them into the data structures. It then runs the computations, and passes the selected results back to the optimisation routine to evaluate the objective function (instead of sending them to output files as in the standard version of PHREEQC);
(3) a *termination* mode which runs the model with the final set of parameter values, outputs the results to file and clears the data structures from memory.

The objective function is constructed as a weighted sum of squared differences between corresponding measured and simulated values. The weighting factor for each measurement is set by the user. The two main considerations in setting the relative weights for the different measured values are uncertainty about the accuracy of the measurement, and the relative importance of the model predictions of different quantities. Thus, if the model were a true representation of the physical system, measurements that are considered more reliable should always get higher weightings. However inadequacies in the model may require a compromise in fitting the measured data for different elements, for example. Depending on the purpose to which the model will be put, the weighting factors can be used to improve the fit for elements considered more important, at the expense of a poorer fit for the less important elements.

3.3. Ash mineralogy-literature considerations

Studies on the mineral composition show that quartz (SiO_2), glass and mullite ($Al_6Si_2O_{13}$) form the principal matrix of the majority of fly ashes reported [16]. In terms of the iron, calcium and magnesium-bearing compounds reported to be present in fly ashes, hematite (Fe_2O_3), magnetite (Fe_3O_4), anhydrite ($CaSO_4$), lime (CaO) and periclase (MgO), are the most frequently reported with minor fractions of these elements also present in the glassy phase [16].

The mineral compositions of South African fly ashes (including Secunda and Tutuka ashes) are similar, with quartz, glass and

Table 1
Total elemental concentrations (mmol/kg) in Secunda and Tutuka ashes (acid digestion).

Element	Secunda fly ash	Tutuka fly ash
Ca	937.02	1546
Mg	470.21	368.89
Na	315.62	259.24
K	104.89	79.3
SO_4^{2-}	1245.29	1574.28
Si	10,593.24	12,062.66
Al	2270.72	1487.03
Cr	3.15	3.85
Mo	0.054	0.079
Sr	20.86	8.49
Ni	0.75	1.29
Fe	344.85	736.26
Li	36.31	25.94
Zn	0.56	0.58
Ti	213.12	197.99

mullite being the most commonly identified mineral phases [17]. Previous studies of fly ashes from South African Power stations have shown mineral phases most commonly to be detected were quartz, mullite, hematite, magnetite, maghemite (Fe_2O_3), anhydrite, portlandite ($Ca(OH)_2$), lime, periclase and titanium oxides [18,19,20].

The formation of secondary solid phase during hydration of ash wastes has been previously investigated [3,16,21,22,23]. Secondary mineral phases that have been identified in weathered ash are ettringite ($Ca_6Al_2 (SO_4)_3(OH)_2 \cdot 26H_2O$), proto-imogolite ($Al_2SiO_3(OH)_4$), Ca-aluminates, Ca-silicates, calcite ($CaCO_3$), portlandite ($Ca(OH)_2$), gypsum ($CaSO_4 \cdot 2H_2O$) and amorphous iron oxyhydroxide (FeOOH).

Investigations have revealed that for many fly ashes in contact with water, the aluminium concentration was controlled by the solubility of $Al(OH)SO_4$ when pH values were less than ∼6.0, by amorphous $Al(OH)_3$ when the pH is between ∼6.0 and 9.0, and by crystalline gibbsite ($Al(OH)_3$) when the pH was greater than 9.0 [16,21,24]. These Al phases are neo-formed by ash hydration.

Silicon concentration is governed by the solubility of quartz at pH lower than 10 and by the solubility of wairakite ($CaAl_2Si_4O_{13} \cdot 2H_2O$) at a higher pH. Other possible aluminium-silicate minerals that have been proposed as likely solubility controlling minerals for silicon include proto-imogolite, laumontite ($CaAl_2Si_4O_{12} \cdot 4H_2O$), or mullite [21,23].

The minerals that have been identified by different authors to control the calcium concentrations are anhydrite, gypsum ($CaSO_4 \cdot 2H_2O$), calcite or portlandite [3,21,25]. Closely related to calcium activities, Fruchter et al. [3] has found that the dominant sulphur species in the solids was SO_4^{2-} with negligible amounts

Table 2
Mineral phases of Secunda and Tutuka ashes as identified by CCSEM: primary phases and secondary phases formed after prolonged contact with water.

Primary fly ash phases	Secondary phases
CaMgoxide	Al-hydroxide/Al-oxide
Ca-oxide/CaP-oxide	Amorphous C-Ca-silicate
Fe-oxide/pyrite	Amorphous C-Ca-aluminosilicate
Kaolonite	Mg-rich silicate/aluminate
Kaolonite (carbonate, pyrite)	Hydrocalumite
Kaolinite (carbonate Ca <40)	Hydrocalumite (Si)
Kaolinite (carbonate <40 altered)	NaCl
Kaolonite (carbonate Ca >40)	Ba/Sr-oxide
Kaolonite (pyrite)	
Mica/orthoclase	
Quartz60Kaolonite40	
Quartz80Kaolonite20	
Quartz	
Ti-oxide	

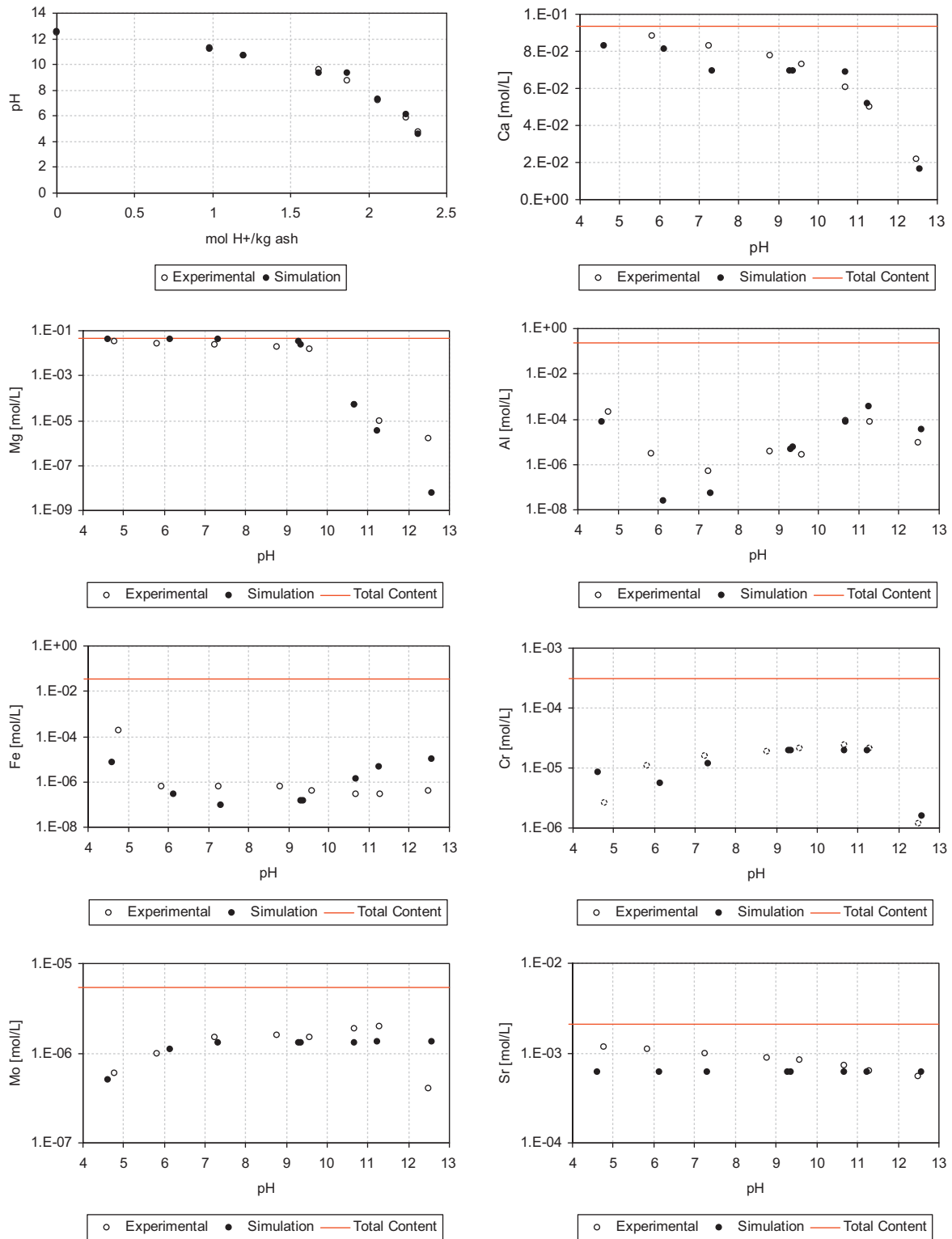**Fig. 2.** Experimental data, simulation results for Secunda ash – ANC test.

of SO_3^{2-} and $S_2O_3^{2-}$ being also present. Iron concentrations have been reported [3,22] to be controlled by amorphous ferric hydroxides.

In terms of the minor elements present in ash, the literature information is limited, with a few hypotheses given. In [3] barium and strontium concentrations are likely to be controlled by co-precipitated $(Ba,Sr)SO_4$, rather than barite $(BaSO_4)$ or celestite $(SrSO_4)$. Barium and strontium were also found to be independent of pH, throughout the measured pH range, which suggests witherite $(BaCO_3)$ and strontianite $(SrCO_3)$ were not the solubility controlling solids. Powellite $(CaMoO_4)$ appears to control the Mo concentration in extracts with hot water while the leaching of chromium has been suggested to be controlled by $BaCrO_4$ and $Ba(S,Cr)O_4$, with the possibility of
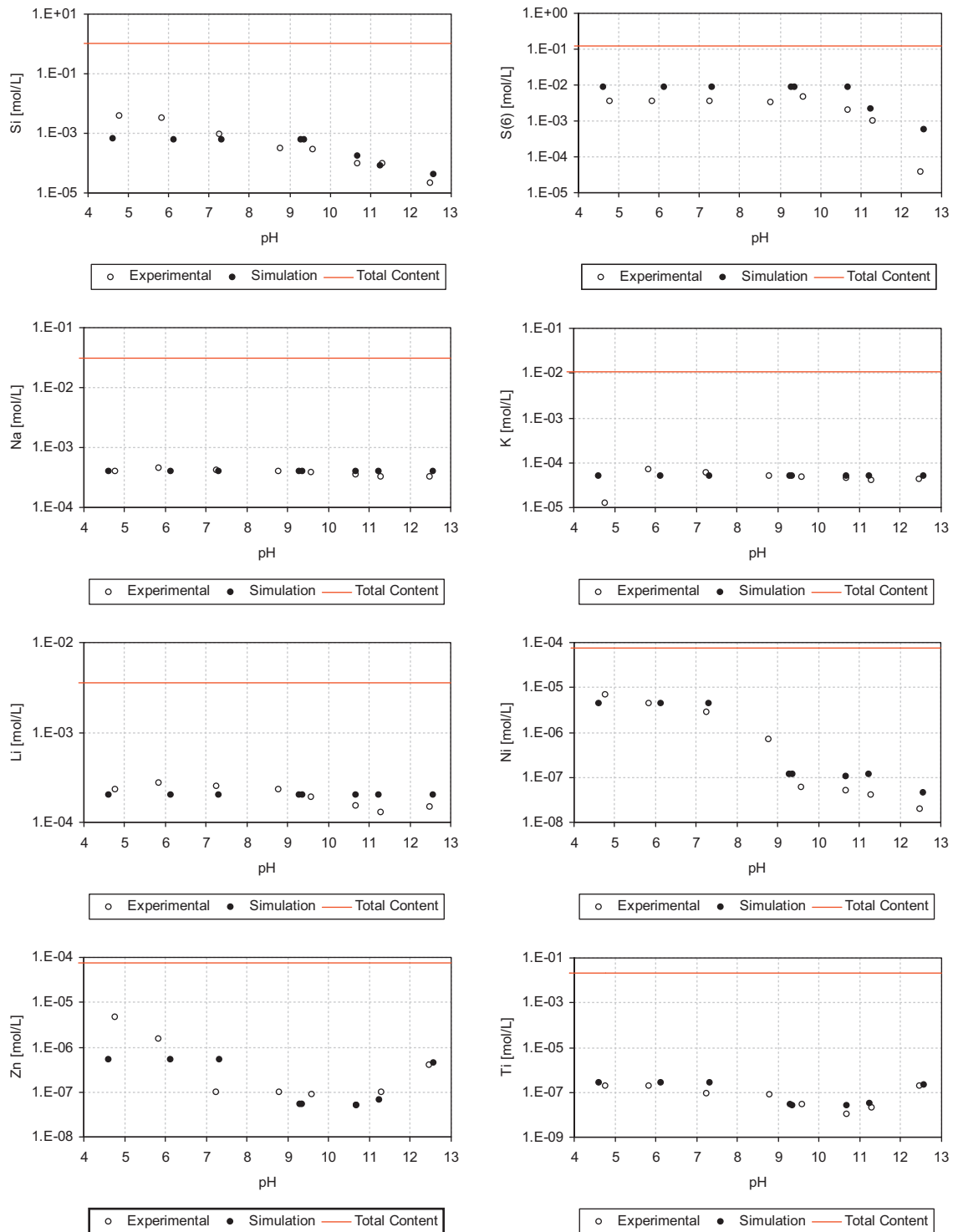
Fig. 2. (*Continued*).

4. Results and discussion

4.1. Experimental results

The elemental total content determined by acid digestion is presented in Table 1. The X-ray diffraction results for both Secunda and Tutuka fly ash used in this study show the presence of quartz, mullite, lime and minor amounts of calcite [11].

chromium also being in equilibrium with amorphous or crystalline $Cr(OH)_3$ [2].

The X-ray diffraction technique is limited in that it can only detect mineral phases that are greater then ~3% mass, and can only detect mineral phases that are crystalline in nature. In order to overcome the XRD limitation, the CCSEM spectroscopic technique (considerably more sensitive with respect to minor mineral or amorphous phases) was used. Mineralogical results from this technique are shown in Table 2 [12]. Fresh Secunda and Tutuka fly ashes were analysed and the mineralogy documented (primary phases). Thereafter fly ash samples were exposed to brine water in order to ascertain the fly ash reactivity over periods of months
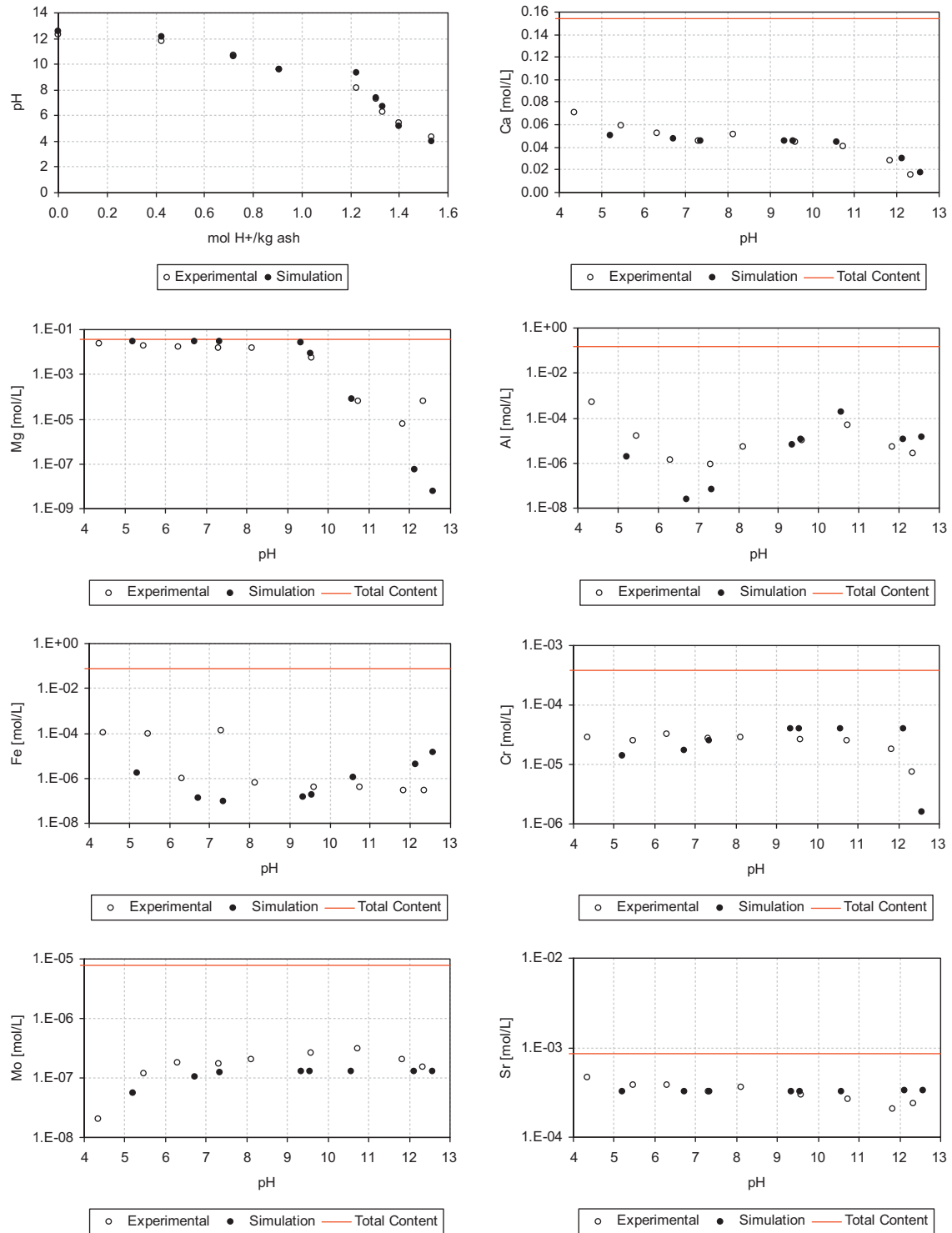
Fig. 3. Experimental data, simulation results for Tutuka ash – ANC test.

and a CCSEM analysis was again performed. Table 2 shows primary mineral phases and the new phases identified after ash/brine interaction. The main conclusion from this study was that the model should consider, among others, the possibility of obtaining ettringite, amorphous Ca-aluminosilicates and hydrocalumite ($Ca_2Al(OH)_7 \cdot 2H_2O$) as newly formed phases in contact with water (Table 2).

The ANC test results (Figs. 2 and 3) show a typical behaviour already encountered for coal ashes from other origins [2]. Both Secunda and Tutuka ashes have an important acid neutralisation capacity, the pH of the ash/water mixture being 12.48 for Secunda and 12.34 for Tutuka ash. The elements Na, K, Li, and Sr show a constant solubilisation or very weak variation as a function of pH. Cr and Mo have a similar behaviour (solubility increasing with pH) suggesting a surface complexation phenomenon. Only Ca and Mg solubilisation are close to the total content at acid pH. SO_4^{2-} follows a similar trend to that of Ca but the solubilisation seems to be incomplete in the low pH region (probably
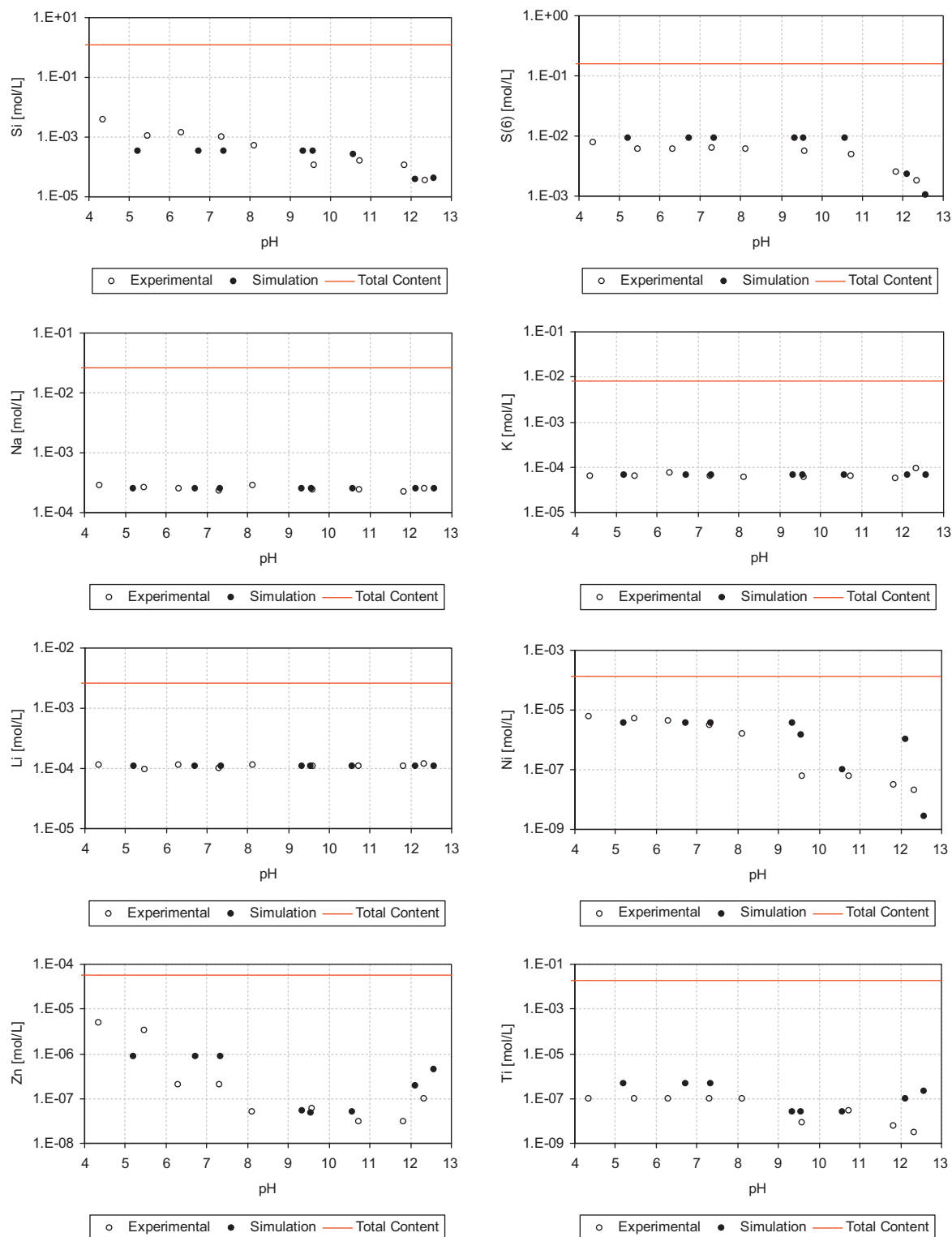
Fig. 3. (Continued).

other forms of S exist). Al, Zn and Ti have a minimum solubility at neutral pH while Si, Fe and Ni solubility decrease with the pH increase.

4.2. Geochemical model

Among the identified phases by XRD and CCSEM, the following are selected as initial phases in the model because potentially reac-

tive under the ANC test conditions: lime, periclase, calcite, pyrite (FeS$_2$), hematite, kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), mullite, and for trace elements silicates and/or oxides. Anhydrite was selected based on literature information.

Among the initial phases several can be at dissolution equilibrium or partially dissolved and could also be identified by SI close to zero. Zn$_2$TiO$_4$ (SI = 0.1), Ni$_2$SiO$_4$ (SI = −0.6), SrSiO$_3$ (SI = −1) and millerite (NiS) (SI = 0.2) were

Table 3
Initial and neo-formed phases together with the fraction of the total elemental content considered in the mineralogical model for Secunda fly ash.

Initial phases	mmol/kg fly ash	Element	% of total content	Possible neo-formed phases
Anhydrite ($CaSO_4$)	76.5	Ca	88.41	$Al(OH)_3$(mC)
$CaCrO_4$	0.196	Mg	88.54	Brucite[a]
Calcite ($CaCO_3$)	136.4	Na	1.26	Bunsenite[a]
$CaMoO_4$	0.0132	K	0.47	Celestite
Hematite (Fe_2O_3)[b]	141.1	SO_4^{2-}	7.03	Csh_gel_0.8[a]
Kaolinite ($Al_2Si_2O_5(OH)_4$)[b]	23.5	Si	0.50	$Cr(OH)3(A)$[a]
Lime (CaO)	615.2	Al	2.10	Ettringite[a]
Millerite (NiS)[b]	0.00116	Cr	6.22	$Fe(OH)_3$(am)-CF[a]
Mullite ($Al_6Si_2O_{13}$)[b]	0.126	Mo	24.44	Gypsum
Ni_2SiO_4[b]	0.0214	Sr	29.17	Magnesite
Periclase (MgO)	416.3	Ni	5.86	$Ni(OH)_2$
Pyrite (FeS_2)[b]	5.4	Fe	83.42	$NiCO_3$
$SrSiO_3$[b]	6.1	Li	5.51	Portlandite[a]
Zn_2TiO_4[b]	0.00267	Zn	0.95	SiO_2(am)
Na^+	5.0	Ti	0.0012	$Sr(OH)_2$
K^+	1.0			$Zn(OH)_2$(gamma)
Li^+	2.0			

[a] Phases for which precipitation occurs, as calculated by PHREEQC.
[b] Phases which cannot precipitate in experimental conditions used.

selected in this way (in parentheses are SI at material's pH-value).

For Na, K and Li one observes that the concentration in the different eluates of ANC test is not dependent on pH, demonstrating that they come from very soluble phases (salts or oxides). Consequently these elements were introduced in the model as free ions (initial phases totally dissolved). It must be emphasised that only a small fraction (those considered in the model) of the total content of these elements is soluble in the ANC test conditions.

Phases such as quartz, mullite, kaolinite, pyrite, hematite, millerite and generally the silicates dissolve slowly and/or cannot precipitate, thus they are not at equilibrium with the eluates. However a certain quantity can dissolve enriching the eluates in elements like Si, Al, S, Fe. The dissolved quantity is lower than the total one and was evaluated by fitting the model using the optimisation method described in Section 3.2.

Kaolinite is slightly soluble in normal conditions and a certain quantity can dissolve in test conditions. At temperatures between 200 and 600 °C it loses water and turns into very reactive phases like metakaolin [26]. It is also legitimate to consider that some amount of kaolinite in fly ash is in an activated state, so able to react in the presence of lime like a cement material. The only silicate phases precipitating in these conditions are cement like phases i.e. calcium silicate hydrate gels (CSH). This reaction is possible to occur during the ANC test (about 2 days). On the other hand other hydration products like amorphous hydrated-Calcium aluminates (e.g. hydrocalumite) need more time to precipitate.

Concerning Cr and Mo, no mineralogical data were available for the studied ashes, and thus information from literature together with the ANC results were used for explaining their behaviour. Chromate and molybdate are the most soluble species of Cr and Mo elements respectively, so only the reactive parts of these elements were considered in the model. A surface complexation model was introduced in order to explain the particular behaviour of chromate and molybdate species in function of pH. The material contains iron in initial phases hematite and pyrite, and generates iron hydroxides as neo-formed phases in contact with water. The diffuse layer model was used with the complexation constants of Dzombak and Morel, supplied by the LLNL database. According to this model the sorption surfaces on amorphous ferric hydroxides are of two types, i.e. high-capacity/low affinity and low capacity/high affinity, with site densities of 0.2 mol/mol Fe and 0.005 mol/mol Fe respectively. The model considered amorphous ferrihydrate surface (denoted ($Fe(OH)_3$)(am)-CF). This phase is neo-formed, and its quantity, calculated by the model, depends on Fe^{3+} availability (Figs. 4 and 5).

The eluate compositions from the ANC test allowed the identification of equilibrium phases by calculation of Saturation Indices for the different pH conditions. Generally the neo-formed phases during the test are at equilibrium state with the leachate. They are mostly hydroxides, sulphates, and amorphous silicates (for the studied conditions). Not all of the proposed phases precipitate effectively. The proposed neo-formed phases and those calculated by PHREEQC to precipitate under different pH conditions are listed in Tables 3 and 4. Figs. 4 and 5 show the newly formed phases and their quantities for both ashes (phase quantity in mol/L vs. pH). As expected, the most neo-formations occur in the basic pH domain and control the elements' concentration in eluates.

Tables 3 and 4 also show the model mass balance by element. For each element, the fraction of the total content (experimentally determined) used in the geochemical model was calculated. The quantities of all elements in the model are less than the respective total content determined experimentally. The order of magnitude of the loading fraction in the model varies for the different elements. This is to be expected, since only the reactive part of the material could be quantified by the approach based on leaching tests. The quantities of all initial phases considered in the model were all calculated by fitting the model to the experimental data (pH vs. H⁺ added) and (concentration vs. pH) using the optimisation procedure.

The simulation results and the experimental data for all elements are presented in Figs. 2 and 3. A very good fit between experimental data and simulations can be seen for the neutralisation curve and for almost all species concentrations. For several elements (Al, Fe, Mg, Zn) occurring as different solid phases, small discrepancies are observed for certain pH domains which could be explained by three main reasons: (1) the real solid compound is not that considered in the model; (2) the solubility constant of the controlling phase is not correct; (3) experimental errors for eluate analysis. The first is less probable while, in this case, the differences between experimental and simulated concentrations should be much higher. The second seems to be the major cause and is a common aspect encountered in geochemical modelling, especially when amorphous phases are involved for which a solubility constant value is difficult to determine (case of Fe, Al, Zn hydroxides). The third reason is also possible knowing that colloidal forms are difficult to separate from eluates and could lead to a concentration overestimation (supposed in the case of Mg at pH >11).

Table 4
Initial and neo-formed phases together with the fraction of the total elemental content considered in the mineralogical model for Tutuka fly ash.

Initial phases	mmol/kg fly ash	Element	% of total content	Possible neo-formed phases
Anhydrite ($CaSO_4$)	78.1	Ca	32.52	$Al(OH)_3(mC)$
$CaCrO_4$	0.392	Mg	77.39	Brucite[a]
Calcite ($CaCO_3$)	51.82	Na	0.96	Bunsenite[a]
$CaMoO_4$	0.02	K	0.84	Celestite
Hematite (Fe_2O_3)[b]	314.7	SO_4^{2-}	5.8	Csh_gel_0.8[a]
Kaolinite ($Al_2Si_2O_5(OH)_4$)[b]	1.4	Si	0.16	$Cr(OH)3(A)$[a]
Lime (CaO)	372.5	Al	3.06	Ettringite[a]
Millerite (NiS)[b]	0.0352	Cr	10.18	$Fe(OH)_3(am)-CF$[a]
Mullite ($Al_6Si_2O_{13}$)[b]	7.12	Mo	25.31	Gypsum[a]
Ni_2SiO_4 [b]	0.0214	Sr	38.54	Magnesite
Periclase (MgO)	285.5	Ni	2.72	$Ni(OH)_2$
Pyrite (FeS_2)[b]	6.57	Fe	86.36	Ni_2SiO_4
$SrSiO_3$ [b]	3.27	Li	4.20	$NiCO_3$
Zn_2TiO_4 [b]	0.00441	Zn	1.52	Portlandite[a]
Na^+	2.5	Ti	0.0022	$SiO_2(am)$
K^+	0.7			$Sr(OH)_2$
Li^+	1.1			$Zn(OH)_2(gamma)$

[a] Phases for which precipitation occurs, as calculated by PHREEQC.
[b] Phases which cannot precipitate in experimental conditions used.
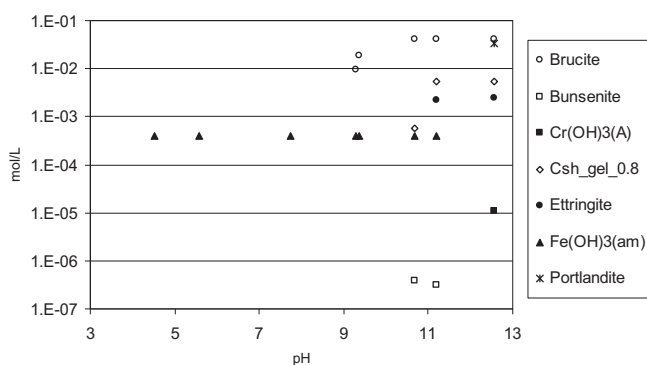

Fig. 4. Neo-formed phases during the leaching test for Secunda ash.
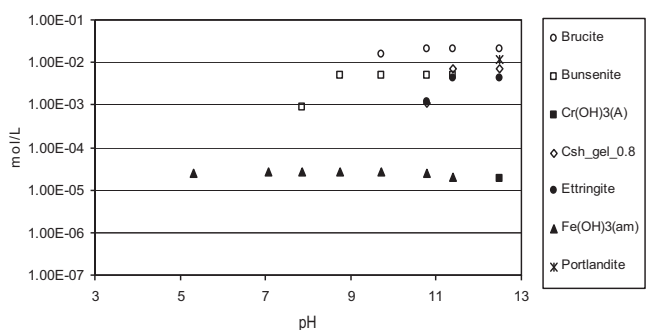

Fig. 5. Neo-formed phases during the leaching test for Tutuka ash.

5. Conclusion

The modelling methodology was based on mineralogical analysis and on leaching tests. The information obtained from the leaching tests complements the mineralogical analysis, in the sense that minor phases not observed by mineralogical analysis (as sophisticated as it may be) could be identified on the basis of their solubility in different leachants. It must be emphasised that mineralogical models based on leaching tests are limited to phases having certain reactivity in water for the experimental conditions chosen.

When the mineralogical model becomes complex, a numerical procedure is necessary in order to evaluate the quantities of different phases involved. Coupling the speciation model (PHREEQC) with an optimisation code (such as those supplied with MATLAB) made it possible to handle a model with many parameters and to obtain a set of rigorously fitted parameters. The modelling tools presented here are new in the field of leaching tests interpretation for waste characterisation. As stated in the bibliography discussion, coupling geochemical modelling and leaching tests is not new, different approaches are encountered. Nevertheless, the adjustment method of unknown parameters still remains an obscure aspect in most of the published work. The present work provides a thorough calibration method for a geochemical model developed in PHREEQC.

The studied ashes originate from the same type of coal but have been processed in different ways. The mineralogical analysis as well as the ANC leaching test showed similarities in terms of identified phases and leaching behaviour for different pH conditions. This experimental result is confirmed by the modelling approach and the simulations performed. The same mineralogical consortium described both ashes, and the quantities of the reactive phases were of the same order of magnitude.

The study presented here is continuing with other experimental and modelling aspects as parts of a larger research program. The presented geochemical model is the starting point for in progress developments taking into account different leaching conditions (water/waste contact modes, time frames, leachant compositions) representing the real disposal scenarios, and the modelling tools will be completed with laws describing dynamic phenomena in an appropriate manner (kinetic laws, transport mechanisms).

Acknowledgements

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