NEW APPROACH TO LEACH TESTING OF
BAUXITE RESIDUE TO SUPPORT MANAGEMENT DECISIONS IN VIEW
OF BENEFICIAL APPLICATION AND STORAGE

Carter, CM[1*], Cooling, D[1], Matheson, T[1], van der Sloot, HA[2] and van Zomeren, A[2]

[1]Technology Delivery Group, Alcoa World Alumina, Kwinana, Western Australia
[2]ECN, Department Clean Fossil Fuels, Environmental Risk Assessment, Petten, The Netherlands

Abstract

Bauxite residue storage, treatment and re-use practices are receiving increasing attention as refineries strive to reduce the potential environmental impact of their operations. In the past, leaching tests such as the Toxicity Characteristic Leaching Protocol (TCLP) and the Australian Standard Leaching Protocol (ASLP) test have been used to evaluate wastes for their potential to release trace elements. These tests are limited in their usefulness, as they provide leaching data at a limited number of pH values, and do not provide information about the long-term behaviour of the residue. A new approach to characterisation of leaching behaviour, previously developed by the Energy Research Centre of the Netherlands (ECN) and Vanderbilt University (Nashville, US), has been applied to various bauxite residue samples. This approach involves characterising the leaching behaviour of bauxite residue using a standardised pH dependence leaching test over a pH range from 4–12, and a standardised percolation leaching test. The leaching data was modelled using a geochemical speciation program to determine which chemical processes are controlling the leaching behaviour of bauxite residue. This approach, when applied to bauxite residue, shows that the nine residue samples examined behave very similarly for most elements, even when generated by different refineries that utilise bauxite from different sources. This implies that the solubility controlling minerals and other release controlling factors are most likely the same for this wide range of samples. Residue treatments such as carbonation and seawater neutralisation do affect the leaching of some elements, resulting in a change in the leaching behaviour of the treated material as compared with the untreated sample. Using geochemical speciation modelling the changes are largely explained, which provides a basis for prediction of long term behaviour.

1 Introduction

As alumina refineries strive to become more sustainable and environmentally accountable, it is inevitable that bauxite residue management practices will continue to improve. New approaches to residue management, such as residue neutralisation and re-use of residue are increasingly being investigated as ways to lessen the potential environmental impact of refinery operations. Whether residue is left in residue storage areas (RSAs) or exposed to different environments through re-use opportunities, understanding residue behaviour has become critical in evaluating the potential impacts associated with the alternative methods for managing residue.

In the past, leaching tests such as the Toxicity Characteristic Leaching Protocol (TCLP, 1990), and the Australian Standard Leaching Protocol (ASLP) test (Standards Australia, 1997) have been used to evaluate wastes for their potential to release trace elements. These tests are limited in their usefulness, as they provide leaching data at a limited number of pH values, and do not provide information about the long-term behaviour of the sample [van der Sloot, 1996]. The TCLP and ASLP leaching tests do not generate data that can be used to predict the leaching behaviour of the sample in an environment that differs in pH and Eh from that of the leaching test. Moreover, the chemical processes that determine the leaching behaviour are unknown.

A new scenario approach to characterisation of leaching behaviour was jointly developed by the Energy Research Centre of the Netherlands (ECN) and Vanderbilt University (Nashville, US) [Kosson et al., 2002], and has been applied to various bauxite residue samples. This technique involves characterisation of the leaching behaviour of bauxite residue using a standardised pH dependence leaching test over a pH range from 4 – 12, and a standardised percolation leaching test. The data is subsequently analysed using geochemical speciation models to determine which processes are controlling leaching. This approach has also been used successfully for a range of contaminated soils [Dijkstra et al., 2004]. The purpose of this work is to assess the leaching behaviour of red mud under various conditions and to understand the underlying chemical processes that determine the leaching behaviour. This work will enable a better understanding of the environmental impact of bauxite residue and might facilitate the development of improved utilisation and disposal scenarios.

2 Experimental

2.1 *Materials*

Bauxite residue slurry samples (super thickener underflow or last washer underflow) were collected from each of Alcoa's nine alumina refineries and filtered (GF/B) to provide a consolidated sample with similar moisture content to residue in a storage area (approximately 70% solids by weight). Sea water neutralised residue slurry was prepared by mixing the unfiltered underflow sample (2.0 to 3.2kg) with seawater (approximately 60kg) for 48 hours. After this time the sample was allowed to settle overnight, the supernatant solution decanted, and the neutralised residue filtered to provide a wet residue cake. After neutralisation, the samples were stored in closed containers prior to testing. Carbonated residue slurry was prepared by sparging unfiltered residue slurry with carbon dioxide, until the pH reached either 9.0 (Australian residue) or 10.5 (all other residue samples). The samples were left over night, and where the pH had rebounded the samples were again sparged with carbon dioxide until the desired pH had been obtained. After carbonation, the residue samples were stored in closed containers prior to testing. All residue samples satisfied the required grain size of 95% less than 1mm.

2.2 *Leaching Test method*

The filtered residue samples were subjected to a pH dependent leaching test as described in CEN standard PrEN 14429. PrEN 14429 involves leaching the sample (at 20°C, with a mixing rate at approximately 10rpm) over a pH range of 4 to 12 (including the sample's natural pH), for a period of 48 hours. In order to prepare leachate solutions that equilibrated at the desired pH, a preliminary acid neutralisation capacity (ANC) test was performed on the samples prior to the pH leaching test to estimate the amount of acid or base needed.

The leaching test was performed at a liquid to solid (L/S) ratio of 10 (L/kg dry weight). The preliminary ANC data was used to prepare eight leachate solutions of 15.6M nitric acid and/or 2M sodium hydroxide that gave a final solution pH in the desired pH range. The mass of sample required (to give 15 ± 1.5g dry weight) was weighed into 250mL polypropylene (PP) bottles, and one third of the leachate solution added. The solution was equilibrated for 30 minutes in a rotating water bath (20°C, 10rpm), before the next third of the leachate solution was added. The solution was equilibrated for another 90 minutes before the last portion of leachate was added. The sample was then allowed to equilibrate under continuous rotation for a further 44 hours. The solution pH was measured 4, 44 and 48 hours after the initial leachate addition.

At the end of the 48 hour equilibration period the bottles were centrifuged and then filtered through 0.45µm membrane filter. The sample pH at 44 and 48 hours did not vary by more than 0.3 pH units for any sample, satisfying the condition for approaching equilibrium. The filtered leachate solutions and the entrained pore water of the sample collected prior to leach testing were analysed for total organic carbon (TOC) by an O.I. Analytical Model 1010 Wet Oxidation TOC analyser, chloride was determined colourimetrically, fluoride by ion specific electrode measurement and a range of major, minor and trace elements (Au, Ag, As, Ba, Be, Bi, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, La, Li, Lu, Mo, Nb, Nd, Pb, Pd, Pr, Pt, Rb, Re, Sb, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, U, W, Y, Yb, Zr) were determined by Inductively Coupled Plasma (ICP) Mass Spectrometry, or by Inductively Coupled Plasma (ICP) Optical Emission Spectrometry (Co, Cu, Ni, Sc, Zn, Al, B, Ca, Cr, Fe, K, Mg, Mn, Na, P, S, Si, Ti, V).

A sample of last washer underflow from one of Alcoa's alumina refineries was subjected to percolation leach tests [PrEN 14405]. The percolation test was run as an up-flow column test at the natural pH of the sample, where deionised water was used as the leachant. The eluates were collected at specified liquid solid (L/S) ratios between 0.1 and 10. This same sample was subjected to the concise leaching test [Kosson and van der Sloot, 1997], which consists of 4 extractions. Two extractions are carried out as a serial batch test similar to EN 12457-3 at L/S=1 (instead of L/S=2) and cumulative L/S=10 using demineralised water and a contact time of 24 hours. Two additional extractions are carried out as pH controlled leaching tests at pH values deviating from the natural pH of the material, such that the major pH domains (around 4, around neutral pH and at mild alkaline pH) are covered. The eluates are analysed for dissolved organic carbon (DOC) and total inorganic carbon (TIC) using a Shimadzu TOC 5000a analyser and various major, minor, and trace elements by ICP-Atomic Emission Spectrometry (AES). The species Cl, F, ammonium and sulfate were analysed by ion-chromatography.

2.3 *Geochemical modelling*

Leaching tests cannot be used directly to assess relevant concentrations under field conditions or release in field scenarios. Therefore, answering the questions posed in the introduction requires modelling to provide a better understanding of the chemical speciation aspects that control release in the long term, or to obtain a source term for release under influence of changes in material properties with time by external factors. Modelling can be carried out to predict leaching of all elements, and to identify the solubility controlling processes using the recently developed JAVA-based modelling tool ORCHESTRA [Meeussen, 2003] as chemical speciation code. Partitioning between free ion and complexed metal species in solution as well as element partitioning in the solid phase can be assessed. The element interaction with mineral phases, aluminium-oxide, iron-oxide, clay surfaces,

particulate and dissolved organic matter can be quantified provided that the relevant information is available (e.g., clay content, organic matter content and the amount of reactive Fe and Al surfaces obtained by selective extractions). The model approach is based on a combination of a number of recently developed mechanistic adsorption models such as the NICA-Donnan approach for adsorption to organic matter [Kinniburgh et al., 1999], and the Diffuse Layer model of Dzombak and Morel for adsorption to hydrous ferric oxides [Dzombak and Morel, 1990]. An example of the successful application of this modelling approach to prediction of release for bauxite residue will be given in the results.

3   Results and discussion

3.1 *Benefits of the Scenario Approach*

The leach testing protocol developed by ECN and Vanderbilt University is part of a scenario approach, which is designed to ultimately understand the behaviour of a material of interest in a particular utilisation or storage scenario. The initial steps are to define the problem, and collate any data that already exists. The material is characterised to understand the release of elements with time (percolation test) under the environmental conditions that the material will be subjected to (pH leach test). The data is used with the storage or re-use details to model and evaluate the scenario from a regulatory and treatment perspective; i.e. can the material be safely stored, remediated or re-used? This approach is underpinned by a database/expert system that collects data in a unified format, and allows modelling and comparison of laboratory data against field data. This is outlined in Figure 1.

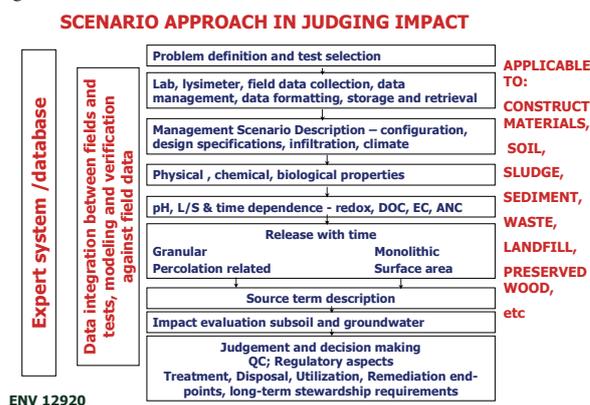**SCENARIO APPROACH IN JUDGING IMPACT**

Figure 1: Outline of the database/expert system for environmental impact assessment based on release as derived from leaching tests.

The characterisation tests used for granular material (such as bauxite residue) have significant advantages over the current regulatory tests (such as the TCLP and ASLP tests). The data produced is much more extensive, and can be used for modelling and predicting future behaviour. In short, the advantages of the pH leach test include:
- Identification of sensitivity of leaching to small pH changes
- Provides information on pH conditions imposed by external influences (e.g. carbonation or imposed neutralisation)
- Basis for comparison of international leaching tests (e.g. TCLP, ASLP)
- Basis for geochemical speciation modelling
- Provides acid neutralisation capacity information
- Mutual comparison of widely different materials to assess similarities in leaching behaviour
- Recognition of factors controlling release (dissolved organic carbon interaction, redox)
- For non-interacting species it is possible to assess the sub-sampling error
- Applicable to almost any material

The advantages of the percolation test include:
- Identification of solubility control versus wash out (see Figure 2)
- Indication of pore water concentrations relevant to field leachate from low L/S data
- Local equilibrium established quite rapidly

- Basis for geochemical speciation modelling
- Allows comparison with lysimeter and field data provided L/S value can be obtained from such measurements
- Projection towards long term behaviour possible
  • Solubility controlled release
  • Wash-out of non-interacting species
- Applicable to many materials (limitation for materials with low permeability)

An example of the pH leach test and the percolation test results is given in Figure 2. This data was not generated from a bauxite residue sample. The pH dependent leaching is given for fluoride and chloride in the left graph. Fluoride shows a pH-dependent leaching pattern indicating chemical processes that determine the leaching behaviour at different pH values. On the other hand, chloride is a very soluble element which is not complexed by the matrix. Hence the pH dependent leaching pattern results in a straight line.

The middle and right side graph show the results of the percolation test as the cumulative leaching (mg/kg) and the leached concentrations in each fraction. First, the cumulative leached amount in the percolation test is closely related to the leached amount in the pH dependence test (see arrow) at the native pH of the sample. This shows the consistency between both leaching tests.

It can be seen that fluoride leaching is solubility controlled by the straight line of the cumulative release curve (slope=1) and by the concentration plot. Hence, the chemical process that determines the leaching of fluoride maintains a constant equilibrium concentration.

The cumulative leaching of chloride however, shows a typical wash out effect. The samples gets depleted as the L/S ratio is increased, this is also reflected in the concentration graph for chloride.

When evaluating bauxite residue material for storage or re-use scenarios, specific environmental conditions will exist. Using the pH leach test, the data that is relevant to the scenario can be used (Figure 3), instead of applying data generated in the laboratory under pH conditions that are different from the pH of the scenario [van der Sloot et al., 1997].
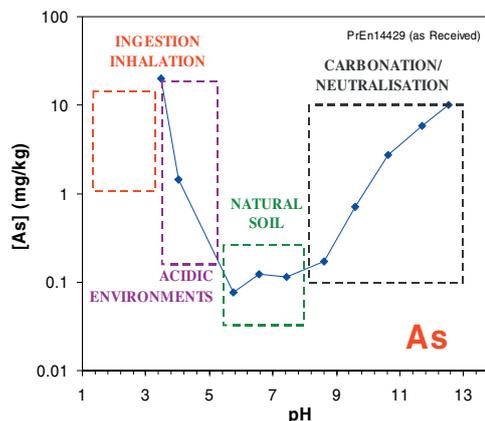
Figure 3: Evaluation of different questions in relation to utilisation and storage of bauxite residue using pH dependent leaching test data.

The percolation test has proven to be good at predicting the leaching behaviour of a material of interest in the field, and is useful for predicting the long-term behaviour of a material in the environment [van der Sloot et al., 2003]. Leach data, in addition to information on the scenario the material will be used in, can be used to predict leaching behaviour of material over a range of 100 – 1000 years.

3.2 *Acid neutralisation capacity (ANC)*

The final pH of each leachate solution in TS 14429 (CEN Standard) can be used to generate the acid neutralisation capacity curve of the material tested. The acid/base addition is calculated as mol H^+/kg (dry weight sample), with base addition expressed as a negative value.

The acid neutralisation capacity of the residue samples vary considerably, depending not only on the type of treatment they have received, but also on the refinery in which it was generated (Figure 4). Neutralisation reduces the native pH of the material, and decreases the material's ANC. ANC behaviour is likely to be dependent on the refinery operating conditions, particularly in regard to lime addition and residue washing. Using the ANC, the time period for residue to be completely neutralised due to atmospheric carbonation, for example, can be predicted. This information is useful in modelling the effects of treatment and the long-term leaching behaviour of residue.
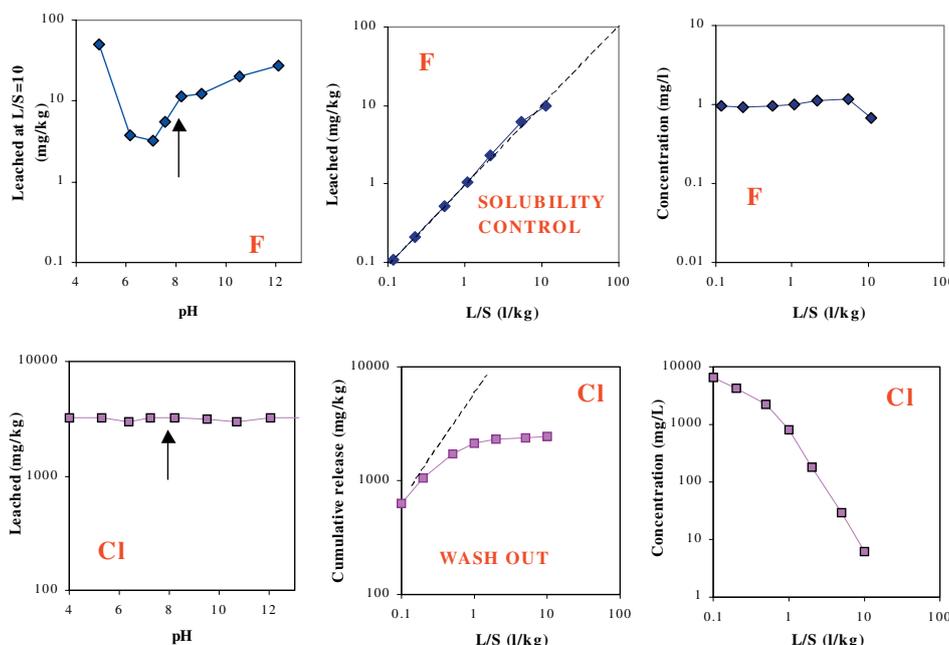
Figure 2: Example of release processes for fluoride and chloride. Examples of solubility control (F) and wash out (Cl) are given based on the results of a pH leach test (left graph) and a percolation test (middle and right graph).
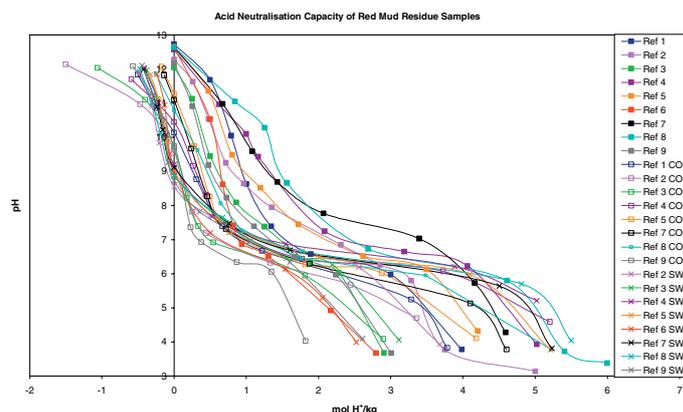
Figure 4. Acid neutralisation capacity (ANC) curves for residue samples as received, after carbonation (CO2)
and after seawater neutralisation (SW).

3.3 pH leaching tests

The leaching data can best be represented as the amount leached (expressed in mg/kg on a log scale) against the leachate pH. This manner of representation allows the effect of pH on leaching to be readily discerned, as changing pH can change the amount leached by orders of magnitude. This type of information cannot be obtained from a single step leaching test, but is highly relevant for a proper judgement of environmental impact.

Aluminium leaching from residue varies over four orders of magnitude in the pH range 4 to 12 (Figure 5). Clearly pH is a major factor in determining aluminium leaching from residue, a point that would not be obvious from the regulatory ASLP or TCLP tests. The leaching behaviour is very similar for each untreated residue sample tested, indicating that the chemical processes controlling leaching are the same for each sample. Geochemical modelling of last washer underflow leaching data indicated that aluminium leaching was controlled by the solubility of amorphous $Al(OH)_3$, and at low pH (< 5) by the solubility of Boehmite.

Residue carbonation did not significantly change the leaching behaviour of aluminium compared with untreated residue (Figure 5). However, seawater neutralisation of residue decreased the amount of aluminium leached from residue at pH > 9; this change was independent of the pH change that occurred due to neutralisation. Geochemical speciation modelling of the data indicates that at pH > 9 the mineral controlling aluminium leachability has changed from amorphous $Al(OH)_3$ in untreated residue to Diaspore. Around neutral pH organic matter is an important controlling factor in sea water neutralised residue.

Calcium leaching from residue is strongly affected by pH, and varies by over nearly four orders of magnitude in the pH range 4 – 12 (Figure 5). Residue neutralisation by carbonation and sea water treatment reduced the calcium leached for all residue samples; this change is independent of the imposed pH change due to neutralisation.

Geochemical modelling of a last washer underflow sample indicated that anhydrite or gypsum (both $CaSO_4$) controlled calcium solubility at pH < 7, while at pH > 7 beta-TCP ($Ca_3(PO_4)_2$) seemed to be the controlling phase. Modelling of calcium leaching may be improved by the inclusion of stability constants for Bayer specific lime solids such as tricalcium aluminate hexahydrate (TCA6) into the thermodynamic database.

In Figure 6 the relationship between the pH dependence leaching test, the percolation test and the concise test is shown illustrating a very consistent interrelationship. This implies that the less intensive concise leach test might be used to identify deviations from the observed behaviour as determined with the characterisation leaching tests (pH dependence and percolation test). The combination of tests allows for extrapolation of data beyond the actual test conditions since the factors controlling release and release mechanisms can be identified. The consistency between batch (pH) and column (percolation) data, as well as between porewater data and column data, is promising.
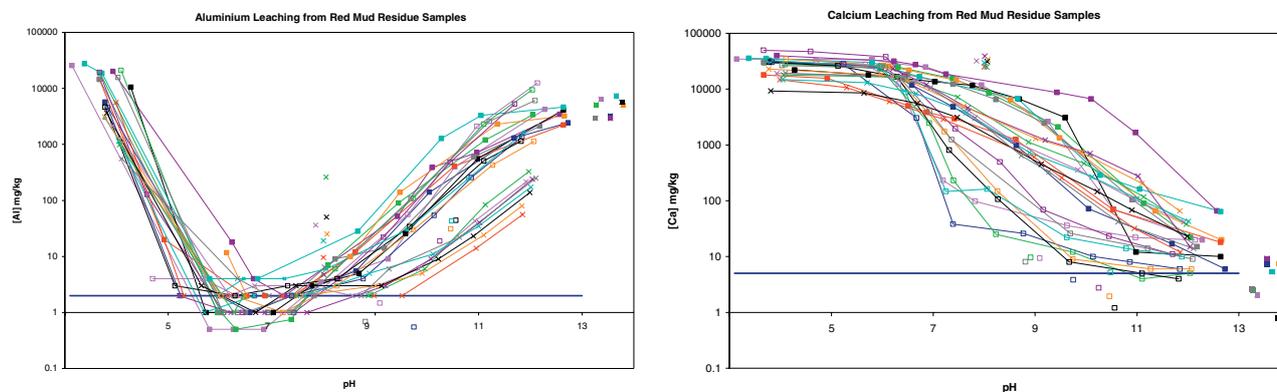

Figure 5. Aluminium and calcium leaching from untreated residue samples (solid squares), carbonated residue samples (open squares)
and seawater neutralised residue satmples (crosses) as a function of pH. Isolated symbols are porewater samples,
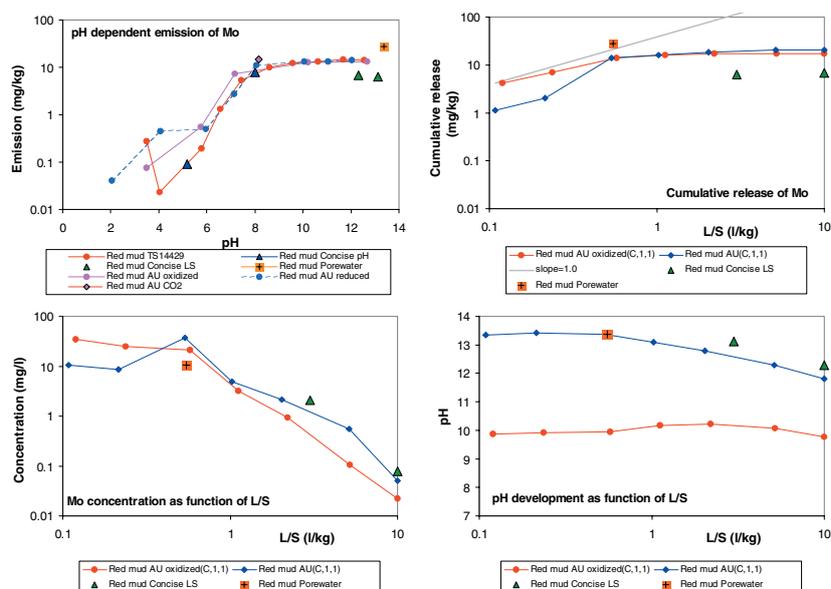and the horizontal line shows the detection limit.

Figure 6: Relationship between pH dependence test, percolation leaching test,
concise test and porewater analysis for molybdenum leaching from bauxite residue.

Geochemical speciation modelling using element availabilities, quantities of Fe-oxide phases, Al-oxide phases, organic matter in solid and liquid and selected minerals provides a prediction of release for all elements in comparison with the actually measured pH dependence leaching test data. The agreement between model and measurement is shown in Figure 7 for four elements, which demonstrates that this modelling approach is very promising. The degrees of freedom to vary any one parameter is becoming very limited, as many elements are interrelated and an improvement in the modelling of one element may deteriorate the match for other elements. When the model predictions closely meet the data, the chemical processes that determine the leaching behaviour are understood and the partitioning of elements between solid and liquid phases can be assessed.

The modelling as performed allows the quantification of element partitioning between dissolved (free and DOC bound) and particulate species (bound to Fe-oxide, Al-oxide, minerals and particulate organic matter). For Mo and Zn the partitioning is shown in Figure 8. This type of partitioning (based on relatively limited data) will prove to be highly informative for material modification, bioavailability and judgement of transport since DOC bound elements are carried further into the soil groundwater system than the free elements (McCarthy and Zachara, 1989). Free elements will bind to iron oxides, clay or solid organic matter, limiting their transport through the soil profile. In the case of Zn, an increased level of reactive Fe would reduce leachability for neutralised bauxite residue, but would have no or marginal effect under alkaline conditions. Specific mineral phases have been identified as controlling release. For Ca, calcite, dolomite, fluoroapatite and fluorite can be identified as relevant solubility controlling phases active in different pH domains.
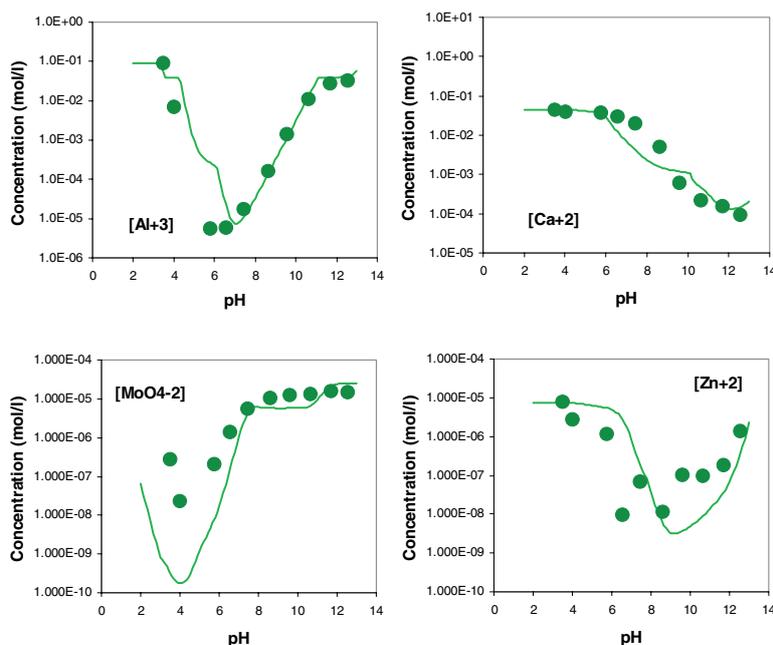

Figure 7: Prediction of leaching behaviour of bauxite residue based on element availability, Fe oxide, AL oxide, particulate and dissolved organic matter properties and a selection of relevant solubility controlling minerals as identified in preliminary geochemical speciation calculations.
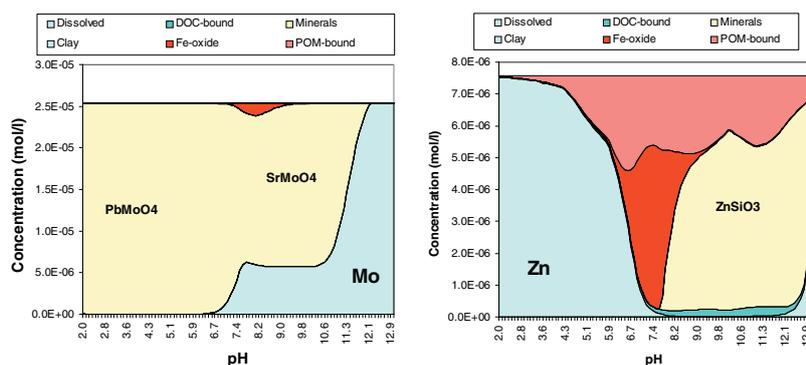
Figure 8: Partitioning of Mo and Zn in bauxite residue between dissolved (free and inorganically complexed), DOC bound, Fe-oxide sorbed, clay sorbed, mineral phases and particulate organic matter bound.

4   Conclusions

The application of the pH dependence test on bauxite residue provides a significantly increased understanding of the residue leaching behaviour. In combination with sophisticated geochemical modelling it allows a very advanced understanding of element partitioning between dissolved and particulate phases. In addition, it provides the means to describe leaching behaviour under conditions deviating from those tested in the laboratory. Furthermore, it allows for describing a source term of release from red mud as a function of time to be used in the prediction of release under specific utilisation and storage scenario conditions.

Well-defined mineral phases as well as the role of Fe, Al and organic matter (dissolved and particulate) can be shown to be controlling the release behaviour of a wide range of major, minor and trace elements from bauxite residue. Apart from the increased understanding of solubility controlling processes, it immediately presents potential for durable improvement of residue quality.

This modelling approach provides the development of more durable solutions to residue management than single step tests ever can. Although utilisation and storage scenarios based on the present full thermodynamic description of bauxite residue leaching is still to be done, the potential for predicting release with associated partitioning is a major step ahead in environmental impact evaluation.

References

Dijkstra, J. J., Meeussen, J. C. L., Comans, R. N. J. Environmental Science and Technology 2004, 38(15), 4390-4395.

Dzombak, D. A., Morel, F. M. M. Surface complexation modelling: hydrous ferric oxide; John Wiley & Sons, Inc.: New York, 1990

Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K., Borkovec, M., Benedetti, M. F., Avena, M. J. Colloid Surface A 1999, 151, 147-166.

Kosson, D.S. and Van der Sloot, H.A. Integration of Testing Protocols for Evaluation of Contaminant Release from Monolithic and Granular Wastes. In: Waste Materials In Construction – Putting Theory into Practice . Studies in Environmental Science 71. Eds. J.J.J.M. Goumans, G.J. Senden, H.A. van der Sloot. Elsevier Science Publishers, Amsterdam, 1997, 201-216.

Kosson, D. S., van der Sloot, H. A., Sanchez, F. and Garrabrants, A. C. (2002). An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. Environ Eng Sci. 19, 159 – 204.

McCarthy, J.F., and Zachara, J.M., Subsurface Transport of Contaminants. Environ. Sci. Technol., Vol. 23., No. 5, pp. 496- 502, 1989.

Meeussen, J. C. L. Environ. Sci. Technol. 2003, 37, 1175-1182

PrEN14429 (2002). Characterisation of waste: Leaching behavior tests – pH dependence test with initial acid/base addition, CEN/TC 292 WG6

PrEN14405 (2002). Characterisation of waste: Leaching behavior tests – up-flow percolation test, CEN/TC 292 WG6

Standards Australia, (1997). Wastes, sediments and contaminated soils. Part 3: Preparation of leachates – Bottle leaching procedure, AS4439.3-1997.

Toxicity Characteristic Leaching Procedure (TCLP). Federal Register, Vol. 261, 29 March, 1990. Government Printing Office, Washington DC.

Van der Sloot, H. A. (1996). Developments in evaluating environmental impact from utilization of bulk inert wastes using laboratory leaching tests and field verification. Waste Management, 16, 65 – 81.

Van der Sloot, H. A., Heasman, L. and Quevauviller, P., Eds (1997). Harmonization of Leaching/Extraction Tests. Studies in Environmental Science, Vol 70. Amsterdam: Elsevier Science Publishers.

Van der Sloot, H.A., van Zomeren, A., Dijkstra, J. J., Hoede, D., Jacobs, J., and Scharff, H. (2003). Prediction of long term leachate quality and chemical speciation for a predominantly inorganic waste landfill. 9th International Waste Management and Landfill Symposium, October 2003, Sardinia.