

# TRANSPORT OF BAUXITE RESIDUE LEACHATE THROUGH CLAY LINERS OF STORAGE IMPOUNDMENTS: A SYNTHESIS OF EXPERIMENTAL AND SIMULATED DATA

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## Abstract

Although many alumina refineries use bores situated around their residue areas to monitor the integrity of storage liners there has been little published work on the effects of alkaline liquor from bauxite residue on clay liners of storage impoundments. At high temperatures, alkaline fluids have been shown to rapidly react with bentonite clays, resulting in dissolution of bentonite after formation of calcium silicate hydrate and calcium-aluminium silicate hydrate mineral phases. Reaction rates decrease exponentially with decreasing temperature and become very low at pH<10.5. Modelling suggests that alkaline dissolution and subsequent precipitation of minerals are likely to occur in approximately similar quantities. These reactions, though initially decreasing permeability, may ultimately lead to a degradation of the clay structure and thus an increase in permeability.

The objective of this work was to predict the life times of existing clay liners from detailed analysis of the integrity of cores collected from a residue storage area. Four cores sampled from a clay liner of a storage impoundment at an Alcoa location were examined. The clay liner had been exposed, at the time of sampling, to bauxite residue for periods of 20-23 years.

Profile distributions in the cores of alkalinity, Na, Cl and Br were measured and compared with results obtained by numerically simulating the transport of Na. Linear extrapolation in time of profile distributions of alkalinity and Na suggests, that in the absence of a reduction in alkalinity (which occurs as a result of the reaction of the leachate with clay) times for breakthrough of leachate through the clay liner may be of the order of 30 to 70 years in the absence of hydraulic head reduction. However, a considerable amount of alkalinity is removed from solution after reaction with clay minerals and is not readily exchangeable. The 'on-going' reaction of alkaline residue leachate with clay progressively slows its movement in a non-linear fashion. Resulting 'breakthrough times' of residue leachate through clay liners are thus likely to be greater than estimated from a linear extrapolation in time of the profile distributions in cores.

The outcome of this work has resulted in Alcoa developing methods for the reduction of hydraulic heads in residue areas where breakthrough may be a risk. Over the last decade, Alcoa has also taken several steps to enhance containment of residue leachate in new residue facilities, including the use of geomembrane-clay composite seals and the newly developed Carbon Capture process which significantly lowers the pH of residue leachate.

## 1. Introduction

Little detailed work has been published on the effects of alkaline liquor from bauxite residue on clay liners of storage impoundments (McKelvey 1996, Savage *et al.* 2002).

Concentrations of Al and Si in extracts of clays with caustic soda are invariably found to be less than expected for equilibrium with clay minerals. Calculations with 'PHREEQC' (Parkhurst & Appelo 1999) confirm this and indicate that various hydrated Ca-aluminates can form at high pH, such as  $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 19\text{H}_2\text{O}$  and tricalcium alumina hydrates (TCA: such as katoite:  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3(\text{OH})_{4x}$  ( $x=1.5-3$ )). Similar results are reported by Whittington and Cardile (1996) and Savage *et al.* (2002). Possibly more important at high concentrations of NaOH is the formation of 'desilication products', which are aluminosilicates with a high content of Na and relatively low content of Si, such as zeolites as sodalite ( $\text{Na}_4\text{Al}_3(\text{SiO}_4)_3\text{Cl}$ ) and cancrinite ( $\text{Na}_7\text{CaAl}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2$ ) (Thornber & Hughes 1987, Bauer & Berger 1998, Gualtieri *et al.* 1997, Mashal *et al.* 2005). A considerable amount of alkalinity is absorbed in these 'minerals' and is only slowly dissolved, when extracting with water (Thornber & Hughes 1992).

Much recent work on reactivity of clays in alkaline media has centered on nuclear waste disposal in bentonite/cement barrier systems (Ramírez *et al.* 2002, Takatoshi *et al.* 2005, 2006, Sakamoto *et al.* 2007, Savage *et al.* 2007, Yamaguchi *et al.* 2007). Alkaline fluids have been shown to react rapidly with bentonite

clays at high temperature, resulting in complete dissolution of bentonite after formation of calcium silicate hydrate and calcium-aluminium silicate hydrate mineral phases (Tajima *et al.* 2003). Reaction rates decrease exponentially with decreasing temperature and appear to cease below pH<10.5 (Tajima *et al.* 2003). It has also been observed through modelling that alkaline dissolution and subsequent precipitation of minerals are likely to occur in approximately similar quantities (Savage *et al.* 2002, Watson *et al.* 2004). The literature quoted for this section also shows how important long-term effects of slow 'weathering' reactions in alkaline media are in transforming and dissolving bentonite. These reactions are complex and strongly dependent on pH and temperature and, though initially lead to marked decreases in permeability, can ultimately (over decades to geological time!) lead to increases through collapse of the bentonite structure.

Bauxite residue leachate is dominated by Na cations and their counter ions  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{OH}^-$  (alkalinity). Transport of  $\text{Na}^+$  and alkalinity through a clay liner is both by advection, driven by an hydraulic head, and by diffusion, driven by a concentration gradient.

Advection of  $\text{Na}^+$  in clays is the net result of hydraulic and an opposing osmotic transport of ions and water in combination with retardation by ion-exchange and chemical reactions (Keyzer & Loch 2001, Malusis *et al.* 2002ab, 2003, Shackelford & Lee 2003, Rowe *et al.* 2004, Loch *et al.* 2005, Bader & Kooi 2005).

Molecular diffusion of Na<sup>+</sup> in clays is decreased by ion exchange, by reactions with clay materials and by coupling of Na<sup>+</sup> with slower moving counter anions. The latter is caused by charge exclusion of anions (e.g. Malusis & Shackelford 2002b, Loch *et al.* 2005, Bader & Kooi 2005). Resulting effective diffusion coefficients can be orders of magnitude smaller than the corresponding (unrestricted) diffusion coefficients in a sandy soil (Arcos *et al.* 2000, Rowe *et al.* 2004).

## 2. Methods

### 2.1 Experimental

Four cores were drilled from the clay liner in a residue area at an Alcoa location. Details of the cores are listed in Table 1. The clay liner was constructed from a local smectitic clay.

Samples from core sections at different depths were extracted with water (water/clay ratio 3:1) and analysed for major and minor ions at the Chemistry Centre of WA using standard methods.

Concentrations of major ions, leaching and diffusing into the clay liner from the bauxite residue above are taken as the reported averages for bauxite residue leachate at the Alcoa location and are listed in Table 2. Analysis data for samples from cores of the clay liners and their water extracts used in simulations (sections 2.2 and 3.2) are given in Table 3.

### 2.2 Simulation

Leaching of solutes from bauxite residue leachate (BRL) through a clay liner can be described with a mass balance equation for transport of step changes in concentrations (Raats *et al.* 1982):

$$\partial C_m / \partial t [1 + K_d \theta^1] = D \partial^2 C_m / \partial z^2 - V_{\text{pore}} \partial C_m / \partial z + S \quad (1)$$

where: t=time, C<sub>m</sub> and C<sub>s</sub> are solute concentrations in the (mobile) water phase in the clay and adsorbed to the clay respectively, θ is moisture content of clay, D is the dispersion coefficient, V<sub>pore</sub> is pore water velocity and z is distance migrated in the direction of advection, K<sub>d</sub> is the distribution coefficient describing the relationship between adsorbed and dissolved

solute concentrations (K<sub>d</sub>=∂C<sub>s</sub>/∂C<sub>m</sub>) and is assumed here to be a constant (=linear adsorption isotherm), S is a 'sink' term and describes a reaction of the solute with clay.

Dividing (1) by the retardation factor R<sub>f</sub> = [1+K<sub>d</sub> θ<sup>1</sup>] gives:

$$\partial C_m / \partial t = D_{\text{eff}} \partial^2 C_m / \partial z^2 - V_{\text{eff}} \partial C_m / \partial z + S^* \quad (2)$$

where: D<sub>eff</sub> and V<sub>eff</sub> are the effective dispersion coefficient and mobility of a solute respectively and S\* is the decrease in solute concentration in the water phase through reaction(s) with clay minerals.

$$D_{\text{eff}} \text{ and } V_{\text{eff}} \text{ in (2) are respectively given by } D_m \tau^{-1} R_f^{-1} \text{ and } V_{\text{pore}} R_f^{-1} \quad (3)$$

where: D<sub>m</sub> is the coefficient for molecular diffusion only (excluding mechanical dispersion at the very low velocities in clay liners), τ is a tortuosity factor (~1.5: Sweerts *et al.* 1991, Berezhovskii *et al.* 2003) and R<sub>f</sub> is the retardation factor [1+K<sub>d</sub> θ<sup>1</sup>] in (1).

(2) was solved numerically, following Gerritse (1994), for Na with a K<sub>d</sub> estimated from (6) for dissolved Na in the top section(s) of the clay liner cores, and for D and V<sub>pore</sub> (~ hydraulic conductivity K<sub>h</sub> as given in (7)), fitted to experimentally obtained profile distributions. The 'sink' term S\* was treated as reversible and included in the K<sub>d</sub> of (1). Dispersion coefficients were initially estimated from molecular diffusion coefficients reported for Na in clays (Arcos *et al.* 2000, Rowe *et al.* 2004) and then fitted to experimentally obtained profile distributions of dissolved Na.

Concentrations of solutes in pore water (C<sub>pore</sub>) in the clay liner are related to concentrations measured in 1:3 water extracts of clay samples by:

$$C_{\text{pore}} = C_{\text{extract}} (K_{\text{de}} + (3 + \theta') / (1 - \theta')) / (K_d + \theta' / (1 - \theta')) \quad (4)$$

where: C<sub>pore</sub> is solute concentration in pore water of the sample from the clay liner, C<sub>extract</sub> is solute concentration in the 3:1 clay/water extract, θ' is moisture content of moist clay (as sampled), K<sub>de</sub> is the distribution coefficient for a solute in the 1:3 clay/water

Table 1. Details for cores sampled from the clay liner in a residue area at an Alcoa location.

Core	Depth of Clay	Visibly Reacted Clay	Hydraulic Head	Years under Residue	Bulk Density δ	Mineral Density ρ	Moisture θ	CEC Range
	m	m	m		t/m <sup>3</sup>	t/m <sup>3</sup>	m <sup>3</sup> /t	me%
F-145	0.38	0.21	27.5	23	-	-	0.30	22-38
F-146	0.34	0.11	27.3	23	-	-	0.27	20-50
*F-147	0.27	0.21	23.9	23	-	-	0.26	20-34
F-151	0.4	0.05	13.7	20	1.58	2.62	0.25	20-100
Local Clay	-	-	-	-	-	-	0.35	30-40

Cores were sampled in sections of 2-4 cm. Samples were processed at the Chemistry Centre of WA using standard methods. Moisture and densities are given as averages per tonne of 'dry' clay.

\* For core F-147 it is likely that the 27 cm sampled was from the basal part of the clay liner. An initial upper ~10 cm may well have eroded away during operational activities (deposition of residue) at the residue area.

Table 2. Solution concentrations (CBRL) of major and minor ions in leachate from bauxite residue (BRL) at the Alcoa location.

Analyte	Units	C <sub>BRL</sub>	Analyte	Units	C <sub>BRL</sub>
pH	-	12.5	Cl	mg/L	800
Eh	mV	-350	Br	mg/L	100
Total Alkalinity	mg/L	19000	F	mg/L	180
Oxalate (C <sub>2</sub> O <sub>4</sub> )	mg/L	2200	S-SO <sub>4</sub>	mg/L	260
Na	mg/L	9000	S <sup>2-</sup>	mg/L	0.9
K	mg/L	10	Si-SiO <sub>2</sub>	mg/L	4.0
Ca	mg/L	0.6	Al	mg/L	1000
Mg	mg/L	0.05	Fe	mg/L	0.35

**Table 3. Selected analysis data for samples from sections of clay liner cores (pH, Cl, Na, oxalate are for concentrations in 1:3 clay-water extracts; Total Na, CEC and Exchangeable Na are for total concentrations in clay). CEC is 'cation exchange capacity' of clay.**

Core	Depth	pH	Cl-extract	Na-extract	Oxalate-extract	Total Na	CEC	Exchangeable Na
	cm	-	mg/L	g/L	mg/L	g/kg	meq%	g/kg
F-145	2.5	10.3	17	23.0	22	32.9	34	21.4
F-145	7.5	10	17	14.0	90	30.1	37	19.3
F-145	12	9.3	24	6.9	100	18.8	38	17.3
F-145	16.5	7.6	34	5.1	1	11.4	34	11.2
F-145	21	7.7	41	5.2	1	10.5	34	9.8
F-145	24.5	8	37	5.2	1	10.2	34	8.7
F-145	27.5	7.8	43	4.7	1	11.5	38	9.2
F-145	31	7.8	46	5.5	1	8.7	37	8.2
F-145	36	7.1	31	8.2	1	7.0	30	6.5
F-145	40.5	9.4	21	9.5	12	11.6	22	8.3
F-146	3.5	10.2	70	18.0	45	27.4	50	22.7
F-146	9.5	10.3	62	21.0	36	16.5	45	22.2
F-146	13.5	10.2	29	12.0	16	8.1	34	15.5
F-146	16.5	8.1	76	4.6	1	6.2	33	9.4
F-146	20	7.5	52	5.7	1	7.9	19	3.6
F-146	23.5	7.6	55	3.4	1	8.3	26	5.1
F-146	27	7.6	97	3.4	1	7.0	39	7.4
F-146	31	7.7	79	4.3	1	6.9	32	4.6
F-146	34.5	7.4	87	7.2	1	7.6	36	6.1
F-146	37.5	7.2	84	12.0	1	7.7	36	6.4
F-147	1.5	10.3	12	8.5	240	8.5	23	10.7
F-147	4.5	10.7	22	12.0	110	16.6	34	18.0
F-147	7.5	11	24	11.0	100	19.0	34	16.5
F-147	10.5	11.1	33	10.0	140	22.8	34	15.4
F-147	13.5	10	33	10.0	210	20.9	31	15.1
F-147	16.5	10.4	37	10.0	200	19.7	30	14.7
F-147	20	8.8	53	4.8	1	15.0	26	11.4
F-147	24	8.1	49	5.6	1	8.4	20	6.8
F-147	27.5	8.1	54	6.6	1	8.0	20	6.9
F-151	2	12.1	37	7.1	49	26.0	67	22.4
F-151	8	12.3	50	9.1	67	42.7	100	32.5
F-151	15	12.2	48	9.2	54	29.8	30	9.7
F-151	22	12.2	45	8.9	49	20.0	30	10.7
F-151	25	12.2	43	8.5	42	27.2	30	6.4
F-151	27	12	22	5.5	2.5	11.7	22	6.6
F-151	29.5	11.4	33	3.5	13	6.8	23	4.7
F-151	32	6.3	75	0.9	0.1	2.0	25	0.5
F-151	37	6.2	63	0.8	0.1	6.2	17	0.5

extract phase system,  $K_d$  is the 'in-situ' distribution coefficient of a solute in the liner clay (in equilibrium with pore water).

The distribution coefficient  $K_{de}$  in (4) is given by:

$$K_{de} = [X]_{\text{exch}} / C_{\text{extract}} \quad (5)$$

where:  $[X]_{\text{exch}}$  is the total concentration of exchangeable solute X in the clay (ion-exchangeable+reacted),  $C_{\text{extract}}$  is as described for (4).

The 'in-situ' distribution coefficient  $K_d$  in (4) is generally difficult to estimate. In top sections of clay liners where pH >10 in water extracts (Table 3),  $C_{\text{pore}}$  can be assumed equal to the concentration in BRL (Table 2) and  $K_d$  can then be estimated from:

$$K_d = [X]_{\text{exch}} / C_{\text{BRL}} \quad (6)$$

In sections of clay liners where pH < 10 in water extracts (Table 3),  $K_d$  was estimated with 'PHREEQC' (Parkhurst & Appelo 1999), assuming ion-exchange only to apply.

### 3. Results and Discussion

#### 3.1 Quality Control

Electro-neutrality (EN) balances for major ions in water extracts of samples from the upper sections of cores of the clay liners were commonly between -5% and +5%. EN balances for extracts of samples from lower sections were often >5% and unacceptably high in some cases. Both total Si and reactive SiO<sub>2</sub> were analysed in water extracts of the clay liner, the difference was assumed to be associated with fine (colloidal) suspended particulate matter. Large positive EN balances invariably occurred in extracts with total Si much greater than reactive Si and appeared to be

associated mainly with excess Na. Concentrations of Na were corrected for these samples to balance EN.

Equivalent concentrations of Na and alkalinity in 1:3 clay/water extracts of samples from cores of the clay liner at the residue area at the Alcoa location are plotted in Figure 1. A ratio of one between the equivalent concentrations of Na and alkalinity is expected for alkalinity derived from bauxite residue leachate (BRL) only and applies (Figure 1) to extracts from the upper sections of clay cores, but not from the lower sections.

Concentrations of  $\text{SO}_4^{2-}$  in water extracts of lower sections of clay cores were high and it was suspected, particularly as core sections had been stored several months before subsamples were extracted with water, that pyrite ( $\text{FeS}_2$ ) was present and had oxidized appreciably to form  $\text{H}_2\text{SO}_4$  (Appelo & Postma 2005).

Sulphuric acid thus formed would have consumed alkalinity and displaced Na ions from clay through ion-exchange, resulting in high background concentrations of Na in water extracts from the basal sections of cores of clay liners (Figure 2). When equivalent concentrations of  $\text{Na}^+$  are plotted against the sum of alkalinity and  $\text{SO}_4^{2-}$ , a good fit results with a slope of one (Figure 1), confirming a suspected generation of  $\text{H}_2\text{SO}_4$  and associated consumption of alkalinity.

### 3.2 Clay Liner Cores

Solution composition in upper sections of clay liner cores is dominated by  $\text{Na}^+$  and by anions, associated with alkalinity, from infiltrating BRL. Profile distributions in clay cores of concentrations in pore water of  $\text{Na}^+$ , alkalinity and  $\text{Cl}^-$  are given in Figure 2 relative to concentrations in BRL.

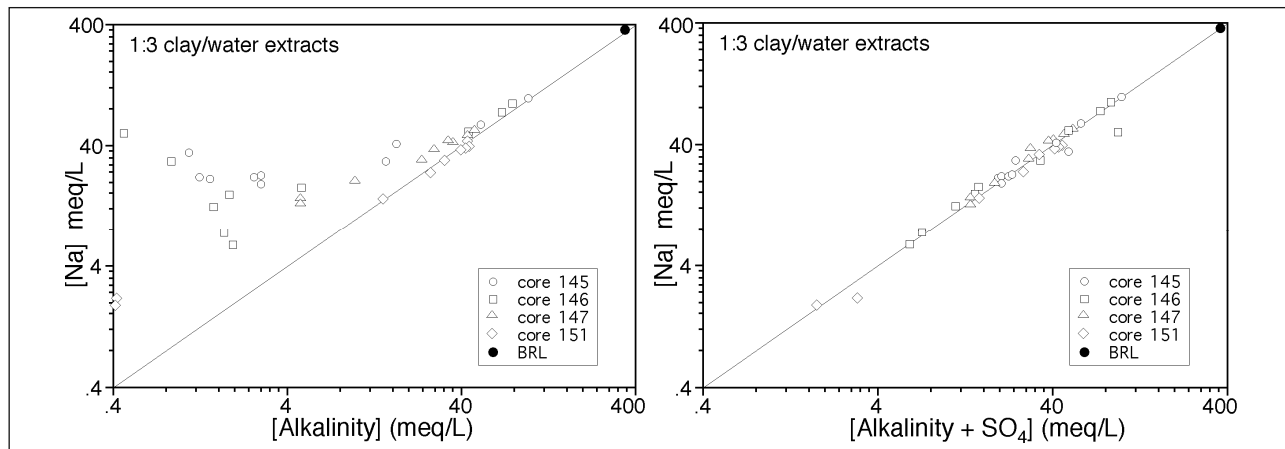


Figure 1. Log-log plots of equivalent concentrations of Na against alkalinity and the sum of alkalinity and  $\text{SO}_4$  in water extracts of samples from sections across cores of the clay liner at the residue area at the Alcoa location.

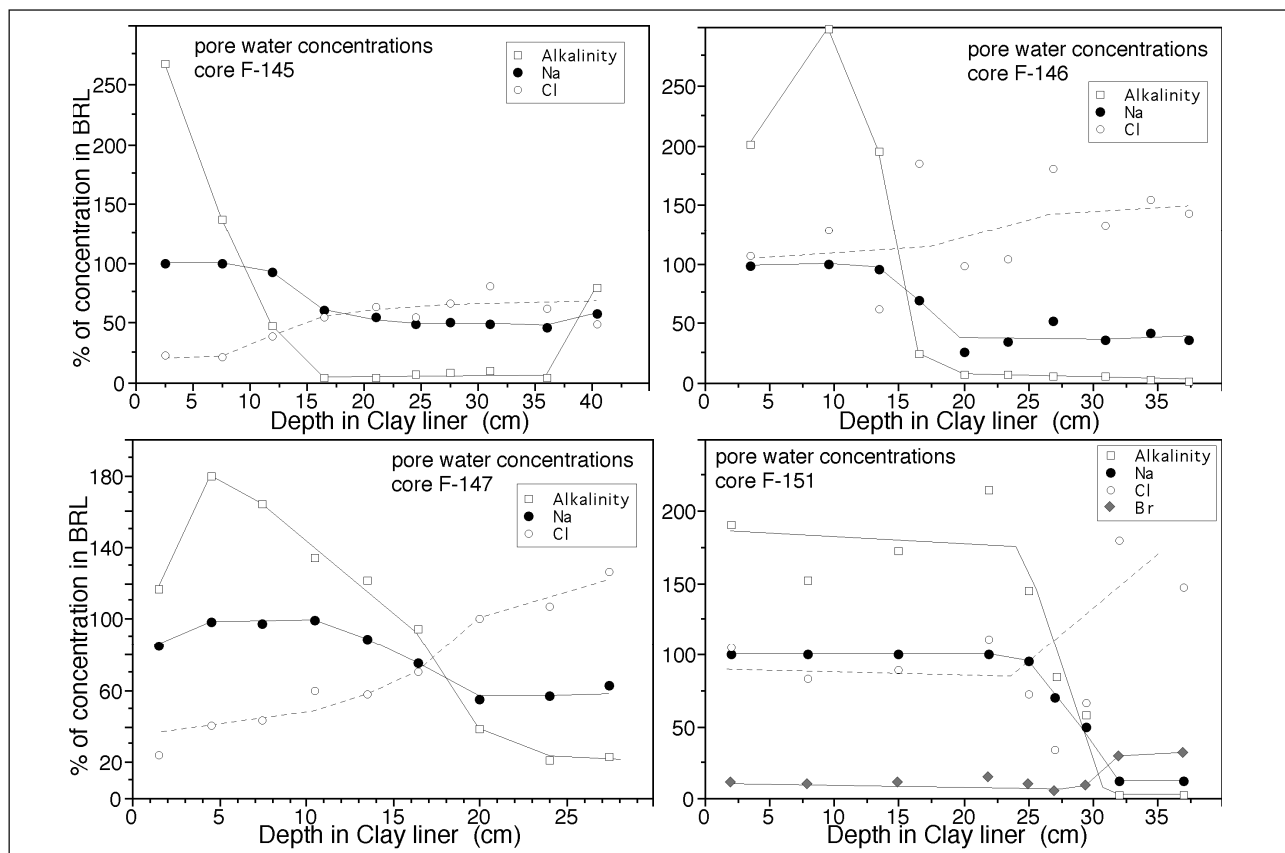


Figure 2. Profile distributions in cores of clay liners of pore water concentrations of Na, Cl, Br and alkalinity. Concentrations were calculated with (5) and are expressed relative to the respective concentrations in bauxite residue leachate ( $C_{\text{BRL}}$ , Table 2).

Concentrations of Cl<sup>-</sup> and alkalinity in Figure 2 were calculated with (4) from concentrations in water extracts, assuming  $K_d$  and  $K_{de}$  to be zero (=no reaction and no adsorption). This should apply to Cl<sup>-</sup>, though pore water concentrations, calculated in this way, are commonly less than expected from concentrations in BRL because of charge exclusion of anions from small pores.

Data in Figure 2 suggest that Cl<sup>-</sup> is excluded from about 60-80% of pores in the alkaline sections of clay liner cores F-145 and F-147, from about 10% of alkaline pores in clay liner core F-151 and is not excluded from alkaline pores in clay liner core F-146. Charge exclusion of the larger anion Br<sup>-</sup>, which was measured in the F-151 core only, is even greater with about 90% of alkaline pores not accessible to Br<sup>-</sup> (compared with about 10% for Cl<sup>-</sup>). Scatter of data for Cl<sup>-</sup> and Br<sup>-</sup> in Figure 2 suggests a significant variability in the pore space not available to Cl<sup>-</sup> and Br<sup>-</sup>, particularly in clay liner cores F-146 and F-151. Though Cl<sup>-</sup> and Br<sup>-</sup> are conservative, i.e. not retarded, preservation of electrical neutrality forces Cl<sup>-</sup> and Br<sup>-</sup> to follow the same displacement pattern as the retarded (through reaction and adsorption) and dominant counter Na<sup>+</sup> cations. Data in Figure 2 confirm this.

Pore water concentrations calculated from water extracts for alkalinity in the upper sections of cores (Figure 2) are much greater than in BRL (Table 2), indicating that significant amounts of alkalinity have reacted with clay (in association with Na) and are partly leachable. Pore water concentrations of Na<sup>+</sup> in Figure 2 for sections of clay cores with a pH>10 in water extracts, calculated for  $K_d$  and  $K_{de} = 0$  with (4), were capped at 100% where results were >100% BRL. For sections with pH<10 in water extracts, pore water concentrations were estimated with (4) for  $K_d$  and  $K_{de} \neq 0$  (i.e. allowing for reaction and adsorption). The required  $K_{de}$  was calculated from analysis data on water extracts (Table 3) and  $K_d$  was estimated with 'PHREEQC' (Parkhurst & Appelo 1999), assuming ion-exchange only, from analysis data on water extracts and exchangeable cations (Table 3).

Oxalate was also analysed in water extracts of clays and follows the infiltration of Na<sup>+</sup> from BRL (Table 3). Results are, however, difficult to quantify as % of BRL as oxalate can react variably with Ca and Mg, released through ion-exchange with Na<sup>+</sup>. Solubility Indices (SI: Appelo & Postma 2005) suggest calcite (CaCO<sub>3</sub>) and magnesite (MgCO<sub>3</sub>) are formed in alkaline affected sections of clay liner cores.

Advective and diffusive transport of Na through clay liner cores was simulated numerically with (2) for the time of exposure of the liner to BRL and assuming a reversible reaction term ( $S^*$  in (2)). Results are given in Figure 3 together with the fitted parameters. Simulated profile distributions of Na are compared in Figure 3 with pore water concentrations estimated from water extracts (Figure 2) and scaled to between 0% and 100% after correcting for background.

Saturated hydraulic conductivities in a clay liner can be estimated empirically for low velocities with the Blake-Kozeny equation (Bird *et al.* 2002):

$$K_h = \varepsilon (\Delta P/L)^{-1} V_{pore} \approx 10^4 (\varepsilon^4/(1-\varepsilon)^2) d_p^2 / (150 \eta) \quad (7)$$

where:  $K_h$  is the hydraulic conductivity (m/s),  $\Delta P/L$  is the pressure gradient from the overlying water column across the clay liner (m/m),  $L$  is thickness of clay liner (m),  $\varepsilon$  is porosity,  $V_{pore}$  is pore water velocity (from (1) in m/s),  $d_p$  is particle diameter (m),  $\eta$  is viscosity (N s/m<sup>2</sup>).

Results of calculations with (7) for different particle diameters are given in Table 4. Hydraulic conductivities ( $K_h$ ) of clay liner cores were not measured separately in a laboratory. Laboratory measurements of  $K_h$  from previous work on comparable clay

liners at another residue area at the Alcoa location ranged from  $0.2 \times 10^{-12}$  to  $4 \times 10^{-12}$  m/s as opposed to  $10 \times 10^{-12}$  to  $90 \times 10^{-12}$  m/s calculated numerically for the cores examined in this work (Figure 3). It should be noted in this respect that laboratory measurements of  $K_h$  are conducted in pressurized cells at relatively high velocities, which could result in greater electro-osmotic counter forces, decreasing the net  $K_h$  when compared with 'in-situ' conditions (Keyzer & Loch 2001, Malusis & Shackelford 2002b, Loch *et al.* 2005, Bader & Kooi 2005). The  $K_h$  is strongly affected by the ionic composition of the permeating solution, increasing with concentrations of polyvalent cations and decreasing with monovalent cations (Jo *et al.* 2005). Also  $K_h$  is measured in the laboratory for sections of cores from clay liners, selected with as few imperfections as possible, while examination of the entire core often revealed preferred pathways with greater conductivity from sand lenses and occasionally from tree roots.

Assuming (7) to apply, a comparison of simulated hydraulic conductivities in Figure 3 with Table 4 suggests particle sizes in clay liners of the residue area to be mainly about 1000 Å (= 0.1 µm). Particle sizes below 2 µm were not specifically measured in the clays from liner cores. Average pore radius was measured in clay from core F-151 and was about 40 Å within a range of 10 to 300 Å.

**Table 4. Saturated hydraulic conductivities estimated with (7) for different particle sizes in clays.**

Porosity	Viscosity	Particle size	Hydraulic Conductivity
$\varepsilon$	$\eta$	$d_p$	$K_h$
m <sup>3</sup> /m <sup>3</sup>	N s/m <sup>2</sup>	Å (10 <sup>-10</sup> m)	m/s
0.4	0.001	100	$4.7 \times 10^{-13}$
0.4	0.001	300	$4.3 \times 10^{-12}$
0.4	0.001	1000	$4.7 \times 10^{-11}$
0.4	0.001	3000	$4.3 \times 10^{-10}$
0.4	0.001	10000	$4.7 \times 10^{-9}$

The molecular diffusion coefficient ( $D_m$ ), fitted to the numerical simulation of advective and diffusive transport of BRL through the clay liner at the residue area, is about  $7 \times 10^{-12}$  m<sup>2</sup>/s (Figure 3). This value is at the lower end of a range of  $4 \times 10^{-12}$  to  $2 \times 10^{-10}$  m<sup>2</sup>/s, reported for diffusion of Na<sup>+</sup> in clays by Arcos *et al.* (2000).

The rate of spread of the alkaline front from diffusion can be approximated by (e.g. Crank 1956):

$$V_{diffusion} \sim 6 (D_m/t)^{0.5} \varepsilon^{-1} \tau^{-1} \quad (8)$$

where  $V_{diffusion}$  is the diffusive velocity of the alkaline front (m/s), 't' is the residence time in the clay liner and 'τ' is a tortuosity factor (see (3)).

The advective velocity follows from the fitted pore water velocity (Figure 3, (7)). Results of calculating advective and diffusive velocities for the clay cores from data in Table 1 and Figure 3 are given in Table 5. Data in Table 5 are compared with depth of infiltration (L) and halfwidth ( $W_{0.5}$ ) of the diffusive fronts for the profiles in Figure 3.

Ratios in Table 5 of  $V_{pore}$  and  $V_{diffusion}$  and of L and  $W_{0.5}$  reflect the ratios of contributions of advection and diffusion to infiltration of residue leachate in the clay liners. Advective transport dominates, but diffusive transport also contributes to transport of alkalinity in the clay liners.

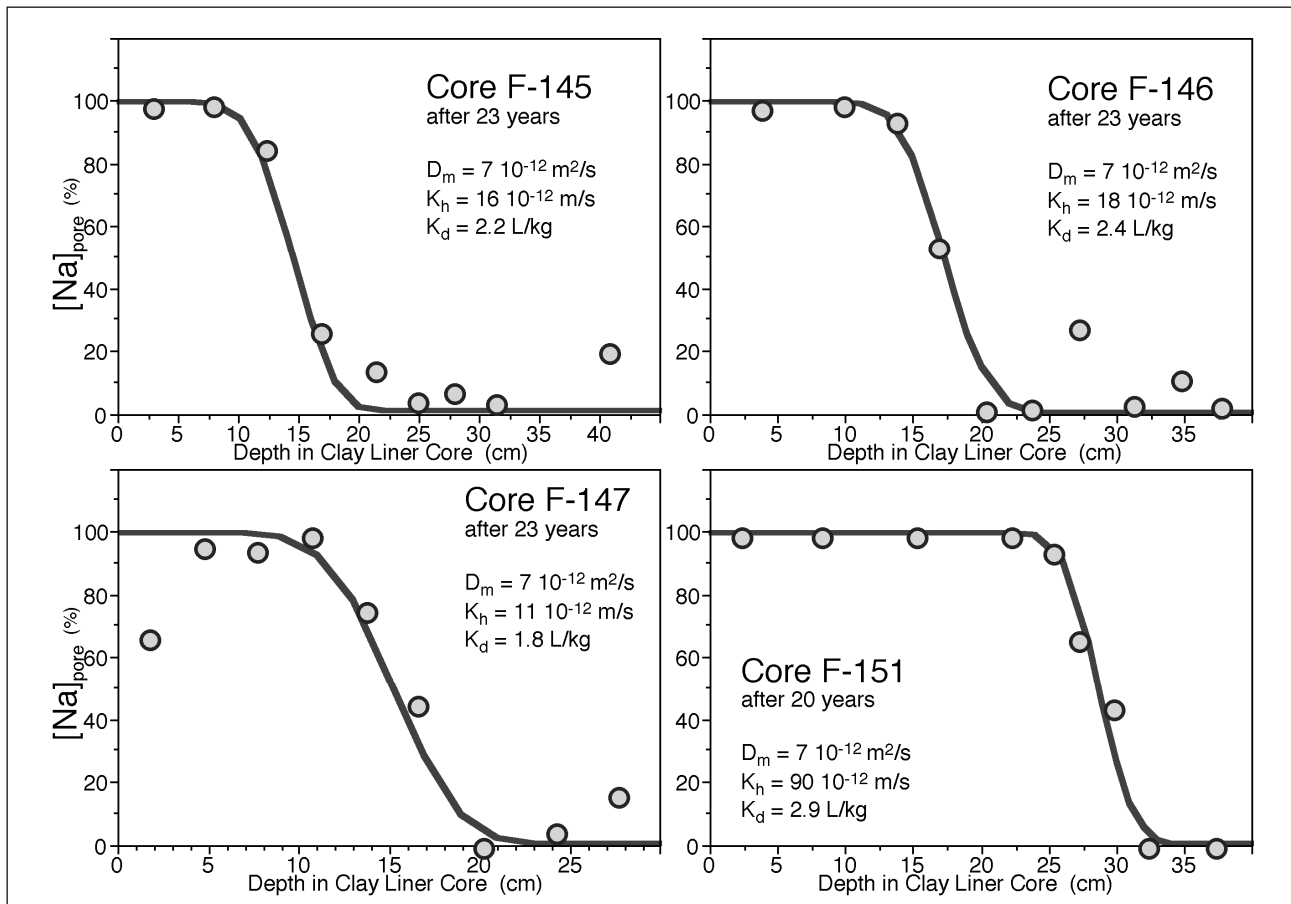


Figure 3. Comparison of concentrations of Na, analysed in pore water of clay liners (circles), with distributions (solid curves), calculated by numerically simulating advection and diffusion with (2) and (3) and fitted parameters  $D_m$  and  $V_{pore}$ . Concentrations of Na in pore water were estimated from concentrations in water extracts and were scaled after correcting for background to between 0% (=background) and 100% (=concentration in BRL).  $D_m$  is molecular diffusion coefficient;  $K_h$  is hydraulic conductivity, calculated from  $V_{pore}$ ,  $\epsilon$ ,  $\Delta P$  and  $L$  as in (7);  $K_d$  is distribution coefficient, estimated with (6).

Table 5. Ratios of depth of infiltration ( $L$ ) and halfwidth ( $W_{0.5}$ ) of the diffusive fronts and ratios of porewater ( $V_{pore}$ ) and diffusive ( $V_{diffusion}$ ) velocities for bauxite residue leachate in cores of the clay liner at the residue area at the Alcoa location.

Core	$L$	$W_{0.5}$	$L/W_{0.5}$	$V_{pore}$	$V_{diffusion}$	$V_{pore}/V_{diffusion}$
	cm	cm	-	m/s	m/s	-
F-145	14.5	5.5	2.6	$1.7 \times 10^{-9}$	$0.8 \times 10^{-9}$	2.1
F-146	17.5	6	2.9	$2.4 \times 10^{-9}$	$0.9 \times 10^{-9}$	2.7
F-147*	>15	6	>2.5	$>1.6 \times 10^{-9}$	$0.9 \times 10^{-9}$	>1.8
F-151	28.5	5	5.7	$5.8 \times 10^{-9}$	$1.0 \times 10^{-9}$	5.8

\* see note in Table 1

Linear extrapolation of profile distributions in Figure 3 suggests the time for breakthrough of alkalinity from BRL at the base of the clay liner to be between about 30 and 70 years. It should be realized, however, that experimental and simulated concentration-time profile distributions in Figure 3 cannot be linearly extrapolated to calculate the 'breakthrough time' for the clay liner (before breakthrough of alkalinity at the base). This is because of the ongoing slow reaction of infiltrating alkaline BRL with clay minerals.

The ongoing slow reaction of BRL with clay is expressed by a 'sink' term  $S$  in the transport mass balance equations (1) and (2). Only part of this 'sink' term will be reversible and can then, as was done in the numerical simulation for Figure 3, be included as an approximation in the distribution coefficient  $K_d$  for (1). The remainder, however, represents part of the reaction of alkaline

BRL with clay minerals that is not or only slowly reversible. Inclusion of the complete 'sink' term would result in a greater effective  $K_d$ , progressively increasing with time, and thus a progressively decreasing movement of the alkaline front in the clay liner (determined by  $V_{eff}$  in (3)). The associated fitted pore water velocity  $V_{pore}$  and hydraulic conductivity  $K_h$  (calculated from  $V_{pore}$  with (7)), would then become greater than for the simulation conditions in Figure 3 (assuming no changes in time of porosity and particle structure).

In view of the ongoing slow reaction of infiltrating alkaline BRL with clay minerals, results in Figure 3 should be considered a snapshot in a non-linear time frame, i.e. the alkaline front in the clay liner moves downwards in proportion to some power of time  $<1$  (e.g.  $\sim t^b$ , where  $b < 0.5$  for soil reacting with phosphate and glyphosate: Gerritse 1994, Beltran *et al.* 1998). Actual 'breakthrough times' for the clay liner will then be significantly greater than estimated from linear extrapolation of the 'snapshot' situation.

#### 4. Conclusions

Linear extrapolation in time of numerically simulated distributions of Na and alkalinity in leachate moving through the clay liner of the residue storage area of an alumina refinery, assuming no reduction of alkalinity caused by reactions with clay, suggests a time for breakthrough of the order of 30-70 years. However, a considerable amount of alkalinity is, in fact, removed from solution after reaction with clay minerals and is not readily exchangeable. This 'on-going' reaction of residue leachate with clay progressively slows movement of the alkaline front in a non-linear fashion. Resulting 'breakthrough times' of residue

leachate through clay liners are thus likely to be significantly greater than estimated from a linear extrapolation in time of profile distributions in cores.

Results of this work have resulted in Alcoa developing methods for reducing hydraulic heads in residue areas where breakthrough may be a risk. Over the last decade, Alcoa has also taken several steps to enhance containment of residue leachate in new residue facilities, including the use of geomembrane-clay composite seals and the newly developed Carbon (dioxide) Capture process which significantly lowers the pH of residue leachate.

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