Influence of sodium adsorption ratio on sodium and calcium breakthrough curves and hydraulic conductivity in soil columns

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Abstract. The paper examines the effects of electrolyte concentration and sodium adsorption ratio (SAR) on the relative saturated hydraulic conductivity (RHC) and the ionic behaviour of calcium (Ca) and sodium (Na) ions in the Na–Ca exchange complex. Batch binary exchange and saturated column transport experiments were carried out to quantify these effects using an agricultural Balkuling soil and a mining residue. Generally, RHC has been found to decrease with time, with increasing SAR, and with decreasing electrolyte concentration. The more rapid decrease in RHC in the mining residue, particularly at the lowest concentration (1 mmol/L), was consistent at all SAR values. The decreases in RHC were likely to be caused by partial blocking of pores by dispersed clay particles, as evidenced by the appearance of suspended clay particles in the effluent during leaching. Significant differences in RHC were observed in the passage of fronts of decreasing electrolyte concentrations for $CaCl_2$ and SAR 15 solutions through the soil columns. These differences were attributable to structural alterations (slaking) of the media and the nature of the particles released and mobilised within the porous structure at any given point in the column. Measurements at the critical threshold concentration and turbidity concentration at SAR 15 revealed structural breakdown of the pore matrix system as evidenced by decreased RHC. The increase in SAR to 15 is initially accompanied by erratic RHC, presumably due to the break up of soil aggregates under the increased swelling forces. The less coherent mining residue soil was substantially more vulnerable to blockage of pores than the Balkuling soil in which clay particles are likely to be more readily mobilised, and hence available to re-deposit and occlude the matrix pores.

Additional keywords: sodium adsorption ratio, exchange reactions, saturated hydraulic conductivity, calcium and sodium ions, breakthrough curves.

Introduction

Interactions of sodium (Na) and calcium (Ca) ions with clays affect the ionic transport (Ersoz *et al.* 2001) as well as the stability of the pore matrix structure, particularly in arid and semi-arid soils with little biomass or soil organic matter to sustain soil structure (Miller and Donahue 1995). While excessive Na ions on the exchange complex were found to deteriorate soil structure and impair soil drainage (So and Aylmore 1993; Keren and Ben-Hur 2003) and also to increase runoff and erosion (Menneer *et al.* 2001; Crescimanno and De Santis 2004), few studies have shown that Na–Ca soils can cause these deleterious effects, in particular, for soils under low quality irrigation water regime. Thus, increased exchangeable sodium percentage (ESP) in soils was found to lower the permeability (Oster and Shainberg 2001). For example, ESP as low as 2–5 can cause adverse effects to pore matrix structure, thus blocking the water-conducting pores (Crescimanno *et al.* 1995). The causes of soil structural deterioration by increased ESP were associated with the mechanisms of clay swelling and dispersion and slaking of silt-sized micro-aggregates (Abu-Sharar *et al.* 1987; Shainberg *et al.* 2001). Further the process of particle disintegration in the natural subsurface soils can be influenced by solution chemistry (Frenkel *et al.* 1978; Pupisky and Shainberg 1979). Decreased saturated hydraulic conductivity (HC) with a decrease in electrolyte concentration and with ESP as well as with sodium adsorption ratio (SAR) has been extensively studied (Quirk and Schofield 1955; Pupisky and Shainberg 1979; Sumner 1993; Keren and Ben-Hur 2003).

For a mixed Na–Ca cation system, the Na–Ca exchange equilibrium can be described with the following Gapon equation (Gapon 1933):

$$\frac{Na_x}{Ca_x} = K_G * \frac{[Na]}{[Ca]^{0.5}} \tag{1}$$

where Na_x and Ca_x are fractions of the exchange complex occupied by those ions, K_G is the Gapon constant, and the square brackets indicate concentrations (mmol/L) of the ions in solution. The concentration of specific ions in the exchange complex can be quantified by measuring the normality (N), for a Na/Ca binary system defined as $N = [Na] + 2[Ca]$. The Gapon equation relates to the exchangeable sodium ratio (ESR), (Sumner 1993) as follows:

$$ESR = K_G * (SAR) \text{ or } SAR = \frac{[Na]}{\sqrt{[Ca]}} \tag{2}$$

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If structural problems in soils containing high levels of Na/Ca are to be minimised, it is necessary to maintain an electrolyte level above the threshold value for that particular soil. Quirk and Schofield (1955) defined the 'threshold concentration' as the concentration of the percolating solution that would give rise to a 10–15% decrease in the relative permeability at a given SAR, and the 'turbidity concentration' as that at which dispersed clay was first observed in the effluent. These concentration levels have implications on the structural stability of the pore matrix and solute or ionic transport. For instance, a solution with high sodium concentration will increase the ESP due to the ion exchange processes. These processes occur dynamically, with an 'ESP front' expected to move through the column causing soil structural deterioration behind the front. In a Na/Ca binary ion exchange system, the Na front may be retarded during transport (Green *et al.* 1994; Hinz and Selim 1994; Evangelou and Lumbanraja 2002).

It is evident that calcium ions are efficient in flocculating soil colloids (Rengasamy 1983); thus, the addition of calcium salts in sodic soils is important in maintaining the threshold level of electrolyte (Rengasamy *et al.* 1986). Decreases of HC were observed for SAR >3 (Rengasamy *et al.* 1986) and are attributed to clogging of pores due to dispersion and re-deposition of particles (Dikinya *et al.* 2006). The adverse effects of soil sodicity on hydraulic properties (Rengasamy 1998; Levy *et al.* 2005) and the dependency of HC on the composition of exchangeable cations and the composition of electrolyte in the soil solution were also studied in detail (Quirk and Schofield 1955). Further, Crescimanno *et al.* (1995) suggested that the relationship between ESP and structural properties may be described as a continuum, with an ESP as small as 2–5 causing adverse effects at low electrolyte concentrations. Similarly, Crescimanno *et al.* (1995) reported decreases in HC of 25% at low concentration. However, Struckman (2001), using soil samples with similar structural characteristics as used in this study, estimated the threshold concentration and turbid concentrations, as defined by Quirk and Schofield (1955), to occur at SAR 15 at low electrolyte concentration. We adopted this concept in this study's experimental design. The present study was therefore designed to examine the effects of SAR at decreasing electrolyte concentration on the dynamics of (*a*) saturated hydraulic conductivity along the soil columns, and (*b*) the electrolyte breakthrough during the Na–Ca exchange reactions at the threshold of SAR 15, for 2 soils of significantly different mineralogical composition (Table 1) and physico-chemical properties (Table 2).

Materials and methods

Soil samples and analyses

Two different soil samples (Balkuling soil and mining residue) with significant differences in clay mineralogical composition (Table 1) and other physico-chemical properties (Table 2) were used in this study. The physico-chemical properties were measured using standard methods (Day 1965; Klute 1986). Balkuling soil is an agricultural soil extensively used for cropping and pasture throughout the Western Australian wheatbelt. It is a duplex soil classified as brown loamy earth (WA soil group, McArthur 1991), or sodic manganesic brown Kandosol (Australian Soil Classification, Isbell 2002) and is also classified as Vertic Ferralsol (World Reference Base for soil classification, FAO 1998). The soil often shows some build-up of salts (especially sodium) in the subsoil, has a potential for structural breakdown, and is subject to water repellence (McArthur 1991). The Balkuling soil samples were collected from 'Yalanbee', the CSIRO research station farm near Bakers Hill, Western Australia. In contrast, samples of the mining residue or spoil were collected from the Cable Sands (WA) Ltd Sandalwood mine site, 5 km north of Brunswick Junction, Western Australia. This sample consisted of waste products (>63 µm tailings sands and <63 µm fines) and is classified as Anthroposol (Soil Taxonomy classification, Soil Survey Staff 1996).

Table 1. Clay mineralogical properties and the specific surface area (SSA) of soil samples

Soil material	Type of mineral	SSA (m^2/g)
Balkuling soil	Kaolinite with traces of gybisite	6.8
Mining residue	Smectite and kaolinite with traces of quartz	12.5

Table 2. Selected measured physico-chemical properties of the soil samples

CEC, Cation exchange capacity; ESP, exchangeable sodium percentage

Property	Balkuling soil	Mining residue
Sand (%)	83.3	89.0
Silt (%)	6.6	1.9
Clay (%)	10.1	9.1
Texture	Sandy loam	Loamy sand
Bulk density (g/cm^3)	1.61	1.58
Electrical conductivity (µS/cm)	42	380
pH(water)	6.1	8.7
CEC (cmol/kg)	3.4	8.1
ESP	2.5	27
Organic carbon (%)	0.3	0.55

Exchange reactions: Theory

Theoretically, cation exchange behaviour is described by exchange characteristics of mixed ions such that for the Na–Ca exchange system:

$$\mathrm{CEC} = E_{x\,\mathrm{Na}} + E_{x\,\mathrm{Ca}} \tag{3}$$

where CEC is the cation exchange capacity and $E_{x\,\mathrm{Na}}$ and $E_{x\,\mathrm{Ca}}$ are the activity of exchange phase of Na and Ca, respectively. According to Vanselow, the selectivity coefficient $K_{\mathrm{Ca}}^{\mathrm{Na}}$ can be expressed by the following (Vanselow 1932):

$$K_{\mathrm{Ca}}^{\mathrm{Na}} = \left[\frac{M_{\mathrm{Na}}}{(M_{\mathrm{Ca}})^{1/2}}\right]\left[\frac{(\alpha\mathrm{Ca})^{1/2}}{\alpha\mathrm{Na}}\right] \quad \text{for} \quad \alpha_i i = c_i \gamma_i \tag{4}$$

where M is mole fraction of the ionic species and c_i and γ_i are the concentration and the activity coefficient of species i, respectively. The molar fractions are given by:

$$M_{\mathrm{Na}} = \frac{E_{x\,\mathrm{Na}}}{E_{x\,\mathrm{Na}} + E_{x\,\mathrm{Ca}}} \tag{5}$$

$$M_{\mathrm{Ca}} = \frac{E_{x\,\mathrm{Ca}}}{E_{x\,\mathrm{Na}} + E_{x\,\mathrm{Ca}}} \tag{6}$$

Further, the soils' preference to either Na^+ or Ca^{2+} adsorption in the exchange complex can be assessed using the following isotherm equation (Sposito 1981*b*):

$$E_{Na} = \left[1 + \frac{2}{FN_T}\left\{\frac{1}{E'^2_{Na}} - \frac{1}{E'_{Na}}\right\}\right]^{-1/2} \qquad (7)$$

where E_{Na} equals the equivalent fraction of Na^+ on exchanger phase, $F = \gamma^2_{Na}/\gamma_{Ca}$, N_T represents the total cation normality, and E'_{Na} represents equivalent fraction of Na^+ in the solution phase.

Experiment 1: Binary Na–Ca exchange reactions

A batch technique was employed in the analyses of Na–Ca exchange reactions. Triplicate 10-g samples of each soil (Balkuling soil and mining residue) were saturated with a 30-mL solution of the Na/Ca mixture at different Na/Ca ratios: 0.9, 0.7, 0.4, 0.2, and 0.1. The 30-mL Na/Ca mixtures were initially saturated with 0.5 mol/L solution (to ensure equilibration with the exchanger sites) and were added into separate 50-mL vials for centrifugation. The 0.5 mol/L saturated samples were placed on a reciprocating shaker for 24 h (to disrupt soil aggregates) and centrifuged, and the supernatant was discarded. This procedure was repeated twice with the final retained sample added to a 50-mL vial saturated with a reduced concentration of 0.005 mol/L solution. This was repeated 6 times, after which 1 mol/L of ammonium acetate (NH_4OAc) solution was added for the cation extraction. The 30 mL of each 1 mol/L NH_4OAc solution was adjusted, using acetic acid and ammonium hydroxide solutions, to a pH 6 and 7.5 for the Balkuling soil and the mining residue, respectively. The samples were also shaken for 24 h and centrifuged while the pH of each retained solution was measured. This was repeated 3 times while the 3 retained samples were washed into 100-mL vial making a 90-mL solution for the determination of CEC using an atomic adsorption spectrometer (AAS).

Experiment 2: Hydraulic conductivity and SAR

The experiment was carried out using laboratory soil columns as schematically shown in Fig. 1. Samples (<2 mm) of each soil were initially mixed with acid-washed sand (0.9–1 mm) to provide a rigid skeletal structure. To enhance the conductivity of the soil columns, the samples were mixed at the following proportions: 50% soil – 50% sand for the Balkuling soil and 70% soil – 30% sand for the mining residue. The soil columns were wet-packed and saturated with solutions of different SAR values (3, 5, 15, and 30) at various electrolyte concentrations (1, 10, and 100 mmol/L). The samples were left overnight for complete saturation. The pressure heads were measured online using an Agilent data logger system (Agilent Technologies 2003), while a peristaltic pump was used to pump the feed solutions at constant flow rate or flux of 1 cm^3/min (Table 3).

Experiment 3: Breakthrough curves at SAR 15

Using similar soil materials, Struckman (2001) found the threshold and turbidity concentrations to occur at approximately 10 and 2.5 mmol/L, respectively, at SAR 15. The breakthrough experiment was set up, with the electrolyte concentration of the solution decreased through these values while maintaining an input SAR value of 15. Column samples were preconditioned by leaching the column with 6 pore volumes of 50 mmol/L $CaCl_2$ solution until the equilibrium was attained. The equilibrium was monitored by measuring the electrical conductivity (EC) of the effluents collected into the fraction collectors. The input concentration was then lowered to 10 mmol/L $CaCl_2$ and the breakthrough of the less concentrated solution was followed to equilibrium by measuring the EC of the effluent. After this preconditioning, the input solution concentration was progressively changed through 10 and 2.5 mmol/L at SAR 15 (see Table 3). The effluent samples were collected into the fraction collectors and later analysed for both Na and Ca concentrations using AAS,

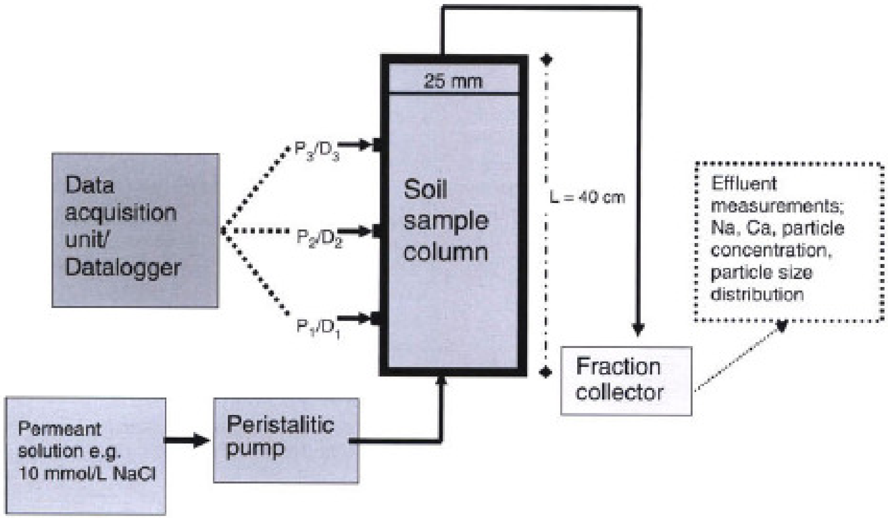

Fig. 1. Schematic diagram of the laboratory online pressure head measurements. Samples were leached with solutions of various electrolyte concentrations and different SAR values. P_1, P_2, and P_3, and D_1, D_2, and D_3 represent positions of pressure transducers and depths, respectively.

Table 3. Column physical properties of samples during leaching with 50 mmol/L $CaCl_2$, 10 mmol/L $CaCl_2$, and SAR 15 (10 and 2.5 mmol/L)

Salt concentration (mmol/L)	Water content^A (cm^3/cm^3)	Flux (cm^3/min)	Pulse time (min)	Pore volume
Balkuling soil at pore volume of 66.8 cm^3/min at density of 1.69 g/cm^3				
50 mmol/L $CaCl_2$	0.381	1.10	380	5.7
10 mmol/L $CaCl_2$	0.381	0.96	700	10.4
SAR 15 (10 mmol/L)	0.381	1.00	1200	18.0
SAR 15 (2.5 mmol/L)	0.381	1.04	1200	18.0
Mining residue at pore volume of 77.1 cm^3/min at density of 1.60 g/cm^3				
50 mmol/L $CaCl_2$	0.423	1.01	500	6.5
10 mmol/L $CaCl_2$	0.423	1.00	750	9.7
SAR 15 (10 mmol/L)	0.423	1.02	1200	15.6
SAR 15 (2.5 mmol/L)	0.423	1.00	1200	15.6

^A Saturated water content.

Table 4. Sodium–calcium exchange on samples for different concentrations ratios (Na/Ca) for Balkuling soil and mining residue

r (Na/Ca)	pH	ExNa	ExCa (mmol/kg)	$\sum$Exi^A	K^{Na}_{Ca}
			Balkuling soil		
0.9	6.1	1.10	11.50	12.60	0.28
0.7	6.6	0.64	11.10	11.74	0.21
0.4	6.3	0.46	11.14	11.86	0.23
0.2	6.6	0.20	12.50	12.70	0.18
0.1	6.6	0.18	12.20	12.38	0.31
			Mining residue		
0.9	7.5	1.16	21.78	22.94	0.16
0.7	7.4	0.78	20.34	21.12	0.14
0.4	7.0	0.64	19.22	19.86	0.19
0.2	7.0	0.40	14.57	14.97	0.30
0.1	7.3	0.40	14.47	14.87	0.57

^A Exi denotes concentration of adsorbed cations and $\sum$Exi total adsorbed cations.

while the remainder of the samples were analysed for particle size distributions using a Malvern Mastersizer analyser. While the breakthrough leaching experiments continued, the pressure head were simultaneously measured at 3 points or column depths ($D_1 = 50$, $D_2 = 150$, $D_3 = 250$ mm) along the columns under constant pore volume velocity of 66.8 and 77.1 cm^3/min, for the Balkuling soil and the mining residue, respectively (see Table 3).

Results and discussions

Binary exchange isotherm reactions

Generally the effects of composition of mixed ions on exchange reactions demonstrated strong preference for Ca^{2+} ions in both soils with a stronger preference for Na^+ on the exchange complex of the agricultural Balkuling soil than for the mining residue. This is attributable to the initial low ESP of Balkuling soil therefore having more affinity to Na-adsorption. The exchange isotherms were computed using Eqns 3–7. The experimental Ca–Na exchange data together with the exchange capacity ($\sum$Exi) and exchange selectivity coefficients (K^{Na}_{Ca}) over different Na/Ca ratios are presented in Table 4. Based on K^{Na}_{Ca} values, the results demonstrated a non-exchanger preference for Ca^{2+} ions in both soils, with the average values of K^{Na}_{Cs} 0.24 and 0.27 for Balkuling and mining residue, respectively. This minor variation in the selectivity coefficient (K^{Na}_{Ca}) was consistent with the smaller variation in exchanger phase composition (Table 4). However, there were also minor variations of solution pH of these Na–Ca binary systems across the entire isotherm observed, with the pH varying from 6.1 to 6.6 and 7.0 to 7.5 for Balkuling and mining residue, respectively. Ideally, pH, ($\sum$Exi), or CEC should be constant across the entire isotherm to generate cation-exchange isotherm or estimate the cation selectivity coefficients.

Effects of sodium adsorption ratio on saturated hydraulic conductivity

The relative saturated hydraulic conductivity (RHC), defined here as the ratio of the measured or actual hydraulic conductivity to the initial hydraulic conductivity, was measured as a function of electrolyte concentration, following leaching of the soil columns with solutions of SAR 3, 5, 15, and 30 (Fig. 2). Generally, the RHC decreased with time, with increasing SAR, and with decreasing electrolyte concentrations. It was clear that in the case of the Balkuling soil the RHC was maintained for SAR 3 and SAR 5 at a concentration of 100 mmol/L. In contrast, Rengasamy *et al.* (1986) observed a decrease in RHC for SAR >3. However, for the mining residue this criterion was not achieved, suggesting a greater potential for mobilisation of the finer particles at low SAR values and even at concentrations as high as 100 mmol/L. A similar observation was made by Rengasamy *et al.* (1986), who found a decrease in hydraulic conductivity for SAR >3. The mining residue also showed a more rapid decrease in RHC particularly at the lowest concentration (1 mmol/L) and this was consistent at all SAR values. Furthermore, the RHC seems to strongly fluctuate in particular for the lowest concentration (1 mmol/L) and lowest SAR in the Balkuling soil.

The results also demonstrated that the initial and the final pH remained constant during leaching, while the EC decreased with decreasing electrolyte concentration. This may imply that the pH did not influence any particle re-arrangement. However, the decrease in EC with electrolyte concentration suggested an influence of EC on particle deposition that might have subsequently blocked pores with subsequent reduction in RHC.

Generally, the highest SAR solutions produced the most stable curves for both the Balkuling soil and the mining residue, although the RHC dropped fastest to the lowest values. This seems to imply that blocking of pores (or pore clogging) occurs, in this case, very fast and thus creating a new pore structure that is not prone to changes in any experimental conditions. In contrast, the lower SAR treatments seem to generate a system that fluctuates between stages where the clogging dominates followed by stages with particle dislodgement and a temporary increase in the RHC. Goldenberg *et al.* (1993), using a micro model, also observed how clay suspensions clog pore networks. One of the observations was that larger flocs or aggregates form and clog pores. Depending on hydrodynamic conditions they either grow or break down. It is conceivable that such processes

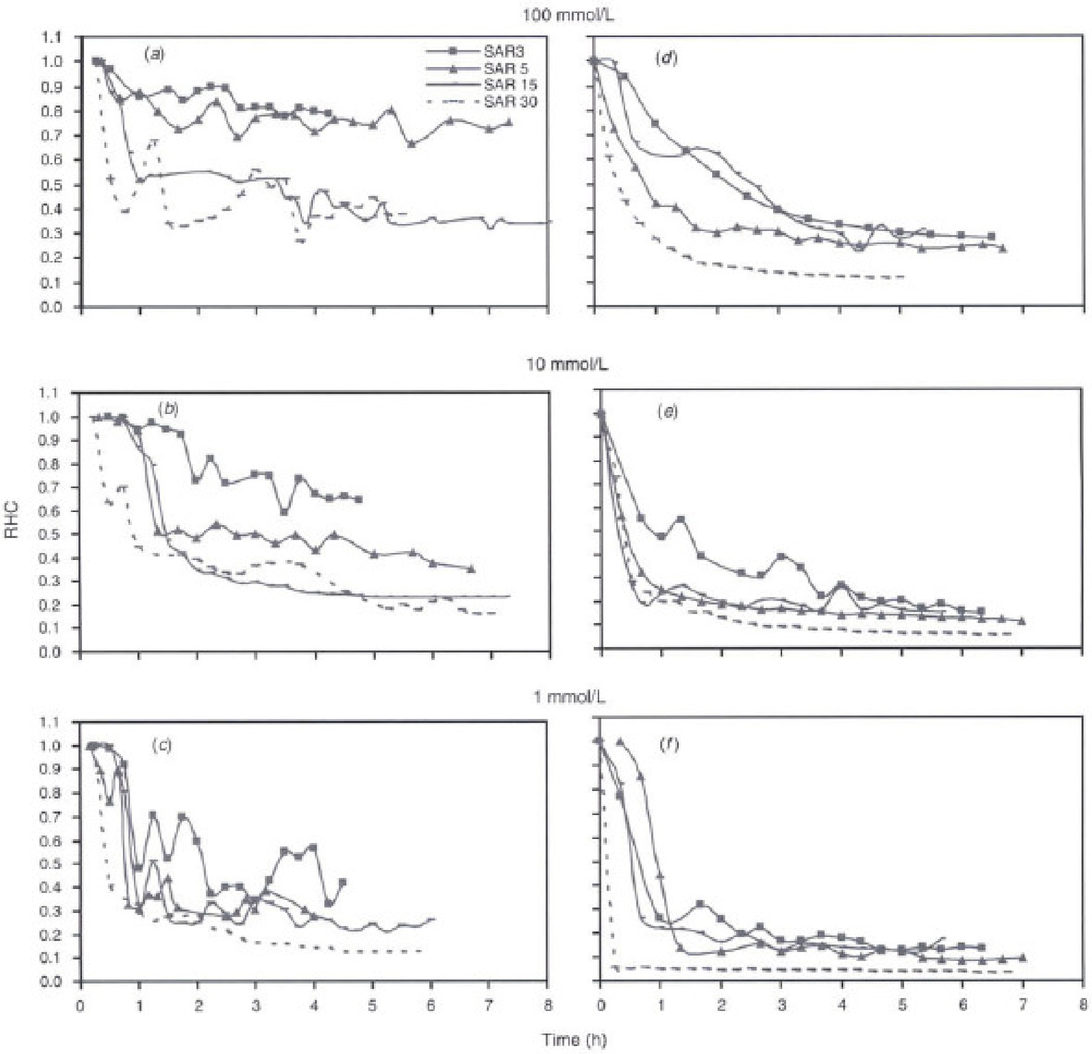

Fig. 2. Relative saturated hydraulic conductivity (RHC) as a function SAR and electrolyte concentration for (*a*–*c*) Balkuling soil and (*d*–*f*) mining residue.

occur in the column studied, in particular when a constant flow rate is maintained. Temporary clogging of pore throats can cause a build-up of pressure and may increase shear forces that cause the flocs to break down. This in turn opens up pores that will, on average, temporarily increase the hydraulic conductivity.

The effects of clay mineralogy are evident with the kaolinite-smectitic mining residue having a more marked decrease in RHC with increasing ionic strength compared with the kaolinitic Balkuling clays. Similar observations were made by Anderson and Lu (2001), who reported higher void ratio for Na/Ca-montmorilllonite than for kaolinite decreasing with increasing ionic strength.

Critical concentrations and breakthrough curves

Figure 3 shows the breakthrough curves for the 2 soils during leaching with 10 mmol/L $CaCl_2$ following the pre-conditioning of the soil columns by leaching with 50 mmol/L $CaCl_2$. The input and equilibrium concentrations are presented in Table 5. The equilibrium with the 50 mmol/L solution was reached rapidly for both soils as demonstrated by the stable EC (Figs 3 and 4).

The RHC for the Balkuling soil initially decreased rapidly and stabilised at essentially constant but differing values at the 3 measured points along the column, with relatively insignificant further change following change in the input concentration to 10 mmol/L (Figs 3 and 4). As previously observed, the greatest

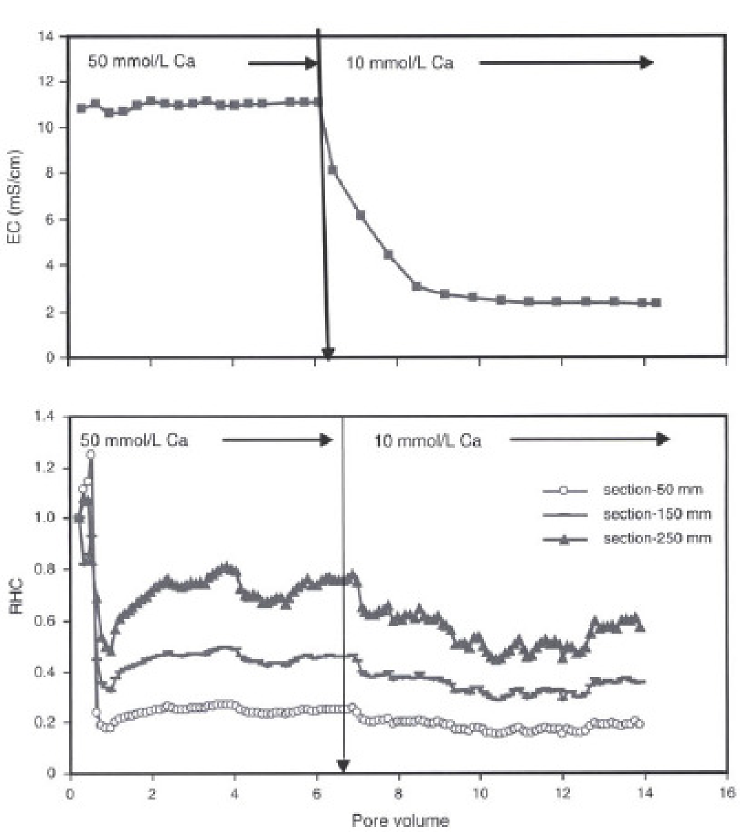

Fig. 3. Relative saturated hydraulic conductivity (RHC) and electrical conductivity (EC) during leaching and conditioning of the soil with 50 and 10 mmol/L $CaCl_2$ solutions for Balkuling soil.

Table 5. Input and equilibrium conditions during breakthrough measurements
EC, Electrical conductivity; PVeq, pore volume to reach equilibrium

Solution concentrations	Input conditions (or solution)				Equilibrium conditions				
	Na (mmol/L)	Ca (mmol/L)	SAR (%)	EC (dS/m)	Na (mmol/L)	Ca (mmol/L)	SAR (%)	EC (dS/m)	PVeq
				Balkuling soil					
50 mmol/L $CaCl_2$	n.a	n.a	n.a	11.11	n.a	n.a	n.a	10.96	5.7
10 mmol/L $CaCl_2$	n.a	9.9	n.a	2.33	n.a	10.1	n.a	2.29	10.4
SAR 15, 10 mmol/L	9.52	0.39	15.24	1.28	10.10	0.44	15.2	1.30	18.0
SAR 15, 2.5 mmol/L	2.5	0.03	14.6	0.35	2.61	0.033	14.4	0.37	18.0
				Mining residue					
50 mmol/L $CaCl_2$	n.a	n.a	n.a	11.11	n.a	n.a	n.a	10.5	6.5
10 mmol/L $CaCl_2$	n.a	10.0	n.a	2.33	n.a	10.1	n.a	2.35	9.7
SAR 15, 10 mmol/L	9.48	0.387	15.2	1.28	10.2	0.42	15.6	1.29	15.6
SAR 15, 2.5 mmol/L	2.48	0.027	15.1	0.35	2.58	0.03	15.1	0.34	15.6

reduction in RHC occurred within the input section of the column, presumably because slaking under the hydraulic flow exerts the most effect in this region, thus shielding the lower parts of the column. Little if any dispersion would occur at these concentrations of $CaCl_2$. Much greater reductions in RHC are observed at all measured points for the mining residue, no doubt

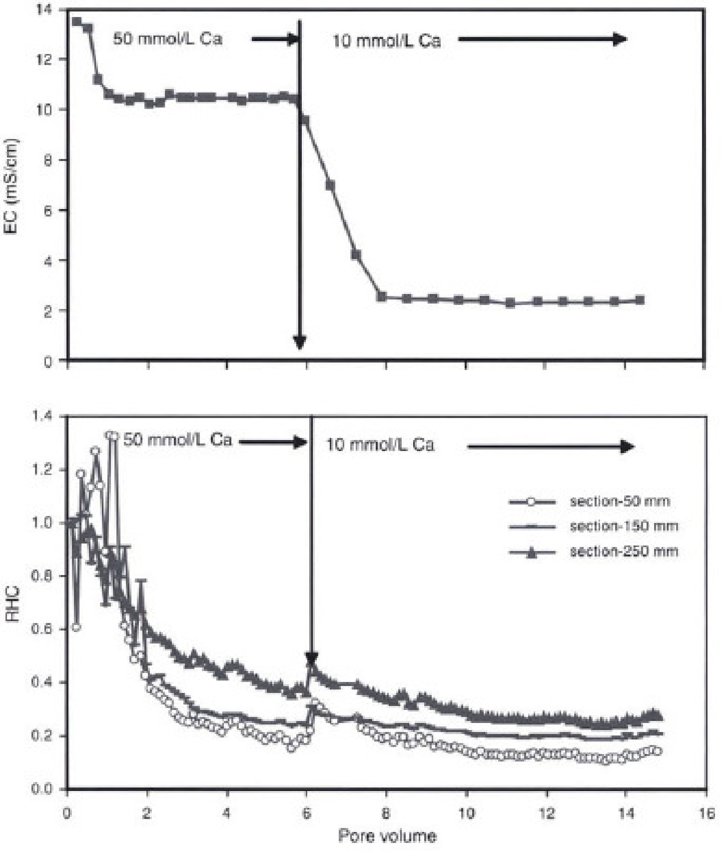

Fig. 4. Relative saturated hydraulic conductivity (RHC) and electrical conductivity (EC) during leaching and conditioning of the soil with 50 and 10 mmol/L $CaCl_2$ solutions for mining residue.

reflecting the lower structural stability within the column. This behaviour of the mining residue presents structural problems in the rehabilitation of mining sites.

Figures 5 and 6 show the outgoing effluent concentrations of Na and Ca ions, SAR, and RHC for the breakthroughs with different input concentrations (threshold concentration 10 mmol/L and turbidity concentration 2.5 mmol/L), while maintaining a constant input SAR of 15, at positions 50, 150, and 250 mm along the columns. Table 5 shows the input concentration of the Na and Ca ions.

For both soils an initial increase in the effluent Na concentration following commencement of the input of the 10 mmol/L SAR 15 solution occurred rapidly, and was followed by subsequent rapid decreases with decreasing electrolyte concentration of the input solution to 2.5 mmol/L. The Ca concentrations in the effluent decreased progressively with decreasing input concentrations as would be expected. However, for both soils, more than 15 pore volumes were required for the effluent SAR to reach that of the input solution. These responses are slightly more rapid in the case of the Balkuling soil, presumably reflecting its more open pore structure associated with the presence of micro-aggregates. Interestingly, the EC closely followed the decrease with normality of the solutions (Figs 5and 6).

The approach to equilibrium hydraulic conductivity during the changeover from SAR 0 to SAR 15 at 10 mmol/L concentration was initially accompanied by rather erratic RHC behaviour, undoubtedly reflecting the particle rearrangement in the porous structure. This erratic behaviour is consistent with the early observations (Fig. 2) which showed that the RHC of the low to intermediate SAR treatments and low ionic strength seem to generate the most variable responses. At the threshold concentration, one would expect slaking to occur with perhaps some dispersion as the micro-aggregate structure is disrupted by the swelling forces induced. Once this has happened, uniformity occurs and the subsequent change to 2.5 mmol/L produces a rapid decrease to a uniform RHC for both soils. A most surprising feature of the results is the relative coincidence of the responses at the different measuring points along the column for both soils despite the clear indication of a gradual breakthrough of the SAR front moving through the columns during the change from the 10 mmol/L $CaCl_2$ solution to 10 mmol/L at SAR 15. Gaston and Selim (1990) and Hinz and Selim (1994) attributed the movement of cation fronts through soil solution to the distribution of exchanger species between solution and adsorbed phases.

The subsequent reduction in the input concentration to 2.5 mmol/L (the turbidity concentration) occurred rapidly in the effluent, producing uniformly lower RHC along the columns of both soils (Figs 5 and 6). The reduction was substantially greater for the less cohesive mining residue. The dilution of high-sodicity soil irrigation water can cause swelling, aggregate

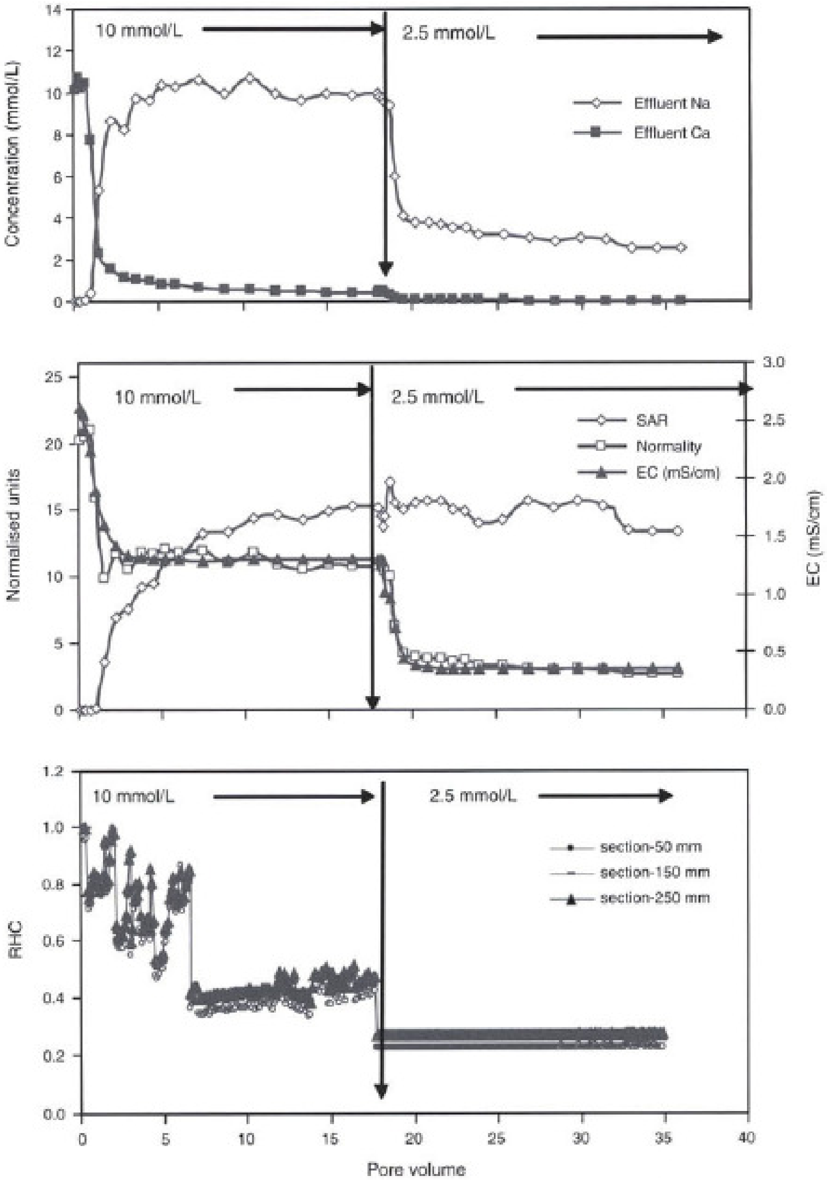

Fig. 5. Breakthrough curve (Na–Ca exchange reactions) and relative saturated hydraulic conductivity (RHC) following leaching with SAR 15 (at threshold concentration 10 mmol/L, and turbidity concentration 2.5 mmol/L) for Balkuling soil after column conditioning with 10 mmol/L Ca.

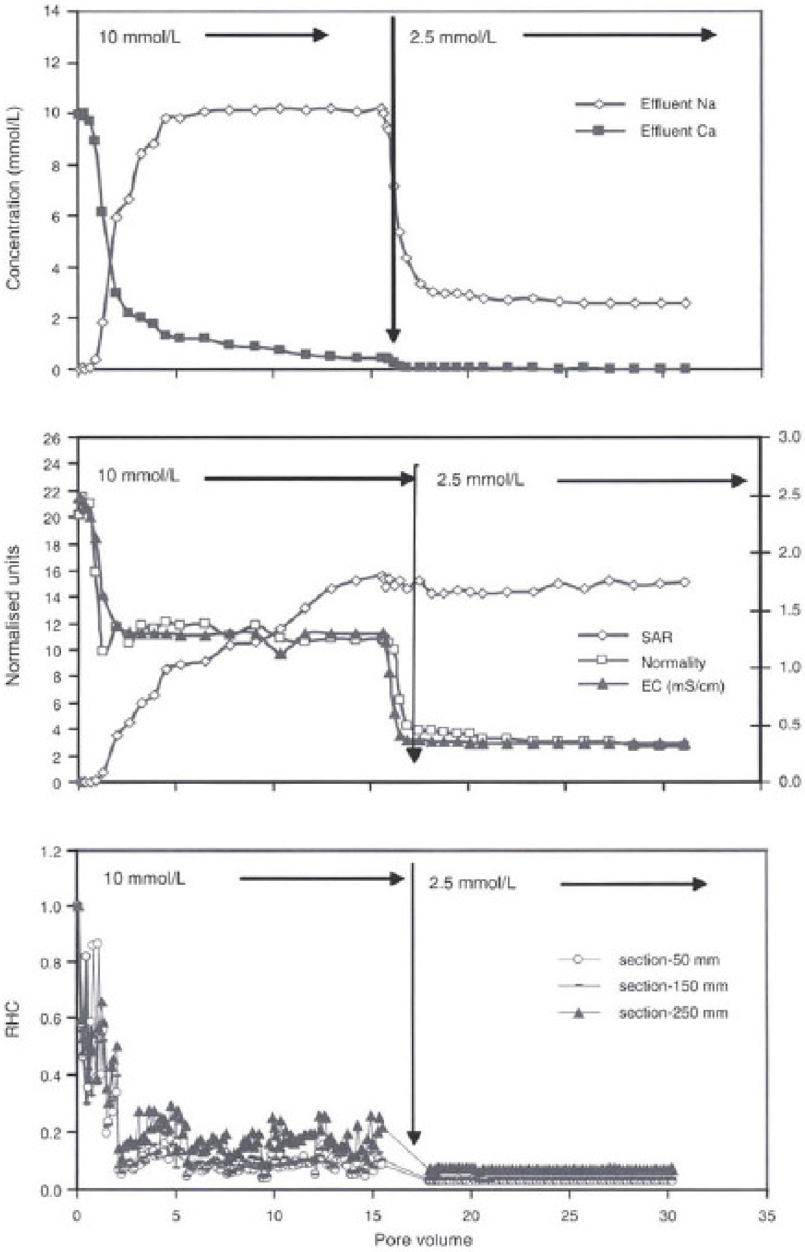

Fig. 6. Breakthrough curves (Na–Ca exchange reactions) and relative saturated hydraulic conductivity (RHC) following leaching with SAR 15 (at threshold concentration 10 mmol/L, and turbidity concentration 2.5 mmol/L) for mining residue after column conditioning with 10 mmol/L Ca.

slaking, and particle clay dispersion (Bagarello *et al.* 2006), and the reductions in RHC here were likely to be caused by partial blocking of pores by dispersed clay particles, as evidenced by the appearance of suspended clay particles in the effluent during leaching. Again the flush of the material occurred earlier for the Balkuling soil, whereas for the mining residue there was more delay due to self-filtration. The effluent for the Balkuling continued to reflect the presence of a wide range of particle sizes, while that for the mining residue clearly showed a predominance of clay-sized material (Fig. 7).

The particle size distribution of the effluents (Fig. 8) shows some increase of particle size with decreasing electrolyte concentration. However, these wider effluent particle size distributions as associated with particle release (Fig. 7) indicated the presence of both the clay domains and clay-sized particles. While the particle release occurs almost continuously from the Balkuling soil column with an initial peak at some 8 pore volumes passed, the release for the mining residue occurs much later at 10–15 pore volumes.

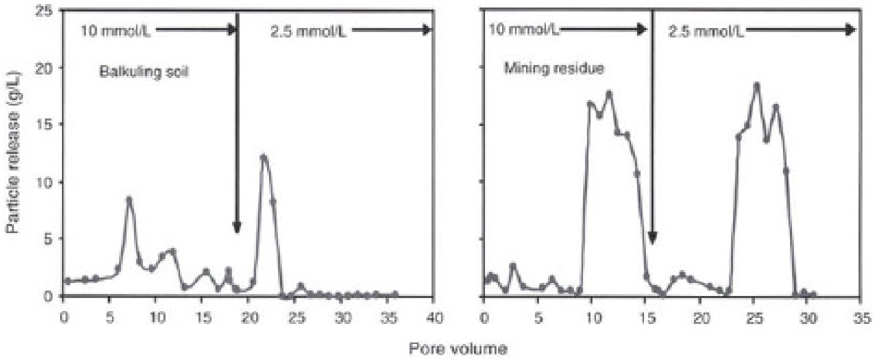

Fig. 7. Particle release of effluents following leaching with SAR 15 at 10 mmol/L and 2.5 mmol/L concentration for Balkuling and mining residue.

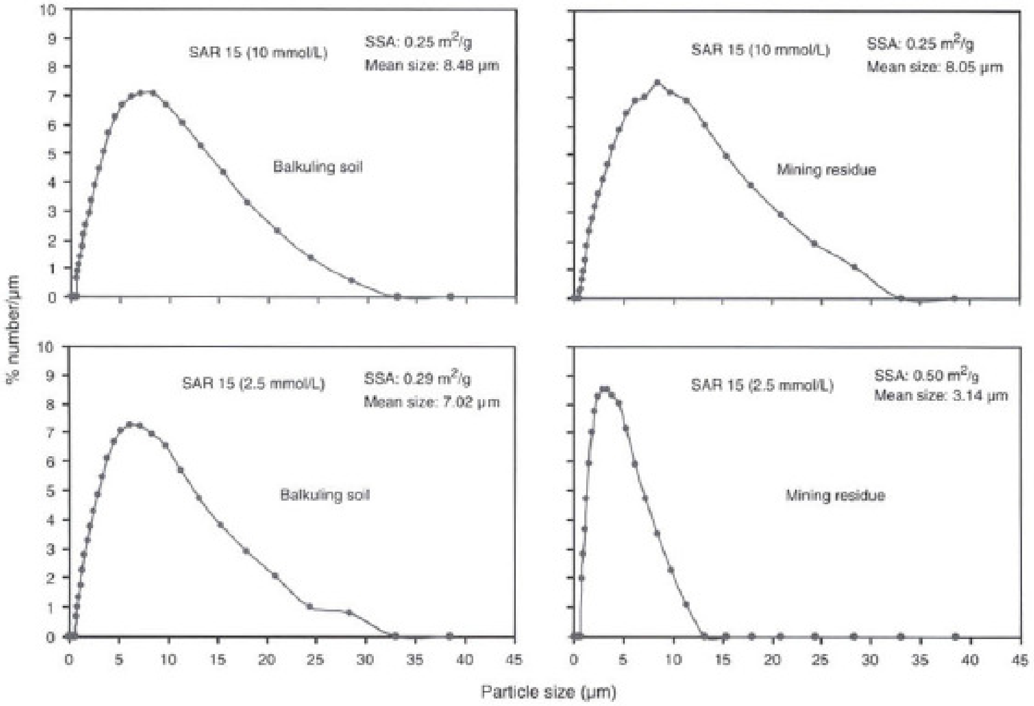

Fig. 8. Particle size distribution of effluents following leaching with SAR 15 at 10 and 2.5 mmol/L concentration for Balkuling and mining residue.

Summary and conclusions

The effects of composition of mixed ions on exchange reactions demonstrated strong preference for Ca^{2+} ions in both soils with a stronger preference for Na^{+} on the exchange complex of the agricultural Balkuling soil than for the mining residue. This is attributable to the initial low ESP of Balkuling soil therefore having more affinity to Na-adsorption. Generally, the RHC of both soils has been shown to decrease with time, with increasing SAR and with decreasing electrolyte concentration. In the case of the Balkuling soil, the RHC was maintained for SAR 3 and SAR 5 at a concentration of 100 mmol/L. However, for the mining residue this criterion was not achieved, suggesting a greater potential for mobilisation of these soils' particulate matter at low SAR values and even at concentrations as high as 100 mmol/L. The mining residue also showed a more rapid decrease in HC, particularly at the lowest concentration (1 mmol/L), although this was consistent at all SARs. The effects of clay mineralogy are evident, with the kaolinite-smectitic mining residue having a more marked decrease in RHC with increasing ionic strength than the kaolinitic Balkuling clays.

Significant differences in RHC were observed in the passage of fronts of decreasing electrolyte concentrations for $CaCl_2$ and SAR 15 solutions through the soil columns, reflecting structural alterations (slaking) of the media, the nature of the particles mobilised within the porous structure at any given point in the column. The increase in SAR to 15 is initially accompanied by erratic RHC, presumably due to the break up of soil aggregates under the increased swelling forces. The mining residue soil was substantially more vulnerable to pore clogging than the Balkuling soil. This is likely related to the less coherent state of the mining residue and the nature of its clay constituents, with Balkuling soil being predominately kaolinite and the mining residue containing an equal amount of kaolinite and smectite clay particles. The latter are likely to be more readily mobilised, and hence available to re-deposit and occlude matrix pores.

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