

Kinetics of Ion Removal from an Iron-Rich Industrial Coproduct: I. Chloride

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ABSTRACT

An industrial TiO_2 extraction process results in a Fe-rich material (IRM) that contains substantial chlorides. Recent investigations showed that washed IRM may serve as a soil amendment for agricultural use. Yet, washing processes at the industrial production facility are currently problematic and costly, and it is essential to devise effective procedures for Cl removal. This study was conducted to determine the mechanism of Cl retention, and to ascertain whether the rate of Cl removal was governed by time-dependent surface-chemical kinetics or diffusion (transport)-controlled kinetics. The IRM samples we used throughout the study were homogenous. It was physicochemically characterized and concentrations of heavy metals were determined. The IRM batch studies revealed negative Cl adsorption, even though its point of zero charge was 8.3. Column studies showed that 92% of the Cl was removed with the first pore volume. Additionally, the salt removal decreased the electrolyte concentration, caused dispersion, and, ultimately, lowered the hydraulic conductivity. Stirred-flow kinetic studies established that Cl leaching was a function only of the total volume that flowed through the chamber, and that no chemical kinetics were involved.

THE DISPOSAL of industrial byproducts and coproducts is an increasing problem that is confronting industrialized nations. Manufacturing processes produce a myriad of waste products that may contain high concentrations of heavy metals, salts, and other potential contaminants to the environment. These byproducts have many potential uses such as soil amendments and as fertilizer sources. Their disposal, however, is often precluded by a lack of information on the accompanied environmental impacts. Therefore, to assure that rational decisions are made concerning the proper land disposal of these waste products, research must be conducted on their environmental soil chemistry.

The IRM or filter-cake used in this study was a coproduct from an industrial process that generates a TiO_2 pigment. The waste contained significant amounts of Fe-oxides as well as other heavy metals. The Ti ore

is processed with HCl to produce the TiO_2 pigment. Neutralizing the remnant slurry with lime results in a mixture of metal-(hydr)oxides and salts. To remove the chlorides the slurry is leached several times in water tanks and squeezed in presses to produce the filter-cake material. About 50 000 Mg of IRM, on a dry weight basis, are produced annually in the mid-Atlantic region of the USA and are stored in unlined slurry ponds or stockpiled at the surface. Agricultural uses, for instance, as a component in synthetic topsoil or as a growth medium amendment, seem promising (Goyette, 1992). The initial, Cl concentration in the slurry at the industrial production facility, however, was $\approx 134 \text{ g Cl kg}^{-1}$ dry matter, and washing processes are currently problematic and costly. Excessive Cl levels are of concern from both plant growth and water quality aspects. Therefore, determining the mechanism and rate of Cl removal by water from the IRM is important if one is to devise effective procedures for its removal and subsequent use of the IRM for agricultural purposes.

Equilibrium and kinetic measurements can be useful in determining the extent of Cl adsorption-desorption on sorbents such as IRM. Surface protonation on Fe-oxides results in considerable pH-dependent charge. Below the point of zero charge (PZC), Cl^- can be retained on Fe-oxides by electrostatic adsorption (Hingston et al., 1967).

Few studies have appeared on the kinetics of Cl adsorption-desorption on soils and soil components. Thomas (1963) compared the pattern of the Cl breakthrough curve (BTC) obtained from a column of Wyoming bentonite (a clay that adsorbed no Cl) to that of a column of FeCl_3 -treated Georgia kaolinite. When evaluating the BTC for the kaolinite, he observed an asymmetry or *tailing* effect, which was attributed to a first-order reaction, apparently hydrolysis of Cl from the hydrous Fe-oxide adsorption sites. The conclusions, however, were supported primarily based on the shape of the BTC, and no rate measurements were presented.

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Abbreviations: BTC, breakthrough curve; CV, the coefficient of variation; DTA, differential thermal analyses; DW, deionized water; EC, electrical conductivity; IRM, iron-rich material; NLLS, nonlinear least squares; ODE, ordinary differential equations; PZC, point of zero charge; SF, stirred-flow technique; SP, saturated paste; XRD, x-ray diffraction.

Laboratory column studies are often used to evaluate mobility and sorption of ions on soils. Barry et al. (1986) provided an analytical approximation method for describing irreversible kinetics in soil columns. Devitt (1989) periodically measured the Cl concentrations in drainage samples taken from soil columns irrigated with saline water.

The transport of solutes through soils is an important process in leaching of salts from the soil profile. A number of adsorption models have been proposed, many assuming instantaneous equilibrium between the solute in soil solution and the amount of solute adsorbed, and others (e.g., Rao et al., 1979; Nielsen et al., 1986; Selim et al., 1989) based on time-dependent adsorption processes (Selim and Mansell, 1976).

Time-dependent terms in adsorption models, however, do not necessarily refer to chemical kinetics. In soil systems, many kinetic processes are a combination of both chemical kinetics or reaction-controlled kinetics, and diffusion or transport-controlled kinetics (Sparks, 1989). For that reason, interpretations of the shape and asymmetry of experimental BTCs may be classified into two model categories (Rao et al., 1979). In the first group of conceptual models, the observed asymmetry in the BTCs was attributed to chemical reactions. In the second group, processes such as diffusion of adsorbate molecules through the soil solution, were assumed to be responsible for the observed tailing.

The stirred-flow (SF) technique can be used to investigate the rates and amounts of ion adsorption-desorption (Carski and Sparks, 1985) under uniform mixing conditions (Seyfried et al., 1989). Stopped-flow experiments, using the SF technique, can be employed to distinguish between instantaneous equilibrium and time-dependent processes (Bar-Tal et al., 1990).

The objectives of this research were to determine the mechanism of Cl retention on the IRM, and to examine whether its removal rate was governed by surface-chemical or diffusion (transport)-controlled kinetics.

MATERIALS AND METHODS

Characterization Analyses of the Iron-Rich Materials

This study dealt with Cl removal after the IRM had been leached several times in water tanks and squeezed in filter presses, about 3 mo after industrial production. The Cl concentration was then 0.745 g Cl kg⁻¹ dry IRM, and the gravimetric water content (w) was 0.85 ± 0.02 kg kg⁻¹. Six filter-cake batches from different production lines were sampled. Each batch was mixed (in a bucket) and 1 kg of the material was air-dried and ground to pass a 2-mm sieve. Then, the ground IRM from all the batches were mixed thoroughly, so that the IRM samples used throughout the study were homogenous. The analyses were performed in quadruplicate.

X-ray diffraction (XRD) analyses were completed using a random powder mount technique, and differential thermal analyses (DTA) were also performed. Electrophoretic mobility measurements, using a ζ - meter (ZM-80; Zeta Meter, Long Island City, NY) were determined at three different ionic strengths (0.001, 0.01, and 0.1 M NaNO₃, at 298K). ζ - potentials were calculated using the Helmholtz-

Smoluchowski equation: $\psi_{\zeta} = (4 \pi \eta \mu) \varepsilon^{-1}$, where ψ_{ζ} is the ζ - potential (mV), η is the viscosity of the water, ε is the dielectric constant of bulk water, and μ is the electrophoretic mobility [($\mu\text{m s}^{-1}$) (V cm^{-1})⁻¹]. The effective cation-exchange capacity of the IRM samples was determined by the BaCl₂ method (Jackson, 1958). The anion-exchange capacity (AEC) of the IRM was analyzed using the compulsive exchange method of Uehara and Gillman (1981). The C and the Fe-sulfide source in the IRM is coke that was added to the IRM in the industrial process. Total C concentration was analyzed with a CHNS-O analyzer (Carlo Erba Model 1501, Carlo Erba, Valencia, CA).

The pH of all IRM suspensions in the study was determined using a combination electrode. The suspensions were then passed through a 0.45- μm filter, and electrical conductivity (EC) was measured with a Radiometer EC-meter, and elemental analyses were performed. Ligands were determined by high-pressure liquid chromatography and metals by inductively coupled plasma spectroscopy.

Chloride Equilibrium Studies

Equilibrium studies were conducted on the IRM samples to estimate the water-soluble and acid-soluble Cl content, and to test if and how easily Cl is removed by sequential washings. The extent of Cl adsorption-desorption on the IRM was also determined. Four IRM deionized water (DW) saturated pastes (SP) (Rhoades, 1982) were extracted by vacuum following a 24-h equilibration period, and Cl and major elemental analyses were performed using procedures given above. To evaluate the leachability of Cl, 1:5 slurries (20 g IRM with 100 mL DW) were filtered, following 1 h of shaking. After filtration, the IRM samples were dried at 378 K for 24 h. The dried materials were then shaken for 1 h with 100 mL DW, and filtered as before. This protocol was repeated four times. Chloride was determined in the extracts, and the first extract was also analyzed for major elements.

Acid-soluble Cl content of the IRM samples was determined by adding 4 mL of concentrated (10.3 M) HNO₃ to 1 g dry (378 K for 24 h) IRM in 96 mL DW, followed by 1 h of mixing using a magnetic stirrer (Extract 1). The same HNO₃ extraction procedure was used to determine the acid-soluble Cl content of a dried IRM that was previously washed (1:5) with DW (Extract 2). The water-soluble Cl concentration in the 1:5 supernatant of Extract 2 was also measured. The IRM from Extract 2 was dried, and washed again with DW (1:5). One gram of this washed IRM was dried and water-soluble and acid-soluble Cl were determined as before (Extract 3).

For the Cl sorption study, one batch of IRM was prepared by combining and mixing the four samples used previously for the water-soluble Cl analyses (from which Cl had been extracted by four 1:5 leachings). Twelve solutions of DW (10 mL) with different initial pH values (3.61 through 11.12) were prepared, using minute quantities of NH₄OH and HNO₃ to adjust the pH. All the solutions had an initial concentration (Cl₀) of 16.2 mg Cl L⁻¹. One gram IRM was added to each of the 12 vials and the slurries were agitated for 40 h, pH was measured, and the slurries were filtered and Cl was determined in the solutions. The amount of adsorbed Cl was determined as the difference between the initial and the final Cl concentrations.

Kinetics Studies

The SF technique was used in the kinetics studies. A detailed description of the apparatus and its operation is given in Eick

et al. (1990). Dried IRM (0.5 g) was loaded into the reaction chamber and 7.43 ± 0.10 mL of DW was added. This volume (V_{ch}) was maintained throughout the reaction period. A steady flow-rate (Q) of 0.85 ± 0.074 mL min^{-1} was maintained, using a Microperpex peristaltic pump (LKB 2132; Bromma, Sweden), and the effluent fractions were collected at 5-min intervals, using a fraction collector (LKB Ultra II 2070). The effluent was analyzed for EC, Cl, and SO_4 .

Column Studies

Preliminary leaching studies, using IRM columns 80 cm long and a 10-cm hydraulic head, had indicated that the flux (even under those saturated conditions) was quite slow. Therefore, column studies were designed to create saturated flow while establishing a larger hydraulic head. For this, three plexiglass tubes, 45 mm in diam. and 1 m long, were packed with IRM of known mass to give columns 10 cm long. The tubes were filled with free-flowing (air-dried <2 mm) IRM and, subsequently, compacted by tapping the bottom end of the filled tube on a hard surface. Average bulk density (ρ_b) of the packed material in the three columns was 0.91 ± 0.01 g cm^{-3} . Porosity (ϕ) was estimated by considering a particle density (ρ_s) of 2.89 g cm^{-3} (Table 1). A 1-mm mesh plastic screen attached to the bottom of the column held the IRM material. Glass beads, 3 mm in diam., were laid in three layers on top of the column. A reservoir discharge kept a constant 80 cm DW head on top of the IRM and maintained a stationary water level in the vertical columns. As soon as the solution percolated through the IRM, effluent samples were taken every 1 h, using a fraction collector (LKB Ultra II 2070). The pH, EC, Cl, SO_4 , and comprehensive cationic analyses were performed as before. Total carbonates, NO_3 , and PO_4 concentrations were minor (<1 mg L^{-1}).

The saturated hydraulic conductivity (K_s) was calculated using Darcy's law, $q = -K_s \cdot \Delta H/L$, where q (cm d^{-1}) is the leachate flux [$q = Q/A$, where Q is the flow-rate (cm³ d^{-1}) that was evaluated by measuring time and effluent volumes, and A is the cross-sectional area of the column (cm²)], and $\Delta H/L$ is the hydraulic gradient, in which $\Delta H = L + b$, where L is the length of the IRM (cm), and b is the hydraulic head above the IRM (cm)].

Table 1. Selected physical properties of the iron-rich material (IRM).

Surface area (BET)†	153	m ² g ⁻¹
Total pore area (MIP)‡	104	m ² g ⁻¹
Average pore diameter (MIP)	36.3	nm
Bulk density [ρ_b] (MIP)	0.78	g cm ⁻³
ρ_b Measured from mass and volume in the columns	0.91 ± 0.01	g cm ⁻³
Particle density [ρ_s] (MIP)	2.89	g cm ⁻³
Porosity [ϕ]¶	0.69 ± 0.006	
Hygroscopic water content (378 K)	0.067	kg kg ⁻¹
Particle-size distribution†	— μm —	— % —
	<2	5.0
	2-20	35.0
	20-200	50.0
	200-2000	10.0

† The particle-size distribution of the IRM was determined by a sedimentation procedure (Page et al., 1982). The texture was sandy loam.

‡ BET represents surface area as measured by the Brunauer, Emmett, and Teller equation (Brunauer et al., 1938) using N_2 .

§ MIP is mercury intrusion pressure.

¶ $\phi = 1 - \rho_b / \rho_s$.

Methods of Computation

The REG procedure of SAS was employed to analyze data by linear regression (SAS Inst., 1989). When a model was expressed using a system of ordinary differential equations (ODEs), its parameters were fitted using nonlinear least squares (NLLS). The AR program of BMDP (Dixon, 1990) was used for NLLS fitting because it allows the expressions of the model as a system of ODEs (the AR program solves systems of ODEs numerically).

Simple (r^2) and multiple (R^2) determination coefficients were used to assess the fit of linear models. For nonlinear models the Pseudo R^2 statistic was used. Pseudo R^2 is defined as: $1 - (\text{Residual SS} / \text{Corrected Total SS})$, where SS is the sum of squares. In order to express the precision of the parameters in relative terms, the coefficient of variation (CV) is used. The CV is defined as standard error/estimated value.

Modeling the Chloride Removal

Model predictions, which are described below, were compared with experimental data collected from the column and SF studies to verify the assumptions of the models. Estimation of model parameters by best fit to experimental data, and not by independent measurements, may lead to erroneous conclusions (Davidson et al., 1976; Rao et al., 1979; Selim et al., 1989). Thus, whenever possible, we estimated parameters for which either independent estimates or theoretical values were available. For example, in the SF study discussed later, the parameter ξ is known theoretically to be the reciprocal of the chamber volume (V_{ch}). In the same SF study, the parameter M_o (initial mass of Cl in chamber) could be determined directly from the data and compared with the value estimated by the model.

RESULTS AND DISCUSSION

Characterization of the Iron Rich Material

Some of the physical characteristics of the IRM samples are provided in Table 1, and selected chemical properties in Tables 2, 3, and 4. The XRD and DTA analyses showed that amorphous Fe-oxides were prevalent in the IRM samples (70-75% by weight). The XRD analyses also indicated the presence of Fe-sulfide (pyrrhotite-11C) (Salingar et al., 1994a), Fe-Cr-oxide (chromite aluminian), and Mn-oxide (wodginite) (Salingar et al., 1994b) in the IRM. Electrophoretic mobility measurements showed that the PZC of the IRM samples was pH 8.3. This value was comparable to PZC values for

Table 2. Selected chemical properties of the saturated paste (SP) and the first 1:5 iron-rich material (IRM) extraction.

	SP†	First 1:5
pH	6.55 ± 0.07	7.14 ± 0.04
Electrical conductivity	1.59 ± 0.05	0.65 ± 0.01
Ca	172 ± 12.7	50 ± 2.7
Mg	118 ± 5.7	29.4 ± 0.33
Na	2.86 ± 0.28	1.58 ± 0.90
K	2.76 ± 0.22	1.53 ± 0.05
Cl	506 ± 14	149 ± 0.82
SO_4	NA‡	7.7 ± 0.33

† ω was 1.05 ± 0.04 . Concentrations are in mg L^{-1} . EC is expressed in dS m^{-1} .

‡ NA means no data available.

Table 3. Selected chemical properties of the saturated paste (SP) and the IRM's solid phase.

	SP†	HF‡	XRF§
	mg L ⁻¹	g kg ⁻¹	g kg ⁻¹
Al	15.4 ± 0.4	11.9	19.1
Cr	9.5 ± 1.5	1.67	2.3
Cu	6.4 ± 0.5	0.06	NA#
Fe	401 ± 127	335	513
Mn	274 ± 17	12.3	19.4
S	NA	4.11	7.2
Si	NA	NA	18.2
Ti	NA	70.6	46.8
Zn	61 ± 35	0.3	NA
Total C¶	NA	13.4 ± 1.2	NA

† ω was 1.05 ± 0.04.

‡ Total digestion, modified from Bernas (1968): HF + HNO₃ + HClO₄, in a teflon bomb, at 378K, for 12 h.

§ X-ray fluorescence (semiquantitative analyses).

¶ Total C was determined separately with CHNS-O analyzer.

NA means no data available.

Fe-oxides and tropical soils that lie in the range of pH 7.5 to 9.3 (Schwertmann and Taylor, 1989).

Equilibrium Studies

The SP and the first 1:5 extraction analyses are provided in Table 2. The pH values in the SP were lower, and, due to a lesser water content, salinity and ion concentrations were higher than for the first 1:5 IRM extraction. Figure 1A shows the four 1:5 DW sequential Cl extractions. Figure 1B gives the acid-soluble (HNO₃ extracted) Cl concentrations in the IRM, before and after being first leached with DW. Hence, it was shown that Cl was leached easily by DW, and the amounts of retained Cl in the IRM were recovered by HNO₃.

In the study of Cl sorption at various pH values, extract number 4 (Fig. 1A) used for this experiment contained only 8 mg Cl L⁻¹ (0.004% of dry solid weight), and the initial Cl concentration of the added solution (Cl₀) was 16.2 mg L⁻¹. A further increase in solution Cl occurred, however, as indicated by negative sorption (Fig. 2A).

The pH values of the supernatants in the Cl sorption studies (Fig. 2A) deviated significantly from the initial pH values of the 12 solutions (Fig. 2B). Final pH values, that were initially below and above the PZC of the IRM (8.3), converged at pH 7.76 to 7.88 (except for the initial solution pH of 11.12, which decreased to pH 10) resulting in a positively charged surface. Except for pH 10, the deviation was linearly related to the initial pH ($r^2 = 0.95$). The reason for the pH values clustering around pH 7.84 (Fig. 2A) may be a result of the system's need to attain electroneutrality, as reflected in the linear deviation around the PZC (Fig. 2B). An adsorption ligand (SO₄) exchange mechanism discussed elsewhere (Salingar et al., 1994a) may account for the process. Because of the convergence in the final pH values, there was no trend between Cl sorption and pH (Fig. 2A), excluding

Table 4. Selected chemical properties of the iron-rich material (IRM).

	pH 8.3	
Point of zero charge	5.63 ± 1.40	cmol. kg ⁻¹
Cation-exchange capacity	0.335 ± 0.125	cmol. kg ⁻¹
Anion-exchange capacity		

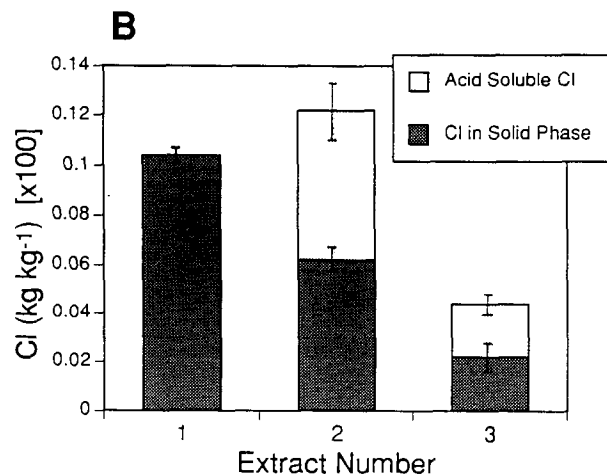
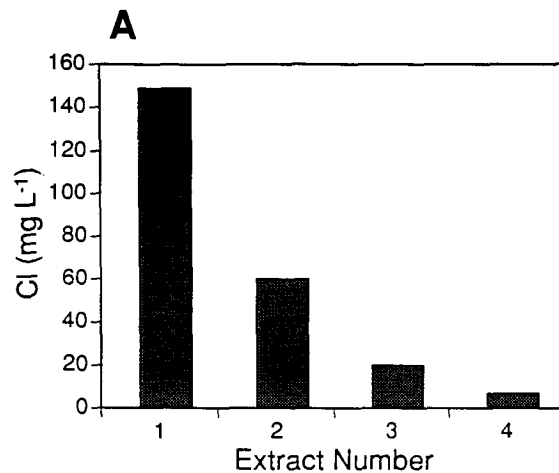


Fig. 1. Chloride concentrations in the (A) sequential 1:5 leachates, and (B) sequential HNO₃ extractions of the solid phase and the DW leachates.

much higher desorption at pH 10, where the surface was negatively charged.

Stirred-Flow Studies

Theoretical Approach

The simplest model for describing the SF reactor in this study is where all the Cl in the solid phase is in solution as soon as water is introduced. From this approach and the assumption of uniform mixing in the SF chamber (Seyfried et al., 1989), one can derive a mathematical model upon which to test the hypothesis against the experimental data. The model gives Cl removal as a function of volume of water flowing through the SF chamber. It was fitted to the data, and parameters were predicted and compared with known values.

The above is an instance of the familiar salt tank problem of differential equations. The mass is governed by (Kreyszig, 1972),

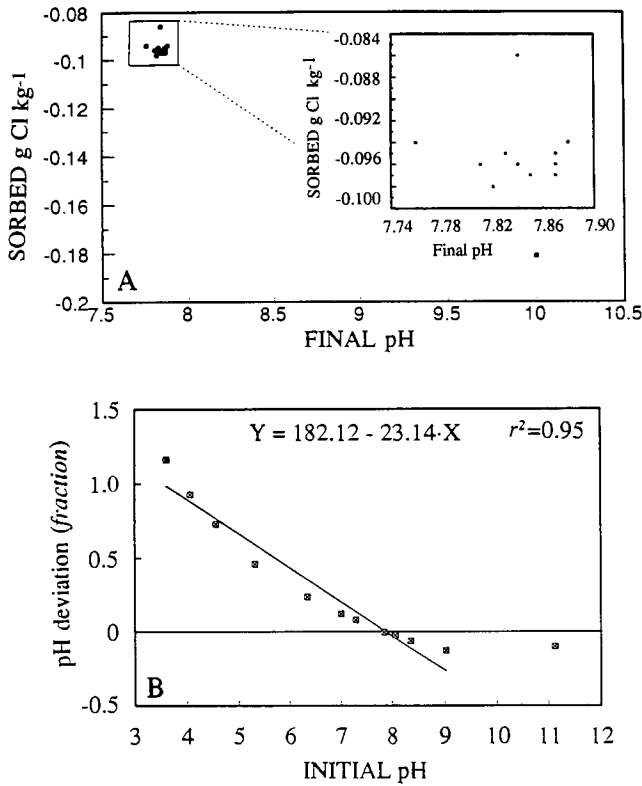


Fig. 2. Chloride sorption (A) vs. final pH values, and (B) fractional change from the initial pH values after shaking with IRM.

$$\frac{dM}{dV_{ac}} = -\zeta M, \quad M = M_0 \text{ for } V_{ac} = 0 \quad [1]$$

where M is mass of Cl in the chamber (mg) at a given volume, V_{ac} is accumulated volume pumped out of the chamber (mL), $\xi = 1/V_{ch}$ ($=135 \text{ L}^{-1}$) in which V_{ch} is volume of the chamber (7.43 mL), and M_0 is the initial mass of Cl in the chamber (mg). The explicit solution of Eq. [1] is,

$$M = M_0 \exp(-\xi V_{ac}) \text{ or } M/M_0 = \exp(-V_{ac}/V_{ch}) \quad [2]$$

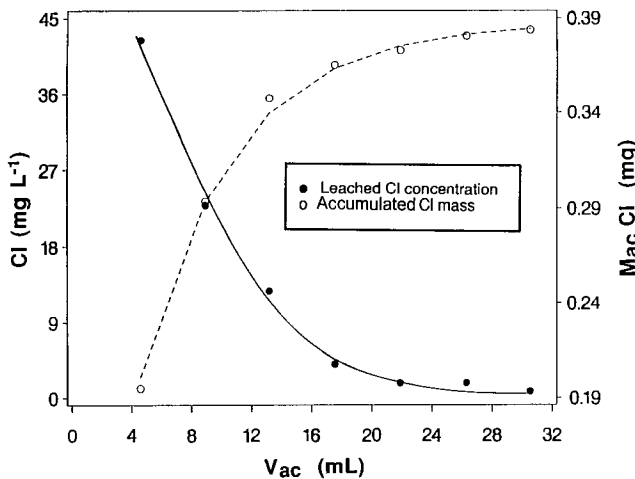


Fig. 3. Leached Cl concentration and accumulated Cl mass (M_{ac}) in the stirred-flow (SF) effluent, vs. distilled water volume that had flowed through the chamber (V_{ac}). Dashed line is M_{ac} fitted by the SF Cl model.

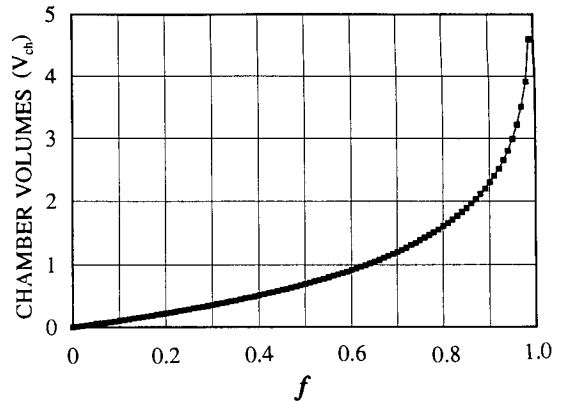


Fig. 4. Number of stirred-flow chamber volumes (V_{ch}) of distilled water required to remove a fraction f of the initial Cl (M_0) from the chamber.

Chloride concentrations measured in the effluent and the accumulated mass of Cl (M_{ac}) vs. V_{ac} are shown in Fig. 3.

When the fraction f of Cl is removed from the chamber, one finds,

$$M_0 (1 - f) = M_0 \exp(-\xi V_{ac}) \quad [3]$$

Solving Eq. [3] for V_{ac} one obtains,

$$V_{ac} = -(\ln(1 - f)) V_{ch} \quad [4]$$

A general solution is presented in Fig. 4. If, for example, $f = 0.99$, then $4.6 \times V_{ch}$ of water has to flow through the chamber.

Modeling

Of course, M cannot be observed directly but M_{ac} , the accumulated Cl removed from the chamber (mg), can be measured. Considering Eq. [1], and because one assumes that $dM/dV_{ac} = dM_{ac}/dV_{ac}$, and $M_0 = M + M_{ac}$ then,

$$\frac{dM_{ac}}{dV_{ac}} = \zeta (M_0 - M_{ac}) \quad M_{ac} = 0 \text{ when } V_{ac} = 0. \quad [5]$$

A numerical solution was favored in this study because an explicit solution demanded constant flow-rate (Q). In the SF system however, Q remained relatively constant throughout the study, but at times it deviated slightly ($Q = 0.85 \pm 0.074 \text{ mL min}^{-1}$). The evaluated parameters for the model along with the CV and the pseudo R^2 values for the fit of M_{ac} (Fig. 3) are given in Table 5. The model estimate for ξ (159 L^{-1}), was in good agreement with its theoretical value (135 L^{-1}). A good fit to the theoretical M_0 (the end M_{ac} datum in Fig. 3, 0.384 mg) was also predicted by the model (0.387 mg).

Table 5. Theoretical and estimated† values for ξ and M_0 in the stirred flow (SF) model (Eq. [5]).

Parameter	Theoretical	Estimated	CV	Pseudo R^2
$\xi \text{ (L}^{-1}\text{)}$	135	159	0.027	0.996
$M_0 \text{ (mg)}$	0.384	0.387	0.006	

† ξ is the reciprocal of the volume of the SF chamber; M_0 is the initial mass of Cl in the chamber.

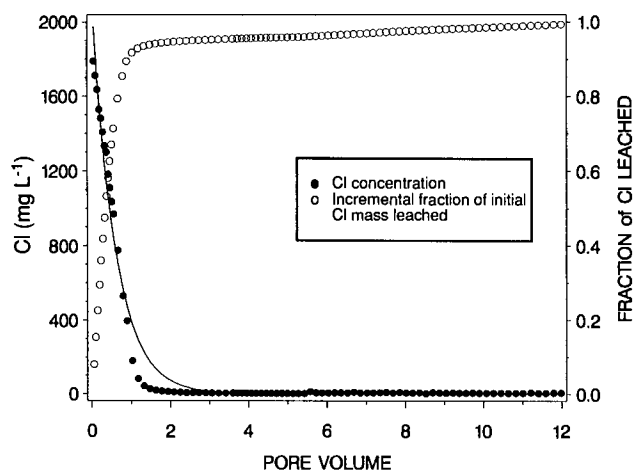


Fig. 5. Chloride leaching vs. pore volume in the column. Solid line represents the fitted model (Eq. [6]).

The model showed good agreement with the experimental data, and made reasonable predictions of known parameters. Thus, the SF study showed that Cl removal from the IRM was a function only of the total volume that flowed through the chamber. As long as the assumption of mixing is valid, flow-rate (or time) is not a necessary parameter.

Column Studies

Chloride Removal

Column studies were performed to ascertain ligand and metal removal behavior from IRM. The columns simulated field leaching conditions better than the batch experiments, which used large solution-to-IRM ratios, and the SF technique which employed mechanical mixing. Additionally, the column studies provide information about the hydraulic properties of the porous medium.

A model of Cl concentration in the column effluent vs. pore volume (ρ) was fitted using NLLS (Fig. 5),

$$Cl = M_i \exp(-k_1 \rho) \quad [6]$$

where M_i is the Cl concentration (mg L^{-1}) at $\rho = 0$, and k_1 is a constant (ρ^{-1}). Estimated values and CV for M_i and k_1 , along with pseudo R^2 for the fit are given in Table 6. The concentration of Cl in the first effluent sample collected from Column A was 1808 mg L^{-1} , and from Columns B and C 1524 mg L^{-1} . Considering the dilution factor (measurements were taken only after ≈ 20 mL of effluent was collected), and extrapolating the Cl line in Fig. 5 to $\rho = 0$, the model estimation for M_i (2142 mg L^{-1}) was plausible. The incremental fraction of Cl mass removal vs. ρ is also depicted in Fig. 5.

Table 6. Estimated parameters† for the model describing Cl removal from the iron-rich material (IRM) in the column vs. pore volume (Eq. [6]).

Parameter	Estimated	CV	Pseudo R^2
M_i (mg L^{-1})	2142	0.020	0.98
k_1 (ρ^{-1})	1.69	0.035	

† k_1 is a constant. M_i is the theoretical initial Cl concentration in the column.

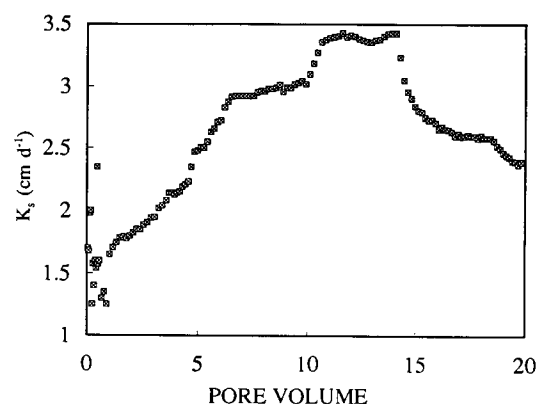


Fig. 6. Saturated hydraulic conductivity (K_s) vs. pore volume in the column.

Most (0.92) of the Cl was removed with the first ρ . It is therefore evident that Cl removal from the column is a function only of leaching, and no chemical kinetics are involved in the process.

The Influence of Chloride on the Hydraulic Conductivity

The calculated saturated hydraulic conductivity (K_s) vs. ρ is shown in Fig. 6. The air-dried IRM used in the columns was in a granular form. The large porosity of the packed material ($0.69 \text{ cm}^3 \text{ cm}^{-3}$, Table 1), despite its sandy loam texture, was also an indication that the IRM material was aggregated. Despite these physical attributes, the IRM had a poor water conductivity, hence the first drops of effluent were observed at the bottom of the 10-cm long columns only after 2 to 2.25 h from the time the large water heads were established. This, and the fact that K_s values during the initial wetting stages (up to 1ρ) were noisy, but remained low throughout the leaching process (K_s maximal value, achieved after 13.7ρ was $\approx 3.4 \text{ cm d}^{-1}$), suggested that the IRM was hydrophobic. The water conductivity increased with ρ , and for $1 < \rho < 11.6$, K_s is linearly correlated to ρ ($r^2 = 0.953$),

$$K_s = 1.561 + 0.165 \rho \quad [7]$$

Starting from 14.1ρ , K_s declined precipitously. A feasible explanation was that the column was partly clogged due to dispersion as a result of salt leaching and a lowering in the electrolyte concentration. Most of the Cl was removed from the column within the first ρ , therefore it may be postulated that the dispersion effect started shortly after the leaching began. To test this hypothesis, the K_s data for $14.1 < \rho < 19.8$ were shifted 14.1 pore volumes backwards and plotted, together with the first 39 Cl concentration data, vs. the first 4.5 pore volumes (Fig. 7). Both parameters showed a similar pattern. For $0 < \rho < 1.33$, during which most of the Cl was leached out, the shifted K_s was dependent on the Cl concentration. The fitted polynomial model (18 data points) had an R^2 value of 0.997.

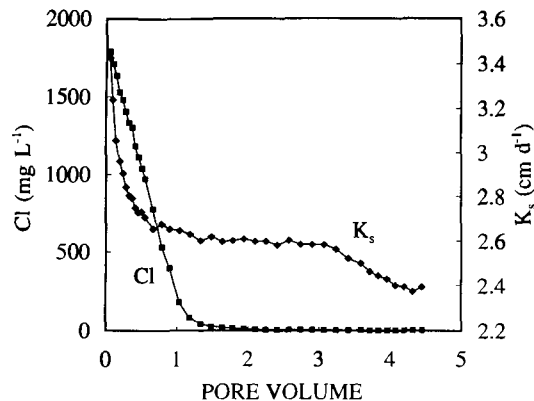


Fig. 7. Chloride and hydraulic conductivity (K_s) vs. pore volume (p) in the column. The K_s data are for $14.1 < p < 19.8$, and they were shifted 14.1 pore volumes backwards.

CONCLUSIONS

Although in most soils Cl moves with less retardation or loss than other major ions, Cl removal processes from the IRM at the industrial production facility were problematic and costly. Data from batch, SF, and column studies showed that even though the PZC of the IRM was 8.3, Cl removal was a function only of the total volume of the leaching water, and no chemical kinetics were involved. Chloride removal lowered the electrolyte concentration in the column which induced dispersion, and resulted in a diminution in K_s values.

We are not aware of publications on salt removal from high-Fe wastes. This study provides a procedure for examining the environmental soil chemistry of high salt-containing waste products with potential agricultural uses. The results can assist one in making rational decisions about the proper land disposal of waste products.

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