

# IMPLICATIONS OF CATION EXCHANGE ON LONG-TERM MIGRATION OF NATURALLY OCCURRING SOLUTES IN UNOXIDISED CLAY TILL



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## INTRODUCTION

The long term migration of solutes in thick clay till, is the focus of a multidisciplinary research program at several sites in southern Saskatchewan, Canada.

Understanding geochemical controls on solute transport is important because naturally occurring salts are concentrated in the oxidized surficial zone. However, thick, unoxidized tills of low permeability are thought to provide a barrier overlying regional freshwater aquifers.

This research will be of direct application to the agricultural and mining industry. For example, effective containment of hog effluent and potash brines requires knowledge of geochemical reactions and potential impacts on the hydraulic conductivity of deep clay barriers.

The goal of this research is to characterize and quantify the role of exchange reactions on the transport of solutes. Minimally disturbed core samples and porewater samples were obtained from a field site for laboratory analysis and centrifuge modeling.

## STUDY APPROACH

- develop and assess the viability of conducting transport experiments in a UFA centrifuge
- analyze and interpret effluent breakthrough for major elements and a deuterium isotope tracer
- analyze retardation factor  $R_d$
- model transport parameters including partition coefficient  $K_d$  using numerical computer codes

## UNIQUE CHALLENGES

The nature of the test material means that conventional column testing for solute transport is not practical:

- very small sample volumes and long testing times due to very low  $K_v$
- saline porewater corrodes reactive materials

It is difficult to distinguish ion exchange reactions from precipitation and dissolution reactions of:

- relatively low Ca, Mg,  $\text{HCO}_3$  concentrations
- high carbonate content of till

## APPLICATIONS OF CENTRIFUGE MODELING

Centrifuge modeling is a useful technique for a range of geo-environmental problems including porewater extraction, and leachate compatibility testing for clay liners.

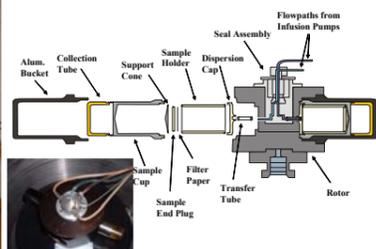
Flow is driven through core by centrifugal force, rather than by hydraulic gradient, which becomes insignificant at >400 RPM. Darcy's Law may be expressed as:

$$K = q / \rho \omega^2 r$$

Where K is hydraulic conductivity, q is flux,  $\rho$  is density,  $\omega$  is angular velocity, r is centripetal radius.



Centrifuge Rotor and Seal Assembly



Physical modeling by application of centrifugal force is advantageous because in situ stress of the sample may be replicated. Published scaling relationships for various physical parameters, enable modeled values to be converted to realistic prototype values.

## EQUIPMENT

Specialized equipment used in this study includes:

- UFA Beckman J6-MI centrifuge and HySed 40J rotor ( $r = 87 \text{ mm}$ ,  $\text{RPM}_{\text{max}} = 3000$ ,  $N_{\text{max}} \sim 880$ )
- ion-specific microelectrodes for real time analysis of  $\sim 0.2 \text{ ml}$  sample volumes, incl. pH, EC, Eh, Cl, Na, Ca, K
- autotitrator for volume corrected alkalinity titrations for  $\sim 1 \text{ ml}$  samples using inflection point method



## FIELD SITE

The hydrogeology and porewater chemistry of the King site have been thoroughly characterized, providing a unique opportunity to verify centrifuge modeling of solute transport.

A regionally extensive basal till, the Battleford Formation, occurs at this site to a depth of 45 m. The unit is clay-rich (35 wt. %), contains dolomite and carbonate (10 wt. %) and has a cation exchange capacity (CEC) of 26-56 meq/100g, with >50% of exchange sites occupied by Ca. The very low hydraulic conductivity, K of the till ( $10^{-12}$  to  $10^{-11} \text{ m/s}$ ) limits downwards porewater flux to 0.5-0.8 m per 10,000 years.

Naturally occurring solutes, principally comprised of Na and  $\text{SO}_4$ , are concentrated at  $\sim 70,000 \text{ mg/L}$  TDS in the oxidized zone (0 to  $\sim 3 \text{ m}$  depth), and gradually decrease to background concentrations of 3,200 mg/L at  $>15 \text{ m}$  depth.

## EXPERIMENTAL SETUP

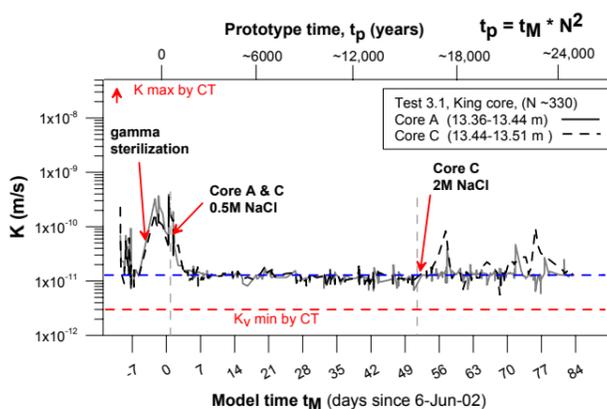
Duplicate core subsamples were obtained from  $\sim 13 \text{ m}$  depth. The cores were described, dissected, double waxed and stored at  $4^\circ\text{C}$  in a humidity controlled room until testing. The cores were sterilized by gamma radiation, saturated under vacuum and installed in a UFA modeling centrifuge. Influent solution (chemistry equivalent to *in situ* porewater) flowed from a micro-burette reservoir through the cores to effluent collection caps within the centrifuge. Centrifuge speed was gradually increased so that stresses at the base of the core were equivalent to *in situ* preconsolidation pressures ( $\sim 500 \text{ kPa}$ ). After establishing steady flow and initial hydraulic conductivity ( $K_v$ ), determined from flow rate, the reservoir water was replaced ( $t=0$ ) with dilute NaCl brine (0.5 M). At  $t = 48$  days, the influent for Core C was replaced with 2.0 M brine. The modeling ended at  $t = 90$  days.

## RESULTS

### Hydraulic conductivity

Flow driven by accelerated gravity ( $\sim 330 \text{ xg}$ ) meant that a day of centrifuge modeling was equivalent to about 300 years of solute transport at prototype scale.

Initial K values were very low at  $1.2 \times 10^{-11} \text{ m/s}$ . These results are consistent with independent K values for similar depth at this site, which were determined by falling head permeameter, consolidation testing and triaxial testing.



### Verification of hydraulic conductivity testing

\* Centrifuge test  
# Shaw & Hendry 1998 (13-34 m depth)

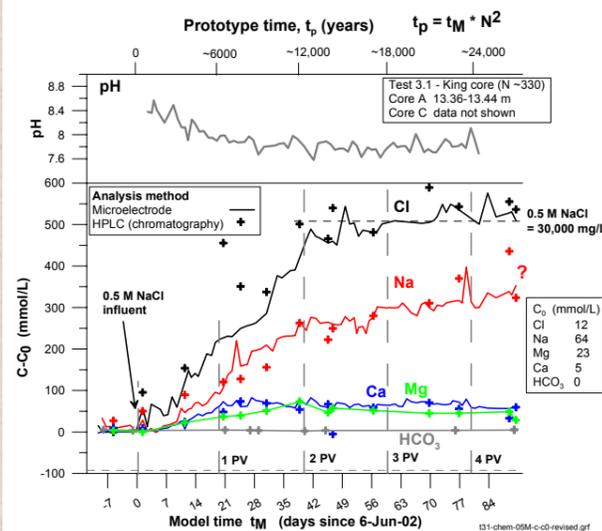
### Test method

Test method	K ( $\times 10^{-11} \text{ m/s}$ )
Centrifuge test (CT)*	1.0 to 1.4
Consolidation test #	2.0 to 2.6
Falling-head test*	1.6
Triaxial constant-head*	2.9

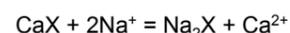
Permeation of dilute brine through the core did not cause a significant increase of K. This confirms that confining stress at depth prevents physico-chemically induced microstructural changes that otherwise lead to increased K.

## Geochemical processes

Breakthrough ( $C/C_0 = 0.5$ ) of the conservative solute Cl occurred at  $t = 20$  days. Minor retardation of Na was observed for 0.5 M NaCl ( $R_d \sim 2.5$ ) and slight Na retardation for 2.0 M NaCl ( $R_d \sim 1.5$ ). Both breakthrough curves were characterized by a lengthy tail below  $C_0$ , although no early arrival was evident.



The deficient of Na appeared to be balanced by an increase of Ca and Mg concentrations in porewater. This suggests that ion exchange of Na onto clay is the dominate geochemical process controlling transport.

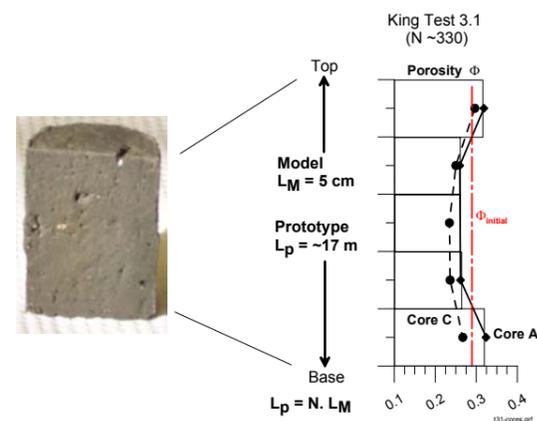


A small quantity of Ca also appeared to be contributed by carbonate dissolution during the early stages of breakthrough.



## Core analysis

Core analysis is in progress to further characterize vertical variability of density, gravimetric moisture, porosity, CEC, porewater chemistry and wt. % carbonate. Selected parameters are analyzed both before and after centrifuge modeling. At the completion of centrifuge modeling, the core is sectioned vertically and horizontally.



## SUMMARY AND CONTINUING WORK

Preliminary results indicated that hydraulic conductivity of till at depth does not change significantly when permeated by dilute brine. Minor retardation of Na was observed during centrifuge modeling. Associated increase of Ca in porewater indicated that geochemical reactions were dominated by ion-exchange. Carbonate dissolution reactions prior to breakthrough appeared to be of secondary importance.

Continuing work includes completion of core analysis, additional centrifuge modeling and solute transport modeling using numerical computer codes. The similitude of reactions between the model and prototype (ie. the King site) at different scales are yet to be determined.

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