

takes place at a slow rate.

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#### MOVEMENT OF RADIUM THROUGH SOIL

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The movement of Ra<sup>2+</sup> below a tailings dam was simulated by laboratory soil column experiments, employing Ba<sup>2+</sup> and Ca<sup>2+</sup>, due to the limitation of the amount of Ra<sup>226</sup> that can be handled in the laboratory, and their chemical similarities as alkaline earth cations. The results of the experiments show that these cations are adsorbed by soil by an ion-exchange process, which consists of an instantaneous portion and a time dependent portion.

#### INTRODUCTION

Disposal of mining and processing wastewaters by ponding in lagoons has been practised for a long time. For large volumes containing a high percentage of solids, ponding may represent the only economical alternative for disposing a wastewater. Ponding relies on water loss through evaporation and seepage. Once a pond is filled with solids, it is then covered with a layer of soil. This method of wastewater disposal is environmentally acceptable provided that no toxic solute leaches to the groundwater and transported by groundwater flow to surface water or groundwater aquifer.

In the milling of uranium ores, tailings are usually disposed of by ponding. The tailings are composed of finely ground parent material depleted of most of its original uranium content, together with process water and used chemical reagents. Its solids to liquid ratio varies from 1:1.5 to 1:2.5. Because of the small concentration of uranium in the ore (less than 1%), one tonne of concentrator waste is produced per tonne of ore processed. Up to 85% of the radioactivity originally contained in the ore may be present in the tailings due to the presence of uranium daughter nuclides, ranging from Thorium to Polonium (1). Some members of the U<sup>238</sup> decay scheme are noted for their persistence and chemical and radio-toxicity. Ra<sup>226</sup> is considered the most hazardous: it has a half-life of 1620 years and is extremely radiotoxic. It decays through a series of short lived, high energy alpha emitting daughters constituting an extreme health hazard if ingested. Water quality standards throughout the world limit Ra<sup>226</sup> concentration to less than 10 pCi/l for potable water.

The ability of soils to retain certain constituents from percolating water

has long been known, and much attention has been given in recent years to determine the value of soils as pollution buffers at municipal and industrial waste disposal sites. The removal of cations by soils have been established to be due to clay minerals (montmorillonite, kaolinite), mineral oxides and hydroxides (particularly of iron, aluminium and manganese), and organic matter present in the soils (2 to 11). Cation exchange, complexation by organic matter, precipitation by reaction, hydrolysis or oxidation-reduction, and specific adsorption have been suggested as mechanisms by which cations may be removed.

This paper describes the results of soil column experiments for removing calcium and barium using soil from a tailings dam of a pilot uranium mill at Kalgoorlie, Western Australia.

#### SOLUTE TRANSPORT EQUATION

The one dimensional movement of a solute through a soil column can be described by (12):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - p \frac{\partial s}{\partial t} \quad (1)$$

where  $c$  = concentration of solute in solution

$s$  = concentration of solute in soil

$t$  = time

$x$  = distance

$D$  = dispersion coefficient

$v$  = superficial solution velocity

$p$  = conversion factor to make units for  $s$  and  $c$  uniform.

The relationship between  $c$  and  $s$  under equilibrium condition is usually described by Freundlich or Langmuir isotherm. If the Freundlich relationship is applicable

$$s^* = m c^n \quad (2)$$

$$\text{and } \frac{\partial s}{\partial t} = m n c^{n-1} \frac{\partial c}{\partial t} \quad (3)$$

Where  $m$  and  $n$  are constants, and the asterisk indicates equilibrium concentration. Under flow condition such as in a soil column it has been observed that only part of the solute in the flowing solution is adsorbed instantaneously (12). Here

$$\frac{\partial s}{\partial t} = \frac{\partial s_1}{\partial t} + \frac{\partial s_2}{\partial t} \quad (4)$$

where  $s_2$  represents the solute that is adsorbed instantaneously

$$\frac{\partial s_2}{\partial t} = m^* n c^{n-1} \frac{\partial c}{\partial t} \quad (m^* < m) \quad (5)$$

while  $s_2$  represents the time dependent adsorption

$$\frac{\partial s_1}{\partial t} = k (s^* - s) \quad (6)$$

$k$  = adsorption rate constant

Solution to equations 1 and 4 with the appropriate initial and boundary conditions gives the concentration of the solute in solution as a function of position and time in the column.

#### EXPERIMENTAL

In assessing the potential for  $Ra^{2+}$  removal by soil beneath the tailings dam, three aspects needed to be given close attention: the total cation removal capacity of the soil, the cation removal mechanism, and the potential for  $Ra^{2+}$  removal from the chemical environment of the tailings liquor.

The cation removal capacity and the removal mechanism were determined by adsorption experiments using soil from the tailings basin and  $BaCl_2$  solution.  $BaCl_2$  solution was used for a number of reasons:

(i) The amount of  $Ra^{226}$  which could be purchased and used in adsorption experiments was limited by licence restrictions and cost, and thus restricted the type of experiments which could be undertaken.

(ii) Analysis of low level Radium samples requires large samples and the procedure is time consuming.

(iii) Ba and Ra appear in the same column of the periodic table, and are consecutive alkali earth elements. In view of the behavioural trends demonstrated by the other alkali earths, it would be expected that the adsorption behaviour of  $Ba^{2+}$  would be very similar to  $Ra^{2+}$  and thus could successfully be used as a substitute in adsorption experiments.

(iv) The use of pure solutions in initial experiments creates a simpler study system, in which behavioural trends are more easily recognized and interpreted.

#### Soil

Soil for the experiments was taken from the floor of the tailings dam of the Western Mining Corporation uranium pilot plant in Kalgoorlie. Analyses of the soil included determinations of soil type, clay mineral type and cation exchange capacity. The hydraulic conductivity of the soil was found to be very low (0.17 m/day), and to enable soil column experiments to be completed in a reasonable time, the soil was blended with Bassendean sand, a highly permeable leached sand found in Perth, W.A., in the proportion of 25% soil, 75% Bassendean

sand.

#### Adsorption isotherm

An equilibrium adsorption isotherm for  $Ba^{2+}$  on the soil blend was determined by measuring the decrease in dissolved  $Ba^{2+}$  when 50 ml solutions of varying initial concentrations (80 to 3000 ppm  $Ba^{2+}$ ) were contacted with 20 g of soil previously saturated with  $Ca^{2+}$  in a shaking water bath set at 15°C.

#### Approach to equilibrium

To determine the rate of approach to equilibrium the batch soil solution contact tests were repeated at several points and determining the  $Ba^{2+}$  concentration in solution as a function of time of contact.

#### Soil column experiments

A 60 cm long 2 cm diameter Perspex column fitted with a sintered glass disc was used. One kg of the soil blend was packed to a bulk density of 1.61 g/cm<sup>3</sup> giving a hydraulic conductivity of 1.34 m/day. The column was hydraulically saturated with 0.010 N  $CaCl_2$  solution. The soil was therefore also saturated with  $Ca^{2+}$ . The solution in the column was then displaced with 0.0077 N  $BaCl_2$  solution until complete breakthrough took place. The  $Ba^{2+}$  in the column was then re-displaced by  $CaCl_2$  solution until breakthrough was again complete. Flow rate was controlled by throttling the outlet flow. Superficial velocities of 5.5 cm/hr and 1.8 cm/hr were used. The pH and conductivity of the liquid leaving the column were continuously monitored, and samples were collected using a fraction collector for analysis of  $Ba^{2+}$  and  $Ca^{2+}$ . Analysis for Ba was by adding 1.36  $\mu Ci$  of  $Ba^{133}$  as  $BaCl_2$  per  $\mu l$  of  $BaCl_2$  solution and determining it using a Searle 1197 gamma scintillation counter.  $Ca^{2+}$  was analysed using an EEL flame photometer.

#### Hydrodynamic Dispersion

Hydrodynamic dispersion coefficient, D, was determined using the column set up described above by displacing 0.01 N  $CaCl_2$  solution in the column by a 0.01 N  $Ca(NO_3)_2$  solution at the two flow rates used. Since both chloride and nitrate are not adsorbed by the soil, measurement of the breakthrough of nitrate provides a means for determining the dispersion coefficient. Nitrate concentration was determined using a Technicon Autoanalyser.

### RESULTS

#### Soil characteristics

The soil from Kalgoorlie had the following characteristics: pH = 6.2, organic matter = 6.3%, clay = 51.2%, silt = 9.4%, sand = 39.4%. On the basis of texture it was classified as sandy clay. X-ray diffraction scan indicated that the clay size particles were predominantly kaolinite. Its total cation

exchange capacity was 17.7 meq/100g. The Bassendean sand used consisted of fine to medium sand with very little organic matter with a total cation exchange capacity of 0.5 meq/100g.

#### Adsorption isotherm

The isotherm covering equilibrium  $Ba^{2+}$  solution concentration from 0.3 mg/l to 1832 mg/l can be represented by a Freundlich relationship, Equation 2, with  $m = 550$ , and  $n = 0.22$ , within  $\pm 3\%$ .

#### Approach to equilibrium

Table 1 shows the results of batch tests to determine the rate of approach to equilibrium with four initial solution concentrations.

TABLE 1: Change in  $Ba^{2+}$  concentration in solution equilibrated with soil.

Time (hours)	s mg/kg	c mg/l	s mg/kg	c mg/l	s mg/kg	c mg/l	s mg/kg	c mg/l
0	0	3000	0	1875	0	1406	0	655
0.125	1830	2268	1567	1248	1462	821	1046	216
0.250	1842	2263	1575	1245	1472	817	1105	213
0.500	1850	2260	1587	1240	1482	813	1110	211
1.00	1862	2255	1600	1235	1496	807	1117	208
2.00	1905	2238	1660	1211	1513	801	1142	198
24.00	2920	1832	2500	875	2185	532	1435	81

A substantial portion of  $Ba^{2+}$  was adsorbed by the soil in less than 7½ minutes, with the rest adsorbed at a fairly slow rate. The instantaneous portion can be correlated by Equation 5, with  $m^* = 334$  and  $n = 0.22$ . From the initial rate of adsorption in the slow rate adsorption regime,  $k$  in Equation 6 is found to be  $0.045 \text{ hr}^{-1}$  ( $\pm 0.005$ ).

#### Column breakthrough curves

Figure 1 shows the breakthrough curve for  $Ba^{2+}$  when  $BaCl_2$  solution displaced  $CaCl_2$  solution at a superficial velocity of 1.8 cm/hr. Shown also are the pH, conductivity and  $Ca^{2+}$  in the solution leaving the column as a function of the number of pore volumes of solution passing through the columns. One pore volume is the volume of solution contained within the column.

#### Dispersion coefficient

When the  $Ca(NO_3)_2$  solution displaced  $CaCl_2$  solution in the column, the breakpoint of  $NO_3^-$  occurred at about 0.65 pore volumes and breakthrough was complete at about 1.30 pore volumes. Employing Brenner's method (13) D was found to be  $4.7 \text{ cm}^2/\text{hr}$  and  $1.0 \text{ cm}^2/\text{hr}$  at 5.5 cm/hr and 1.8 cm/hr liquid

superficial velocities respectively.

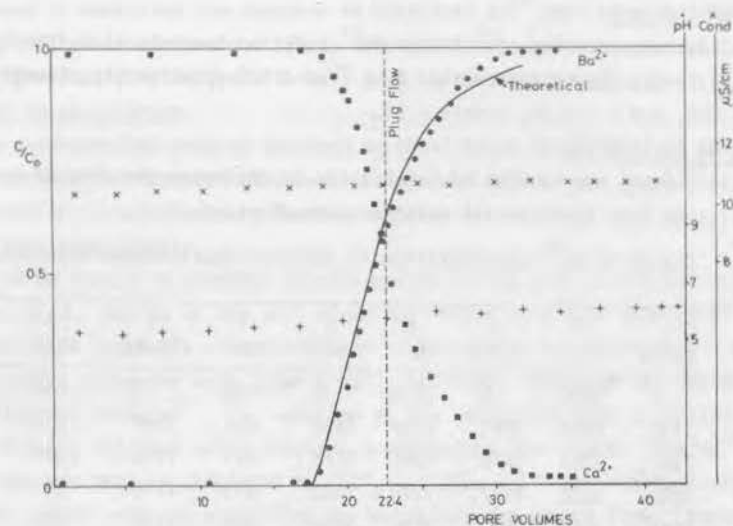


Figure 1. Breakthrough Curve For Displacement of  $\text{CaCl}_2$  By  $\text{BaCl}_2$

## DISCUSSION

### Adsorption capacity of soil

The results of the batch tests and column experiments show that the sandy clay soil studied has a substantial ability to remove  $\text{Ba}^{2+}$  from solution. The CEC of 17.7 meq/100g is equivalent to 12,125 mg/kg of  $\text{Ba}^{2+}$  removal ability. When other cations are present this figure may be reduced depending on the total cations concentration and the relative adsorption preference of the soil for cations.

### Adsorption mechanism

The column breakthrough curves show that adsorption is reversible and that exchange between  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  is stoichiometric. This rules out precipitation and specific adsorption, which is characterised by a lack of stoichiometry of exchange, a reduction in solution conductivity and a tendency toward the acid range in column effluent (5), and points to ion-exchange, which is in agreement with studies reported in the literature (3, 4).

The results of the batch contact tests show that ion exchange takes place in two stages: an instantaneous portion for 61 percent of the cations ( $m^*/m = 334/550$ ) and a rate dependent portion with a first order rate of  $0.045 \text{ hr}^{-1}$ . The column breakthrough curves also show that this is the case (see Figure 1). A plug flow model with instantaneous ion-exchange gives a vertical line for the breakthrough curve at a pore volume of 22.4. A model incorporating hydrodynamic dispersion gives a curve that starts at pore volume 22 and reaches  $c/c_0 = 1.0$  at pore volume 23. The effect of hydrodynamic dispersion on the shape of the breakthrough curve is therefore minimal. Solution of Equations 1 and 4 with appropriate initial and boundary conditions and  $m^* = 74$  and  $k = 0.90 \text{ hr}^{-1}$  gives a very good fit to the experimental curve. The portion that is adsorbed instantaneously ( $m^*$ ) in the column is much smaller than in the batch test, while the rate of exchange ( $k$ ) in the column is much larger. This can be explained by the difference in the ways the solution contacts the soil in the two cases, and in the ratios between soil and solution, being low in the batch test and high in the column.

### Application to Radium adsorption

On the basis of the preference of adsorbent materials for alkali earth cations,  $\text{Ra}^{2+}$  would be expected to be adsorbed by the soil in the same way as  $\text{Ba}^{2+}$ , and if they are both present in solution  $\text{Ra}^{2+}$  would be preferentially adsorbed. Preliminary batch contact tests using  $\text{RaCl}_2$  solution of initial concentrations ranging from  $5 \times 10^2$  to  $1 \times 10^6$  pCi/l of  $\text{Ra}^{2+}$  gave an isotherm of the form  $s = 5c^{0.7}$ . In diluted simulated tailings solutions containing other cations the adsorption was depressed by a factor of approximately 10.

A column experiment again indicated that ion-exchange was the mechanism of adsorption as adsorbed  $\text{Ra}^{2+}$  could be displaced by  $\text{Ca}^{2+}$ . Modelling of the breakthrough curve was not possible since large samples were required for analysis of  $\text{Ra}^{226}$ , and the experimental breakthrough curve was in the form of a histogram with large steps. It is thought, however, that the model developed for  $\text{Ba}^{2+}$  adsorption is applicable.

An implication of the ion-exchange mechanism to the management of the tailings dam is the need to ensure that re-leaching of  $\text{Ra}^{2+}$  does not occur once the dam is completed by preventing rain or flood water from percolating down.

## CONCLUSIONS

The sandy clay studied has a significant capacity for adsorbing alkali earth cations including  $\text{Ra}^{226}$ , and the mechanism for adsorption is ion-exchange. Part of the ion exchange takes place instantaneously, while the remaining part