

**PRELIMINARY STUDIES OF THE EFFECTS OF OXIDATIVE
AND REDUCTIVE LEACHES ON THE ION EXCHANGE
BEHAVIOUR OF MARINE SEDIMENTS**

by
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**OCEAN DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTE
A RESEARCH REPORT PREPARED FOR THE DEPARTMENT
OF THE ENVIRONMENT**

**NATURAL ENVIRONMENT
INSTITUTE OF OCEANOGRAPHIC SCIENCES
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Abstract:

Cation exchange is a surface property of all sediment particles. Measurement of cation exchange capacity (C.E.C.) is a useful indicator of the likely ability of a sediment to retain radionuclides. C.E.C of a particle is derived from the particular mineral grain at the core and coatings of iron and manganese oxides and organic matter deposited on the grain during its progress from continent to ocean floor. Reaction of the surface of the grain with surrounding solution gives rise to a specific chemical composition at its surface which is determined by the composition of both surface and solution. The simplest approach to determining the contribution of oxide and organic coatings to the C.E.C. of the sediment is to remove them chemically. The aim of this work was to evaluate methods for doing this, which would then be used in further studies applied to deep sea sediment.

Keywords: 299, 94, 112, 115, 123.

This work has been commissioned by the Department of the Environment as part of its radioactive waste management research programme. The results will be used in the formulation of Government policy, but at this stage they do not necessarily represent Government policy.

ABSTRACT

In order to achieve an understanding of the extent to which the adsorption/exchange properties of sediment are determined by the organic matter, and, manganese and iron oxides which coat the surfaces of individual sediment mineral grains, the simplest approach is to compare the properties of the sediment before and after these coatings have been removed. A large number of methods have been proposed for the removal of organic matter and oxides. None of these methods are completely effective or selective. Two of the more commonly used and practical methods for removing organic matter and two for removing oxides have been evaluated specifically in the light of their effect on the cation exchange capacity of sediment material. As a result of these studies sodium hypochlorite (to remove organic matter) and buffered oxalic acid (to remove iron and manganese oxides) will be used in further studies applied to deep sea sediments.

INTRODUCTION

The overall aim of this work is to understand how the solid phases present in marine sediment control ion exchange behaviour. From this knowledge predict the ion exchange behaviour of sediment assemblages with respect to the mobility of radionuclide waste components through them.

Frequently when abyssal sediments are put forward as a suitable repository for radioactive waste material their high ion exchange capacity is given as a major supporting argument. Adsorption of nuclides onto exchange sites on sediment surfaces will slow their effective rate of migration from the buried canister to the sediment surface, increasing the break through time. However it should be pointed out that it is an assumption that marine sediments have a high cation exchange capacity. I have so far been able to find only four published papers in which the cation exchange capacities of recent marine sediments have been reported and none of these measurements was for pelagic material. (McALLISTER 1964; RASHID 1969; ROSENFELD 1979 and BOATMAN et. al., 1982). It is though probably a good assumption based on our knowledge from the soil science literature that the components of pelagic sediment, fine grained clays and shells, and organic and amorphous oxide coatings all tend to produce high exchange capacity material.

What we would like to know is:-

- (1) What is the ion exchange capacity of marine sediment.
- (2) How does the composition of a particular sedimentary horizon determine the

exchange characteristics of that horizon.

(3) What changes in exchange capacity result from natural diagenetic processes, or will be precipitated by canister emplacement in the sediment.

This work will require a stringent re-evaluation of the methods used to measure ion exchange, to see how well methods developed for the treatment of soil samples can be applied to marine sediments. A critical factor in this will be an assessment of the way in which sample handling effects the measured exchange capacity. Initially this work will be concerned with the measurement of total cation and anion exchange capacity, for a wide range of sediment types. We will seek to identify the physical and chemical properties which determine exchange capacity and the functional groups on the sediment surface which are the exchange sites. Later studies will be of the specific sorption behaviour of elements analogous to active waste components. Because of the complexity of the system we have to be very aware of the systematic errors which may obfuscate the true nature of the processes being studied. For example as pointed out by SAYLES et al., (1977), RUSSEL (1970) reported erroneous results for the ratios of the major ions adsorbed on river sediment on entering the sea. Russel rinsed excess sea water from his clays with distilled water before displacing the major ions. The decrease in ionic strength seen by the clay during rinsing increases the preference of the clay surface for divalent ions. This produced a considerable discrepancy between his results and those of SAYLES et al., where rinsing was avoided. Interpretation of results must also involve an awareness of the complexity of the surfaces that are being dealt with and the limitation that this complexity imposes on the degree to which results can be interpreted quantitatively. For example RASHID (1969) measured the cation exchange capacity of coastal sediment samples before and after treatment with hydrogen peroxide to remove the organic component in the sediment, and the exchange capacity of humic acid extracted from the sediment. He then estimated the organic matter contribution to the total exchange capacity of the sediment on the basis of exchange capacity of the humic acid and the organic carbon content of the sediment. This is invalid because it is not known how uniformly the organic matter is dispersed in the sediment. It is not therefore possible to know the effective surface area per unit weight of humic acid. Also the extracted humic acid is only a portion of the organic matter in the sediment; and that may well have been modified by the extraction process. Similarly any other process which is used to modify the surface of the sediment by removing a sediment component cannot be

used to quantify the contribution of that sediment component to the exchange capacity of the sediment unless we know how that component is distributed in the virgin sediment. What such treatments do reveal is a qualitative indication of the activity these phases contribute to the surface.

For a clay mineral, and clay sized minerals there are three possible sources of cation exchange capacity (GRIM 1968). Broken bonds around the edges of silica-alumina units give rise to unsatisfied charges, which are balanced by adsorbed cations. This is probably the major cause of exchange capacity for kaolinite minerals. Substitutions within the lattice structure result in unbalanced charges in the structural units of some clay minerals. In montmorillonites this gives rise to about 80% of the exchange capacity. The third and minor cause of cation exchange capacity, is exchange with the hydrogen of structural hydroxyl groups. Exchange capacity due to broken bonds will increase with decreasing particle size, whereas exchange capacity due to lattice charges and structural hydroxyl groups is independent of changes in particle size. Exchange capacities of clay minerals range from about 1 meq/100 g for well crystallised kaolinites to over 100 meq/100g for some fine grained montmorillonites.

Organic matter present in sediments will tend to block the clay exchange sites, and so dominate the exchange behaviour of the sediment (GREENLAND, 1971). Humic acids extracted from sediment have exchange capacities of several hundred meq/100g (SCHNITZER et al., 1972; RASHID 1969). When present in the sediment its effective exchange capacity will depend on how it is dispersed within the sediment. The work of HUNTER (1977) on the surface properties of particles in coastal waters suggest that carboxyl is the major functional group in the organic matter on these particles. Similar techniques to those used by Hunter may be applied to marine sediment particles, to assess what are the major functional groups present in pelagic sediment organic matter.

The third source of exchange capacity in sediments is the amorphous oxide component, which is dominantly iron and manganese oxides. This is the most difficult phase to deal with because it will have a tendency to undergo both simple ion exchange (an electro static process, as displayed by clay mineral and organic surfaces) which is rapidly reversible - and specific sorption processes which may involve redox reactions between the adsorbed cation and the oxide (HEM 1977) which may not be easily reversible.

LEACHING EXPERIMENTS

We have compared:- for the removal of organic matter the hydrogen peroxide, and sodium hypochlorite oxidation methods; and for the removal of amorphous oxides the acid ammonium oxalate and the sodium dithionite - citric acid - sodium bicarbonate reduction methods.

Each of these methods is in common use for the preparation and analysis of sediment and soil samples. The method chosen for a particular task depends on the nature of the experiment. None of the methods is specific. Previous work would suggest that sodium hypochlorite would be the preferred oxidizing agent because problems are known to arise with hydrogen peroxide in that it dissolves manganese oxides (JACKSON 1979) and is known to disrupt clay mineral structures (DROSDOFF et al., 1928). However its ability to break down marine organic matter may be greater than that of sodium hypochlorite.

Clear differences have been shown in the extent to which the oxalic acid and dithionite solutions attack iron oxide phases. (HEATH et al., 1977; FEY et al., 1977). Oxalic acid is the more specific reagent only attacking amorphous oxides, crystalline goethite is not dissolved (LANDA et al., 1973). No reports of the influence of these reagents on the surface properties of clay minerals have been published.

The comparison was done to see which pair of methods would be the most suitable for application to our samples. The criteria for selection being least disruption to the cation exchange behaviour of crystalline material, apparent specificity and ease of use.

METHODS

All the experiments were carried out on about 500mg of sediment which was retained in the same 50ml polypropylene centrifuge tube throughout processing (except for the peroxide treatment where heating was carried out in a glass beaker).

Sodium Hypochlorite Oxidation:-

- (1) Dry sediment is weighed into the centrifuge tube.
- (2) pH of hypochlorite solution is adjusted to pH 8.5 with 6N hydrochloric acid (about 5ml/100ml of hypochlorite).
- (3) 10ml of hypochlorite is added to sediment and mixed thoroughly. The tube is

placed in a boiling water bath and heated 15 minutes.

(4) a further 15ml of hypochlorite is added, the sediment is dispersed using an ultra-sonic disruptor, then returned to water bath for a further 15 minutes.

(5) The sediment is then rinsed once with distilled water and three times in a 80% methanol 20% water solution.

Hydrogen Peroxide Oxidation:-

(1) Dry sediment is weighed and placed in 50ml glass beaker.

(2) 10ml of 30% v/v hydrogen peroxide is added and the mixture stirred.

(3) Warm carefully (avoid frothing over) on a hot plate to speed reaction - control by adding distilled water.

(4) Evaporate to near dryness and add a further 10ml of peroxide, warm until reaction ceases.

(5) Transfer quantitatively to a centrifuge tube.

(6) The sediment is then rinsed once with distilled water and three times with an 80% methanol 20% water solution.

Dithionite - Citrate - Bicarbonate Reduction:-

Reagents (a) 0.3M sodium citrate (88g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_6 \cdot 2\text{H}_2\text{O}/1$).

(b) 1.0M sodium bicarbonate (84 g/1).

(c) sodium dithionite (powdered).

(1) Weigh sediment into centrifuge tube.

(2) Mix citrate and bicarbonate solutions 8+1, and add 30g of this solution to sediment.

(3) Place in water bath and warm to 80°C.

(4) Add 0.66g sodium dithionite (solid) stir, wait one minute and add further 0.66g dithionite.

(5) Digest for 15 minutes.

(6) Disperse using ultra-sonic disruptor, add a further 0.66g dithionite.

(7) Return to water bath and heat further 15 minutes.

(8) The sediment is then rinsed once with distilled water and three times with 80% methanol 20% water solution.

Acid Ammonium Oxalate Reduction:-

Reagents (a) 0.2M ammonium oxalate (28.4 g/l)

(b) 0.2M oxalic acid (25.2 g/l)

(1) Weigh sediment into centrifuge tubes.

(2) Mix oxalate solutions 1+1 and adjust to pH 3.0 with concentrated ammonia solution.

(3) Add 30ml mixed reagent to sediment.

(4) Shake in dark for two hours.

(5) The sediment is then rinsed once with distilled water and threetimes with 80% methanol 20% water solution.

Measurement of Total Cation Exchange Capacity:-

Reagents (a) 1.0 N ammonium chloride in 80% methanol: 20% water solution (53.5g $\text{NH}_4\text{Cl}/1$).

(b) 0.1 N ammonium chloride, aqueous solution (0.54 g/l).

(c) Filtered seawater.

(d) 80% methanol.: 20% water solution.

(1) Weigh centrifuge tube and cap (wt A)

(2) Weigh sediment into each tube (wt B)

(3) Rinse three times 80% methanol 20% water solution

(4) Rinse 2 times 1 N ammonium chloride first one shaken four hours, second exchange shaken over night.

(5) Rinse 3 times 0.01 N ammonium chloride. Centrifuge decant off supernatant and weigh wet sediment (wt C).

(6) Suspend in seawater. Rinse 3 times with at least one hour shaking per rinse. Collect and consolidate supernatants, measure volume collected (V mls).

(7) After final rinse weigh wet sediment (wt D).

(8) Dry to constant weight (wt E).

(9) Measure ammonia content and the change in alkalinity of the seawater.

CALCULATION

Final wt of sediment $F = (E-A) - [(D-E) \times (\phi - 1)]$

where ϕ is the density of the seawater.

Corrected final volume of seawater $V = V + [D-E]/\phi$

Change in alkalinity and corrected ammonium in V

$$\Delta \text{ cations (meq)} = \left(\frac{\text{meq/l NH}_4 \times V}{1000} - \frac{0.01 [C - (C - (F+A))]}{1000} \right) + \frac{\Delta \text{alk} \times V}{2000}$$

$$\text{Exchange capacity} = \frac{\Delta \text{ cations}}{F} \times 100 \text{ (meq/100 g)}$$

EXPERIMENTAL DETAILS AND RESULTS

The solid substrates used in these experiments where:-

Standard Clays (a) Kaolin well crystallised Washington County Georgia (KWC).

(b) Kaolin poorly crystallised Washington County Georgia (KPC).

(c) Illite Morris Illinois (I).

(d) Montmorillonite Belle Fourche South Dakota (M).

(e) Chlorite El Dorado County California (C).

Natural Assemblage

(a) Organic Rich Coastal Sediment. About 3% organic carbon, quartz kaolin and feldspar (OR).

(b) Iron coated sediment, mainly quartz (IRS).

OXIDATION EXPERIMENTS

Humic acid was extracted from a large sample of coastal sediment (OR) using 0.5 N NaOH, reducing the pH and then freeze drying the precipitate. This material was subjected to the peroxide and hypochlorite treatments, and the weight loss calculated. A hundred percent weight loss would not be expected due to inorganic impurities in the extract. In this test hypochlorite gave the better result giving a weight loss of 86% as opposed to 58% for the peroxide.

In a second experiment with the extracted humic acid it was mixed with kaolinite and the exchange capacity of the clay and clay humic mixture was measured before and after treatment with peroxide and hypochlorite. The results (Table 1) show that both reagents appear to be equally efficient at

removing the humic acid exchange capacity, in this case peroxide gave the more complete removal. No effect on the clay is discernible.

Investigation of possible effects on the cation exchange capacity of crystalline material was extended to a wider range of standard clays. The results (shown in Table 2) show similar changes for both peroxide and hypochlorite attack. When applied to the organic rich coastal sediment with an initial cation exchange capacity of 57 meq/100g peroxide reduced it to 35 meq/100g and hypochlorite to 39 meq/100g.

REDUCTION EXPERIMENTS

Of primary importance in selecting use of oxalic acid or dithionite for amorphous oxide removal is whether or not the known greater iron extracting power of dithionite leads to an excessive disruption of the mineral surfaces. In parallel to experiments on standard clays with the oxidising reagents reactions with oxalic acid and dithionite were run. The results (Table 2) show considerable increases in the exchange capacity of the montmorillonite and chlorite when exposed to attack by dithionite. Changes shown in Table 2 in ion exchange capacity cannot be simply related to the amount of iron, aluminium and silicon removed by the leaches shown in Table 3. To examine the selectivity of the reagents for amorphous phases and iron, a series of sequential leaches was carried out comparing the effects on two kaolins of similar composition but differing crystallinity, and the iron coated sediment. The results are shown in Figs. 1A, B and C. These results clearly show the greater extracting power of dithionite, but also show the low selectivity of its attack. For example dithionite attacks the well crystallised kaolin solubilising progressively more silicon with each leach whereas, the amount of silicon solubilized by the oxalic acid is negligible.

At this stage in the investigation it was decided that the reducing reagent to be used in further experiments would be oxalic acid on the basis that it was probably more specific in its attack on amorphous phases than dithionite. Hypochlorite was also chosen as the oxidising agent because it appeared to be as efficacious as peroxide, but was easier to handle and less likely to disrupt crystalline material (DROSSDOFF et al. 1938).

The next experiment was to see if a greater degree of specificity could be achieved by carrying the oxalic acid leach out at pH5, and what effect increasing the time to an overnight leach had on the yield of the leach. The results shown in Table 4, show that pH5 did not produce a more iron

specific leach. Increasing the leach time increased the yield of iron but at the expense of a greater proportional rise in dissolved silicon. On this basis it was decided normally to carry out leaches at the pH3 for 2 hours as originally recommended by SCHWERTMANN (1964).

SEQUENTIAL LEACHING

The expected effect of leaching would be that as amorphous phases with high exchange capacities were removed from the surface of a mineral grain its exchange capacity should decrease. Further, if the exchange capacity was mainly due to either the organic or the amorphous oxide coating then this should show up as a more marked reduction in exchange capacity when this coating was removed. With this idea in mind, sequential leaching was performed on the organic rich sediment, to see if a drop in exchange capacity was associated with a particular leach, and whether or not it was associated with the order in which the leaches were done.

The results (Table 5) of the experiment when carried out with the total sediment passing through a 200 mesh sieve show that the leaches actually increased the exchange capacity. The trend in the changes was independent of the order of leaching - the first leach produced an increase in exchange capacity, the second leach reduced the exchange capacity, but not to a value as low as that of the starting material. When the experiment was repeated for a leach sequence of hypochlorite followed by oxalic acid, using the less than 2 μ m portion of the sediment, the hypochlorite leach produced little change in the exchange capacity, the oxalic acid produced a 30% drop. In both these experiments it was noted that leaching produced a progressively more fine grained material which took longer to centrifuge down. Noticeably the drop in exchange capacity was accompanied by a considerable weight loss, much greater than the amount of material dissolved by the leach.

DISCUSSION

The only unambiguous result reported above which involved measurement of cation exchange was for the experiment where kaolinite was mixed with a known quantity of humic acid and the humic acid was then destroyed. In the other leaching experiments where a natural material was used interpretation of the results is plagued by not really knowing what the material is that we are dealing with.

What appears to be a reasonable indication of the problem is that during processing we can tell from the way that leached samples take longer to centrifuge down that leaching is producing smaller particles. Records of weight loss show

that due to fine particles not been effectively removed from suspension at all stages in processing - percentage weight losses can be quite large. So we are dealing with two changes in the mineral assemblage which probably act in opposite directions to change the exchange capacity measured on a weight basis.

Decreasing the particle size will increase the surface area per gram of the sample and hence increase the exchange capacity. Losing finer grained material will tend to have the opposite effect. The results in Table 5A are probably dominated by the creation of smaller particles, whereas the results in Table 5B are dominated by loss of fine grained material.

The obvious answer to this problem would seem to be to relate the cation ion exchange capacity to a measure of the area of surface involved, rather than the weight of the sample (of ALBERTS et al. 1979). Cation exchange capacity would be a measure of the activity of the mineral surface.

CONCLUSIONS

Use of sodium hypochlorite to remove organic matter and buffered oxalic acid to remove amorphous oxides provide simple methods for preliminary studies of the removal of these materials, which do not appear to produce marked changes in the cation exchange behaviour of standard clays. However some ambiguity into the actual extent to which they alter surface properties will remain until the cation exchange capacity of a material is related to surface area rather than weight.

I recommend that further experiments of the type reported here be coupled with particle size and surface area measurements of the sediment being studied.

TABLE 1

Cation exchange capacity of kaolin and kaolin humic acid mixtures when subjected to hydrogen peroxide or sodium hypochlorite oxidation.

	Cation exchange capacity meq/100g		
	Before	After H ₂ O ₂	After NaOCl
Kaolin (KWC)	3.8,3.8	3.8,4.4	3.5,3.5
Kaolin plus humic acid	20.3,19.8	4.5,4.3	6.4,6.6

TABLE 2

Cation exchange capacity of standard clay minerals (less than 2 μ m fraction) when subjected to hydrogen peroxide, sodium hypochlorite, oxalic acid and sodium dithionite attack.

Clay	Cation exchange capacity meq/100g				
	Before	H ₂ O ₂	NaOCl	Oxalic	Dithionite
Kaolin (KPC)	9	9	10	12	11
Illite	30	33	33	30	27
Montmorillonite	99	79	86	11	246
Chlorite	7	7	10	9	15

TABLE 3

Amounts of iron, aluminium and silicon removed from standard clays by a single reaction with oxalic acid or sodium dithionite, corresponding to changes shown in Table 2.

Clay	Amount leached mg/g					
	Fe		Al		Si	
	Ox	Di	Ox	Di	Ox	Di
Kaolin (KPC)	0.1	2.4	0.1	0.1	0.2	3.4
Illite	3.4	13	0.1	0.2	0.2	8.9
Montmorillonite	0.2	2.5	0	0.6	0.5	7.7
Chlorite	39	14	1.0	0.4	30	7.1

TABLE 4

Influence of pH and time on oxalic acid attack on the iron coated sediment (IRS).

	Fe		Al		Si	
	mg/g		mg/g		mg/g	
	pH3	pH5	pH3	pH5	pH3	pH5
2 hours	2.9	1.6	0.8	0.5	0.2	0.1
18 hours	4.2	2.4	1.2	0.6	0.5	0.2

TABLE 5

Cation exchange capacity of organic rich sediment before and after oxidising and reducing leaches. 3 samples subjected to each treatment figure in brackets mean percentage weight loss.

(A) Sediment sieved through 200 mesh sieve.

Cation Exchange Capacity meq/100 g		
Before	Oxalic Acid	Hypochlorite
8.6	13.2	12.5
8.5	12.1	12.1
8.1	10.9	9.3
(4)	(6)	(9)
	Oxalic Acid then Hypochlorite	Hypochlorite then Oxalic Acid
	8.2	9.0
	11.6	8.6
	11.6	8.4
	(11)	(13)

(B) Starting material less than 2 μ m

Before	Hypochlorite	Hypochlorite then Oxalic
48.6	48.2	33.5
49.4	48.2	33.7
54.1	49.4	35.4
(3)	(15)	(38)

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FIGURE 1 The cumulative amount of A. Silicon, B Aluminium and C, Iron, removed by sequential treatments of sediments with dithionite plus ● iron coated sediment ▲ poorly crystallized kaolin ▼ well crystallized kaolin; and oxalic acid with ○ iron coated sediment Δ poorly crystallized kaoline, ▽ well crystallized kaolin.



