

Clay minerals as sorbents for nuclear reactor activation products

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A comparison is presented of cobalt and chromium uptake on different clays. It is shown that clay minerals are good adsorbents for cobalt and chromium in waste effluents. The sorption of cobalt and chromium on the clays studied was by ion exchange and surface complex formation, respectively. In addition, the percentage of either cobalt or chromium removed in a mixed solution environment is higher than the individual adsorption in single-component experiments. This proves a synergistic mechanism. The optimum uptake of each metal ion from mixed species was achieved by montmorillonite clay in the calcium form.

1. Introduction

Stainless steel is widely used in the construction of nuclear reactor core components and when in service neutron activation products are formed in their matrices. These radioactive products are ^{60}Co and ^{51}Cr . The decommissioning of nuclear reactors will produce waste contaminated with these and other radioactive isotopes. Current disposal philosophy envisages that the waste will be consigned to underground repositories designed on the basis of multiple barriers to the subsequent movement of the radioactivity. One of these barriers will be adsorbent material used to back-fill the repository when it is closed, and clay materials have been proposed for this purpose. The present work explored the use of three common clay materials, bentonite, kaolinite and montmorillonite, for this purpose. Technical feasibility has been evaluated in bench-scale experimentation using simulated waste mixtures to examine which clay form is most appropriate for cobalt and chromium exchange.

2. Previous work

The adsorption of multivalent and, especially, transition metal ions on to oxide and clay mineral surfaces has been studied by a variety of techniques over a long period because of its significance in plant nutrition, water treatment and flotation behaviour [1, 2]. The importance of clay minerals in many process industries has led to their being extensively studied in the past. Unfortunately, much of the early data is vitiated by the fact that most clay minerals are unstable in aqueous solution, especially at low pH. Slow dissolution of silica and especially alumina from crystal edges [3] and redeposition on the crystal faces, has been shown to lead to considerable uncertainty and variability in surface properties, particularly when the clay is "purified" by electro dialysis techniques.

Grutter *et al.* [4] have studied adsorption and desorption of some radionuclides on glaciofluvial deposits and have shown that the isotherms for sorption and exchange on these materials are non-linear. The investigators reported that part of the non-linearity can be accounted for by the collapse of the c-spacing for vermiculite clay.

The simple ion-exchange process between a proton and a metal cation with a valency z may be represented by the following reversible equation



The subscript s refers to the material in the solid phase. The adsorption of heavy metals on clays is often dominated by surface complex formation with a single coordinated OH group on the edge of the surfaces.

Fig. 1 portrays the general layered structure of a clay mineral with two types of strata, the T-layer is a silica tetrahedral one and the O-layer represents octahedral gibbsite/brucite $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$ [5, 6].

The clay minerals used in this study included kaolinite ($\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$) which is a non-expanding aluminosilicate that has a two-layered structure (T–O/T–O/T–O/...) and a medium cation exchange capacity (CEC). Secondly, we studied montmorillonite $[(\text{Na},\text{K})_{x+y}(\text{Al}_{2-x}\text{Mg}_x)_2(\text{Si}_{1-y}\text{Al}_y)_8 \text{O}_{20}(\text{OH})_4(\text{H}_2\text{O})_n]$ an expanding aluminosilicate which has a three-layered structure (T–O–T/M $^{n+}$ /T–O–T) and a high CEC. In the T-layer there are possible Al/Si substitutions, while in the O-layer Mg^{2+} , Fe^{3+} or Cr^{3+} can substitute for aluminium ions. The main component of bentonite, the third clay studied, is smectite with a theoretical formula of $(\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4)$ without considering the lattice substitution.

The main ion-exchange processes occur in the O-layer and either H^+ ions (in the free form or acid-washed clay) or M^{n+} (Na^+ , Ca^{2+}) in the conditioned

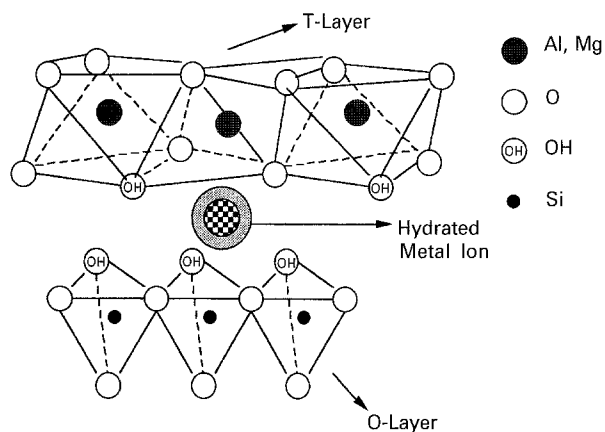
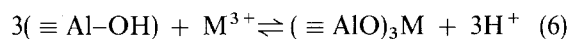
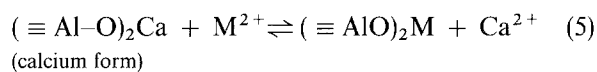
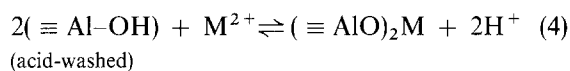
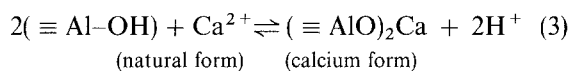
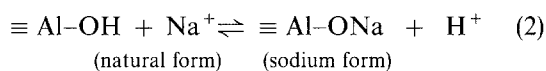


Figure 1 General structure of a clay mineral.

clays are exchanged with heavy metal ions (Co^{2+} or Cr^{3+}). Some of the mechanisms are as follows



Gordon [7] has given an excellent review of earlier models for metal sorption on clays.

3. Experimental procedure

Preliminary porosimetric studies on the clays were carried out using the "ASAP 2000" Micromeritics (USA) Accelerated Surface Area and Porosity Analyser. This equipment can analyse powders both for adsorption and desorption with various gases and mixtures of them. A mixture of nitrogen and krypton was used for assessing the porosimetric properties of the different clay mineral forms. In this study, it was possible to obtain the average pore size and micropores area. Fig. 2 presents comparative surface data for different clay forms. Fig. 2a gives the micropore area for various clays. This illustration depicts the physical adsorption and desorption results and shows montmorillonite as the best adsorbent based on the surface area only, but not necessarily on ion-exchange potential. In Fig. 2b, the average pore diameter increases accordingly with sodium and calcium treatment for montmorillonite.

In order to study the sorption of both cations and hydrolysed microcolloids on the clay minerals, the pH range studied varied from 2–8 and the minerals were contacted with 20 and 200 p.p.m. (weight basis) solution of both metals. For these sorption experiments, both synthetic and washed raw-clay minerals were selected. The synthetic clays were bought from British Drug Houses (BDH) and Fisons Laboratory supplies, while kaolinite and montmorillonite conditioned with

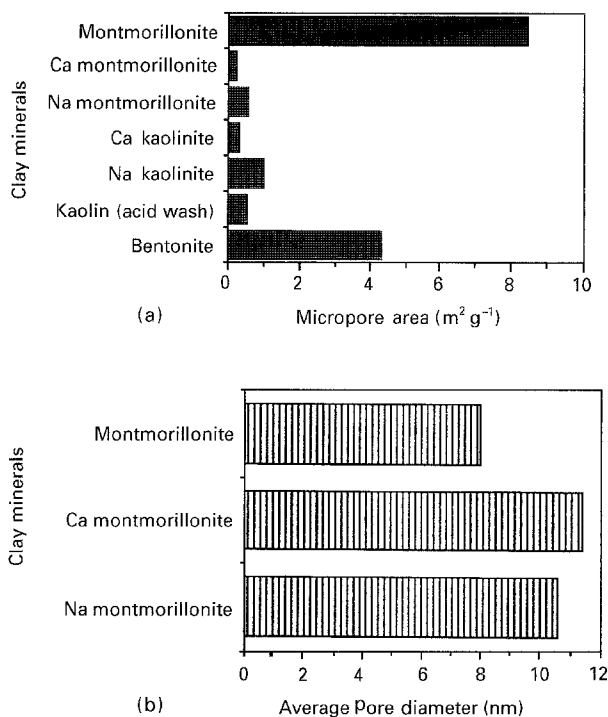


Figure 2 Some surface analysis data for different clay minerals (ASAP 2000). (a) Micropores area for various clays. (b) Average micropore diameter for montmorillonite clays.

sodium and calcium have been characterized elsewhere [8]. Batch-contacting experiments were then carried out with three different sets of solutions at determined pH values, as described below. The desired concentrations of 20 and 200 p.p.m. were prepared from chromium and cobalt "Spectrosol" quality standard. The mixed standard solution contained 100 p.p.m. each of cobalt and chromium. Nitric acid and freshly prepared sodium hydroxide were used in pH adjustments.

In the first set of contacting tests, cobalt or chromium exchange capacity was investigated. For this purpose, 10 ml Co or Cr solution, adjusted to desired pH value, were used. 0.25 g of the different clay minerals were weighed into polyethylene centrifuge tubes. The polyethylene tubes were tightly closed by fitting stoppers of polyethylene after the desired solution had been added. These tubes were placed in a water bath shaker. The shaker bath was maintained at $20 \pm 2^\circ \text{C}$ while the speed was maintained at 140 r.p.m. to guarantee good mixing. Complete equilibration was achieved by shaking 0.25 g of the clay minerals with 10 ml of the adjusted solution for 1 week. After the equilibration experiment, each of the polyethylene tubes was subjected to high-speed centrifugation and the supernatant was removed and filtered. The filtrate was subsequently analysed using a Perkin-Elmer Atomic Absorption Spectrophotometer model 100B. In the second set of experiments, the mixed solutions were equilibrated with the corresponding clay minerals under the same conditions.

4. Results and discussion

The sorption data of each clay mineral form studied were plotted as functions of capacity and solution pH.

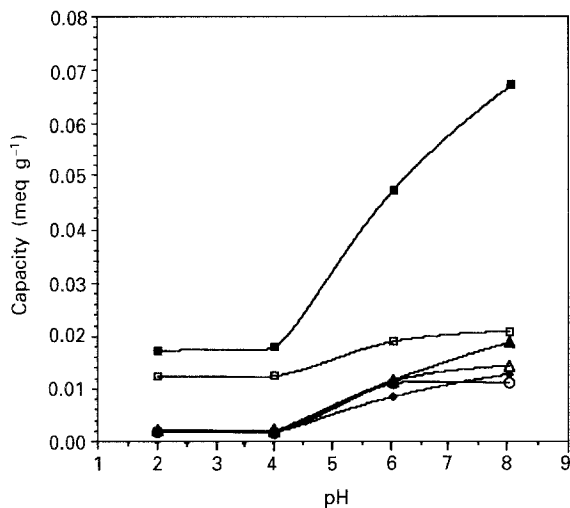


Figure 3 Capacity of different clays for Co(II) 20 p.p.m. (○) Bentonite, (◆) kaolin-H, (△) kaolin-Na, (▲) kaolin-Ca, (□) Montmorillonite-Na, (■) Montmorillonite-Ca.

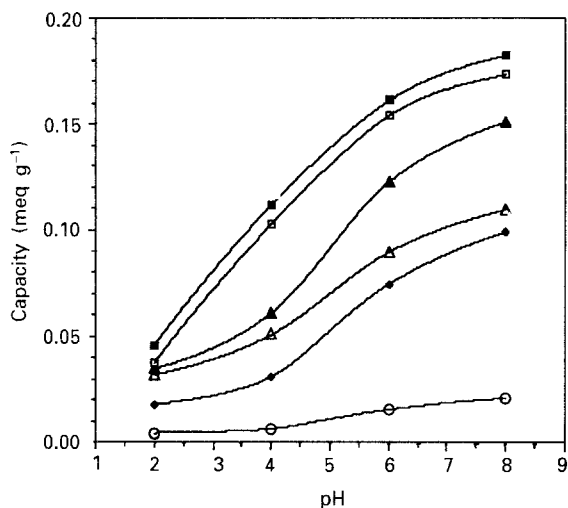


Figure 4 Capacity of different clays for Co(II) 200 p.p.m. For key, see Fig. 3.

The capacities obtained for cobalt are shown in Figs 3 and 4. Fig. 3 gives the data for 20 p.p.m. solutions and Fig. 4 that for 200 p.p.m. ones.

Fig. 4 gives a much clearer picture of the capacity of clays for the Co^{2+} ion. In every case this increases with the pH of the contacting solution. The highest adsorption is obtained with calcium montmorillonite and the worst, by far, is bentonite. The capacity series, beginning with the best is:

1. calcium montmorillonite
2. sodium montmorillonite
3. calcium kaolinite
4. sodium kaolinite
5. acid-washed kaolinite
6. bentonite.

Comans [9] observed similar phenomena with calcium-illite in his study on Cd^{2+} adsorption.

Figs 5 and 6 display the corresponding results for the chromium ion which shows a similar trend to the previous data. Again the clay mineral capacity series is exactly the same. The lower concentration of 20 p.p.m.

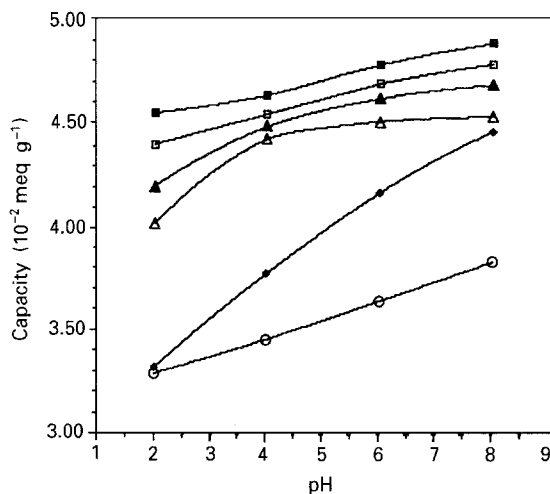


Figure 5 Capacity of different clays for Cr(III) 20 p.p.m. For key, see Fig. 3.

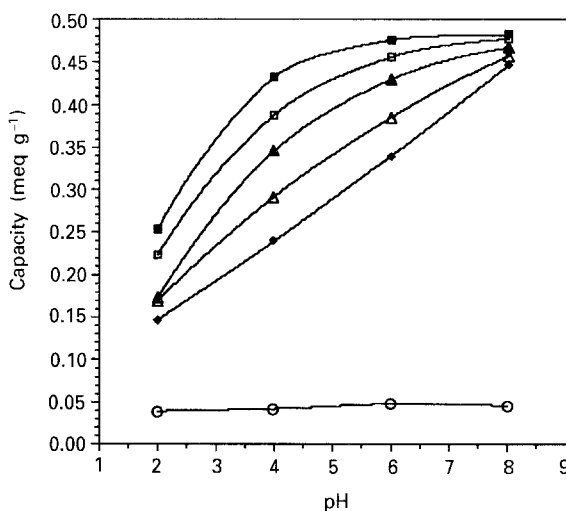


Figure 6 Capacity of different clays for Cr(III) 200 p.p.m. For key, see Fig. 3.

data show some considerable closer capacity values at high pH for some of the clays. In the 200 p.p.m. data, the data cluster together for all the clays showing saturation in chromium. This is due to the fact that most of the chromium had been removed during these particular tests.

On a closer examination of the data for the pH range 4–6 it is clear that the capacities of the clay for the hydrolysed Cr^{3+} species is more than double that of the ionic Co^{2+} ion. The behaviour of chromium in the figures is distinctly different from the corresponding ones for cobalt, and the influence of the clay forms (H^+ , Na^+ and Ca^{2+}) is evident. This figure also provides additional evidence for the concept of physiochemical sorption. In this system, it would seem that bentonite approximates a reference clay which typifies physical adsorption. There is a gradual transition from physical sorption for the reference clay to chemisorption, as observed in the plots moving from acid-washed kaolinite and finally to calcium-treated montmorillonite. The sharp change in slope of the chromium isotherm is remarkable for some of the clays except for bentonite, acid-washed and sodium

kaolinite. Stumm [10] observed that the interaction of alkaline and earth-alkaline ions with clays occurs mostly through ion-exchange processes, while the adsorption of heavy metals on clays is often dominated by surface complex formation with a single coordinated OH group on the edge of the surfaces. It is also important to note that the results obtained in this study confirm previous findings of the fact that bentonite and montmorillonite show a constant zeta potential throughout the entire pH range. The high constant value of 35 mV, as the apparent zeta potential found by Răutiu *et al.* [11] is correlated with their ion-exchange behaviour.

Fig. 7 presents a typical bar chart for percentage adsorption of the six clay mineral forms for single and mixed solution feeds. The mixed contacting solution contained 100 p.p.m. each of cobalt and chromium. In this illustration, the percentage adsorption of chromium contained in a mixed solution of cobalt and chromium is higher than individual adsorption in the single experiments. This proves a synergistic mechanism.

For ideal systems, the higher the valence of the ion, the greater is its exchangeability and the more difficult it is to displace when already sorbed on the clay. The uptake of chromium is thus expected to be more than the divalent cobalt in line with previous study and the chemistry of chromium. This observation is contained in the review by Grim [5]. The factors influencing the sorption selectivity are the charge and effective hydrated radius of the ion, and solution pH. Cobalt exists in solution as the divalent Co^{2+} ion which hydrolyses at pH values above 8, and chromium as the Cr^{3+} cation which hydrolyses at a pH value in excess of 4. The effective hydration radii of the cations are 0.159 and 0.146 nm, respectively [12]. The hydration radii of the functional ions on the clays are Ca^{2+} 0.184 nm and Na^{+} 0.186 nm.

For pH values above 4 for Cr^{3+} and 8 for Co^{2+} hydrolysis plays an important role, and the presence of colloidal species thus influences the sorption on clays. This result proves that the typical trivalent heavy metal (chromium) studied is sorbed by surface complex formation to the OH-functional groups of

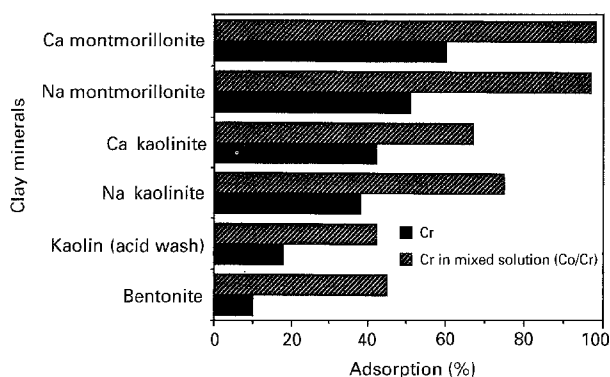


Figure 7 Comparison of chromium adsorption on clay minerals in single and mixed solution environments (pH 4).

the outer surface for an expandable three-layer montmorillonite clay. This observation was also reported by Stumm [10].

In general, kaolinite clays have layers bound more tightly together and permit less substitution of other ions for aluminium and silicon. It is therefore obvious that these structural differences are reflected in relatively low ion-exchange capacity for kaolinite when compared with montmorillonite clays. In the case of three-layered clays, such as montmorillonite, the sheets are bound less tightly. This geometry enhances the sorption capacity. Thus steric factors, such as hydration radii and interlayer spacing, prove to be essential.

An interesting experimental finding not reported previously is the synergism of the $\text{Co}^{2+}/\text{Cr}^{3+}$ co-sorption. This can be explained by the surface sorption mechanism predominating on the simple ion-exchange mechanism. Hence, individual sorption capacities for single systems are lower than co-sorption values for mixed systems.

5. Conclusions

1. The sorption of cobalt and chromium on the clay minerals studied is by ion exchange and surface complex formation, respectively.

2. The evidence from this study is that the percentage of either cobalt or chromium contained in a mixed-solution environment is higher than the individual adsorption in single-component experiments.

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