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REMOVAL OF NICKEL AND COBALT FROM AQUEOUS SOLUTIONS BY Na-ACTIVATED BENTONITE

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Abstract—The ability of Na-activated bentonite to remove Ni^{2+} and Co^{2+} from aqueous solutions at room temperature (22 ± 1°C) was studied under various experimental conditions. The parameters studied were solid-to-liquid ratios and initial cation concentrations. Experiments involved the behavior of bentonite *vs.* Ni and Co separately and where Ni and Co were present in solution at different concentrations and ratios. Bentonite retained substantial amounts of both metals readily, but it showed a higher affinity for Ni. Over-exchange appears when initial metal concentration exceeds the concentration corresponding to the cation exchange capacity (CEC) of bentonite. The presence of both metals in solution may be either synergistic or antagonistic sorption, depending on the initial ion concentrations.

Key Words—Adsorption, Bentonite, Cation Exchange, Clays, Cobalt Removal, Heavy Metals, Nickel Removal, Wastewater.

INTRODUCTION

Heavy metals such as Ni and Co are common constituents of runoff from mining operations, urban stormwater runoff, and industrial effluents. Although in small concentrations they are essential to life, excessive levels may be detrimental. Therefore, heavy metals in wastewater should be minimized to prevent accumulation in the biosphere. Adsorption on smectite-rich clays, *i.e.*, bentonites, is a reliable method of metal removal owing to its simplicity, effectiveness, and low cost, and bentonites are abundant. Common environmental uses of bentonites involve the protection of aquifers from contamination by the sealing of ponds and landfill sites; bentonite holds pollutants and prevents downward movement of wastewater. Hence, it is important to know the retention capacity of bentonite and the factors that govern cation retention.

Bentonite is commercially available and consists mainly of the clay mineral montmorillonite, a member of the smectite family. Smectites display nearly threefold higher sorption of Cd, Cu, Zn, and Ni than illite, with Ni and Zn occupying interlayer sites rather than external surfaces of the clay particles. Ni and Zn have a lower release during desorption. (Rybicka *et al.*, 1995; Brigatti *et al.*, 1994).

Zn^{2+} and Pb^{2+} follow Langmuir-type exchange, with Zn preferred slightly to Pb (Brigatti *et al.*, 1995). Adsorption of Zn^{2+} and Cd^{2+} by smectites might be improved by heat treatment (Pradas *et al.*, 1994). Smectites also absorb Hg at acidic pH through an endothermic process (Viraraghavan and Kapoor, 1994). Reactive sorption sites in soils might be specific or non-specific (Tiller *et al.*, 1984a). Short contact time gives an approximation of total adsorption that underestimates the potential of any soil or clay system. Verburg and Baveye (1994) proposed a two-stage kinetics model for ion exchange. The model emphasizes the key role of activation-energy barriers.

The high affinity of smectites for Cd and Ni was attributed to the hard-soft acid-base rule (Puls and Bohn, 1988; Pradas *et al.*, 1994). Montmorillonite exhibits a harder base character than kaolinite; thus in Cl^-, ClO_4^-, and SO_4^{2-} solutions, montmorillonite is preferred by Ni, which is a relatively hard Lewis acid (Puls and Bohn, 1988). However, both minerals do not readily sorb Ni, especially in the presence of SO_4^{2-}, reflecting their relative softness in an absolute sense. In contrast, kaolinite shows greater relative affinity for Ni than montmorillonite and soil clay fractions rich in 2:1 phyllosilicates display greater preference for Zn than for Cd and Ni, and higher affinities for each metal at pH < 5 than clays rich in Fe (Tiller *et al.*, 1984b).

The objectives of the study are: (1) to investigate the effectiveness of bentonite in removing Ni and Co from aqueous solutions; (2) to examine the effects of contact time and contaminant concentration on the adsorption capacity of bentonite and; (3) to evaluate sorption in the presence of both Ni and Co in aqueous solutions.

MATERIALS AND METHODS

Bentonite characterization

The bentonite used in this study comes from Milos island (Greece) and was supplied by Silver and Baryte Co. in the Na-activated form. It is light tan and has a surface area of 65.6 $m^2\ g^{-1}$ measured by N_2 adsorption following ASTM D4567 (Flowsorb Micromeritics Instrument Corp). The sample was ground to <100 mesh.

A sample of the original calcium bentonite (pre-exchanged form) was analyzed for particle size distribution, by wet sieving for the sand fraction and by

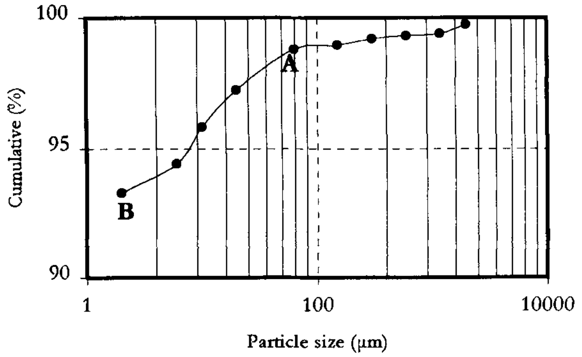

Figure 1. Particle size analysis of Milos-Island bentonite. Point A separates sand from silt fraction whereas point B separates silt from clay fraction.

sedimentation (Andreassen pipette method) for the silt and clay fractions. This sample was a more reliable indicator of the clay content since it was not ground.

Cation exchange capacity (CEC) of the Na-activated bentonite was determined for a sample dried at 100°C for 24 h, by saturation with ammonium acetate at pH 7, subsequent distillation with a Kjeldahl microstream apparatus, and titration against H_2SO_4 (0.05 N). All reagents used were *pro analysis* quality. Chemical analysis for SiO_2 content was performed by fusion at 1000°C in a Pt crucible with a mixture of $NaCO_3$, KCO_3, and borax as flux at a 15:1 flux:sample ratio. Major elements were determined by acid digestion using a mixture of concentrated HF, $HClO_4$, and HNO_3. Loss on ignition (LOI) was determined by weight difference after calcination of an air-dried bentonite sample at 1000°C.

Mineralogy of the Na-activated bentonite was determined by X-ray diffraction analysis (XRD) using a Siemens D5000 X-ray diffractometer (40 kV, 30 mA, Ni-filtered CuKα radiation, and graphite monochromator).

Experimental procedure

Three series of experiments were performed to study the sorption behavior of bentonite for Ni^{2+} and Co^{2+} ions. The first series were performed using Ni solutions of 5 to 500 ppm initial concentration and 1:50, 1:100, 1:500, and 1:100 solid-to-liquid ratios. An analogous set of experiments was performed for Co. In the third series, the solid-to-liquid ratio remained constant (1:100) and the solutions contained Ni and Co. Each solution was characterized by one primary and one secondary cation depending on which cation was of interest. The concentration ratios used for the primary-to-secondary cation were: 1:10, 1:2, 2:1, and 10:1, and the concentration values were 0.5, 2.5, 5, 10, 50, and 100 ppm. Also, control experiments with Ni and Co in the absence of bentonite were conducted to determine if the glass of the containers absorbed any Ni or Co.

All experiments were conducted in 500-mL mechanically-stirred spherical-glass reactors equipped with a Hg contact thermometer and a pH electrode to measure variations in temperature and pH. The aqueous solutions of Ni and Co were obtained from dilutions of stock solutions prepared by dissolving $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ (Merck standards) in deionized water. The experimental procedure was the following: a known amount by weight of bentonite, dried at 100°C for 4 h, was mixed with 400 mL of reacting solution with a specific metal concentration, agitated at a speed of 500 rpm at room temperature (22 ± 1°C).

Preliminary tests showed that the pH of a 5% bentonite suspension was 10.5, and this high value can lead to precipitation of metal hydroxides formed in the over-alkaline environment (Barrer and Townsend, 1976). The chemistry and valences of the hydrolysis products may influence the results in the following way: (1) adsorption of the dissolved Ni and Co on the surface of the bentonite, (2) coagulation of metal species to form colloidal particles, and (3) oxidation or reduction of the metal. Therefore, the pH value of the solutions was adjusted to 3.5 immediately after bentonite dispersion, using 12 N H_2SO_4 to avoid any precipitation of metal hydroxides pH values <3 were avoided because of dissolution of bentonite (Thomas *et al.*, 1950).

In each experiment, samples of 2 mL of the suspension were withdrawn over time. Initial tests indicated that a contact time of 120 min suffices for all experiments. The samples were subsequently filtered through a Whatman 42 filter and analyzed for Ni or Co by atomic absorption spectrophotometry (AAS). The quantity of metal ion sorbed by the bentonite was determined by the difference between the initial metallic concentration and the remaining concentration in the filtrate, since the control tests showed negligible loss from the container. The pH value of the suspensions at equilibrium was found to be <5 in all experiments.

EXPERIMENTAL RESULTS

Wet-sieve and Andreassen-particle size analyses are presented in Figure 1 as cumulative percentage of material whose particle size is smaller than the size noted on the x axis. The chemical analysis, based on wt. % oxide of the dry sample, is: SiO_2, 50.54; Al_2O_3, 19.23; Fe_2O_3, 5.77; TiO_2, 1.97; MgO, 4.74; CaO, 5.62; K_2O, 0.74; Na_2O, 3.29; LOI, 8.10. X-ray data (Figure 2) show the presence of smectite and calcite. Surface area of the bentonite is 65.6 m^2 g^{-1} and the CEC value based on NH_4^+ exchange is 0.96 meq g^{-1}.

The adsorption results for the binary systems of

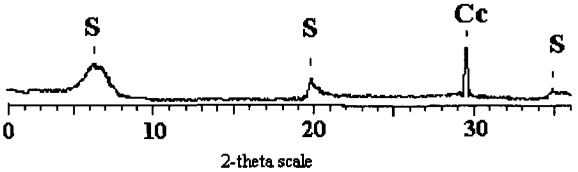

Figure 2. X-ray diffraction pattern of Milos-Island Na-activated bentonite. S = Smectite, Cc = Calcite.

bentonite and either Ni or Co are presented in Figure 3 and equilibrium data are shown in Figure 4. Figure 5 shows the effect of Co upon the removal of Ni by bentonite and vice versa.

DISCUSSION

Bentonite characterization

In Figure 1, all material <2 μm in size essentially corresponds to smectite and calcite, as indicated by the XRD pattern (Figure 2) of the clay fraction. The possibility exists that smectite is present in the coarse fractions also, because smectite may form quasicrystals several microns thick and it can exist in the fine and medium-silt fractions (2–6 and 6–20 μm, respectively) as well. Point B (Figure 1) indicates that the Na-activated bentonite sample contains >93% smectite.

The high smectite content explains the high CEC value, which combined with the chemical analysis, was used to determine the structural formula (van Olphen, 1977) of the smectite present: $(Si_{3.6}Al_{0.4})$-$(Al_{1.4}Fe^{3+}_{0.2}Mg_{0.6})O_{10}(OH)_2(K_{0.2}, Na_{0.6})_{0.8}$. The CEC value is a measure of the degree of substitution, since the exchangeable cations compensate the unbalanced charge from the 2:1 layers of the smectite owing to isomorphous substitutions.

The bentonite is an industrial product and contains calcium, even after Na-activation. The Ca^{2+} exchangeable cations react to form $CaCO_3$ as indicated in Figure 2.

Heavy metal exchange. Figure 3 shows that the removal of metal cations reaches a steady state quickly. After 30 min, a high amount ($Q_{S(I)}/Q_{0(I)}$ where $Q_{S(I)}$ is the quantity of the I cation sorbed by bentonite, Q_0 is the initial quantity, based on meq g^{-1}) of each metal was sorbed by the Na-activated bentonite. This time is similar to that determined by Rybicka *et al.* (1995), Viraraghavan and Kapoor (1994), Brigatti *et al.* (1994), and Pradas *et al.* (1994). Tiller *et al.* (1984a) reported a two-stage adsorption and emphasized that a short contact time of several hours or even days gives only an approximation of total adsorption. Thus, the results are an underestimation of the sorptive po-

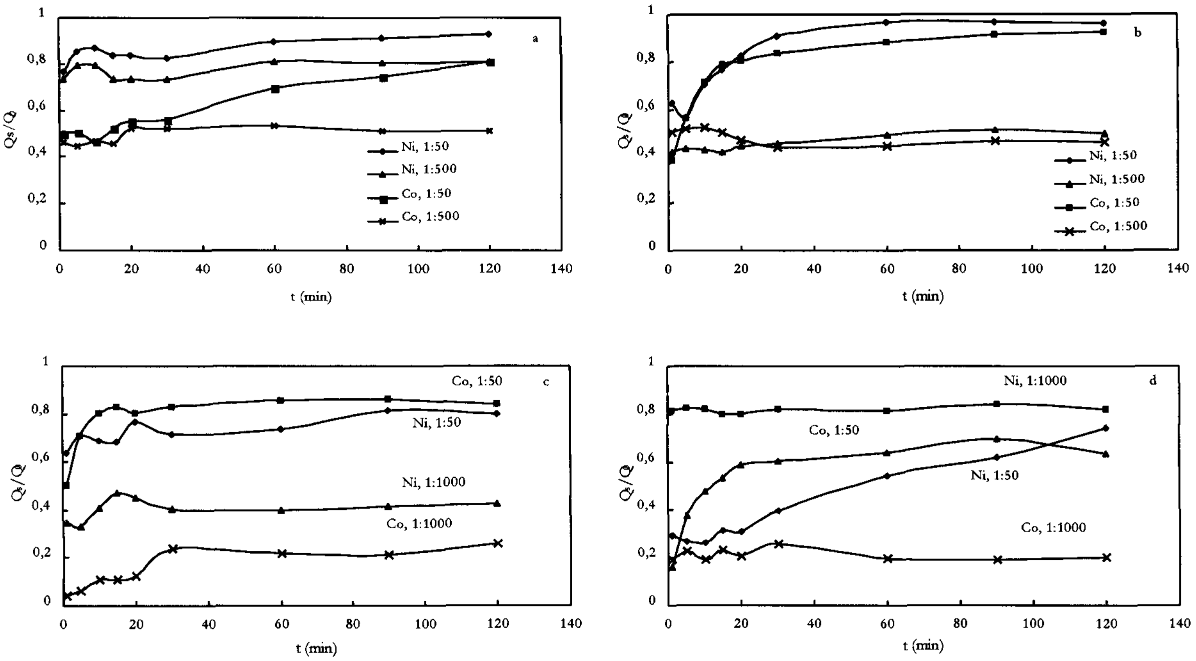

Figure 3. (a) Plot of $Qs(i)/Q_0(i)$ *vs.* time for Ni^{2+} and Co^{2+} absorbed by the Na-activated bentonite. Initial concentration of i cation: 5 ppm for solid-to-liquid ratios of 1:50 and 1:500. $Q_s(i)$ = the quantity of i cation sorbed by bentonite (meq g^{-1} of bentonite), $Q_0(i)$ = the initial quantity of i cation (meq g^{-1} of bentonite). (b) Plot of $Qs(i)/Q_0(i)$ *vs.* time for Ni^{2+} and Co^{2+} absorbed by Na-activated bentonite. Initial concentration of i cation: 20 ppm for solid-to-liquid ratios of 1:50 and 1:500. (c) Plot of $Qs(i)/Q_0(i)$ *vs.* time for Ni^{2+} and Co^{2+} absorbed by the Na-activated bentonite. Initial concentration of i cation: 200 ppm for solid-to-liquid ratios of 1:50 and 1:1000. (d) Plot of $Qs(i)/Q_0(i)$ *vs.* time for Ni^{2+} and Co^{2+} absorbed by the Na-activated bentonite. Initial concentration of i cation: 500 ppm for solid-to-liquid ratios of 1:50 and 1:1000.

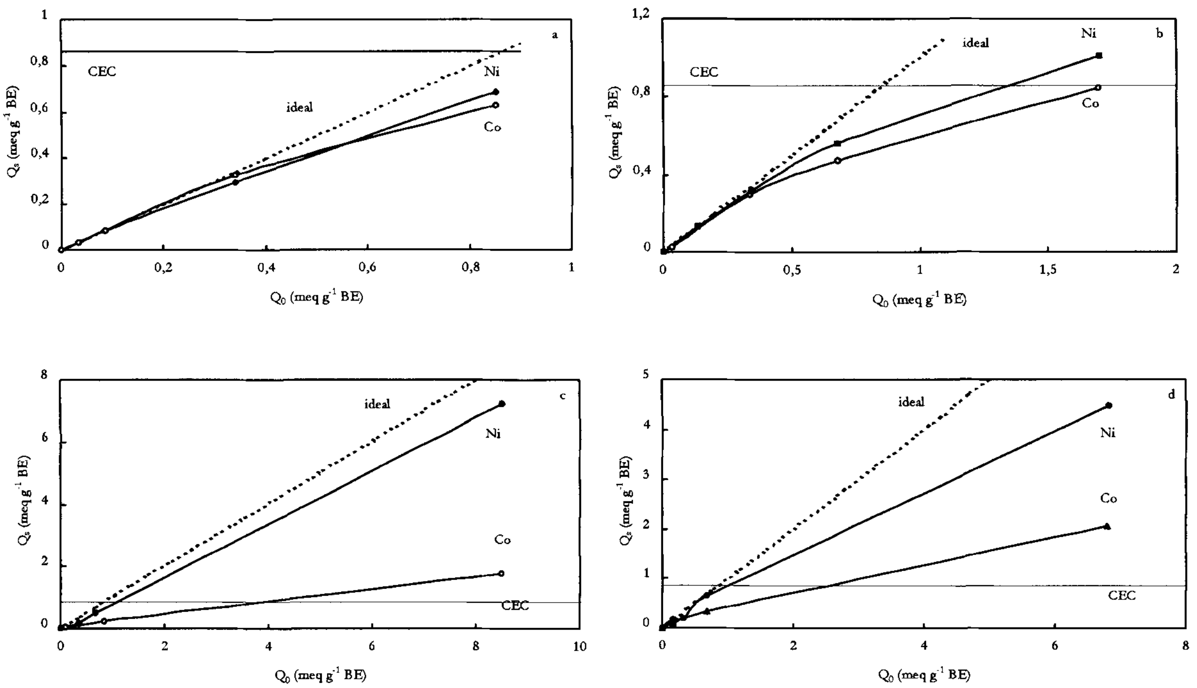

Figure 4. (a) Removal of Ni^{2+} and Co^{2+} by Na-activated bentonite at equilibrium. Solid-to-liquid ratio: 1:50. (b) Removal of Ni^{2+} and Co^{2+} by Na-activated bentonite at equilibrium. Solid-to-liquid ratio: 1:100. (c) Removal of Ni^{2+} and Co^{2+} by Na-activated bentonite at equilibrium. Solid-to-liquid ratio: 1:500. (d) Removal of Ni^{2+} and Co^{2+} by the Na-activated bentonite at equilibrium. Solid-to-liquid ratio: 1:1000.

tential of the clay. In fact, the time required to approach a steady state of adsorption differs with metal ion, sample, and pH. Although this occurs for static systems, the criterion for an industrial application (*e.g.*, wastewater treatment) of bentonite is less stringent and a short contact time is sufficient.

Solid-to-liquid ratio of 1:50. The solid-to-liquid ratio of 1:50 resulted in an increased Ni or Co removal (Figure 3) and a longer time was needed to reach a steady state. Cation removal increased owing to the availability of more sorption sites. The greater time required to reach a steady state was extended until bentonite was satisfactorily dispersed. The sorbent at this density formed aggregates which probably result in a reduced surface area of the smectite.

Ni at a solid-to-liquid ratio of 1:50 (Figure 3d) appeared to be an exception, since the solution showed high Ni depletion. However, the increase in the pH value of the suspension from 3.5 at the beginning of the experiment to 5.0 at the end, may have led to precipitation rather than adsorption of the examined cation (Baes and Mesmer, 1976).

Solid-to-liquid ratio of 1:100. These systems showed that some over-exchange for Ni was observed after the initial metallic concentration exceeded C_{CEC} (concentration corresponding to the cation exchange capacity of bentonite) (Figure 4b). This result may be attributed to broken bonds at the edges of the tetrahedral sheets, which require adsorbed cations for charge balance. The number of such bonds is high for smaller particle sizes. In addition, there is a high possibility of formation of complexes in the metal solutions between the exchange cations and the co-anions, so that hydrogen also exchanges onto the bentonite, which would result in an apparent over-exchange. (Loizidou and Townsend, 1987).

Solid-to-liquid ratio of 1:500. The behavior of the sorbent at the solid-to-liquid ratio of 1:500 (Figure 3a and 3b), is characterized by a small uptake at initial concentrations lower than C_{CEC}; but when the concentration of the cation in the reacting solution becomes larger than the C_{CEC}, the adsorption of additional cations is promoted, owing to sorbate-sorbate forces (Gregg and Sing, 1982). These attractive forces exist owing to van der Waals forces, which promote contact. At these high concentrations, the sorption of Ni by bentonite reaches 80% of its CEC and for Co it goes twice beyond this capacity. During the experiments, the solid dispersed well and there was no increase in the pH value from the initial value of 3.5.

Solid-to-liquid ratio of 1:1000. The behavior of the sorbent at the solid-to-liquid ratio of 1:1000 is similar to that for 1:500 (Figure 3c and 3d). The sorption of both cations exceeds the bentonite capacity at a con-

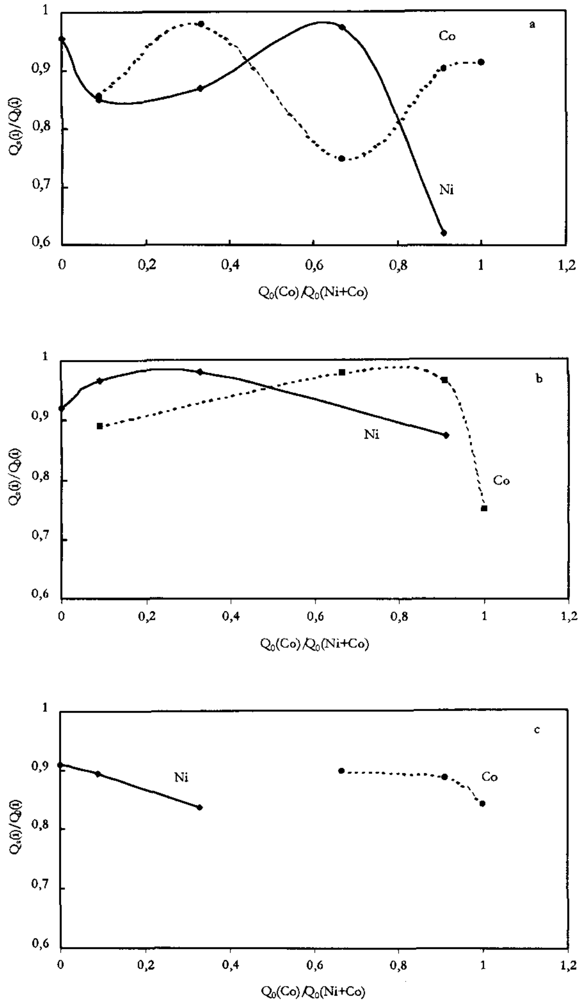

Figure 5. (a) The effect of Co^{2+} present in the Ni^{2+}-dominated solutions and *vice versa.* Initial concentration of i cation is 5 ppm and solid-to-liquid ratio is 1:100. (b) The effect of Co^{2+} present in the Ni^{2+}-dominated solutions and *vice versa.* Initial concentration of i cation is 10 ppm and solid-to-liquid ratio is 1:100. (c) The effect of Co^{2+} present in the Ni^{2+}-dominated solutions and *vice versa.* Initial concentration of i cation is 100 ppm and solid-to-liquid ratio is 1:100.

centration higher than the C_{CEC}; for Ni it is five times the CEC, whereas for Co it is a value twice the CEC.

Generally, at the same experimental conditions, the sorption results indicated an affinity of bentonite for Ni, which was confirmed by the steady state experiments (Figure 4). The relative abilities of the solute-ion species to compete for surface sites of bentonite is governed by intrinsic factors such as valence, ionic radius, pH, and the solution activities. Because the pH of the solution was kept constant and both Ni and Co are divalent cations, the selectivity depends entirely on the hydrated radii of the ions. With a radius of 4.04 Å, Ni is smaller than Co (radius = 4.23 Å) (Nightingale, 1959). Ni is more effective in reacting with the clay particles of bentonite because of its smaller size.

We assume that the solutions are dominated by the cation under study. Thus, the addition of Co to the Ni dominated solutions (Figure 5) acts to reduce the removal of the latter by bentonite. Nevertheless, at initial Ni concentrations of 5 ppm and Co between 50–70%, the phenomenon becomes "synergistic" (Figure 5a) and there is a substantial removal of Ni. Similar results occur at an initial Ni concentration of 10 ppm and Co <50% (Figure 5b).

In contrast, the presence of Ni apparently enhances Co removal. The results are generally synergistic, but there is an exception at low initial Co concentrations; Co retention is reduced ("antagonistic") when Ni is between 10–55% (Figure 5c).

The above results clearly indicate that Ni and Co removal by bentonite is influenced significantly by the ion species present in the reacting solution with results either synergistic or antagonistic. Note that there are a number of possible compounds of Ni and Co at a given valence. These compounds result from surface complex formation of the metal cations with a single coordinated OH group on the edges of the surfaces of smectites. Thus, a surface sorption mechanism may dominate in the simple ion-exchange mechanism. Further discussion of the possible complexes is beyond the scope of this paper. However, the nature of these compounds rather than the quantity is of prime importance for the adsorption process (Adeleye *et al.*, 1995).

CONCLUSIONS

Adsorption studies indicate that Na-activated bentonite readily retains Ni and Co. Contact time may be short (several minutes) for most adsorption to occur. Low solid-to-liquid ratios result in better sorption, but lower values of removal per unit mass of bentonite. Over-exchange appears when initial metal concentration exceeds the concentration corresponding to CEC. Compared to Co, Ni removal is favored probably due to its smaller ionic radius. The presence of both metals in the solution may favor greater sorption or reduce sorption effects depending on the initial ion concentrations.

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