Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Cheong, Jae Hak and Lee, Kun Jai(1996) 'Removal of Co^2 Ions from Aqueous Solution by Ferrite Process', Separation Science and Technology, 31: 8, 1137 — 1160
To link to this Article: DOI: 10.1080/01496399608001339
URL: http://dx.doi.org/10.1080/01496399608001339

SEPARATION SCIENCE AND TECHNOLOGY, 31(8), pp. 1137–1160, 1996

Removal of Co^{2+} Ions from Aqueous Solution by Ferrite Process

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ABSTRACT

A mathematical model was developed to investigate the characteristics of Co^{2+} removal by the pre-formed ferrite process. In this study, surface adsorption, hydrolysis-precipitation, and ion exchange were considered as Co^{2+} removal mechanisms, and incorporated into the model. In addition, a series of batch experiments was performed to remove Co^{2+} ions from aqueous solution, and the removal characteristics of Co^{2+} were analyzed by considering equilibrium pH, shaking time, ionic strength, and the effect of EDTA and Ca^{2+} as a chelating agent and a competing cation, respectively. Finally, the model proposed in this study was applied to the given experimental system, and it turned out that the pH-edge could be successfully predicted by the model. The experimental results were well-fitted by a Freundlich isotherm, and the standard enthalpy change of the reaction was 25.02 $kJ \cdot mol^{-1}$. The removal efficiency was slightly diminished by increasing the ionic strength and the initial concentration of Co^{2+}; however, the effect of the competing cation, Ca^{2+}, was negligible.

INTRODUCTION

Radionuclides existing in the low and intermediate level liquid radioactive wastes generated from nuclear power plants are generally classified into two types; activated corrosion products (mainly transition metals such as Fe, Co, Ni, etc.) and fission products (e.g., Cs, Sr, I, etc.). In the aspect of radiological safety, cobalt (^{58}Co and ^{60}Co), cesium (^{134}Cs and ^{137}Cs), and strontium (^{85}Sr and ^{90}Sr) are major radioactive isotopes

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because of their relatively long half-lives or high concentrations in the liquid wastes (1). Alkali metals (e.g., Cs) and alkaline earth metals (e.g., Sr) exist predominantly as ionic forms in an aqueous solution, and can be separated from the liquid wastes by conventional ion-exchange beds. On the other hand, the aquatic chemistry of cobalt is more complex and much different from the other metal cations coexisting in the liquid wastes. It has been reported that only a portion of cobalt can be removed using ion exchange because cobalt can exist in a variety of chemical forms such as soluble cations, multiply hydrolyzed forms, and colloidal species. Therefore, a series of separation processes such as ion exchange, filtration, and solution chemistry (e.g., pH, solute concentration, etc.) control has been proposed in order to enhance the removal efficiency for the cobalt species (1).

Ferrite is a ferromagnetic mixed valence iron oxide material which has the structure of ccp (cubic close packed) and inverse spinel (2, 3). The ferrite is generally represented by $MO{\cdot}Fe_2O_3$, where M is usually a divalent metal cation such as Fe^{2+}, Co^{2+}, Ni^{2+}, and Mg^{2+}. When M is a ferrous (Fe^{2+}) ion, the material ($FeO{\cdot}Fe_2O_3$ or Fe_3O_4) is termed as iron ferrite or magnetite. Natural magnetite (4) and synthetic magnetite (5, 6) with aging or further treatment have been studied as inorganic adsorbents for metal cation removal. The ferrite is a metal oxide and has common features with conventional inorganic adsorbents; high thermal and radiation stabilities, and great compatibility with the cement matrices that are likely to be used in radioactive waste disposal. Furthermore, it has also been reported that the solubility of the ferrite is very low and a variety of immobilization methods (e.g., cementation and vitrification) can be effectively applied. Especially in the aspect of final disposal safety, therefore, the ferrite process is expected to be applicable to the radioactive waste treatment system. In practice, magnetic materials such as iron ferrite have been used in the nuclear industry to separate actinides from aqueous waste (3), to extract uranium from seawater (7), and to remove corrosion products from the coolant of nuclear power reactors.

The iron ferrite can also be implemented into the liquid waste treatment system in another way, that is, as a ferrite process where freshly precipitated ferrite is directly used as a sorbent (3, 8, 9). It has been reported that the ferrite process has a lot of advantages over conventional chemical precipitation or ion exchange: 1) A variety of heavy metals can be simultaneously removed in one step; 2) Liquid wastes containing highly concentrated heavy metals can be effectively removed; 3) Removal efficiency is not affected by high salt concentrations; 4) Smaller amount of solids are formed and various separation techniques such as magnetic means as well as filtration or centrifugation can be implemented.

The ferrite processes (3) can be classified into an "in-situ process," in which the ferrite is precipitated within the liquid waste medium itself, and a "pre-formed process," where the ferrite is separately prepared in a small volume of aqueous solution and directly added into the waste solution. The ferrite is usually precipitated by increasing the solution pH, and therefore the pH of the total volume of the waste solution should be generally increased in the in-situ process. Compared to the pre-formed process, more chemical reagent such as NaOH is needed for the in-situ process, and this is economically disadvantageous. In addition, the remaining solution is further treated or diluted before discharge into the environment because of its highly alkaline characteristics. On the other hand, a smaller amount of NaOH is spent in the pre-formed process since the ferrite is pre-precipitated separately in a small volume of solution. That is, the pre-formed process is expected to be more practical for treating liquid radioactive wastes although the in-situ process has been reported to be slightly more efficient than the pre-formed process (3).

The metal-removal mechanisms in the ferrite process are very complex, and a few investigators have proposed a series of probable reaction mechanisms including conventional surface adsorption. Boyd et al. (3) proposed possible reaction mechanisms of the ferrite process such as surface adsorption and chemical incorporation of metal ions into the ferrite structure. Kochen and Navratil (8) reported that adsorption occurs through the metal hydroxide species in the ferrite process. However, only a few quantitative or systematic studies have been reported on the removal mechanisms of the ferrite process and on the mathematical modeling for individual metal ion removal.

We have tried to implement the ferrite process in order to remove radioactive transition metals such as cobalt from liquid radioactive wastes. Accordingly, the purpose of this study was to investigate quantitatively the removal characteristics of Co^{2+} ions in the pre-formed iron ferrite process, and to propose relevant reaction mechanisms and a suitable mathematical model. In addition, the effects of various operating conditions (e.g., reaction time, pH, temperature, ionic strength, amount of sorbent, etc.) were experimentally analyzed. The results of this study provide basic information for applying the ferrite process to the liquid radioactive waste treatment system.

MODEL DEVELOPMENT

Ferrite Formation

In the ferrite process of removing Co^{2+} ions from aqueous solution, two kinds of ferrites (iron ferrite and cobalt ferrite) are formed. The iron ferrite is formed at the beginning of the ferrite process as:

$$Fe^{2+} + 2Fe^{3+} + 4H_2O \Leftrightarrow FeO{\cdot}Fe_2O_3 + 8H^+, \qquad K_{IF} \qquad (1a)$$

where

$$K_{IF} = \frac{[FeO{\cdot}Fe_2O_3][H^+]^8}{[Fe^{2+}][Fe^{3+}]^2} \qquad (1b)$$

In the in-situ ferrite process, the iron ferrite is prepared in the waste solution itself. However, in the preformed ferrite process, the iron ferrite is separately synthesized and subsequently poured into the waste solution. The formation of iron ferrite is not a cobalt-removal mechanism but a reaction to prepare a sorbent for cobalt removal. Reaction constant and standard enthalpy change of the iron ferrite formation, Eq. (1a), are listed in Table 1 (10).

It is expected that cobalt ferrite ($CoO{\cdot}Fe_2O_3$), formation plays an important role in the in-situ ferrite process as a cobalt-removal mechanism as:

$$Co^{2+} + 2Fe^{3+} + 4H_2O \Leftrightarrow CoO{\cdot}Fe_2O_3 + 8H^+, \qquad K_{CF} \qquad (2)$$

where K_{CF} is the reaction constant of the cobalt ferrite formation reaction. In the case of the pre-formed ferrite process performed in this study, however, the iron ferrite is prepared before adding it into the Co^{2+}-containing waste solution. Accordingly, it can also be assumed that cobalt removal by the formation of cobalt ferrite will be negligible in the preformed ferrite process.

Hydrolysis and Precipitation of Co^{2+} Ions

One of the most important characteristics of Co^{2+} ions in aqueous solution is that they can be multiply hydrolyzed depending upon the solution chemistry such as pH and concentrations of chemical species. The Co^{2+} ions have been shown (11) to form mononuclear hydrolysis products ranging from $Co(OH)^+$ to $Co(OH)_4^{2-}$. The relative fraction of $Co(OH)_4^{2-}$ is known to be quite small and therefore is generally ignored in aqueous solution equilibrium problems. Therefore, only three of the aqueous hy-

TABLE 1
Reaction Constant and Standard Enthalpy Change of Iron Ferrite Formation

$\log K_{IF}$	-3.737
ΔH_{IF}	$+50.46$ kcal·mol^{-1}

drolyzed species, $Co(OH)^+$, $Co(OH)_2$, and $Co(OH)_3^-$, are considered in this study. The generalized hydrolysis reactions of Co^{2+} ions can be written as

$$Co^{2+} + nH_2O \Leftrightarrow Co(OH)_n^{2-n}(aq) + nH^+, \qquad K_{H,n} \tag{3a}$$

and

$$K_{H,n} = \frac{[Co(OH)_n^{2-n}(aq)][H^+]^n}{[Co^{2+}]} \tag{3b}$$

where n is the degree of hydrolysis and the reaction constants $K_{H,n}$ are listed in Table 2 (11).

The ferrite process has usually been performed at high pH (pH > 9) where the hydrolyzed cobalt species are predominant and can be adsorbed onto the iron ferrite surface (3, 9). The importance of the metal hydroxide species in the ferrite process has been reported by Kochen and Navratil (8).

In addition, one of the aqueous hydrolyzed cobalt species, $Co(OH)_2$ (aq), can be precipitated into the solid phase depending on the solution pH and total cobalt concentration. The hydrolysis and subsequent precipitation can also be an important cobalt removal mechanism, and it is described by the following equation:

$$Co(OH)_2(aq) \Leftrightarrow Co(OH)_2(s) \tag{4}$$

or

$$Co^{2+} + 2H_2O \Leftrightarrow Co(OH)_2(s) + 2H^+, \qquad K_{H,2s} \tag{5a}$$

where

$$K_{H,2s} = \frac{[Co(OH)_2(s)][H^+]^2}{[Co^{2+}]} \tag{5b}$$

TABLE 2
Reaction Constants of Hydrolysis and Precipitation of Co^{2+} Ions

	Hydrolysis	
log $K_{H,1}$	−9.90	Ref. 11
log $K_{H,2}$	−18.80	Ref. 11
log $K_{H,3}$	−31.50	Ref. 11
	Precipitation	
log $K_{H,2s}$	−12.10	Ref. 12

where (aq) and (s) represent the aqueous and solid phases, respectively. The reaction constant $K_{H,2s}$ is also listed in Table 2 (12).

Surface Adsorption

For the adsorption of metal ions onto the surface of metal hydroxides such as nickel ferrite [$NiO \cdot Fe_2O_3$ (13)], magnetite [Fe_3O_4 (4, 5)], hematite [α-Fe_2O_3 (4)], and amorphous iron oxyhydroxide (14), surface adsorption has been shown to be the most important mechanism for metal cation removal. Since iron ferrite is a metal hydroxide, it is expected that the adsorption of Co^{2+} ions onto the surface of iron ferrite will play an important role in the overall cobalt removal mechanisms. The importance of surface adsorption in the ferrite process has been reported by Boyd et al. (3) and Kochen and Navratil (8).

Therefore, we assumed that a portion of cobalt removal will be accomplished by the surface adsorption mechanism in the ferrite process. In this study, a surface complexation model, SGMA (14, 15), was used to consider the surface adsorption phenomena, and the electrostatic effect between the oxide surface and the aqueous phase was described by TLM (triple layer model).

The surface of metal hydroxides has generally shown amphoteric characteristics:

$$SOH_2^+ \Leftrightarrow SOH + H_s^+, \qquad K_{a1}^{int} \tag{6}$$

$$SOH \Leftrightarrow SO^- + H_s^+, \qquad K_{a2}^{int} \tag{7}$$

where

$$K_{a1}^{int} = \frac{[SOH][H^+]_s}{[SOH_2^+]}, \qquad K_{a2}^{int} = \frac{[SO^-][H^+]_s}{[SOH]} \tag{8}$$

The subscript "s" denotes the species existing at surface sites. The activity (or concentration) of a surface chemical species, X, with a charge of z can be related to the activity of X in the bulk solution by considering the potential barrier between the first plane (surface, in this case) and the second plane (bulk electrolyte, in this case) as

$$[X^z]_s = [X^z] \exp\left\{\frac{-ze\psi}{kT}\right\} \tag{9}$$

where $[X^z]_s$ is the concentration of ion X with charge z near the surface, $[X^z]$ is the concentration of X in the bulk solution outside the influence of the charged surface, k is the Boltzmann constant (= 1.380×10^{-23}

J·K^{-1}), e is the electronic charge ($= 1.6021 \times 10^{-19}$ C), ψ is the electrical potential in volts, and T is the absolute temperature in K.

To explain the effect of background electrolyte such as NaCl, the surface complexations of the electrolyte should be considered:

$$\mathrm{SOH} + \mathrm{Na_s^+} \Leftrightarrow \mathrm{SO^-\cdots Na^+} + \mathrm{H_s^+}, \qquad {}^*K_{\mathrm{Na^+}}^{\mathrm{int}} \tag{10}$$

$$\mathrm{SOH} + \mathrm{H_s^+} + \mathrm{Cl_s^-} \Leftrightarrow \mathrm{SOH_2^+\cdots Cl^-}, \qquad {}^*K_{\mathrm{Cl^-}}^{\mathrm{int}} \tag{11}$$

The adsorption of Co^{2+} ions onto the surface sites of iron ferrite can be written as

$$\mathrm{SOH} + \mathrm{Co_s^{2+}} \Leftrightarrow \mathrm{SO^-\cdots Co^{2+}} + \mathrm{H_s^+}, \qquad {}^*K_{\mathrm{Co^{2+}}}^{\mathrm{int}} \tag{12a}$$

where

$$ {}^*K_{\mathrm{Co^{2+}}}^{\mathrm{int}} = \frac{[\mathrm{SO^-\cdots Co^{2+}}][\mathrm{H_s^+}]}{[\mathrm{SOH}][\mathrm{Co_s^{2+}}]} \tag{12b}$$

In some adsorption experiments of metal cations onto inorganic adsorbents, the slope of the adsorption pH-edge is very steep, and this suggests that more than one proton is released per adsorbed metal cation. This phenomenon can be ascribed to the surface complexation of the hydrolyzed metal cations (14) onto the surface or the participation of the bidentate surface site (5). The surface complexation of a monohydrolyzed species of cobalt, Co(OH)$^+$, is often considered in the model as

$$\mathrm{SOH} + \mathrm{Co_s^{2+}} + \mathrm{H_2O} \Leftrightarrow \mathrm{SO^-\cdots CoOH^+} + 2\mathrm{H_s^+}, \qquad {}^*K_{\mathrm{CoOH^+}}^{\mathrm{int}} \tag{13a}$$

where

$$ {}^*K_{\mathrm{CoOH^+}}^{\mathrm{int}} = \frac{[\mathrm{SO^-\cdots CoOH^+}][\mathrm{H_s^+}]^2}{[\mathrm{SOH}][\mathrm{Co_s^{2+}}]} \tag{13b}$$

On the other hand, the participation of the bidentate surface site can be represented by

$$2\mathrm{SOH} + \mathrm{Co_s^{2+}} \Leftrightarrow (\mathrm{SO^-})_2\cdots \mathrm{Co^{2+}} + 2\mathrm{H_s^+}, \qquad {}^*B_{\mathrm{Co^{2+}}}^{\mathrm{int}} \tag{14a}$$

where

$$ {}^*B_{\mathrm{Co^{2+}}}^{\mathrm{int}} = \frac{[(\mathrm{SO^-})_2\cdots \mathrm{Co^{2+}}][\mathrm{H_s^+}]^2}{[\mathrm{SOH}]^2[\mathrm{Co_s^{2+}}]} \tag{14b}$$

The symbol B is used for the reaction constant when a surface reaction involves a bidentate surface site. Thus, the surface complexation reactions given in Eqs. (12a)–(14a) can be considered to participate in the overall cobalt removal mechanisms in the ferrite process.

Ion Exchange of Co^{2+} with Fe^{2+}

In some sorption experiments, it has been shown that an amount of metal cation is removed by the sorbent even in a low pH region ($pH < 4$) when the portion of the negatively charged surface sites (SO^-) is negligible. The metal removal efficiency has usually been underestimated by the surface complexation model (16) in this low pH region. This implies that another removal mechanism besides surface complexation exists in the low pH region. Park and Huang (17) reported that there are three modes of interfacial reactions in the removal of transition metal cations by the hydrous CdS surface; lattice exchange or chemical displacement as well as conventional adsorption and precipitation. In addition, Jeong and Lee (18) proposed a sorption model where adsorption and ion exchange occur simultaneously.

Accordingly, we assumed that ferrous (Fe^{2+}) ions existing in the iron ferrite structure take part in the overall cobalt removal mechanisms. That is, Co^{2+} ions in aqueous solution can be exchanged by Fe^{2+} ions in the iron ferrite structure:

$$Co^{2+} + FeO{\cdot}Fe_2O_3 \Leftrightarrow CoO{\cdot}Fe_2O_3 + Fe^{2+}, \qquad K_{IX} \tag{15a}$$

where

$$K_{IX} = \frac{[CoO{\cdot}Fe_2O_3][Fe^{2+}]}{[Co^{2+}][FeO{\cdot}Fe_2O_3]} \tag{15b}$$

The above reaction has been thoroughly investigated in the field of nuclear reactor coolant water chemistry, and the reaction constant of the reaction, Eq. (15b), has been reported by Massow et al. (19) as $\log K_{IX} = 7.29$ at 298.15 K. However, all the internal Fe^{2+} ions cannot be expected to participate in cobalt removal since a variety of surface species will interfere with the close approach of Co^{2+} ions to the internal structure of the ferrite. This effect is considered by introducing a parameter, α, which represents the fraction of Fe^{2+} ions that can participate in ion exchange with Co^{2+} ions, and which will be derived from the experimental data.

Mathematical Formulation

In this study the electric charge density of each plane can be written

$$\sigma_o = \left(\frac{F}{C_sA_s}\right)\left[\begin{array}{l}[\mathrm{SOH_2^+}] + [\mathrm{SOH_2^+\cdots Cl^-}] \\ -\ [\mathrm{SO^-}] - [\mathrm{SO^-\cdots Na^+}] \\ -\ [\mathrm{SO^-\cdots Co^{2+}}] - [\mathrm{SO^-\cdots CoOH^+}] \\ -\ 2[(\mathrm{SO^-})_2\cdots\mathrm{Co^{2+}}]\end{array}\right] \tag{16}$$

$$\sigma_\beta = \left(\frac{F}{C_sA_s}\right)\left[\begin{array}{l}[\mathrm{SO^-\cdots Na^+}] \\ +\ 2[\mathrm{SO^-\cdots Co^{2+}}] \\ +\ [\mathrm{SO^-\cdots CoOH^+}] \\ +\ [(\mathrm{SO^-})_2\cdots\mathrm{Co^{2+}}] - [\mathrm{SOH_2^+\cdots Cl^-}]\end{array}\right] \tag{17}$$

where F is the Faraday constant (96,485 $\mathrm{C\cdot mol^{-1}}$), σ_o and σ_β are the surface (o-plane) charge density and the charge density in the mean plane (β-plane) of specifically adsorbed counterions in $\mathrm{C\cdot m^{-2}}$, C_s is the concentration of the sorbent in $\mathrm{g\cdot L^{-1}}$, and A_s is the specific surface area in $\mathrm{m^2\cdot g^{-1}}$. The charge density in the diffuse layer at 298.15 K is given by the Gouy–Chapman theory (14, 20) as

$$\sigma_d = -(11.743)\sqrt{I}\,\sinh\left[\frac{ze\psi_d}{2kT}\right] \tag{18}$$

where z is the charge of the supporting electrolyte counterions in the diffuse layer.

All the chemical species and surface structure considered in this study are displayed in Fig. 1, where C_1 and C_2 represent the integral capacitances for the inner and outer regions of the compact layer, respectively, in $F\cdot\mathrm{m^{-2}}$. On the other hand, the electroneutrality throughout the interface must be met as

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \tag{19}$$

The surface charge–potential relationships have been generally reported by many investigators (14–16, 20) and also applied to the model calculation procedure of this study.

The material balance for the surface sites must be satisfied, and it can be written as:

$$N_s = \left(\frac{F}{C_sA_s}\right)\left[\begin{array}{l}[\mathrm{SOH}] + [\mathrm{SOH_2^+}] + [\mathrm{SO^-}] \\ +\ [\mathrm{SO^-\cdots Na^+}] + [\mathrm{SOH_2^+\cdots Cl^-}] + [\mathrm{SO^-\cdots Co^{2+}}] \\ +\ [\mathrm{SO^-\cdots CoOH^+}] + 2[(\mathrm{SO^-})_2\cdots\mathrm{Co^{2+}}]\end{array}\right] \tag{20}$$

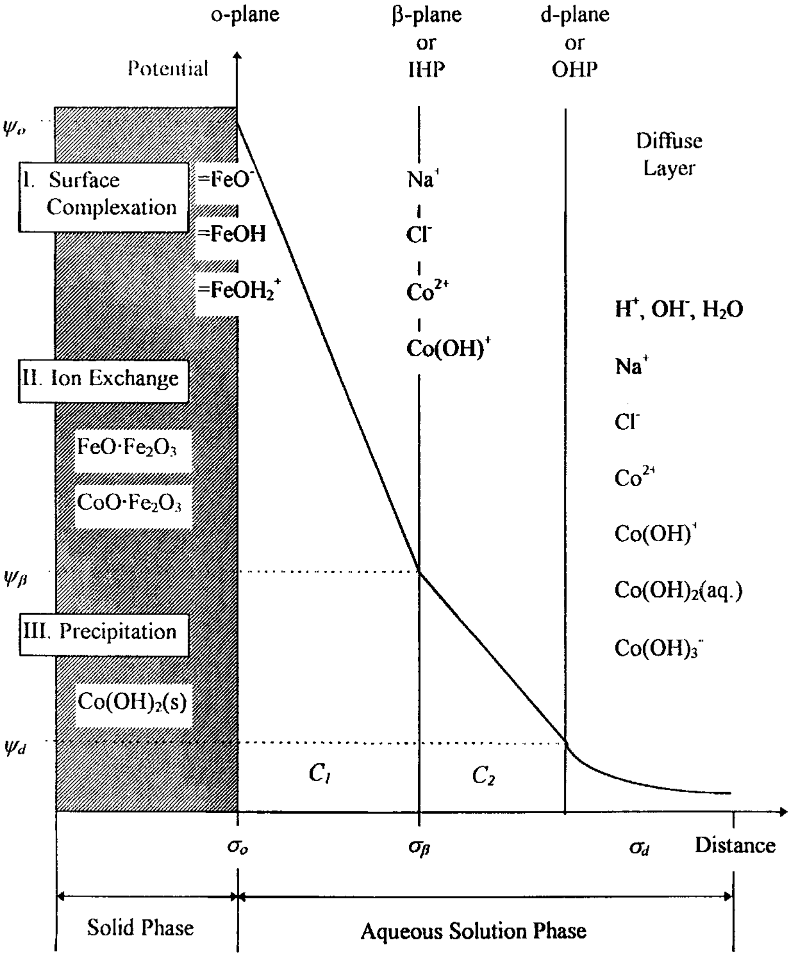

FIG. 1 Chemical species and surface structure considered in this study.

where N_s is the total number density of the surface sites in C·m^{-2}. On the other hand, the material balance for cobalt must also be met:

$$[Co^{2+}]_{TOT} = \begin{bmatrix} [Co^{2+}] + [CoOH^+] + [Co(OH)_2(aq)] + [Co(OH)_2(s)] \\ + [Co(OH)_3^-] + [SO^-\cdots Co^{2+}] + [SO^-\cdots CoOH^+] \\ + [(SO^-)_2\cdots Co^{2+}] + [CoO\cdot Fe_2O_3] \end{bmatrix} \tag{21}$$

Equation (21) is quite different from the material balance for the conventional SCM in that the precipitated species of cobalt and cobalt ferrite are additionally incorporated.

The nominal distribution coefficient (k_d) for cobalt removal in the ferrite process, k_d ($\mathrm{dm^3 \cdot kg^{-1}}$), can be written as:

$$k_d = \frac{\begin{bmatrix} [\mathrm{SO^- \cdots Co^{2+}}] + [\mathrm{SO^- \cdots CoOH^+}] \\ + [\mathrm{(SO^-)_2 \cdots Co^{2+}}] + [\mathrm{Co(OH)_2(s)}] \\ + [\mathrm{CoO \cdot Fe_2O_3}] \end{bmatrix}}{[\mathrm{Co^{2+}}] + [\mathrm{CoOH^+}] + [\mathrm{Co(OH)_2(aq)}] + [\mathrm{Co(OH)_3^-}]} \frac{V}{m} \tag{22}$$

where V is the total volume of the solution in $\mathrm{dm^3}$, and m is the expected dry mass of the iron ferrite formed (as $\mathrm{FeO \cdot Fe_2O_3}$) in kg. The nominal distribution coefficient defined in this study may differ from the conventional concept of distribution coefficient used in adsorption studies, since the ion exchange and precipitation as well as adsorption are considered as cobalt removal mechanisms. Therefore, it is expected that the nominal distribution coefficient will have a larger value compared to the conventional distribution coefficient which considers adsorption only.

The surface species given in Eqs. (16) and (17) can be rewritten by considering the mass action laws and electrostatic effects:

$$[\mathrm{SOH_2^+}] = \frac{[\mathrm{SOH}][\mathrm{H^+}]}{K_{a1}^{\mathrm{int}}} \exp\left\{\frac{-e\psi_o}{kT}\right\} \tag{23}$$

$$[\mathrm{SO^-}] = \frac{[\mathrm{SOH}]}{[\mathrm{H^+}]} K_{a2}^{\mathrm{int}} \exp\left\{\frac{+e\psi_o}{kT}\right\} \tag{24}$$

$$[\mathrm{SO^- \cdots Na^+}] = \frac{[\mathrm{SOH}][\mathrm{Na^+}]}{[\mathrm{H^+}]} {}^*K_{\mathrm{Na^+}}^{\mathrm{int}} \exp\left\{\frac{e(\psi_o - \psi_\beta)}{kT}\right\} \tag{25}$$

$$[\mathrm{SOH_2^+ \cdots Cl^-}] = \frac{[\mathrm{SOH}][\mathrm{H^+}][\mathrm{Cl^-}]}{{}^*K_{\mathrm{Cl^-}}^{\mathrm{int}}} \exp\left\{\frac{e(\psi_\beta - \psi_o)}{kT}\right\} \tag{26}$$

$$[\mathrm{SO^- \cdots Co^{2+}}] = \frac{[\mathrm{SOH}][\mathrm{Co^{2+}}]}{[\mathrm{H^+}]} {}^*K_{\mathrm{Co^{2+}}}^{\mathrm{int}} \exp\left\{\frac{e\psi_o - 2e\psi_\beta}{kT}\right\} \tag{27}$$

$$[\mathrm{SO^- \cdots CoOH^+}] = \frac{[\mathrm{SOH}][\mathrm{Co^{2+}}]}{[\mathrm{H^+}]^2} {}^*K_{\mathrm{CoOH^+}}^{\mathrm{int}} \exp\left\{\frac{2e(\psi_o - \psi_\beta)}{kT}\right\} \tag{28}$$

$$[(SO^-)_2 \cdots Co^{2+}] = \frac{[SOH]^2[Co^{2+}]}{[H^+]^2} \, {}^*B^{int}_{Co^{2+}} \exp\left\{\frac{2e(\psi_o - \psi_\beta)}{kT}\right\} \quad (29)$$

We have assumed that hydrolysis-precipitation, surface complexation, and ion exchange are the three modes of the cobalt removal mechanisms through the pre-formed ferrite process. The main stem of the model developed in this study is the SCM (surface complexation model) which simulates the surface adsorption phenomena of cobalt. The effects of hydrolysis-precipitation and ion exchange are to be incorporated into the SCM in terms of the material balances, Eq. (21), and the mass action laws, Eqs. (3b), (5b), and (15b).

All the equations written above can be solved by a numerical method (e.g., Newton–Raphson method) at a certain pH and bulk solution concentration when a series of required parameters is known (10, 14). In practice, all the equations presented here can be solved simultaneously by chemical equilibrium computer programs such as MINTEQA2 (10) and MINEQL+ (12). MINTEQA2 has been developed by Allison et al. of the US EPA and has been widely used for radionuclide sorption modeling by Turner et al. (21). In this study we used MINTEQA2 for the model calculation by providing related reaction stoichiometries, reaction constants, and any other necessary input parameters obtained from the experimental results.

EXPERIMENTAL

Materials and Instruments

All chemicals used in this study were of analytical grade or higher and used without further purification. Cobalt stock solution were prepared by dissolving $CoCl_2$ (Aldrich) in doubly distilled and deionized water. The pH of the aqueous solution was adjusted with 1.0 and 0.1 N NaOH solutions.

The pH of the aqueous solution was measured using an Orion pH meter (SA 720), and all pH adjustments were made by a magnetic stirrer with a glass-coated magnetic stirring bar. Shaking was accomplished by a reciprocating shaker equipped with a water bath (Lauda MS/2). The centrifugation was done with a Beckman centrifuge (J2-21M/E). The amount of cobalt species remaining after centrifugation in the supernatant was analyzed quantitatively by AAS (atomic absorption spectrophotometer; Perkin-Elmer 3100).

Preparation of Iron Ferrite

It has been reported that iron ferrite can be prepared by wet methods as well as dry methods, and the wet methods can be further classified into neutralization and oxidation methods (9, 22). In the neutralization method the iron ferrite can be prepared from an aqueous solution containing both ferric and ferrous ions by adding an alkaline solution:

$$Fe^{2+} + 2Fe^{3+} + ROH \rightarrow FeO{\cdot}Fe_2O_3 \tag{30}$$

On the other hand, an aqueous solution containing only ferrous ions is oxidized after an alkaline solution is added:

$$3Fe^{2+} + ROH + O_2 \rightarrow Fe_{1-x}O{\cdot}Fe_{2+x}O_3 \tag{31}$$

In this study we prepared the iron ferrite by the neutralization method and almost the same procedure used by Boyd et al. (3). Therefore, 0.025 mmol of ferrous sulfate ($FeSO_4{\cdot}7H_2O$) as a Fe^{2+} source and 0.050 mmol of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) as a Fe^{3+} source were dissolved in 2.00×10^{-2} dm^3 of water, and then NaOH was added to the solution until the pH matched the target point. Then the previously prepared solution was added to the Co^{2+}-containing solution without any other additional treatment.

Batch Experiments

A series of experiments was carried out by the batch method in 0.1 dm^3 polyethylene bottles at 25.0 ± 0.1°C. The pre-formed iron ferrite was added to 0.01 dm^3 of 1.70×10^{-3} M ($\approx$ 100 ppm) Co^{2+} solution. Then the total volume of the mixed solution was increased to 0.05 dm^3. The pH of the aqueous solution was adjusted to reach the equilibrium pH, 9.0 ± 0.1. Therefore, the concentration of the finally prepared Co^{2+} solution was 3.40×10^{-4} M ($\approx$ 20 ppm). The solution was equilibrated by shaking for 2 hours at 60 rpm, and then complete separation of the solid and aqueous phases was accomplished by high-speed centrifuging for 10 minutes at 12,000 rpm. The concentration of Co^{2+} species remaining in the supernatant was analyzed by AAS at 240.7 nm.

Removal Efficiency

The nominal distribution coefficient, Eq. (22), can be calculated from the experimental data by the following equation:

$$k_d = \frac{C_0 - C_f}{C_f}\frac{V}{m} \tag{32}$$

where C_0 is the initial concentration of Co^{2+} in ppm, and C_f is the final concentration of Co^{2+} in ppm. In this study the removal percentage, *P* (%), was also used to quantify the removal efficiency:

$$P = \frac{C_0 - C_f}{C_0} \times 100 = \frac{(100)k_d}{k_d + V/m} \tag{33}$$

RESULTS AND DISCUSSION

Effect of Shaking Time

In this study the removal of Co^{2+} ions using the pre-formed ferrite process was analyzed as a function of shaking time by varying the time from 3 to 960 minutes, as shown in Fig. 2. The reaction proceeded very rapidly up to 30 minutes. The cobalt removal percentage further increased very slowly with time after 30 minutes. More than 99% of cobalt was removed only after 3 minutes.

It is known that the reaction rate of the ferrite process is very high compared to conventional adsorption reactions, and this is one of the most important advantages of the process. For instance, 10 minutes (3) and 30 minutes (9) have been used as reaction times for the ferrite process. As Fig. 2 shows, there was no appreciable increase of the removal percentage after 120 minutes. Therefore, the shaking time for the other experimental systems was set to 120 minutes because the system could be considered to have reached a quasi-equilibrium state by that time.

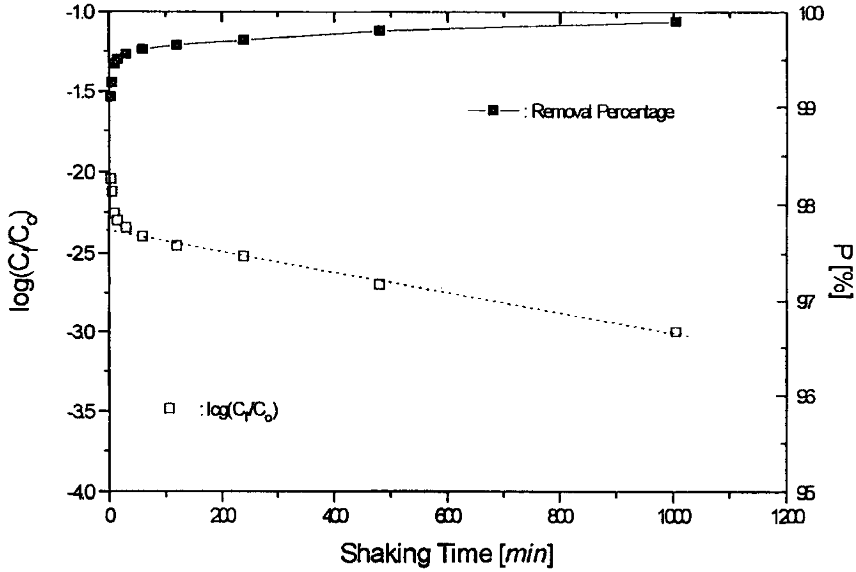

FIG. 2 The effect of shaking time on cobalt removal.

In general, sorption of metal cations on hydrous oxides is a two-step process consisting of a rapid initial uptake followed by a slower step in which the equilibrium sorption density is approached asymptotically. Figure 2 is consistent with these general phenomena. However, the first step proceeds more rapidly compared to the conventional adsorption reactions. This may be attributed to the participation of other cobalt removal mechanisms such as precipitation and ion exchange.

Also, a $\log(C_f/C_0)$ vs shaking time plot is simultaneously displayed in Fig. 2, and it shows that $\log(C_f/C_0)$ decreases linearly with shaking time (>30 minutes). This result is compatible with that of Choi (9) who reported that $\log(C_f/C_0)$ decreases linearly with time (30 to 120 minutes) in the ferrite treatment systems of Ni/Fe_3O_4 and Cr/Fe_3O_4 at pH 10.

Effect of Equilibrium pH

The effect of equilibrium pH on cobalt removal was studied by varying the solution pH from 3.9 to 12.5, and the results (i.e., pH-edge) are displayed in Fig. 3. The removal percentage increases with equilibrium pH, and increases sharply in the medium pH region (pH 6.5 to 8.0). The low removal percentage in the low pH region can be explained by the competitive adsorption of H^+ and Co^{2+} ions onto the adsorption surface sites.

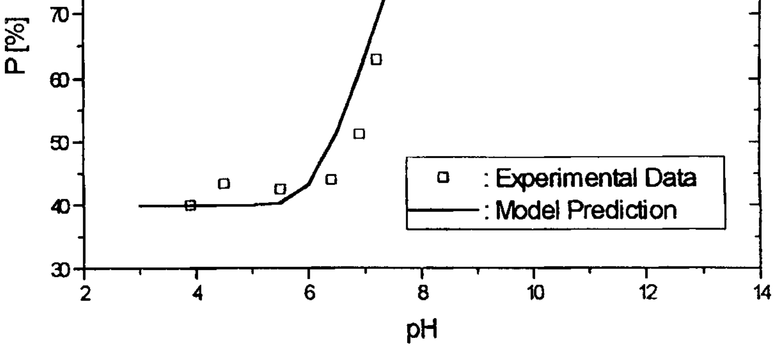

FIG. 3 The effect of equilibrium pH (pH 3.9 to 12.5) on cobalt removal.

The most conspicuous feature of the pH-edge is that an amount of Co^{2+} ions ($\approx$40%) is removed even in a low pH region (pH $<$ 3 or 4). This phenomenon may be due to the ion exchange of Co^{2+} ions in aqueous solution with Fe^{2+} ions existing in the iron ferrite structure. In this study a further increase of cobalt removal efficiency above pH 9 would result from the precipitation of Co^{2+} ions as $Co(OH)_2(s)$. Some investigators have also reported that the removal efficiency can be relatively high in metal/inorganic adsorbent systems at low pH values. For instance, Ahmad et al. (23) showed that about 40% of $^{60}Co^{2+}$ ions can be adsorbed onto a lateric mineral mixture at pH 3, and the removal efficiency remains constant even in a lower pH region (1 $\le$ pH $<$ 3).

All the parameter values used for our model calculations are listed in Table 3. The fraction of available $FeO{\cdot}Fe_2O_3$ participating in cobalt removal through ion exchange, α, was determined from the removal percentage in the low pH region (pH $<$ 4). The values of C_1 and C_2 were set to 1.4 and 0.2 $F{\cdot}m^{-2}$, respectively. These values have been generally adopted by many investigators (10, 14, 16). As a first attempt, log K_{a1} and log K_{a2} were set to 7.29 and -8.93, respectively, as proposed by Dzombak and Morel (16) for iron oxyhydroxide. In addition, log $^*K_{\mathrm{Co}_{2+}}$ and log $^*K_{\mathrm{CoOH^+}}$ were used as free parameters to fit the experimental data. As a result, the values of log $^*K_{\mathrm{Co2^+}}$ and log $^*K_{\mathrm{CoOH^+}}$ were determined to be -2.00 and -8.00, respectively. Results of the model prediction for the pH-edge using the parameter values given in Table 3 are shown in Fig. 3 as a solid line.

The specific surface area (A_s) of inorganic adsorbents has been generally reported (14) as hundreds of square meters per gram. In the case of activated carbon, however, Neely and Isacoff (24) reported that A_s ranges from 600 to 1200 $m^2{\cdot}g^{-1}$ and sometimes up to 3000 $m^2{\cdot}g^{-1}$. We have tried

TABLE 3
Values of Parameters Used in This Study

Parameter	Value	Parameter	Value
T	25°C	C_s	4.63×10^{-2} g·L^{-1}
V	5.00×10^{-2} dm^3	$[Fe_3O_4]_{TOT}$	2.00×10^{-4} M
$[Co^{2+}]_{TOT}$	3.39×10^{-4} M	α	0.675
$[Cl^-]_{TOT}$	6.79×10^{-4} M	log K_{IX}	+7.29
$[SOH]_{TOT}$	6.00×10^{-4} M	log K_{a1}	+7.29
A_s	5.00×10^3 m^2·g^{-1}	log K_{a2}	-8.93
C_1	1.40 F·m^{-2}	log$^*K_{\mathrm{Co2+}}$	-2.00
C_2	0.20 F·m^{-2}	log$^*K_{\mathrm{CoOH+}}$	-8.00

to calculate the theoretical A_s of the freshly precipitated iron ferrite in two different ways. First, we assumed that iron ferrite forms a monolayer sorbent, and the top and bottom sides of each ccp-unit cell take part in the surface adsorption. In this case, A_s can be easily calculated using the method presented by Greenland and Hayes (25):

$$\begin{aligned} A_s &= \frac{2a^2N_A}{M_{fw}} \\ &= \frac{2(8.391 \times 10^{-10}\ \text{m})^2(6.02 \times 10^{23}\ \text{mol}^{-1})}{(231.54\ \text{g·mol}^{-1})} \\ &= 3661\ \text{m}^2\text{·g}^{-1} \end{aligned}$$

where "2" is the factor involving the contribution of both top and bottom sides of each unit cell, a is the lattice parameter of $FeO{\cdot}Fe_2O_3$, and M_{fw} is the formula weight of $FeO{\cdot}Fe_2O_3$. On the other hand, it can also be assumed that each unit cell of the iron ferrite forms a corpuscular structure. In this case, A_s can be calculated by the equation proposed by Osick (26):

$$\begin{aligned} A_s &= \pi a^2 \frac{N_A}{M_{fw}} \\ &= \pi(8.391 \times 10^{-10}\ \text{m})^2 \frac{(6.02 \times 10^{23}\ \text{mol}^{-1})}{(231.54\ \text{g·mol}^{-1})} \\ &= 5751\ \text{m}^2\text{·g}^{-1}. \end{aligned}$$

These values represent the theoretical maximum of the specific surface area of the freshly precipitated iron ferrite.

In the model calculation, A_s of the freshly precipitated iron ferrite was set as 5.00×10^3 $m^2{\cdot}g^{-1}$. This value seems to be very high compared to those of conventional inorganic adsorbents; however, the extent of the increase of cobalt removal in the medium pH region (pH 6.5 to 8.0) could not be well simulated with lower values. The specific surface area decreases with drying, heating, or aging. In this study the iron ferrite is precipitated and added to the experimental system immediately after preparation without separation, aging, heating, or any other further treatments. Therefore, it can be expected that the actual surface area of the iron ferrite taking part in surface adsorption could be very high. The validity of the high A_s value used in the model prediction will be further studied later on.

The log C_f vs pH plot (pH 6.9 to 12.5) is shown Fig. 4. The plot fits the quadratic equation:

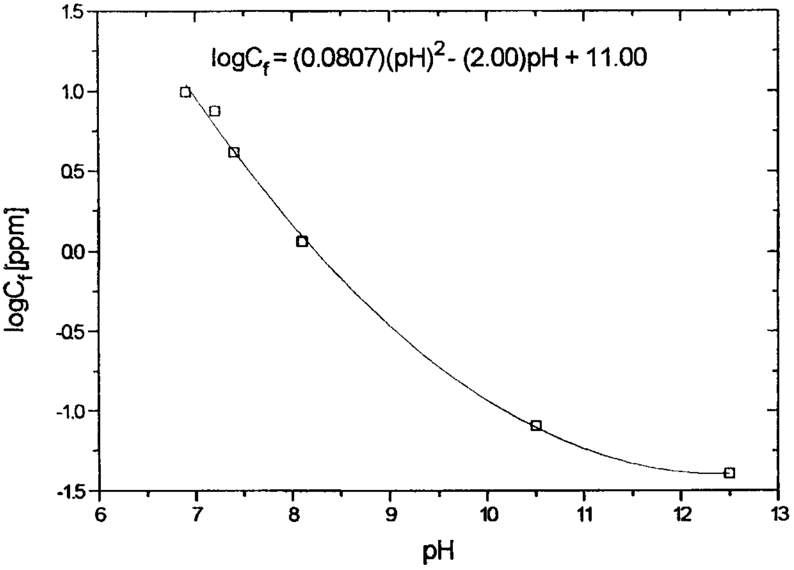

FIG. 4 The effect of equilibrium pH (pH 6.9 to 12.5) on cobalt removal.

$$\log C_f = (8.07 \times 10^{-2})(\mathrm{pH})^2 - 2.00\mathrm{pH} + 11.00 \tag{34}$$

This quadratic relationship has also been reported by Choi (9) for Ni/Fe_3O_4 and Cr/Fe_3O_4 systems in the given pH region (pH 7 to 12). However, the equation cannot be implemented in the low pH region (pH < 7) where log C_f decreases more rapidly with increasing pH. This implies that different reaction mechanisms predominate depending on the equilibrium pH, and thus agrees with the basic assumptions of this study.

Effect of Temperature

The temperature dependence of Co^{2+} removal was studied by performing batch experiments at 25, 35, 55, and 75°C. The standard enthalpy change of the overall ferrite process was assessed by the well-known van't Hoff equation:

$$\ln k_d = -\frac{\Delta H^\circ}{R}\frac{1}{T} + C \tag{35}$$

where ΔH° is the standard enthalpy change in $\mathrm{kJ \cdot mol^{-1}}$, R is the gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), T is the absolute temperature in K, and C is a constant.

Figure 5 shows the temperature dependence of the ferrite process. The standard enthalpy change which can be calculated from the slope of the fitted line was assessed as 25.02 kJ·mol^{-1}, and the overall reaction turned out to be endothermic. This value is comparable to that of a general ion exchange or chemisorption where the standard enthalpy change is normally about 8.37 kJ·mol^{-1} (27) and its maximum value is 41.86 kJ·mol^{-1}. In addition, Tamura et al. (5) reported that the standard enthalpy change of cobalt adsorption onto magnetite is 16.8 kJ·mol^{-1} ($\approx$ 4 kcal·mol^{-1}), and this value is close to the result of this study. The slight difference of the two values may be attributed to additional reaction mechanisms such as ion exchange and precipitation of cobalt species involved in the ferrite process.

Isotherms

The effect of initial Co^{2+} concentration was analyzed by varying the initial concentration of Co^{2+} from 1.70×10^{-5} to 1.70×10^{-3} M (1 to 100 ppm). It is generally known that this effect can be graphically represented as an isotherm, and we used the Freundlich isotherm to fit the experimental data in this study. The Freundlich isotherm is generally writ-

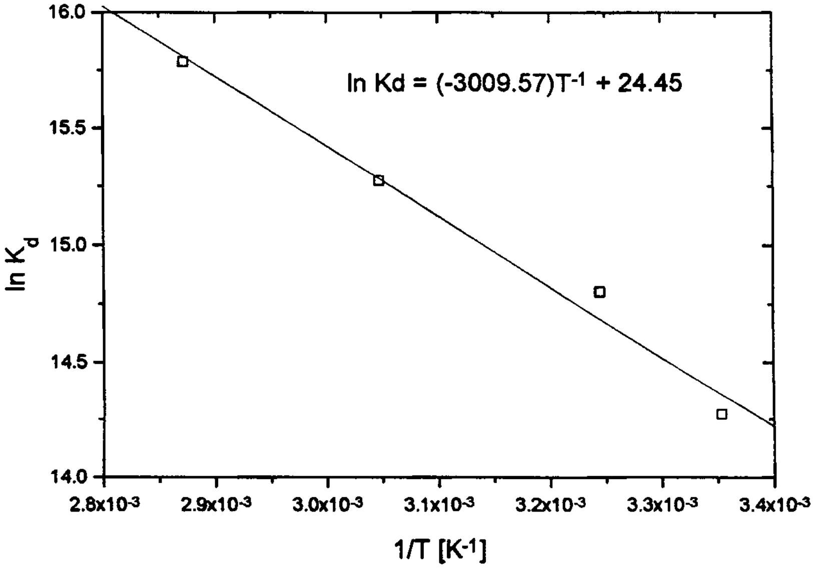

FIG. 5 The effect of temperature on cobalt removal (van't Hoff plot).

ten in logarithmic form:

$$\log X_s = \log P + \frac{1}{n} \log C_f \tag{36}$$

where X_s is the amount of cobalt existing in the unit mass of the solid phase in mg·g^{-1}, C_f is the equilibrium concentration of cobalt in the aqueous phase in ppm, and P and n are empirical constants for a specific system. In Fig. 6 the empirical constants P and n are found from the intercept and slope of the log X_s vs log C_f plot as 5.16×10^3 and 0.93622, respectively.

Effect of Ionic Strength

The effect of the ionic strength of the solution was studied by adding predetermined doses of NaCl electrolyte. The ionic strength of the solution was set to 0.01, 0.1, 0.5, and 1.0 N. As shown in Fig. 7, cobalt removal efficiency is diminished with increasing ionic strength; this has been confirmed by many investigators (28). However, even at a high ionic strength (1.0 N), the removal percentage of Co^{2+} is still high (≈ 90%). The small effect of the ionic strength may be because the electrostatic effect or

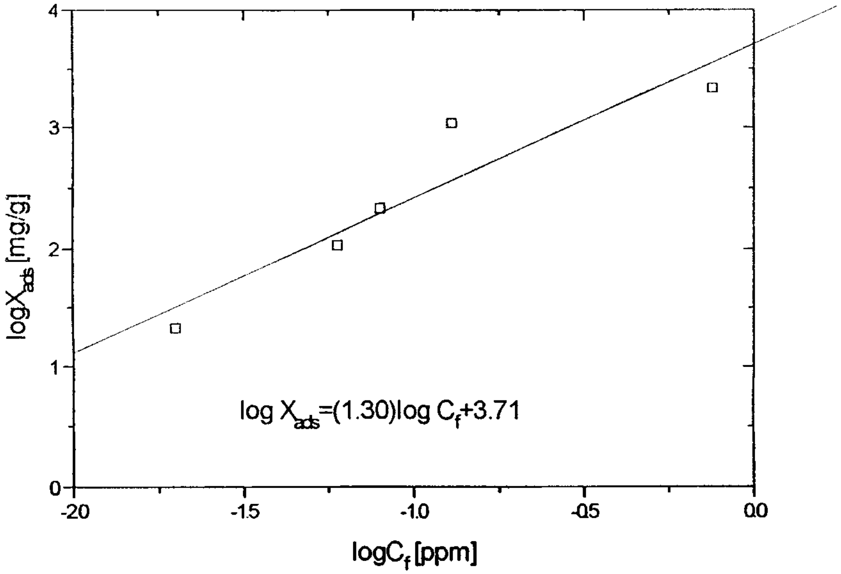

FIG. 6 Freundlich isotherm.

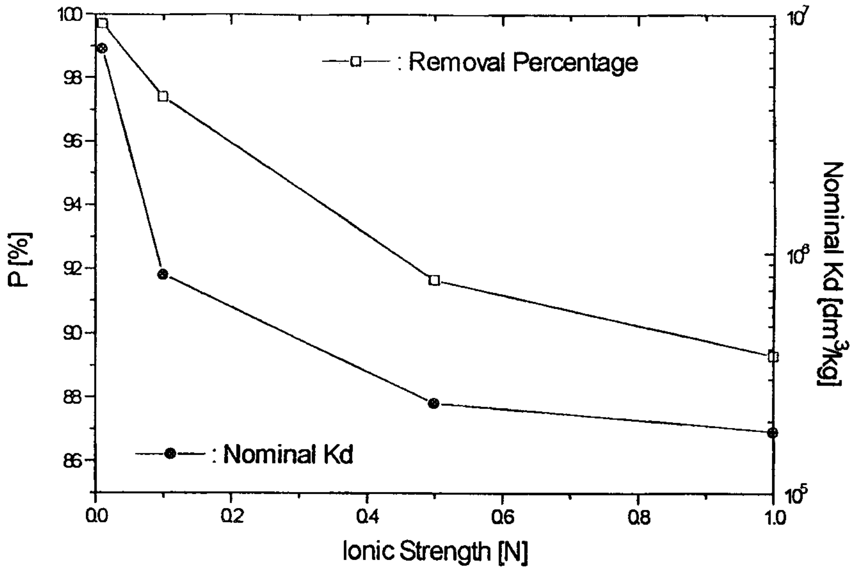

FIG. 7 The effect of ionic strength on cobalt removal.

the contribution of surface adsorption to overall cobalt removal may be relatively small compared to conventional adsorption reactions.

Effect of Chelating Agent

The effect of a synthetic organic chelating agent, EDTA (ethylenediaminetetraacetic acid), was studied by changing the concentration of the disodium salt of EDTA (Na_2EDTA) from 2.00 × 10^{-6} to 1.00 × 10^{-3} M. As shown in Fig. 8, the removal percentage is rapidly decreased when the total concentration of EDTA exceeds 1.00 × 10^{-5} M.

Effect of Competing Cations

The effect of Ca^{2+} ions on Co^{2+} removal by the ferrite process was analyzed. The doses of Ca^{2+} ions were varied from 2.00 × 10^{-6} to 1.00 × 10^{-3} M. It has been generally reported that Ca^{2+} ions compete with Co^{2+} ions and suppress the adsorption of Co^{2+} ions (28). In this study, however, no appreciable reduction of cobalt removal efficiency was observed up to a Ca^{2+} concentration of 1.00 × 10^{-3} M. This implies that the importance of surface adsorption at high pH (i.e., pH 9.0) is small or that Ca^{2+} ions do not compete with Co^{2+} ions in the ferrite process.

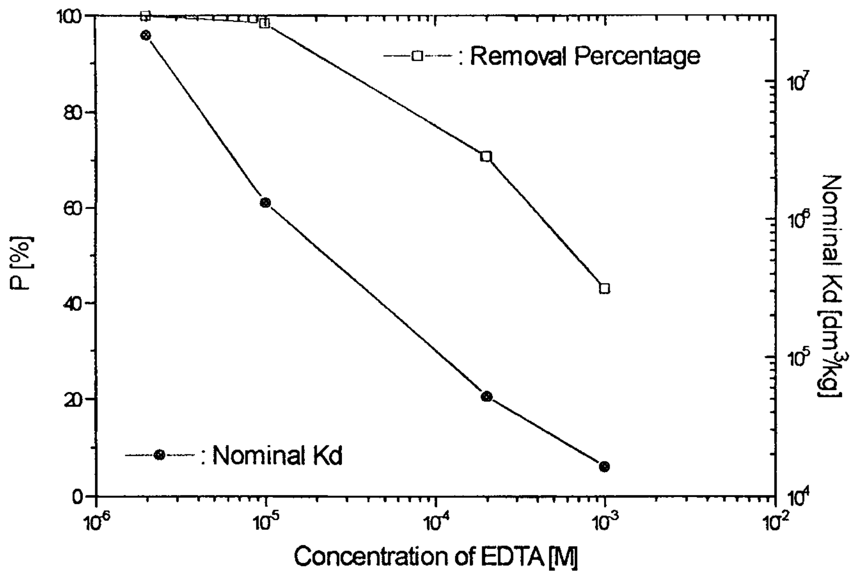

FIG. 8 The effect of EDTA on cobalt removal.

CONCLUSIONS

It has been shown that Co^{2+} ions in an aqueous solution can be effectively removed by using the preformed ferrite process with a relatively small amount of sorbent. Various factors and operating conditions affecting cobalt removal were analyzed by performing a series of batch experiments. As a result, the overall reactions turned out to be endothermic ($\Delta H^\circ = 25.02\ \text{kJ}\cdot\text{mol}^{-1}$), and the effects of ionic strength and chelating agent (EDTA) were relatively small compared with the conventional adsorption of Co^{2+} ions onto the surface of inorganic adsorbents.

In addition, the pH-edge shows a relatively high and constant cobalt removal efficiency in the low pH region ($pH < 4$), a typical surface adsorption curve in the medium pH region ($4 < pH < 8$), and an additional increase of removal efficiency in the higher pH region ($pH > 8$). The ferrite process has been quantitatively modeled by considering such probable removal mechanisms as ion exchange, surface complexation, and precipitation. Finally, it turned out that the pH-edge of the pre-formed ferrite process could be successfully predicted by the newly developed model in this study. From the experimental results of this study it can be anticipated that the ferrite process will show higher cobalt removal efficiency and require smaller amounts of such chemical reagents as NaOH in more alkaline aqueous waste solutions. Accordingly, the process will be suitable for removing radioactive transition metals from alkaline liquid waste streams such as evaporator concentrates.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Korea Science and Engineering Foundation through the Center for Advanced Reactor Research at the Department of Nuclear Engineering, KAIST.

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Received by editor July 26, 1995