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Characteristics of Cobalt Adsorption on Prepared TiO_2 and Fe-Ti-O Adsorbents in High Temperature Water

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ABSTRACT

TiO_2 and Fe-Ti-O adsorbents were prepared by hydrolysis of $Ti(OC_3H_7)_4$ and by alkalizing an equimolar mixed solution of $TiCl_4$ and $FeCl_2$, followed by heat treatment of their hydroxides. Their structures were studied by x-ray diffractometry and TG-DTA. The Co^{2+} adsorption characteristics of the adsorbent in high temperature water were investigated in a stirred autoclave. The prepared Fe-Ti-O adsorbent was found to be a stable nonstoichiometric ferrous/ferric titanium oxide with pseudobrookite and rutile structures. The Co^{2+} adsorption capacity of the Fe-Ti-O adsorbent was determined to be larger (0.38 meq Co^{2+}/g adsorbent at 280°C) than that of TiO_2 at high temperature. The enthalpy changes ($\Delta H°$) of about 34 and 49 $kJ \cdot mol^{-1}$ due to the adsorption of Co^{2+} on the TiO_2 and Fe-Ti-O adsorbents, respectively, indicates that the adsorption is endothermic in the experimental temperature range (150–280°C). It is shown that the specific surface areas of these adsorbents are not dominant factors for Co^{2+} adsorption on oxides at high temperature.

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INTRODUCTION

Inorganic adsorbents (1) for the removal of soluble corrosion products are attractive alternatives for water purification systems in pressurized water reactors or boiling water reactors (the major nuclear plant types in the world) because of the limitations of organic ion-exchange materials in their use: decomposition and oxidation at higher operating temperatures. Higher thermal efficiency and simplification of the clean-up system could be realized by using inorganic adsorbents made of stable oxides at reactor water conditions (150–280°C). The inorganic adsorbents also have an advantage for waste solidification.

A major radiation source in water-cooled reactors is activated corrosion products, mainly ^{60}Co, which is generally considered to be supplied from the primary side of nuclear reactors as Co^{2+} ions. Therefore, replacement of organic resin adsorbents, especially with such inorganic adsorbents compounds as $Zr_2(PO_4)_3$ (2), ZrO_2 (2–7), Al_2O_3 (3, 5), Fe_3O_4 (4), $NiFe_2O_4$ (3, 5), TiO_2 (8–10), TiO_2 supported on Al_2O_3 (11), and composite oxides [Al_2O_3-TiO_2 (12) and Fe-Ti-O (13)], which can be used in high temperature water, has been investigated. Among these inorganic adsorbents, TiO_2 has the highest selectivity for cobalt ion and is recommended for purification of the high temperature system. There are also several potential advantages in using composite oxides, particularly TiO_2-based oxides, with respect to enhancement of their adsorption capacity and hydrothermal stability with leaching resistance at high temperature. Co^{2+} adsorption in high temperature water is known to be mainly controlled by TiO_2 in the composite adsorbent. Thus, some efforts have been made to improve its adsorption capacity and/or selectivity by loading TiO_2 on substrates or by preparing various types of composites, such as supported TiO_2 on stable porous media and TiO_2-based composite oxides. However, few studies on the influence of the preparation methods on material characterization and adsorption characteristics of TiO_2 and Fe-Ti-O adsorbents have been reported.

The purpose of the present paper is to describe the preparation of TiO_2 and Fe-Ti-O adsorbents, to examine their material characterization, and to analyze the Co^{2+} adsorption characteristics of the two adsorbents (adsorption capacity, adsorption isotherm, and adsorption rate) by considering the influence of the preparation methods on adsorption at high temperature.

EXPERIMENTAL

Preparation of Co^{2+} Solution and Adsorbents

All chemicals were of GR grade quality and used without further purification. All Co^{2+} solutions were prepared with deionized water from a

NANOpure purification system (Barnstead 18.5 Mohm). $Co(NO_3)_2 \cdot 6H_2O$ was used for preparing stock solutions in which the Co^{2+} ion concentration was 5.0×10^{-5} mol·dm^{-3}. This concentration is low enough to avoid bulk precipitation of $Co(OH)_2$ at high temperature (14).

TiO_2 Adsorbent

The TiO_2 was prepared by using the sol–gel technique from an alkoxide starting material. The particulate $Ti(OH)_4$ sol solution was prepared by hydrolysis of titanium(IV) tetraisopropoxide [$Ti(OC_3H_7)_4$] while adding 7% ammonium hydroxide (NH_4OH) solution with a stirring speed of 1000 rpm at room temperature for 1 hour. The possible reaction for this hydrolysis is

$$Ti(OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH \quad (1)$$

The different pH values (pH 4–11) of the solution at the end of precipitation in the hydrolysis reaction were made constant before aging the solution overnight. The precipitate was filtered, washed with deionized water, and dried at 100°C. The dried powder was ground, sieved to 100–120 mesh size, and calcined at 600°C for 6 hours.

Composite Oxide (Fe-Ti-O) Adsorbent

A mixed particulate sol solution was prepared by alkalizing an equimolar mixture of 1 M ferrous(II) chloride ($FeCl_2 \cdot 4H_2O$) and 1 M titanium(IV) chloride ($TiCl_4$) solution while adding 2.5 M sodium hydroxide (NaOH) solution with a stirring speed of 1000 rpm at room temperature for 1 hour. The pH value at the end of precipitation was controlled to be 9. The resultant precipitate was aged overnight at the same temperature and pH as after the precipitation reaction, filtered with a 1.0-μm glass fiber filter, washed thoroughly with deionized water in a Soxhlet extractor until no chloride ions could be detected in the rinsed liquid, and dried at 100°C. The dried powder was then analyzed, and the molar ratio of Fe to Ti was found to be about 1. These powders were crushed and sieved, and a fraction of 100–120 mesh size was pressed into pellets (20-mm diameter, 10-mm high) without any binder. The pellets were formed in a cylindrical die at 4 MPa for 0.5 minutes. A typical firing cycle was ambient to 600°C at 10°C·min^{-1}, 600°C to the desired temperature at 5°C·min^{-1}, isothermal hold for 2 hours, and then cooled at 20°C·min^{-1} to room temperature in a box furnace (Nabertherm HT 16/17). The calcination temperatures used in this experiment were between 700 and 1400°C. The heat-treated samples were again crushed and sieved, and a fraction of 100–120 mesh size was used in the following experiments.

Batch Experiments

Adsorption experiments were carried out at elevated temperatures in a 1-dm^3 capacity stirred autoclave (Parr bench top reactor with magnetic drive), which was made of Hastelloy C-276 with a temperature controller (Parr model 4843) as shown in Fig. 1. The temperature in the autoclave was measured by type J thermocouples and maintained with an accuracy of ±2°C. The operation temperature range of the autoclave was 150–280°C. The adsorbed amount of Co^{2+} ion on the adsorbents with 100–120 mesh size particles was determined from the concentration change of the Co^{2+} solution after batch adsorption had reached equilibrium. Adsorption equilibrium time was about 5 hours for 0.2 g of the adsorbent in the stirred autoclave system containing 0.5 dm^3 cobalt solution. In order to avoid errors due to precipitation of $Co(OH)_2$ in the bulk solution, $pH_{25°C}$ was 7. During or after the adsorption experiment, a 5-cm^3 portion of the suspended solution was sampled, centrifuged at 3000 rpm for 10 minutes, and the Co^{2+} concentration of a small portion of the supernatant solution was measured.

Small changes in Co^{2+} concentration in the solution due to adsorption were determined by atomic absorption spectroscopy (Perkin-Elmer 5100PC).

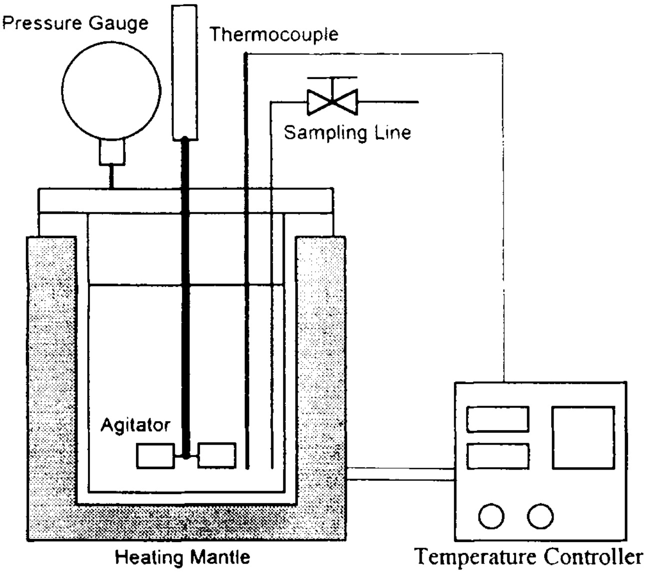

FIG. 1 Schematic diagram of high temperature apparatus.

The equilibrium concentration of Co^{2+}, C (mol·dm^{-3}), and the average amount of adsorbed Co^{2+} per unit adsorbent, q_{av} (mol·g^{-1}), are calculated from the initial concentration of Co^{2+}, C_0 (mol·dm^{-3}), and the fraction of the adsorbed Co^{2+}:

$$q_{av} = \frac{V(C_0 - C)}{W_s} \tag{2}$$

where V is the volume of the solution (dm^3) and W_s is the weight of adsorbent (g). The distribution coefficients, K_d (dm^3·g^{-1}), of Co^{2+} were calculated by the following equation:

$$K_d = \frac{C_0 - C}{C}\frac{V}{W_s} \tag{3}$$

Material Characterization

The specific surface areas of the adsorbents were obtained by the BET method at 77°K using a continuous flow method with the Quantachrome autosorb-6 sorption system (model AS-6/Po). The accuracy of the method was judged to be $\pm 2.5\%$ or better based on the measurements of standard reference materials with known surface areas. The mean apparent density was determined by the liquid pycnometer technique. Thermogravimetric and differential thermal analysis (TG-DTA) with the Netzsch system (STA 409) were used to characterize the thermal processing and crystallization behavior of prepared adsorbent. The rate of temperature increase for TG-DTA operation was 10°C·min^{-1}. The x-ray diffraction (XRD) patterns of the prepared adsorbents were measured to identify the crystal structures at room temperature with a Rigaku Denki (Max/3D) x-ray diffractometer, filtered CuKα_1 radiation (λ = 1.5418 Å) and CoKα_1 radiation (λ = 1.7889 Å) being used at a scanning rate of 2°·min^{-1}.

RESULTS AND DISCUSSION

Effect of Adsorption Temperature

The temperature dependence of Co^{2+} adsorption is exhibited in Fig. 2. The increased Co^{2+} adsorption capacity of the two adsorbents with temperature is attributed to the adsorption of hydrolyzed species of cobalt. Tewari et al. (3–5) reported that the adsorption of Co^{2+} on oxides increases with pH and temperature. Co^{2+} adsorption at high temperature seems to be due to increased hydrolysis of Co^{2+} accompanied by surface precipitation and formation of an insoluble $Co(OH)_2$ followed by reaction with substrate to form an oxide compound with the loss of water. The reaction mechanism suggested is as follows.

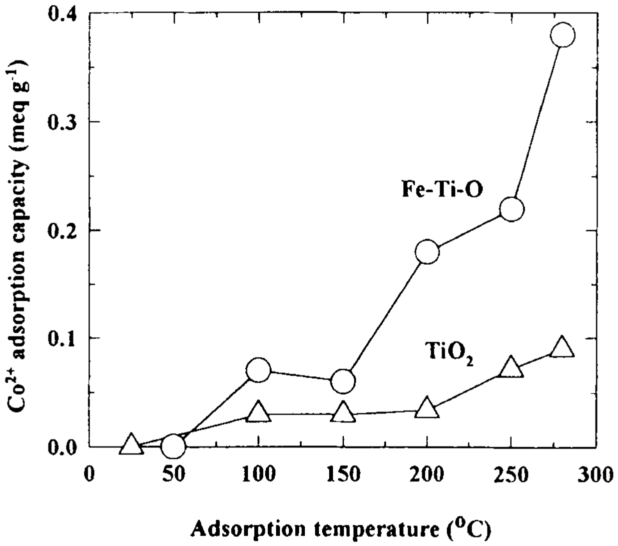

FIG. 2 Variation of Co^{2+} adsorption capacity of adsorbents with adsorption temperature. Initial Co^{2+} concentration: 5.0×10^{-5} mol·dm^{-3}. Adsorption time: 6 hours.

Surface precipitation with hydrolysis reaction:

$$Co^{2+} + H_2O \leftrightarrow Co(OH)^+ + H^+ \qquad (4)$$

$$Co^{2+} + 2H_2O \rightarrow Co(OH)_2(aq) + 2H^+ \qquad (5)$$

Adsorption reactions with substrate:

$$Co(OH)_2(aq) + TiO_2 \rightarrow CoTiO_3 + H_2O \quad \text{for } TiO_2 \text{ adsorbent} \qquad (6)$$

$$Co(OH)_2(aq) + Fe_xTi_yO_z \rightarrow Fe_xCoTi_yO_{z+1} + H_2O \quad \text{for Fe-Ti-O adsorbent} \qquad (7)$$

At high temperature, a strong adsorption mechanism such as the irreversible chemical reaction illustrated by Eqs. (6) and (7) would be dominant. High temperature conditions seem to increase multiple surface coverage of $Co(OH)_2$ by adsorption. Based on the preparation conditions which show favorable adsorption capacities, Co^{2+} adsorption capacity of the composite Fe-Ti-O was found to be about 4 times larger than that of TiO_2 alone at high temperature, as shown in Fig. 2. This is probably due to the electrical conductivity of the crystals, which is higher in the composite oxide compared to TiO_2 alone. Accordingly, it seems that the interaction of the relatively large Co^{2+} ions on the surface of the Fe-Ti-O adsorbent is more favorable than the corresponding interaction onto the surface of TiO_2.

The temperature dependence of adsorption equilibrium, in general, is related to standard enthalpy change by the following equation (van't Hoff equation):

$$\ln K_d = -\frac{\Delta H^\circ}{2.303RT} + C \tag{8}$$

where K_d = distribution coefficient ($cm^3 \cdot g^{-1}$) defined as the ratio of the concentrations of Co^{2+} in the adsorbent and in the solution
ΔH° = standard enthalpy change ($kJ \cdot mol^{-1}$)
R = gas constant ($kJ \cdot K^{-1} \cdot mol^{-1}$)
T = temperature (K)
C = constant

The distribution coefficients (K_d) of Co^{2+} ions as a function of the temperature for TiO_2 and Fe-Ti-O adsorbents are plotted in Fig. 3. Analysis of the slope gives ΔH° of about 34 and 49 $kJ \cdot mol^{-1}$, respectively. The standard enthalpy change of the adsorption reaction of Co^{2+} on prepared adsorbents indicates that the reactions are endothermic and their enthalpy

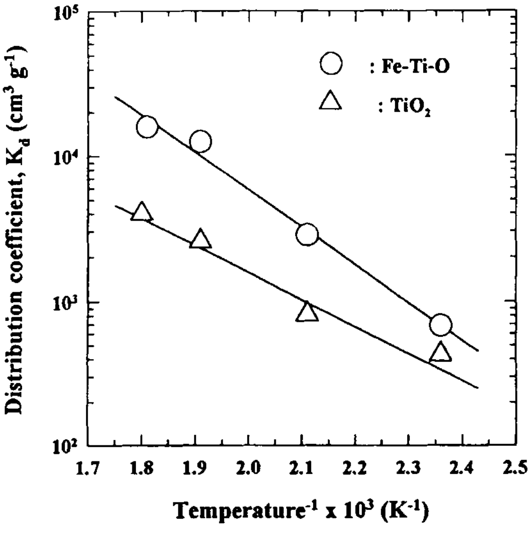

FIG. 3 Distribution coefficient versus temperature. Initial Co^{2+} concentration: 5.0×10^{-5} $mol \cdot dm^{-3}$. Adsorption time: 6 hours.

change is much higher than that of simple ion-exchange reactions. The ion-exchange reactions are generally known to have smaller values of enthalpy changes than 8.4 kJ·mol^{-1}, and the enthalpy changes due to Co^{2+} adsorption on the surface of TiO_2 and Fe-Ti-O adsorbents also exceed that of the dissolution of $Co(OH)_2$ (~19 kJ·mol^{-1}). This result can be explained by multilayer adsorption at higher coverages. At high temperatures the adsorbed cobalt might react with the substrate to produce oxide compounds containing cobalt. The larger values of $\Delta H°$ for cation adsorption on the surface of TiO_2 are probably connected with the formation of spinel-type compounds ($CoTiO_3$), while those of Fe-Ti-O with the formation of nonstoichiometric mixed oxides ($Fe_xCoTi_yO_{z+1}$).

Effect of Preparation pH on Adsorption Capacity of TiO_2

The effects of the preparation pH of TiO_2 adsorbent on the specific surface area and Co^{2+} adsorption capacity are shown in Fig. 4. The specific surface area of the TiO_2 adsorbent increases and the mean pore radius decreases with an increase in the preparation pH at 25°C. The TiO_2 adsorbent showed its maximum adsorption capacity when it was prepared at pH 9. It is known that micropores (less than 20 Å) do not make a contribution to the adsorption of the cobalt complex. A specific surface area with

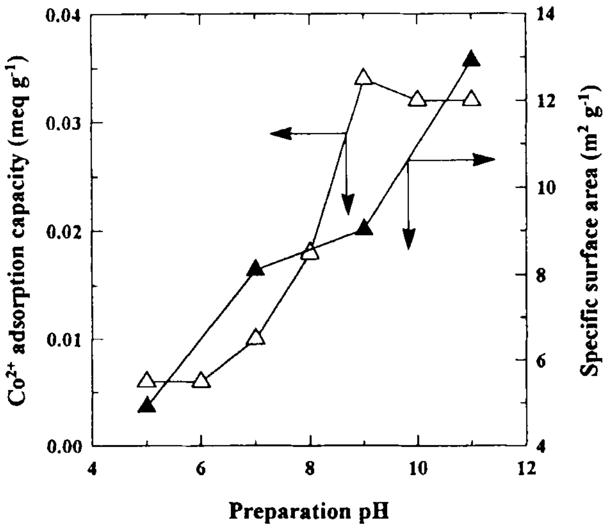

FIG. 4 Effect of preparation pH on specific surface area and adsorption capacity of TiO_2. Calcination temperature: 600°C. Initial Co^{2+} concentration: 5.0×10^{-5} mol·dm^{-3}. Adsorption temperature: 200°C for 6 hours.

a relatively large fraction of micropores is not effective for Co^{2+} adsorption, as shown in Fig. 4, and it seems likely that pores in the mesopore range would be needed if hydrated Co^{2+} ions are to diffuse into pores coated with $Co(OH)_2$ precipitated layers.

Figure 5 shows the x-ray powder diffraction patterns of TiO_2 adsorbent prepared at pH value of (a) 10, (b) 7, and (c) 4, and calcined at 600°C for 6 hours. The peaks for anatase become more dominant and intense with increasing pH. Only anatase peaks appear at pH 10, both anatase and

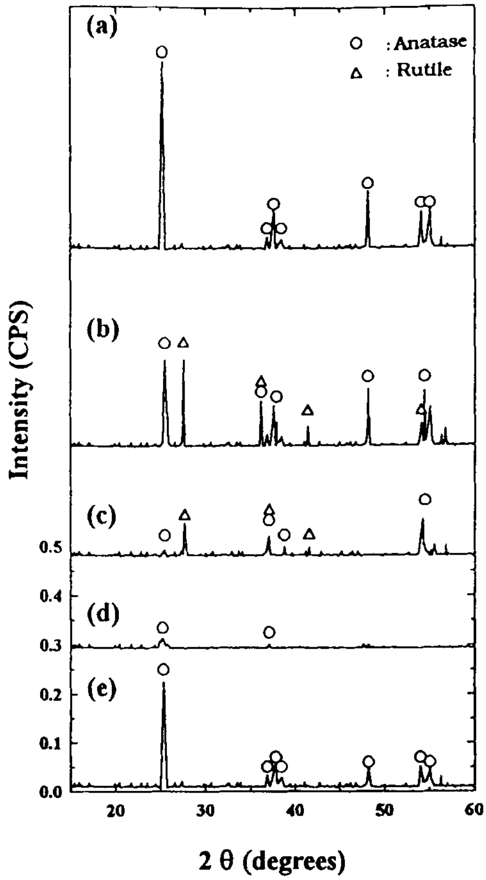

FIG. 5 X-ray diffraction patterns of TiO_2 adsorbents prepared at (a) pH 10 followed by heat treatment at 600°C, (b) pH 7 followed by heat treatment at 600°C, (c) pH 4 followed by heat treatment at 600°C, (d) pH 10 followed by hydrothermal heat treatment at 150°C, and (e) pH 10 followed by hydrothermal heat treatment at 250°C for 6 hours.

rutile peaks are observed at pH 7, and rutile with a trace of anatase peaks exists at pH 4. The percentage of each phase present was determined using the diffraction peak intensities at the (110) peak of the rutile phase and at the (101) peak of the anatase phase at diffraction angles (2θ) of 27.4 and 25.3°, respectively. As shown in Table 1, these results indicate that a higher pH value led to an increase in the concentration of the anatase phase. The apparent densities of the TiO_2 adsorbents prepared at a pH range of 4–10 were about 3.4–3.9 $g \cdot cm^{-3}$. The peaks in (d) and (e) of Fig. 5 show the anatase type of TiO_2 prepared by hydrothermal heat treatment at 150 and 280°C, respectively. Because of the lack of hydrothermal stability (mechanical hardness), TiO_2 adsorbents prepared by hydrothermal heat treatment were found to be easily redispersed as fine particles in high temperature water. Therefore, hydrothermally treated TiO_2 was not used as an adsorbent in the present study.

Effect of Heat Treatment of Fe-Ti-O on Adsorption Capacity

Figure 6 shows the effect of heat treatment temperature on the adsorption capacity of Fe-Ti-O. At a heat treatment temperature of about 1200–1350°C, superior values were obtained in spite of a lower specific surface area in comparison with TiO_2.

In Fig. 7, patterns (a) and (b) illustrate the x-ray diffraction data of Fe-Ti-O powders heat-treated at 1000 and 1350°C, respectively. Pattern (c) in Fig. 7, which is for Fe-Ti-O without heat treatment at room temperature, is shown in comparison with heat-treated Fe-Ti-O. Neither the anatase phase of TiO_2 nor the spinel-like structure of the magnetite phase ($FeO \cdot Fe_2O_3$) is detected in heat-treated Fe-Ti-O whereas these phases appeared in Fe-Ti-O without heat treatment. The x-ray patterns of Fe-Ti-O adsorbents calcined at 1000 and 1350°C for 2 hours showed that phases corresponding to pseudobrookite and rutile structures were present, de-

TABLE 1
Effects of Preparation pH on TiO_2 Characterization

Preparation pH	Apparent density ($g \cdot cm^{-3}$)	Specific surface area ($m^2 \cdot g^{-1}$)	Phase present (%)	
			Anatase	Rutile
4.0	3.91	6.6	22	78
7.0	3.7	8.1	50	50
10.0	3.46	10.9	95	5

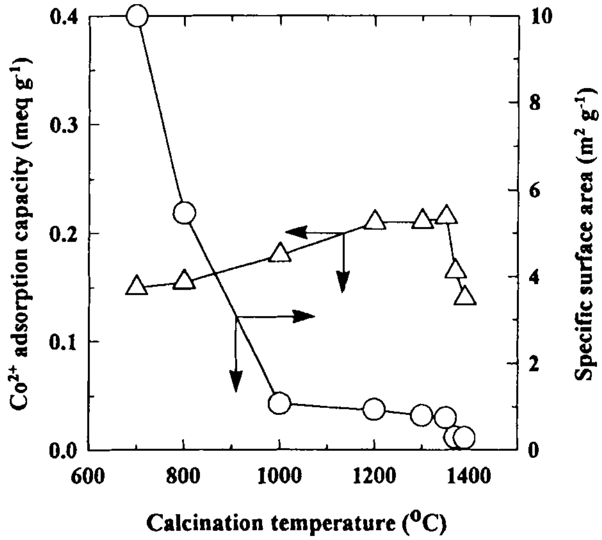

FIG. 6 Effect of calcination temperature on Co^{2+} adsorption capacity of Fe-Ti-O adsorbents. Initial Co^{2+} concentration: 5.0×10^{-5} mol·dm^{-3}. Adsorption temperature: 250°C for 6 hours.

spite the fact that different conditions of heat treatment were used. This result indicates that there is no significant change in the phase composition of the resultant adsorbents due to a temperature change of heat treatment except for the intensity of pseudobrookite structure at room temperature. The adsorbents prepared here have a stable phase at room temperature, and their synthesis requires slow cooling from the calcination temperature. Mixtures of $FeO{\cdot}Fe_2O_3$, and TiO_2 (molar ratio Fe:Ti = 1:1) that are allowed to cool down to room temperature over a period of hours yield Fe-Ti-O composite oxide with a pseudobrookite phase as its major constituent and a small portion of rutile phase. This is typical of nonstoichiometric iron titanium oxide, and suggests that the starting ferrous oxide is partly oxidized during precipitation and calcination in air. These results show that a pseudobrookite-type structure is good for Co^{2+} adsorption and is more stable at high temperature than are other structures. However, heat treatment of the mixed oxide below about 1200°C led to an unstable structure and to a decreased adsorption capacity because of the growth of a decomposition product (rutile) at low temperature. The electrical conductivity of the pseudobrookite-type structure might enhance Co^{2+} adsorption due to an increase of the possibility of valence oscillation be-

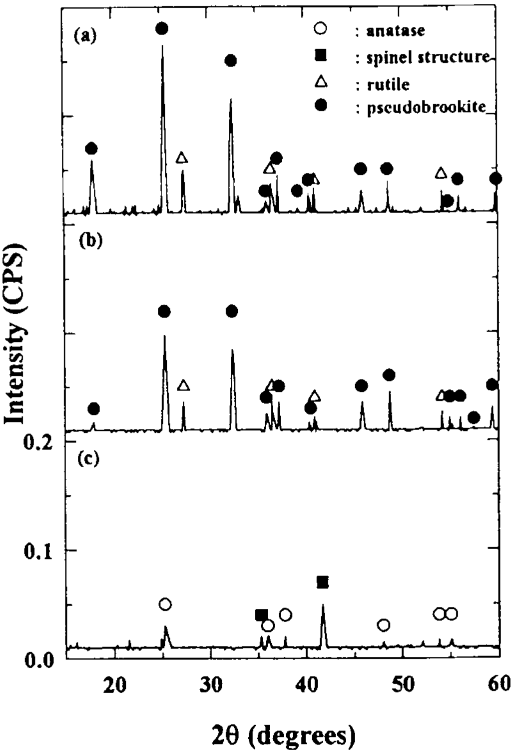

FIG. 7 X-ray powder diffraction patterns of Fe-Ti-O adsorbents heat-treated at (a) 1350°C, (b) 1000°C, and (c) their composite hydroxide before heat treatment.

tween Fe^{2+} and Fe^{3+} sites (15) in contrast to the ilmenite structure of ferrous titanium oxide ($Fe^{II}Ti^{IV}O_3$).

The result of TG-DTA for the prepared Fe-Ti-O adsorbent which was heat-treated at 1350°C is shown in Fig. 8. The DTA profile indicates that a large amount of melting phase was starting to form at 1500°C; there is a single endothermic reaction within a relatively narrow temperature range and then a small weight loss due to evaporation at about 1550°C. These results suggested that the prepared composite oxide was formed as a kind of single phase compound even though its constituents have no congruent melting. The pseudobrookite region corresponding to an equivalent molar ratio of Ti to Fe in the ternary phase diagram of the $FeO-Fe_2O_3-TiO_2$ system with a liquidus temperature line (16) suggests that the Fe-Ti-O

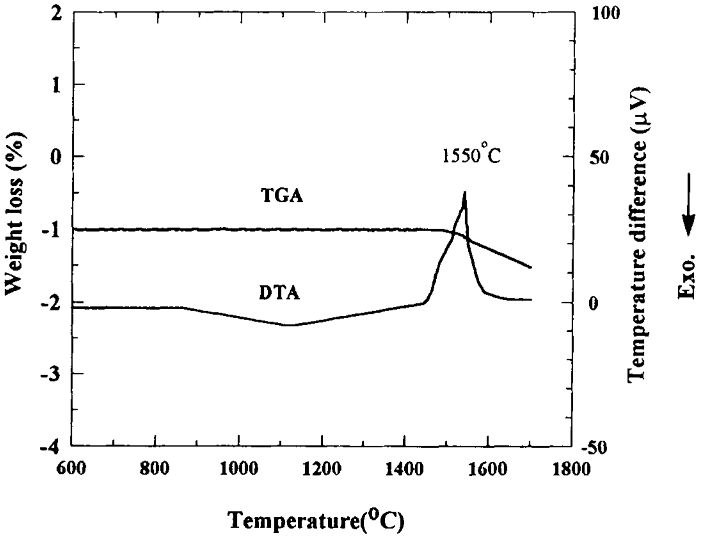

FIG. 8 TG-DTA curve of Fe-Ti-O adsorbent prepared by heat treatment at 1350°C.

adsorbent is nonstoichiometric ferrous and ferric titanium oxide (FeO: Fe_2O_3:TiO_2 ≅ 0.4:0.1:0.5).

After completion of each experiment of Co^{2+} adsorption, neither ferrous/ferric nor titanium ions could be detected in the solution. This result indicates that the adsorbents of Fe-Ti-O have sufficient hydrothermal stability to serve as high temperature adsorbents.

Co^{2+} Adsorption Isotherm and Adsorption Rate

Figure 9 shows the results of adsorption isotherms at 250°C. They can be correlated by the following Freundlich-type equations:

$$q = 0.2C^{1/6.21} \quad \text{for } TiO_2 \tag{9}$$

$$= 1.79C^{1/4.1} \quad \text{for Fe-Ti-O} \tag{10}$$

This was done with a particle weight of 0.05 to 1 g and a solution volume of 0.5 dm^3 with an initial concentration (C_0) range of 1×10^{-5} to 5×10^{-4} $mol \cdot dm^{-3}$.

Assuming that intraparticle diffusion is the rate-limiting step in adsorption, Saulyev's two-point average method was used to estimate the intraparticle diffusivity for a nonlinear (Freundlich-type) isotherm from con-

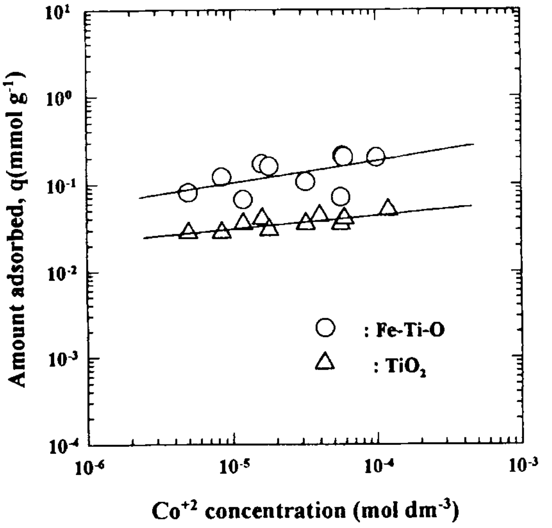

FIG. 9 Log Co^{2+} adsorbed versus log equilibrium Co^{2+} solution concentration on the TiO_2 and Fe-Ti-O adsorbents. Adsorption temperature: 250°C. Adsorption time: 6 hours.

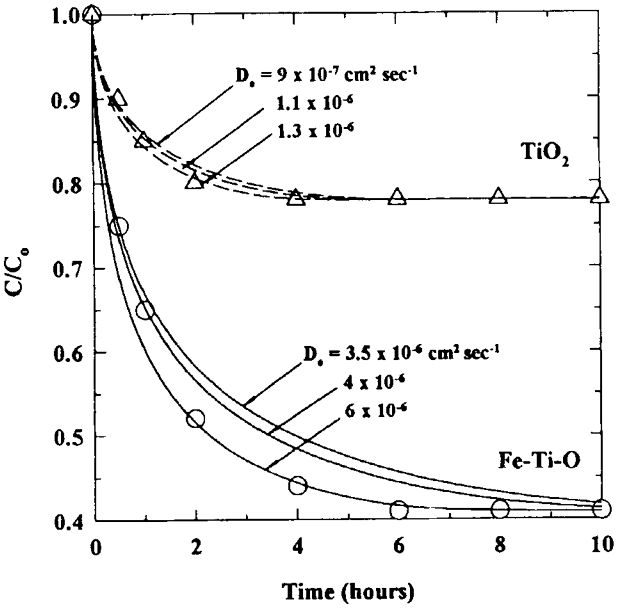

FIG. 10 Adsorption curves for estimation of intraparticle diffusion controlling. (○, △) Experimental data. (——, – –) Theoretical curves. Initial Co^{2+} concentration: 5.0×10^{-5} mol·dm^{-3}. Adsorption temperature: 250°C.

TABLE 2
Calculated Values of the Intraparticle Diffusion Coefficients

Adsorption temperature (°C)	Intraparticle diffusion coefficient, D_e (cm^2/s)	
	TiO_2	Fe-Ti-O
200	8×10^{-7}–9.5×10^{-7}	8.5×10^{-7}–1×10^{-6}
250	9×10^{-7}–1.3×10^{-6}	3.5×10^{-6}–6×10^{-6}

centration decay in a stirred batch adsorber by numerical calculation (17, 18). Then the isotherm curves can be used for curve fitting to find the relation of C_∞/C_0 and t, which gives the values of the intraparticle diffusion coefficient, D_e. In Fig. 10 the theoretical curves obtained for intraparticle diffusion kinetics in the Freundlich isotherm system are plotted with the experimental data for $C_\infty/C_0 = 0.41$ and 0.78 for Fe-Ti-O and TiO_2, respectively. The agreement of experimental data and the curves suggests that the rate of adsorption is controlled by intraparticle diffusion in both TiO_2 and Fe-Ti-O particles. The effective diffusion coefficients of Co^{2+} ion in TiO_2 and Fe-Ti-O particles thus determined in this study are listed in Table 2.

CONCLUSION

The inorganic adsorbents of TiO_2 and Fe-Ti-O were prepared under various experimental conditions and tested for Co^{2+} adsorption at high temperature. The TiO_2 prepared from its hydroxide sol at the aging condition of pH 9 and the Fe-Ti-O heat-treated at 1350°C were shown to have the most favorable adsorption capacities. When these adsorbents were applied in a solution containing Co^{2+} of 5×10^{-5} mol·dm^{-3} at 280°C in batch adsorption experiments, the Fe-Ti-O type composite oxide was found to have a larger adsorption capacity of Co^{2+}, about 0.38 meq·g^{-1}, while TiO_2 alone had only about 0.09 meq·g^{-1} capacity. The enthalpy changes connected with the adsorption of Co^{2+} on the prepared adsorbents are endothermic and suggest that the Co^{2+} adsorption mechanism is accompanied by a certain irreversible chemical reaction. The specific surface area of adsorbents is not a dominant factor for Co^{2+} adsorption on oxides at high temperature, especially in Fe-Ti-O. The prepared Fe-Ti-O adsorbent was a stable nonstoichiometric ferrous/ferric titanium oxide with pseudobrookite and rutile structures. Titanium-based types of composite oxides like Fe-Ti-O seem to be powerful high temperature adsorbents and can be recommended for the removal of ionic contaminants in the primary cooling water of nuclear power plants.

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