

ADSORPTION OF COBALT(II) ION BY TITANIUM-BASED OXIDES IN HIGH TEMPERATURE WATER

Kwang-Rag Kim[†], Sung-Ho Lee, Seung-Woo Paek, Hongsuk Chung and Jae-Hyung Yoo

Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejeon 305-600, Korea

(Received 9 March 1998 • accepted 20 November 1998)

Abstract – Titanium-based adsorbents such as TiO₂ and Fe-Ti-O were prepared by hydrolysis of Ti(OC₃H₇)₄ and alkalizing an equimolar mixed solution of TiCl₄ and FeCl₃ followed by heat treatment of their hydroxides, respectively. The prepared Fe-Ti-O adsorbent was found to be stable nonstoichiometric ferrous and ferric titanium oxides with pseudobrookite and rutile structures. The Co²⁺ adsorption characteristics of the adsorbent in high temperature water were investigated in the autoclave. Co²⁺ adsorption capacity of the Fe-Ti-O adsorbent was determined to be larger than that of TiO₂ at high temperatures. The enthalpy changes of 34 and 49 kJ·mol⁻¹ due to the adsorption of Co²⁺ on the TiO₂ and Fe-Ti-O adsorbents indicate that the adsorption is endothermic in the experimental temperature range (15-280 °C). From this preliminary study, titanium-based oxides are shown to have good potential applicability for reactor water purification as high temperature adsorption media.

Key words : TiO₂, Fe-Ti-O, Adsorbents, Cobalt(II) Ion, Reactor Water Purification

INTRODUCTION

Inorganic oxide adsorbents [Amphlett, 1964] have been reviewed for the removal of soluble corrosion products and are attractive alternatives for water purification systems in pressurized water reactors (PWRs) or boiling water reactors (BWRs) because of the limitations of organic ion-exchange materials in their use, namely decomposition and oxidation at higher operating temperatures. Higher thermal efficiency and simplification of the clean-up system could be realized by using the inorganic adsorbents, made up of stable oxides, which can be operated at reactor water conditions. The inorganic adsorbents also have an advantage for their waste solidification with the direct ceramization of soluble corrosion products on an adsorbent matrix.

In water-cooled nuclear reactors, corrosion products are transported from the structural materials of the primary coolant circuit into the neutron flux in the reactor core, and out again to deposit on out-of-core areas such as the steam generator surface. A major radiation source in water cooled reactors has been identified to be activated corrosion products, mainly ⁶⁰Co, which is generally considered to be supplied from the primary side of nuclear reactors as Co²⁺ ions. Therefore, replacements of organic resin adsorbents, especially with inorganic compounds such as Zr₂(PO₄)₃ [Michael et al., 1961], ZrO₂ [Michael et al., 1961; Tewari and Lee, 1975; Tewari et al., 1973; Tewari and McIntyre, 1975; Ahrlund and Carleson, 1971; Balakrishnan and Buckley, 1988], Al₂O₃ [Tewari and Lee, 1975; Tewari and McIntyre, 1975], Fe₃O₄ [Tewari et al., 1973], NiFe₂O₄ [Tewari and Lee, 1975; Tewari and McIntyre, 1975], TiO₂ [Kikuchi et al., 1978; Kikuchi et al., 1979; Kawamura et al., 1984], and composite oxides with TiO₂ [Fujita et al., 1980, 1985; Hata et al., 1986]

which can be applied in high temperature water, have been investigated. Among these inorganic adsorbents, TiO₂ has turned out to have the highest selectivity for cobalt ion and is recommended for purification in the high temperature system. There are also several potential advantages in using composite oxides, including particularly TiO₂ based oxides, with respect to enhancement of their adsorption capacity and hydrothermal stability with leaching resistance at high temperature. The Co²⁺ adsorption in high temperature water is known to be mainly controlled by TiO₂ in the composite adsorbent. Thus, some efforts have been made to improve its adsorption capacity and/or selectivity by employing the method of loading of TiO₂ on substrates or the preparation of various types of composites such as supported TiO₂ on stable porous media and TiO₂ based composite oxides. However, few studies on the influence of the preparation methods on material characterization and adsorption characteristics of TiO₂ and Fe-Ti-O adsorbents have been reported.

The purpose of the present paper is to describe the preparation of TiO₂ and Fe-Ti-O adsorbents, examine their material characterization, and analyze the Co²⁺ adsorption characteristics of the two adsorbents considering the influence of the preparation methods on adsorption capacity at a high temperature.

EXPERIMENTAL

1. Preparation of Co²⁺ Solution and Adsorbents

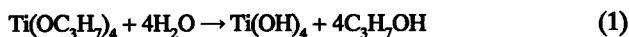
All chemicals were of GR grade quality and used without further purification. All Co²⁺ solutions were prepared with deionized water from a NANOpure purification system (Barnstead 18.5 Mohm). The Co(NO₃)₂·6H₂O was used for preparing stock solution of which Co²⁺ ion concentration was 5.0×10⁻⁵ mol·dm⁻³. This concentration is low enough to avoid experimental error due to the bulk precipitation of Co(OH)₂ in a high temperature

[†]To whom correspondence should be addressed.
E-mail : krkim1@nanum.kaeri.re.kr

aqueous solution [MacDonald et al., 1972].

1-1. TiO₂ Adsorbent

The TiO₂ was prepared by using the sol-gel technique from alkoxide starting material. The particulate Ti(OH)₄ sol solution was prepared by hydrolysis of titanium (IV) tetraisopropoxide (Ti(OC₃H₇)₄) while adding 7% ammonium hydroxide (NH₄OH) solution with the stirring speed of 1,000 rpm at room temperature for 1 hour. The possible reaction for this hydrolysis is:



The different pH values (pH=4-11) of the solution at the end of precipitation in the hydrolysis reaction were set to be constant before the solution was aged overnight. The precipitate was filtered off, 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.

1-2. Composite Oxide (Fe-Ti-O) Adsorbent

Mixed particulate sol solution was prepared by alkalizing an equimolar mixture of 1 M ferrous (II) chloride (FeCl₂·4H₂O) and 1 M titanium (IV) chloride (TiCl₄) solution while adding 2.5 M sodium hydroxide (NaOH) solution with the stirring speed of 1,000 rpm at room temperature for 1 hour. The pH value at the end of precipitation was controlled 9. The resultant precipitate was aged overnight at the same temperature and pH after the precipitation reaction. And then it was filtered with a glass fiber filter of 1.0 μm, washed thoroughly with deionized water in Soxhlet's 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 unity. These powders were crushed and sieved, and a fraction of 100-120 mesh size was pressed into pellets (20-mm diameter, 10-mm height) without binder. The pellets were formed in a cylindrical die at 4 MPa for 0.5 min. 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 1,400°C. The heat-treated samples were again crushed and sieved, and a fraction of 100-120 mesh size was used in the following experiments.

2. Batch Experiments

Adsorption experiments were carried out at elevated temperatures in 1 dm³ capacity of stirred autoclave (Parr bench top reactor with magnetic drive), which was made of hastelloy C-276 with temperature controller (Parr model 4843). 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 in this work was 150-280°C. The adsorbed amount of Co²⁺ ion on the adsorbents with 100-120 mesh size particles was determined from the concentration change of the Co²⁺ solution after batch adsorption had reached equilibrium. An adsorption equilibrium time took about 5 hours for 0.2 g of the adsorbent in the stirred autoclave system containing 0.5 dm³ cobalt solution. In order to avoid errors due to precipitation of Co(OH)₂ in the bulk solution, pH_{25°C}

was kept to be 7. During or after the adsorption experiment, a 5 cm³ portion of the suspended solution was sampled, centrifuged at 3,000 rpm for 10 minutes, and the Co²⁺ concentration of a small portion of the supernatant solution was measured. Small changes in the Co²⁺ concentration of the solution due to adsorption were determined by atomic absorption spectroscopy (Perkin-elmer 5100PC).

The equilibrium concentration of Co²⁺, C (moles·dm⁻³), and the average amount of adsorbed Co²⁺ per unit adsorbent, q_{av} (moles·g⁻¹), are calculated from the initial concentration of Co²⁺, C₀ (moles·dm⁻³), and the fraction of the adsorbed Co²⁺,

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

where V is the volume of the solution (dm³) and W_s is the weight of adsorbent (g). The distribution coefficients, K_d (dm³·g⁻¹), of Co²⁺ were calculated by the following equation.

$$K_d = \frac{C_0 - C}{C} \cdot \frac{V}{W_s} \quad (3)$$

3. Material Characterization

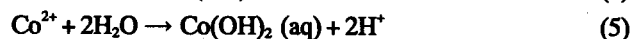
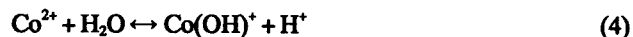
Specific surface areas of the adsorbents were obtained by BET method at 77°K using a continuous flow method with the Quantachrome autosorb-6 sorption system (model AS-6/Po). The accuracy of the method was judged to be ±2.5% or better based on the measurements of standard reference material with known surface areas. And 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 the 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 CuK_α radiation (λ=1.5418 Å) and CoK_{α1} radiation (λ=1.7889 Å) being used at a scanning rate of 2°·min⁻¹.

RESULTS AND DISCUSSION

1. Effect of Adsorption Temperature

The temperature dependence of Co²⁺ adsorption is exhibited in Fig. 1. The increased Co²⁺ adsorption capacity of the two adsorbents with high temperature is attributed to the adsorption of hydrolyzed species of cobalt. Tewari et al. [Tewari and Lee, 1975; Tewari et al., 1973; Tewari and McIntyre, 1975] have reported that the adsorption of Co²⁺ on oxides increases with pH and temperature. The Co²⁺ adsorption at high temperature seems to be due to increased hydrolysis of Co²⁺ accompanied by surface precipitation and formation of an insoluble Co(OH)₂ followed by reaction with the substrate to form an oxide compound with the loss of water. The reaction mechanism is suggested as follows:

surface precipitation with hydrolysis reaction;



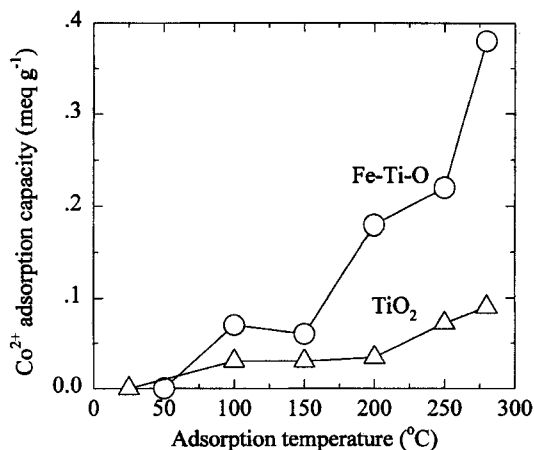
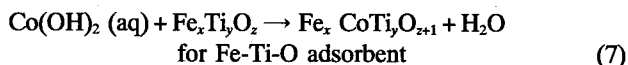
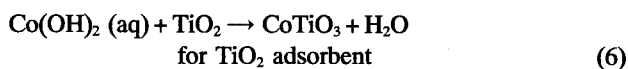


Fig. 1. Variation of Co^{2+} adsorption capacity of adsorbents with adsorption temperature (Initial Co^{2+} concentration: $5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, Adsorption time: 6 hours).

adsorption reactions with substrate;



At a high temperature, the strong adsorption mechanism such as irreversible chemical reaction illustrated by the Eqs. (6) and (7) would be dominative. High temperature conditions seem to increase multiple surface coverage of $\text{Co}(\text{OH})_2$ 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. 1. This is probably due to the electrical conductivity of the crystals, which is higher in composite oxide in contrast 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):

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

where, K_d =distribution coefficient ($\text{cm}^3 \cdot \text{g}^{-1}$), which is defined as the ratio of the concentrations of the Co^{2+} in the adsorbent and in the solution,
 ΔH° =standard enthalpy change ($\text{kJ} \cdot \text{mol}^{-1}$),
 R =gas constant ($\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$),
 T =temperature (K), and
 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 as shown in Fig. 2. Analysis of the slope gives ΔH° of about 34 and 49 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. The standard enthalpy change of the adsorption reaction of Co^{2+} on prepared adsorbents indicates that the reactions are endothermic and their enthalpy

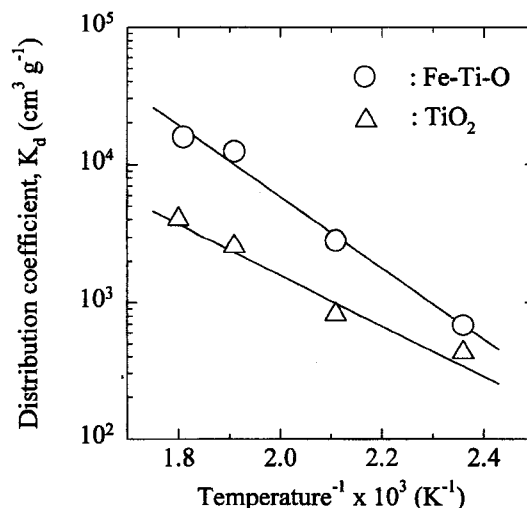


Fig. 2. Distribution coefficient versus temperature (Initial Co^{2+} concentration: $5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, Adsorption time: 6 hours).

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 $8.4 \text{ kJ} \cdot \text{mol}^{-1}$ 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 $\text{Co}(\text{OH})_2$ ($\sim 19 \text{ kJ} \cdot \text{mol}^{-1}$). 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 ΔH° 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 oxide ($\text{Fe}_x\text{CoTi}_y\text{O}_{z+1}$).

Cobalt adsorbed from solutions on the surface of TiO_2 powders has been detected by X-ray photoelectron spectroscopy (XPS). The absolute binding energies of the adsorbed photoelectron lines have been compared to the binding energies for a number of cobalt compounds in order to identify the cobalt species adsorbed on the surface. The mean escape depth for the cobalt 2p electron is 0.6 to 1.0 nm [Tewari and McIntyre, 1975]. The XPS data for cobalt(II) compounds are summarized in Table 1. The $\text{Co}(2p \ 3/2)$ line position observed for cobalt adsorbed at 250°C on the outer surface of TiO_2 is about 781 eV. The observation of these satellites in the adsorbed cobalt spectra confirms that the major adsorbed species are $\text{Co}(\text{II})$, as shown in Fig. 3. These observations match those for $\text{Co}(\text{OH})_2$, which also has a binding energy of $780.7 \pm 0.2 \text{ eV}$ among the values of cobalt species as given in Table 1 and a prominent shake-up satellite in this range.

Table 1. XPS binding energies for some cobalt oxides [Tewari and McIntyre, 1975]

	$\text{Co}(2p \ 3/2) \text{ eV}$	$\text{Co}(3p) \text{ eV}$	$\text{Co}(3s) \text{ eV}$
CoO	779.7 ± 0.15	60.0 ± 0.1	101.9 ± 0.2
$\text{Co}(\text{OH})_2$	780.7 ± 0.2	61.1 ± 0.2	102.9 ± 0.2
Co_2O_3	779.6 ± 0.2	61.4 ± 0.2	103.0 ± 0.2
CoOOH	779.7 ± 0.2	61.2 ± 0.2	103.0 ± 0.2

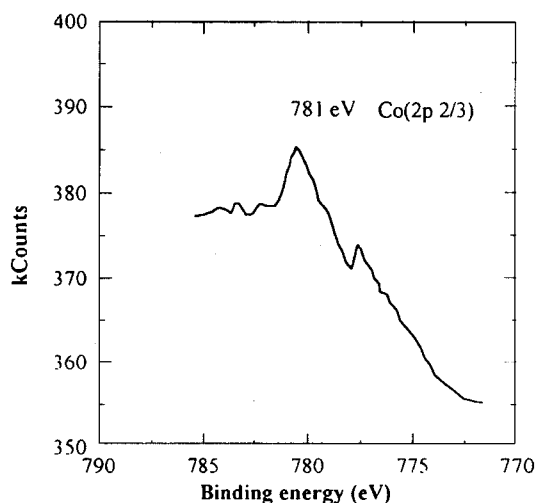


Fig. 3. XPS spectra of surface cobalt in Co(OH)_2 adsorbed on TiO_2 at 250°C by Al-K α X-rays.

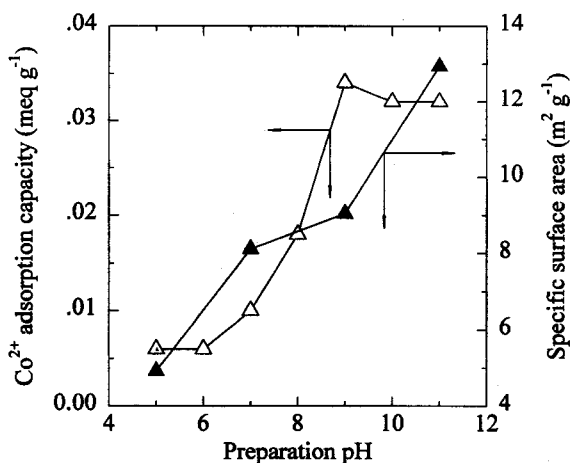


Fig. 4. Effect of preparation pH on specific surface area and adsorption capacity of TiO_2 (Initial Co^{2+} concentration: $5.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, Adsorption time: 6 hours, Calcination temperature: 600°C , Adsorption temperature: 200°C for 6 hours).

2. 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 shows its maximum adsorption capacity when it was prepared at pH 9. It is known that the micro pores (less than 20 \AA) do not make contributions to the adsorption of the cobalt complex. The considerable specific surface area with a relatively large fraction of micro pores in adsorbents is not effective for Co^{2+} adsorption as shown in Fig. 4, and it seems to be likely that the pores in the range of mesopore would be needed to allow the hydrated Co^{2+} ions to diffuse into the pores coated with Co(OH)_2 precipitated layers.

Fig. 5 shows the X-ray powder diffraction patterns of the 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

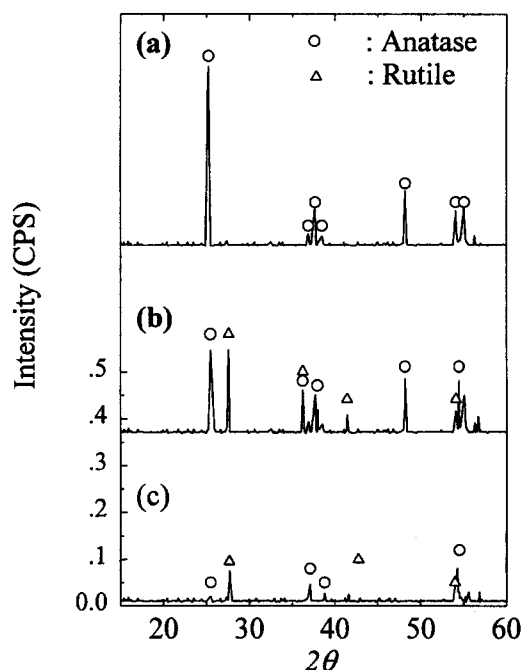


Fig. 5. X-ray diffraction patterns of TiO_2 adsorbents prepared at (a) pH 10, (b) pH 7 and (c) pH 4 followed by heat treatment at 600°C for 6 hours.

became more dominant and intense with increasing pH. Only anatase peaks appear at pH 10, both anatase and rutile are observed at pH 7, and rutile with a trace of anatase peaks exist at pH 4.

The apparent densities of the TiO_2 adsorbents prepared at pH range of 4-10 were about $3.4\text{--}3.9 \text{ g} \cdot \text{cm}^{-3}$. Although this was not confirmed by IR investigations that were expected to show polymerized cluster variations, gels prepared at high pH with high water contents dried to low bulk density and were predicted to have skeletal structures approaching the dense anhydrous oxide [Hench and Ulrich, 1984].

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

Fig. 6 shows the effect of heat treatment temperature on the adsorption capacity of Fe-Ti-O. At about $1,200\text{--}1,350^\circ\text{C}$ heat treatment temperature, superior values were obtained in spite of 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 $1,000$ and $1,350^\circ\text{C}$, respectively. And pattern (c) in Fig. 7, which is for Fe-Ti-O without heat-treatment, is shown in comparison with heat-treated Fe-Ti-O. Neither the anatase phase of TiO_2 nor spinel-like structure of magnetite phase ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) 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 $1,000^\circ$ and $1,350^\circ\text{C}$ for 2 hours showed that phases corresponding to pseudobrookite and rutile structures were present, despite 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 temperature changes in heat treatments except the intensity of pseudobrookite structure at room temperature. The adsorbents prepared here have a stable phase at room tempera-

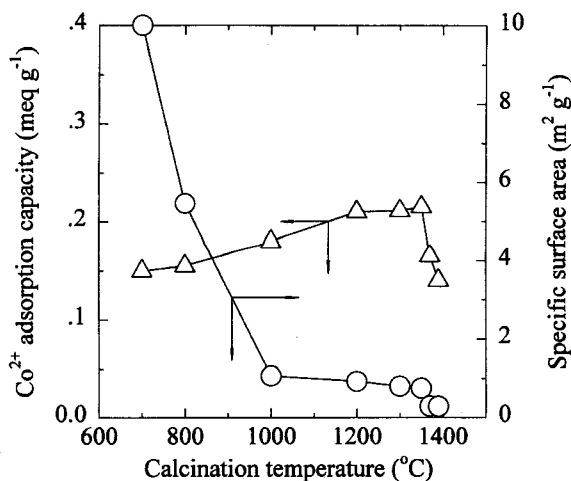


Fig. 6. Effect of calcination temperature on Co²⁺ adsorption capacity of Fe-Ti-O adsorbents (Initial Co²⁺ concentration: 5.0×10^{-5} mol·dm⁻³, Adsorption time: 6 hours, Adsorption temp.: 250 °C).

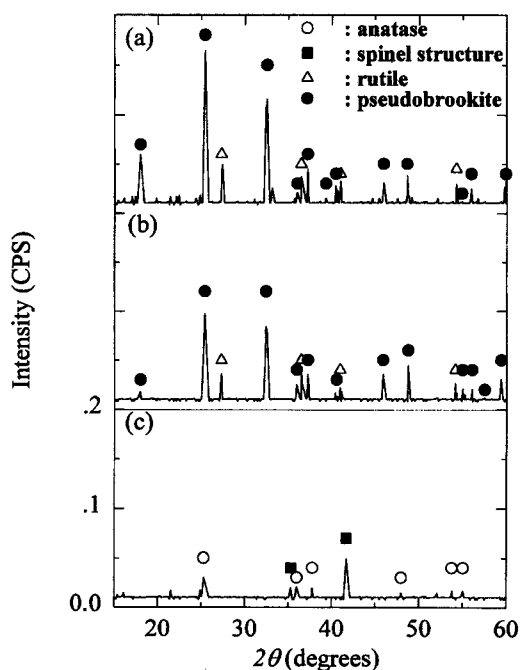


Fig. 7. X-ray powder diffraction patterns of Fe-Ti-O adsorbents heat-treated at (a) 1,350 °C, (b) 1,000 °C and (c) their composite hydroxide before heat treatment.

ture and their synthesis requires slow cooling from the calcination temperature. Mixtures of FeO·Fe₂O₃ and TiO₂ (molar ratio Fe:Ti=1:1) that are allowed to cool down to room temperature over a period of hours yield a mixture of pseudobrookite and small portion of rutile phases as its major constituent. This is typical of nonstoichiometric iron titanium oxide and suggests that the starting ferrous oxide is partly oxidized during the process of precipitation and calcination in air. These results show that pseudobrookite type structure is good for Co²⁺ adsorption and is more stabilized at high temperature than other structures. However, the heat treatment of the mixed oxide at below about 1,200 °C led to an unstable structure and to decreased adsorp-

tion capacity because of the growth of a decomposition product (rutile) at the lower temperature. The electrical conductivity of the pseudobrookite type structure might enhance Co²⁺ adsorption due to the increase of the possibility of valence oscillation between Fe²⁺ and Fe³⁺ sites [Cotton and Wilkinson, 1988] in contrast to the ilmenite structure of ferrous titanium oxide (Fe^{II}Ti^{IV}O₃).

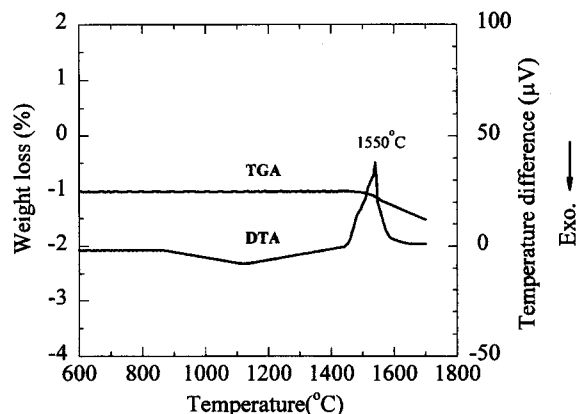


Fig. 8. TG-DTA curve of Fe-Ti-O adsorbent prepared by heat treatment at 1,350 °C.

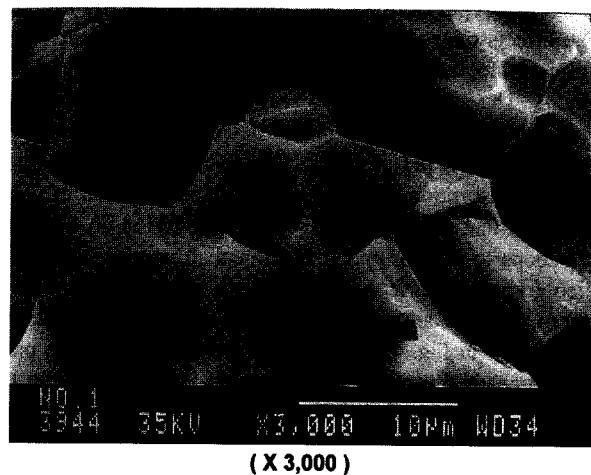
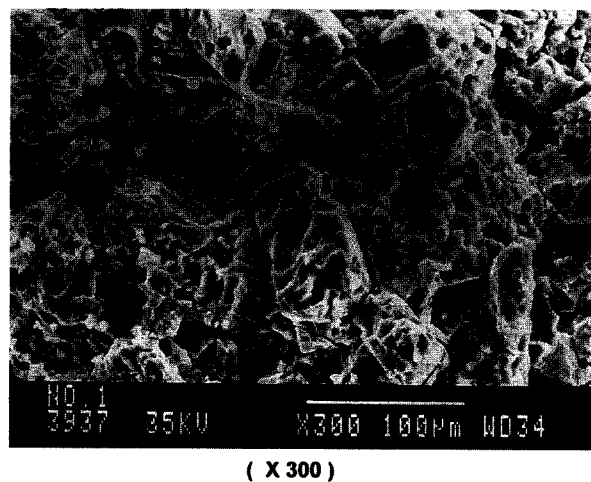


Fig. 9. Scanning electron micrographs of a partially sintered Fe-Ti-O (gel prepared by heat-treating at 1,350 °C).

The result of TG-DTA for the prepared Fe-Ti-O adsorbent which was heat-treated at 1,350°C is shown in Fig. 8. The profiles of DTA indicate that a large amount of melting phase was starting to be formed at 1,500°C which seems to have a single endothermic reaction within a relatively narrow temperature range and then a small weight loss due to evaporation was observed at about 1,550°C. These results suggest 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 the equivalent molar ratio of Ti to Fe in the ternary phase diagram of FeO-Fe₂O₃-TiO₂ system with liquidus temperature line suggests that Fe-Ti-O adsorbent is nonstoichiometric ferrous and ferric titanium oxide (FeO:Fe₂O₃:TiO₂ ≈ 0.4:0.1:0.5). Scanning electron micrographs of a partially sintered Fe-Ti-O are shown in Fig. 9.

After completion of each experiment of the Co²⁺ 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 a high temperature adsorbent.

CONCLUSIONS

The inorganic adsorbents of TiO₂ and Fe-Ti-O were prepared under various experimental conditions and tested for Co²⁺ adsorption at high temperature. TiO₂ prepared from its hydroxide sol at the aging condition of pH 9 and the Fe-Ti-O heat-treated at 1,350°C were shown to have the most favorable adsorption capacities. When these adsorbents were applied in the solution containing Co²⁺ 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 larger adsorption capacity of Co²⁺ with about 0.38 meq·g⁻¹ while TiO₂ alone had only about 0.09 meq·g⁻¹ capacity. The enthalpy changes connected with the adsorption of Co²⁺ on the prepared adsorbents indicate endothermic adsorption and suggest that the Co²⁺ adsorption mechanism was accompanied by a certain irreversible chemical reaction. The specific surface area of adsorbents was not a dominant factor for Co²⁺ 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 could be recommended for the removal of ionic contaminants in the primary cooling water of nuclear power plants.

REFERENCES

Amphlett, C. B., "Inorganic Ion Exchangers," Elsevier Publish-

- ing, Co., Amsterdam (1964).
- Ahrland, S. and Carleson, G., "Inorganic Ion Exchangers-VIII (The Purification of Water at Elevated Temperatures by a Combination of Zirconium Phosphate and Zirconium Hydroxide Gels)," *J. Inorg. Nucl. Chem.*, **33**, 2229 (1971).
- Balakrishnan, P. V. and Buckley, L. P., "Corrosion-Product Filtration in PWRs," EPRI NP-5727 (1988).
- Cotton, F. A. and Wilkinson, G., "Advanced Inorganic Chemistry," Wiley-Interscience, New York (1988).
- Fujita, K., Takeuchi, S. and Yamashita, H., "Characteristics of Cobalt Adsorption on Titanium(IV) Oxide Alumina Composite Adsorbents in High Temperature Water," *J. Chem. Soc. Japan*, **9**, 1656 (1985).
- Fujita, K., Yamashita, H., Takeuchi, S. and Nakajima, F., "Cobalt Adsorption in High Temperature Water Using Titanium Oxide Supported on Alumina," *J. Inorg. Nucl. Chem.*, **43**, 188 (1980).
- Hata, K., Kitao, H., Miyazaki, T. and Ohsawa, Y., "Development of High Temperature Adsorbent," Water Chemistry of Nuclear Reactor Systems 4. BNES, London (1986).
- Hench, L. L. and Ulrich, D. R., "Ultrastructure Processing of Ceramics, Glasses, and Composites," John Wiley and Sons, New York (1984).
- Kawamura, F., Funabashi, K., Kikuchi, M. and Ohsumi, K., "Using Titanium Oxide for Cobalt Removal from High-Temperature Water," *Nucl. Tech.*, **65**, 332 (1984).
- Kikuchi, M., Ga, E., Funabashi, H. and Yusa, H., "Adsorption of Ions on Titanium Oxide at Temperature up to 280°C," *Radiochem. Radioanal. Letters*, **33**(5-6), 331 (1978).
- Kikuchi, M., Ga, E., Funabashi, K., Yusa, H., Uchida, S. and Fujita, K., "Removal of Radioactive Cobalt Ion in High Temperature Water Using Titanium Oxide," *Nucl. Eng. Des.*, **53**, 387 (1979).
- MacDonald, D. D., Shierman, G. R. and Butler, P., Atomic Energy of Canada Ltd. AECL-4138 (1972).
- Michael, N., Fletcher, W. D., Bell, M. J. and Croucher, D. E., "Inorganic Ion-Exchange Materials for Waste Purification in CVTR," Westinghouse Electric Corporation Report CVNA-135 (1961).
- Tewari, P. H. and Lee, W., "Adsorption of Co(II) at the Oxide-Water Interface," *J. Colloid and Interface Sci.*, **52**(1), 77 (1975).
- Tewari, P. H. and McIntyre, N. S., "Characterization of Adsorbed Cobalt at the Oxide-Water Interface," *AIChE Symp. Ser.*, **71**(150), 134 (1975).
- Tewari, P. H., Tuxworth, R. H. and Lee, W., "Specific Adsorption of Co(II) by ZrO₂ and Fe₃O₄," Proc. of Symp. on Oxide-Electrolyte Interface. -J. Electrochem. Soc. (1973).