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Adsorption Characteristics of Cobalt on ZrO_2 and Al_2O_3 Adsorbents in High-Temperature Water

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ABSTRACT

To evaluate adsorbents for the removal of soluble corrosion products, mainly ^{60}Co under PWR reactor coolant conditions, ZrO_2 and Al_2O_3 were prepared by the sol-gel method and hydrolysis of metal alkoxide, respectively. Their structures were studied by x-ray diffractometer and TG-DTA. The Co^{2+} adsorption on ZrO_2 and Al_2O_3 in high-temperature water were investigated in a stirred batch autoclave. The effect of calcination temperature on Co^{2+} adsorption capacity of ZrO_2 and Al_2O_3, the effect of pH on Co^{2+} adsorption capacity of Al_2O_3, the effect of adsorption temperature on adsorption capacity and Co^{2+} adsorption isotherms were studied. The prepared ZrO_2 and Al_2O_3 adsorbents were found to be stable with tetragonal, monoclinic structures and θ, δ, and α phase structures, respectively. The enthalpy changes ($\Delta H°$) due to the adsorption of Co^{2+} on ZrO_2 and Al_2O_3 were 12.8 and 16.1 kJ/gmol, which suggest that the adsorption is an irreversible endothermic reaction in the experiment temperature (150 ~ 250°C). The Co^{2+} adsorption capacities of ZrO_2 and Al_2O_3 at 250°C were 0.16 and 0.18 meq Co^{2+}/g adsorbent, respectively. The thermodynamic function of adsorption of $\triangle H$, $\triangle S$, $\triangle G$, and equilibrium constant K_d were calculated. The process of adsorption was established to be endothermic, and chemisorption was stabilized through thermodynamic functions.

INTRODUCTION

In pressurized water reactors (PWRs) or boiling water reactors (BWRs), even though careful control of water quality can keep corrosion-product concentrations fairly low, small amounts are released into the coolant and are activated in the core to become radioactive corrosion products such as ^{51}Cr, ^{95}Zr,

^{59}Fe, ^{54}Mn, ^{58}Co, and ^{60}Co. Some of these products will deposit on the surfaces of the primary cooling system, e.g., in the steam generators of PWRs or around the recirculation system in BWRs; consequently, the radiation levels will increase with operating time (1). This makes maintenance and repair work difficult. Among the radioactive corrosion products, ^{60}Co is the primary contributor to the radiation levels because of its long half-life ($T_{1/2}$: 5.3 y) and high gamma ray energies (E_γ: 1.17 MeV and 1.33 MeV). Therefore, it is necessary to remove ^{60}Co, as well as nonradioactive Co and Ni ions, which would be activated to produce ^{60}Co to reduce radiation levels.

Ion exchange resins made of organic polymers such as polystyrene are currently used in most reactor water purification systems in PWRs and BWRs. To avoid resin degradation, the water must be cooled below 50°C before passing through the clean-up system. Water pressure must be reduced along with temperature. Therefore, thermal losses become serious as the flow rate of the clean-up system increases. If it were possible to clean the coolant at a higher temperature by using heat-resistant ion-exchanger materials (i.e., inorganics), then a greater amount of reactor water could be purified without energy loss.

To solve such problems, inorganic ion exchangers or inorganic adsorbents such as $Zr_3(PO_4)_4$ (2), ZrO_2 (2–8), Al_2O_3 (4, 6), Fe_3O_4 (5), $NiFe_2O_4$ (4, 6), TiO_2 (9–11), TiO_2 supported on Al_2O_3 (12), and composite oxides [Al_2O_3–TiO_2 (13)], which can be used in high-temperature water, have been investigated. However, few studies on the influence of the preparation methods on material characterization and adsorption characteristics of ZrO_2 and Al_2O_3 adsorbents have been reported.

The purpose of the present paper is to describe the preparation of ZrO_2 and Al_2O_3 adsorbents, to examine their material characterization, and to analyze the Co^{2+} adsorption performance of the two adsorbents by considering the influence of the preparation methods on adsorption at high temperatures.

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 NANO pure purification system (Barnstead 18.5 Mohm). The $Co(NO_3)_2 \cdot 6H_2O$ was used for preparing stock solution in which the Co^{2+} ion concentration was 5×10^{-5} mol/L. This concentration is low enough to avoid bulk precipitation of $Co(OH)_2$ at high temperatures (14).

ZrO_2 Adsorbent

The ZrO_2 was prepared by using the sol-gel technique from zirconyl nitrate [$ZrO(NO_3)_2 \cdot xH_2O$] starting material. The zirconyl sol solution was prepared by 1 M zirconyl nitrate solution while adding 15 wt% ammonium hydroxide (NH_4OH) solution with a stirring speed of 1000 rpm at 70°C for 1 h. Enough of the 15 wt% ammonium hydroxide (NH_4OH) solution was placed in a measuring cylinder such that it occupied about one-third the height of the cylinder (a 200 or 250 mL cylinder was used). The diethyl ether was poured into the graduated cylinder containing the 15 wt% ammonia solution. The glass tube was connected with a dropper to the ammonia lecture bottle using tygon tubing. The NH_3 lecture bottle was opened to start a 100 cc/min flow rate of ammonia through the ether. The zirconyl sol solution was dropped slowly from above into the glass cylinder. The ZrO_2 was precipitated as hydrous oxide.

The possible chemical reaction is

$$ZrO(NO_3)_2 + H_2O + 2NH_3 \rightarrow ZrO_2 + 2NH_4NO_3 \tag{1}$$

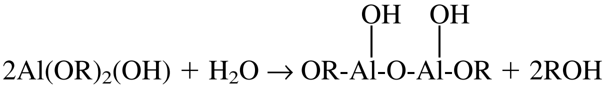
The solution at the end of precipitation in the reaction was made constant before aging the solution overnight. The precipitate was transferred to a wide glass dish, washed with 0.1% NH_3 solution, followed by deionized water, and was dried in an oven at 130°C for 4 h. The dried powder was calcined at various temperatures (600 ~ 1400°C) for 4 h in a box furnace (Nabertherm HT 16/17). The calcined samples were again crushed and sieved to 100 ~ 140 mesh size, and were used in the following experiments.

Al_2O_3 Adsorbent

The Al_2O_3 was prepared by using the hydrolysis-of-metal-alkoxide technique in a dilute solution of alcohol from aluminum isopropoxide [$Al(OC_3H_7)_3$] starting material. The [$Al(OC_3H_7)_3$] was first dissolved in the isopropyl alcohol with mixing by a magnetic stirrer in a water bath. The water-to-alkoxide ratio was kept at around 200 mol water per mol of alkoxide to minimize the heating effect of the exothermic reaction. The boehmite(AlOOH) sol solution was prepared by hydrolysis of aluminum isopropoxide [$Al(OC_3H_7)_3$] while adding deionized water with a stirring speed of 500 rpm at 80°C for 3 h in a water bath to maintain the solution at pH 10 of 0.1 mol of ammonium hydroxide (NH_4OH) solution.

The possible hydrolysis and polymerization reactions are

$$Al(OR)_3 + H_2O \rightarrow Al(OR)_2(OH) + R(OH) \tag{2}$$



$$2Al(OR)_2(OH) + H_2O \rightarrow OR\text{-}\underset{}{\overset{OH}{\overset{|}{Al}}}\text{-}O\text{-}\overset{OH}{\overset{|}{Al}}\text{-}OR + 2ROH \tag{3}$$

The hydroxides were aged at room temperature. The precipitate was filtered and dried in an oven at 110°C for at least 24 h. The dried powder was calcined at various temperatures (600 ~ 1400°C). A typical firing cycle was ambient to the desired temperature at 10°C/min, isothermal hold for 4 h, then cooled at 20°C/min to room temperature in a box furnace (Nabertherm HT 16/17). The calcined samples were again crushed and sieved to 100 ~ 140 mesh size, and were used in the following experiments.

Batch Experiments

Adsorption experiments were carried out at elevated temperatures in a 1L capacity stirred autoclave (Parr bench-top reactor with magnetic drive), which was made of Hastelloy C-276 with a temperature controller (Parr model 4521M). 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 50 ~ 250°C. The adsorbed amount of Co^{2+} ion on the adsorbents with 100 ~ 140 mesh size particles was determined from the concentration change of the Co^{2+} solution after batch adsorption had reached equilibrium. Adsorption equilibrium took about 24 h for 0.2 g of the adsorbent in the stirred autoclave system containing 0.5 L cobalt solution. To avoid errors due to precipitation of $Co(OH)_2$ in the bulk solution, $pH_{25°C}$ was kept to 7. During or after the adsorption experiment, a 5-cm^3 portion of the suspended solution was sampled, centrifuged at 3000 rpm for 10 min, 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 an inductively coupled plasma-atomic emission spectrometer (Jobin Yvon model JY 50P).

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

$$q_{av} = \frac{V(Co - C)}{W_s} \tag{4}$$

where V is the volume of the solution (L) and W_s is the weight of adsorbent (g). The distribution coefficients, K_d (cm^3/g), of Co^{2+} were calculated by

$$K_d = \frac{Co - C}{C}\frac{V}{W_s} \tag{5}$$

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 Micromeritics sorption system (model ASAP 2400). The accuracy of the method was judged to be ±2.5% or better based on the measurements of standard reference materials with known surface areas. The x-ray diffraction (XRD) patterns of the prepared adsorbents were measured to identify the crystal structures at room temperature with a Simens Diffraktometer (D5000) x-ray diffractometer, filtered CuK α_1 radiation ($\lambda = 1.5418$ Å) and CoK α_1 radiation ($\lambda = 1.7889$ Å) being used at a scanning rate of 2°/min.

RESULTS AND DISCUSSION

Effect of Calcination Temperature on Adsorption Capacity of ZrO_2 and Al_2O_3

The effect of calcination temperature on the specific surface area and Co^{2+} adsorption capacity of ZrO_2 is shown in Fig. 1. The specific surface area of the ZrO_2 adsorbent decreases with an increase in the calcination temperature. The ZrO_2 adsorbent showed its maximum adsorption capacity when it was prepared at 600°C calcination temperature. Fig. 2. illustrates the x-ray diffraction data of ZrO_2 powders heat-treated between 600°C and 1400°C, respectively. Amorphous ZrO_2, which is formed above 480°C, crystallizes to tetrag-

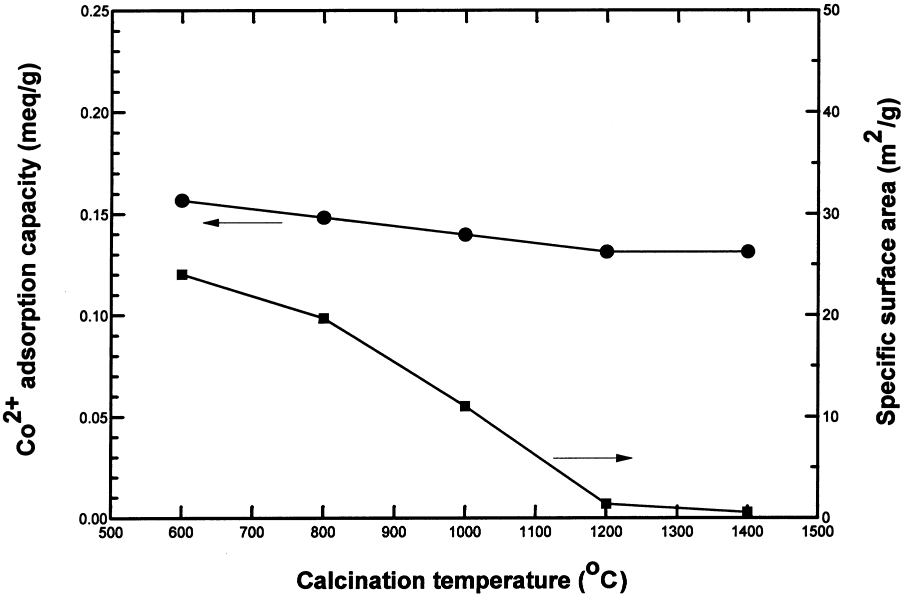


FIG. 1 Variation of Co^{2+}-specific surface area and Co^{2+} adsorption capacity of ZrO_2 adsorbent with calcination temperature. Initial Co^{2+} concentration: 5×10^{-5} mol/L, adsorption temp./time: 250°C/24 h.

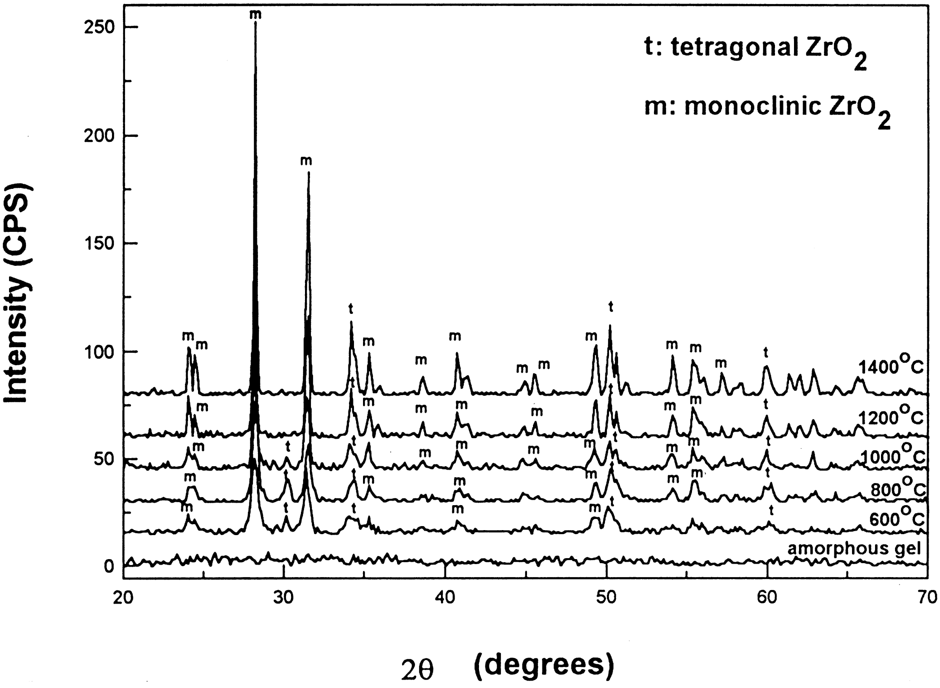


FIG. 2 X-ray diffraction patterns of ZrO_2 powder calcined at various temperatures.

onal ZrO_2. After calcined at 600°C for 4 h, the ZrO_2 powder consisted of 16% tetragonal and 84% monoclinic phase(111) or (11$\bar{1}$), as estimated from the x-ray diffraction peak intensities. The tetragonal ZrO_2 was gradually transformed to monoclinic ZrO_2 as the heating temperature was raised. Only the monoclinic phase was observed after calcined to 1200°C.

Figure 3 illustrates the x-ray diffraction data of Al_2O_3 powders heat-treated between 600°C and 1400°C. X-ray diffraction indicates that the amorphous alumina was transformed to a crystalline by being calcined for 4 h at 500°C. Between 500 and 900°C, crystalline alumina was converted to δ–Al_2O_3. Some conversion of δ-Al_2O_3 to θ-Al_2O_3 was detected above 900°C. Both θ-type alumina and δ-type alumina are presented between 900°C and 1000°C. Above 1100°C, the only phase present is α-Al_2O_3.

Despite the fact that different conditions of heat treatment were used, the results indicate that there is no significant change in the phase composition of the resultant adsorbents due to a temperature change of the heat treatment. These results show that the starting tetragonal ZrO_2 and δ-Al_2O_3 structure are good for Co^{2+} adsorption. However, heat treatment of the monoclinic ZrO_2

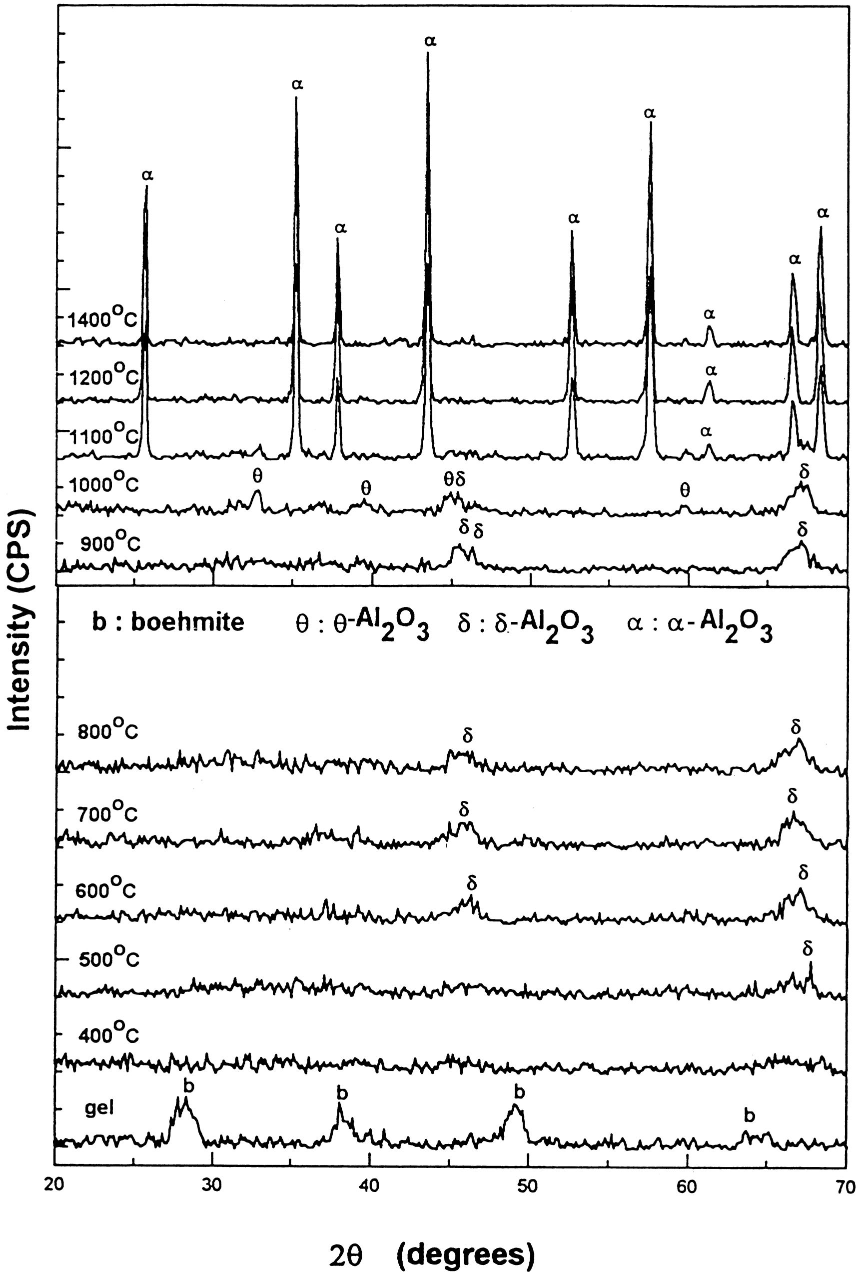


FIG. 3 X-ray diffraction patterns of Al_2O_3 powder calcined at various temperatures.

and α-Al_2O_3 at about 1200°C led to a decreased adsorption capacity because of the growth of a decomposition product at high temperatures.

Effect of Solution pH on Adsorption Capacity of Al_2O_3

Metal oxides such as Al_2O_3 in aqueous solutions usually carry a surface that is very much dependent on the pH of the solution. Hence, the Co^{2+} adsorption of Al_2O_3 adsorbent was examined in aqueous solutions covering a pH range from 4.0 to 10.0. The effects of the solution pH of Al_2O_3 adsorbent on the specific surface area and Co^{2+} adsorption capacity are shown in Fig. 4. The specific surface area of the Al_2O_3 adsorbent increases and the mean pore radius decreases with an increase in the preparation at 25°C. The Al_2O_3 adsorbent showed its maximum Co^{2+} adsorption capacity when it was prepared at pH 10. 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 a relatively large fraction of micropores is not effective for Co^{2+} adsorption, as shown in Table 1, and it seems 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.

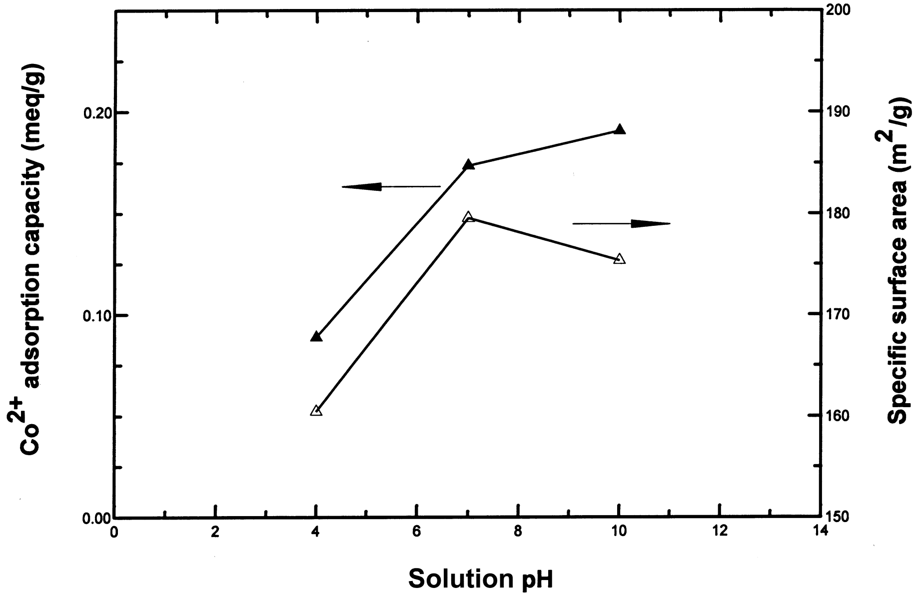


FIG. 4 Effect of solution pH on specific surface area and Co^{2+} adsorption capacity of Al_2O_3. Calcination temperature: 250°C, initial Co^{2+} concentration: 5 × 10^{-5} mol/L, adsorption temp./time: 250°C/24 h.

TABLE 1
Effects of Solution pH on Al_2O_3 Characterization Calcined at 600°C for 4 h

Solution pH	Average pore size (nm)	Specific surface area (m^2/g)
4.0	6.3	161
7.0	10.6	180
10.0	11.3	175

$$\mathrm{MOH} \underset{H^+}{\overset{OH^-}{\rightleftarrows}} \mathrm{MO^-} + \mathrm{H^+} \tag{6}$$

$$\mathrm{MO^-} + \mathrm{Co^{2+}} \leftrightarrow \mathrm{MOCo^+} \tag{7}$$

As the pH becomes greater than the surface of oxide surface, the surface hydroxy groups may dissociate into MO^-, which tends to undergo cation sorption (15). Thus, the increase in the adsorption of Co^{2+} with the pH can be explained by the enhanced dissociation of OH groups in hydrated Al_2O_3 oxide, resulting in the release of hydrogen ions available for the exchange of Co^{2+} ions from solutions as in Eqs. (6) and (7).

Effect of Adsorption Temperature on Adsorption Capacity

The temperature dependence of Co^{2+} adsorption is exhibited in Fig. 5. 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. (4–6) 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 a reaction with the substrate from an oxide compound with the loss of water. The reaction mechanism suggested is as follows.

Surface precipitation with hydrolysis reaction

$$\mathrm{Co^{2+}} + \mathrm{H_2O} \leftrightarrow \mathrm{C_o(OH)^+} + \mathrm{H^+} \tag{8}$$

$$\mathrm{Co^{2+}} + 2\mathrm{H_2O} \rightarrow \mathrm{C_o(OH)_2(aq)} + 2\mathrm{H^+} \tag{9}$$

Adsorption reactions with substrate

$$\mathrm{C_o(OH)_2\,(aq)} + \mathrm{ZrO_2} \rightarrow \mathrm{C_oZrO_3} + \mathrm{H_2O} \qquad \text{for } \mathrm{ZrO_2} \text{ adsorbent} \tag{10}$$

$$\mathrm{C_o(OH)_2\,(aq)} + \mathrm{Al_2O_3} \rightarrow \mathrm{C_oAl_2O_4} + \mathrm{H_2O} \qquad \text{for } \mathrm{Al_2O_3} \text{ adsorbent} \tag{11}$$

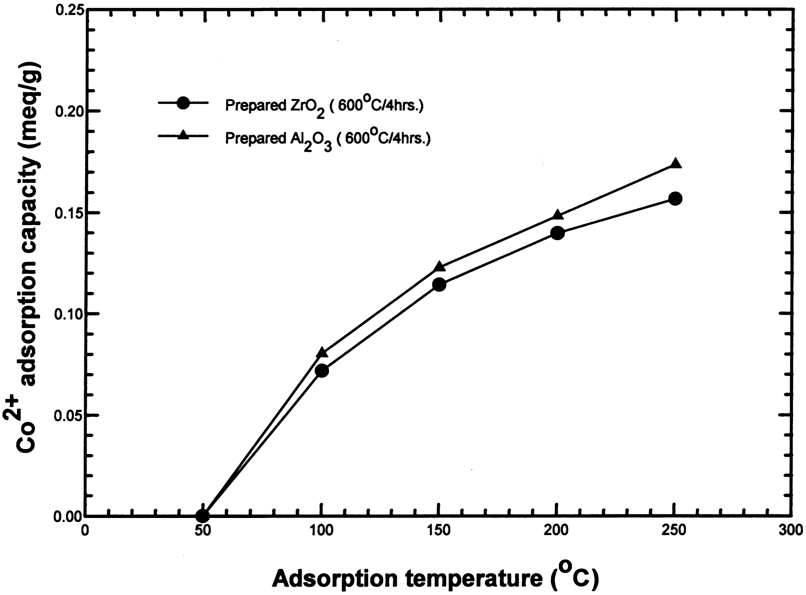


FIG. 5 Variation of Co^{2+} adsorption capacity of adsorbents with adsorption temperature. Initial Co^{2+} concentration: 5×10^{-5} mol/L, adsorption time: 24 h.

At a high temperature, a strong adsorption mechanism such as the irreversible chemical reaction illustrated by Eqs. (10) and (11) would be dominant. High temperature conditions seem to increase multiple surface coverage of $Co(OH)_2$ by adsorption.

The Co^{2+} adsorption capacity of the Al_2O_3 was found to be larger than that of ZrO_2 at high temperatures, as shown in Fig. 6. This is probably due to the electrical conductivity of the crystals, which is higher in the Al_2O_3 compared to ZrO_2. Accordingly, it seems that the interaction of the relatively large Co^{2+} ions on the surface of the Al_2O_3 adsorbent is more favorable than the corresponding interaction onto the surface of ZrO_2.

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

$$\ln K_d = -\frac{\triangle H^\circ}{2.303RT} + C \tag{12}$$

where K_d = distribution coefficient (cm^3/g) is defined as the ratio of the concentrations of Co^{2+} in the adsorbent and in the solution

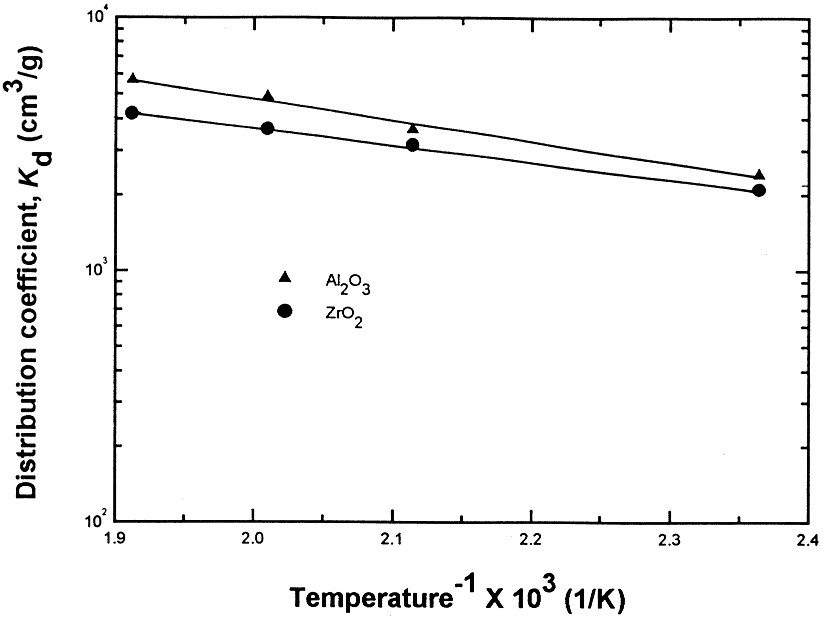


FIG. 6 Distribution coefficient versus temperature. Calcination temperature: 600°C/4 h, initial Co^{2+} concentration: 5×10^{-5} mol/L, adsorption time: 24 h.

ΔH° = standard enthalpy change (kJ/K·mol)
R = gas constant (kJ/K·mol)
T = temperature (K)
C = constant

The distribution coefficients (K_d) of Co^{2+} ions as a function of the temperature for ZrO_2 and Al_2O_3 adsorbents are plotted in Fig. 6. Analysis of the slope gives ΔH° of about 12.8 and 16.1 kJ/mol, respectively. The standard enthalpy change of the adsorption reaction of Co^{2+} on prepared adsorbents indicates that the reactions are endothermic and their enthalpy 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. This result can be explained by a 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 Al_2O_3 are probably connected with the formation of cobalt aluminate ($CoAl_2O_4$), while those of ZrO_2 would be connected with the formation of cobalt meta zirconate ($CoZrO_3$).

Co^{2+} Adsorption Isotherm

Figure 7 shows the results of adsorption isotherms at 250°C. They can be correlated by the following Freundlich-type equations:

$$\log q_{av} = \log A + \frac{1}{n}\log C_e \tag{13}$$

where,

q_{av} = amount of cobalt adsorbed (mol/g)
C_e = amount of cobalt in solution (mol/L)
A and $1/n$ = constants

This was done with a particle weight of 0.05 to 1 g and a solution volume of 500 mL with an initial concentration (Co) range of 1×10^{-5} to 5×10^{-4} mol/L.

The value of the constants A and $1/n$ are computed from the slope and the intercept by means of a linear least-squares fit method and are given in Table 2. The $1/n$ value is usually dependent on the nature and strength of the adsorption process as well as on the distribution of the active sites. Furthermore, the statistical theory of adsorption shows that the isotherm with $0 < 1/n < 1$

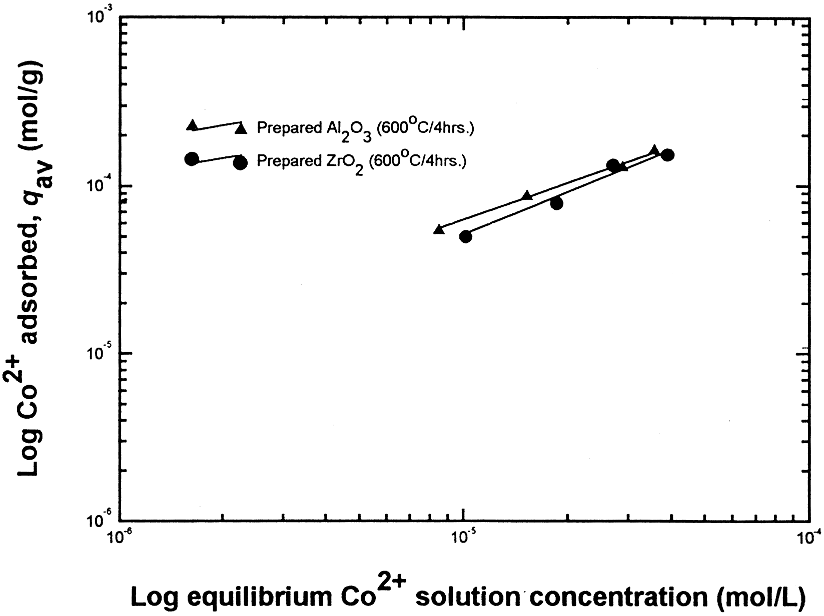


FIG. 7 Freundlich adsorption isotherm for Co^{2+} on the ZrO_2 and Al_2O_3 adsorbents. Adsorption temperature: 250°C, adsorption time: 24 h.

TABLE 2
Constant Parameters of the Freundlich Isotherm

Adsorbents	A(mol/g)	$1/n$
ZrO_2	1.18	0.88
Al_2O_3	0.32	0.74

is attributed to a heterogeneous structure of the surface without any interactions between adsorbed atoms or molecules. In the present findings the lower fractional value of $1/n$ (= 0.744) for Al_2O_3 than $1/n$ (= 0.876) for ZrO_2 corresponds to a heterogeneous surface with an exponential distribution of energy of the adsorption sites (15).

Thermodynamic Studies

Studies of the effect of temperature on the adsorption of Co^{2+} on ZrO_2 and Al_2O_3 were carried out by using the van't Hoff equation:

$$2.303 \log K_d = \frac{-\triangle H}{RT} + \frac{\triangle S}{R} \tag{14}$$

where $\triangle H$, $\triangle S$, K_d, and T are the enthalpy, entropy, distribution coefficient, and temperature in Kelvins, respectively. R is a gas constant in kJ/K·mol. The slope of a graph of log K_d vs. $1/T$ is equal to $-\triangle H/R$, and the intercept is $\triangle S/R$. The main driving force of adsorption is Gibbs free energy ($\triangle G$), which is calculated by using

$$\triangle G = \triangle H - T\triangle S \tag{15}$$

and

$$\triangle G = -RT \ln K_d \tag{16}$$

The values of K_d obtained at different temperatures are given in Tables 3 and 4, which show that these values increase with an increase in temperature. The

TABLE 3
Thermodynamic Parameters of the Adsorption of Co^{2+} on ZrO_2 Calcined at 600°C for 4 h

Temperature (K)	Distribution coefficient K_d (cm^3/g)	ΔG (kJ/gmol)	ΔH (kJ/gmol)	ΔS (J/gmol·K)
423	2,105	−26.88	12.8	93.8
473	3,166	−31.57		93.8
498	3,639	−33.91		93.8
523	4,198	−36.26		93.8

TABLE 4
Thermodynamic Parameters of the Adsorption of Co^{2+} on Al_2O_3 Calcined at 600°C for 4 h

Temperature (K)	Distribution coefficient K_d (cm^3/g)	ΔG (kJ/gmol)	ΔH (kJ/gmol)	ΔS (J/gmol·K)
423	2,410	−27.26	16.1	102.5
473	3,639	−32.38		102.5
498	4,868	−34.95		102.5
523	5,684	−37.51		102.5

plot of log K_d vs. $1/T$ is given in Fig. 6, and values of $\triangle H$ and $\triangle S$ calculated from the slope and intercept are given in Tables 3 and 4.

The negative value of $\triangle G$ calculated from Eq. (16) indicates that the reaction is spontaneous. The positive value of $\triangle H$ reflects that in the inner sphere complex of $Co(H_2O)^2_{+6}$, the hydration zone is disrupted to a greater extent during adsorption, which results in a net endothermic enthalpy change. The positive $\triangle S$ value reveals that elimination of the hydration zone during adsorption of cobalt on ZrO_2 and Al_2O_3 results in a net positive entropy effect.

CONCLUSION

The inorganic adsorbents of ZrO_2 and Al_2O_3 were prepared under various experimental conditions and tested for Co^{2+} adsorption at high temperatures. The ZrO_2 and the Al_2O_3 calcined at 600°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/L at 250°C in batch adsorption experiments, the Al_2O_3 was found to have a larger adsorption capacity of Co^{2+}, about 0.18 meq/g, while ZrO_2 alone had only about 0.16 meq/g capacity. The Co^{2+} adsorption capacities of prepared ZrO_2 and Al_2O_3 were determined to be larger than those of other commercially available adsorbents (1) for this application. 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, solution pH, and hydroxyl group of adsorbents are dominant factors for Co^{2+} adsorption on oxides at high temperatures.

The structure of zirconium oxide gel is transformed with the rise of temperature as follows: amorphous → monoclinic and tetragonal → monoclinic and that of aluminum oxide gel is transformed with temperature as follows: boehmite (AlOOH) → δ-Al_2O_3 → θ-Al_2O_3 → α-Al_2O_3.

ZrO_2 and Al_2O_3 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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