

THE SOLUBILITY OF COBALTOUS SALTS IN SUPERCRITICAL WATER

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This work is to investigate the solubility of cobaltous salts in compressed hot water and to try to propose a general correlation for water's macroscopic properties. The salts investigated are Co(OH)_2 , CoCO_3 , and CoO . The solubility was measured along two isochoric paths with a batch reactor. The temperature investigated ranges from 250 to 420 °C, and the density inside the reactor remained below the water's critical density 0.317 g/cm^3 .

It was found that the most suitable equation to predict the solubility of Co(OH)_2 and CoO is related to the chemical equilibrium constant, formulated as $\log K = A + \frac{B}{T} + C \log \frac{T}{T_o} + \frac{D}{T} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_o} \right)$.

However, the solubility behavior of $\text{CoCO}_{3(\text{aq})}$ differs from those of CoO and Co(OH)_2 . It is presumed that the CO_2 produced on heating up the $\text{CoCO}_{3(\text{aq})}$ may act as an antisolvent to CoO . In this work, the solubility is correlated with the difference of the inverse of dielectricity. It was also found that the decrease of pH value, from 7 to 1.28, generally lowers the solubility of CoCO_3 when the temperature is above water's critical point and increases that, when below water's critical point. The obtained solubility data and model provide useful information for further study on development of the decontamination technology of a nuclear power plant.

INTRODUCTION

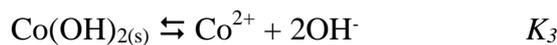
The decontamination technology for decommissioning of nuclear power plant mainly focuses on cobaltous salts, because their half-life of radioactivity is the longest. The water circulation system in a nuclear power plant inevitably creates corroded cobalt, which dissolves into the compressed hot flowing water. The dissolved cobalt becomes radioactive as it circulates through the reactor. The radioactive cobalt will precipitate on the surfaces of the piping, of other equipments in reactor, and of heat exchanger or evaporator. Since precipitation is mostly due to the change of solubility of radioactive cobalt in water, applying near or supercritical water could reverse the precipitation and accomplish the decontamination. Prior to the decontamination study, the variation of the solubility of various cobaltous salts, Co(OH)_2 , CoCO_3 , and CoO , with temperature were studied along two

isochoric paths with a batch reactor. In this work, we measured the solubility of cobaltous salts in water to evaluate the feasibility of decontamination by near or supercritical water.

The literature was scarce for the solubility of metal oxides and salts in high temperature water. Recently, the supercritical water oxidation process has been demonstrated to be an effective process to destruct hazardous wastes and municipal sludge. Although the commercialization of the SCWO process is on its way, the formation of solid salts will hinder its application. To further commercialize the SCWO process, the phase behavior of some salts commonly met in SCWO process was studied. Based on the data available in literature, Anderko has developed an equation of state for the salt solution. Extension of Anderko's equation to ternary system is also possible [1]. Other than the salt solutions, a series of researches done by Tohoku University in Japan showed the feasibility of producing nano-particles of metal oxides in supercritical water [2]. In order to control the size and distribution of the particles and to understand the nucleation mechanism, the solubility of metal oxides should be measured prior to further study and commercialization. Due to lack of phase equilibrium data of metal oxides, no satisfactory generalized equation of state is available to predict the solubility of metal oxides in supercritical water. However, an empirical equation can be obtained when the solubility data found in literatures are employed to correlate with water's macroscopic properties, such as density, pH, or dielectric constant. Simonson et al. and Ziemniak et al. used the following equation to predict the solubility of metal oxide in water [3, 4];

$$\ln[\text{MO}_x \cdot n\text{H}_2\text{O}] = A + \frac{B}{T} + C \ln T + D \ln r \quad (1)$$

In this work, the solubility of cobaltous hydrate, cobaltous oxide, and cobaltous carbonate in hot compressed water is measured and correlated via equation (1). However since the salts and oxides will form complex or hydrate in the presence of water, the chemical equilibrium among them need be considered before satisfactory correlation can be obtained. For cobaltous hydrate, the solubility is attributable to the four possible routes,



Therefore the total solubility of cobaltous ions in supercritical water can be expressed as

$$\begin{aligned} C_T(\text{ppm}) &= \{ [\text{Co(OH)}_{2(aq)}] + [\text{Co(OH)}^+] + [\text{Co}^{2+}] + [\text{Co(OH)}_3^-] \} \times 58.93/1000 \\ &= \left\{ K_1 + \frac{K_2}{[\text{OH}^-]} + \frac{K_3}{[\text{OH}^-]^2} + K_4[\text{OH}^-] \right\} \times 58.93/1000 \end{aligned} \quad (2)$$

Arai et al. has shown that the chemical equilibrium constants depend strongly on water's properties, which can be correlated as [5]

$$\ln K(T, \mathbf{r}) = -\ln K^o(T_o, \mathbf{r}_o) + \frac{\Delta H^o(T_o, \mathbf{r}_o)}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) + \frac{\sum_i w_i}{T} \left(\frac{1}{\mathbf{e}(T, \mathbf{r})} - \frac{1}{\mathbf{e}(T_o, \mathbf{r}_o)} \right) \quad (3)$$

For the purpose of regression, the equation is rewritten as

$$\log K = A + \frac{B}{T} + C \log \frac{T}{T_o} + \frac{D}{T} \left(\frac{1}{\mathbf{e}} - \frac{1}{\mathbf{e}_o} \right) \quad (4)$$

The macroscopic properties of water can be calculated based on the observed pressure and temperature. In this work the density of water was calculated with Patel-Teja equation of state [6], and the dielectricity and the ionic product were calculated with the regression equations derived by Uematsu and Franck [7] and by Marshall and Franck [8], respectively.

EXPERIMENTS AND METHODS

Water (25 or 30g) and various cobaltous salts (0.1g) were loaded into a high pressure vessel. The vessel is made of SS 316L with internal volume of 124 ml and equipped with a pressure gauge, a relief vale, and a filter connected to the sampling system. The loaded vessel is placed in a furnace and heated-up to the designated temperature. In the present work the temperature of the furnace studied ranged from 280 °C to 420 °C. Normally, the pressure in the vessel exhibited a maximum after about 30 minutes of heating, and leveled off to the maximum as the heating continued. The reaction in the vessel was allowed to carry on for an additional period of about 60 minutes after the maximum pressure was first observed. The reaction was then terminated by opening the relief valve. The effluent was filtrated and collected in a sampling system, which is composed of a sample cylinder and a needle valve. The cobaltous content of the collected liquid effluent was analyzed by an AA.

The batch reactor used in this work follows an isochoric path, and the final pressure is in theory predictable for pure water. However, the presence of salts, decomposed gases and condensed liquids in the connector and the tube outside the furnace may render the pressure to deviate significantly from the prediction. Therefore the observed maximum pressure and the temperature of the furnace were used to characterize the state of the water. From the pressure and temperature, the macroscopic properties of water such as density, pH, and dielectricity were calculated and correlated with the solubility data of salts and metal oxides.

RESULTS AND DISCUSSION

The Solubility of Co(OH)₂

Figure 1 shows the influence of temperature on the solubility of Co(OH)₂ along an isobaric path, in which 25 g of water and 0.1 g of Co(OH)₂ were placed in a 124-ml reactor. The circles represent the experimental results, and the solid line is the regression line with equations (2) and (4). Equation (1) was also used to fit the experimental results; however,

no good fit was found. On applying equations (2) and (4), sixteen parameters were needed to fit the seven experimental data. Since the contribution of Co(OH)^+ and Co^{2+} is minor, only the contribution of $\text{Co(OH)}_{2(\text{aq})}$ and Co(OH)_3^- to the solubility is accounted for in this work. The parameters used for the chemical equilibrium constant are listed in Table 1, and the contribution of $\text{Co(OH)}_{2(\text{aq})}$ and Co(OH)_3^- is also depicted in Figure 2. It is observed that the solubility is mostly contributed by Co(OH)_3^- when the temperature is below water's critical point, and mostly contributed by $\text{Co(OH)}_{2(\text{aq})}$ when, above water's critical point. The same parameters employed in Figure 1 was also applied to another experiment with 30 g of water and 0.1 g of Co(OH)_2 in a 124-ml reactor. Both experimental and calculated results are also shown in Figure 3. Although the fit is not as good as that of Figure 1, the trend is predicted adequately. Further study on generalized parameters will improve the fit.

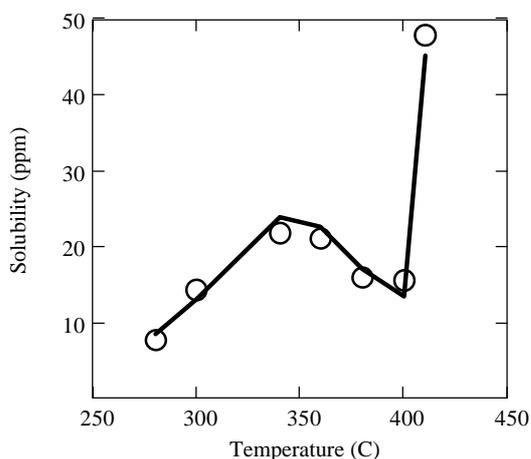


Figure 1 The solubility of Co(OH)_2 along isobaric path; 25 g of water and 0.1 g of Co(OH)_2 in 124 ml vessel.

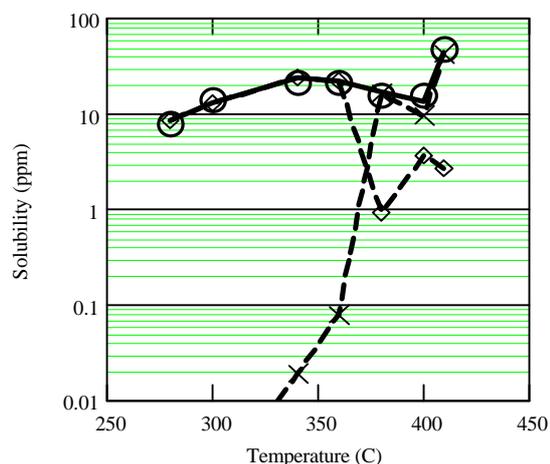


Figure 2 The contribution of $\text{Co(OH)}_{2(\text{aq})}$, symbolized as \times , and Co(OH)_3^- , symbolized as $?$, to the total solubility.

The Solubility of CoCO_3

The solubility of CoCO_3 along two isobaric paths is shown in Figure 4. The trend of the experimental data is roughly consistent with $1/e - 1/e_0$. For each isobaric path an individual empirical equation can be found by correlating with the difference of the inverse of dielectricity, however, no general empirical equation was obtained in this work. The empirical correlations are

$$\left\{ \begin{array}{l} \ln(S) = 7.67 \left(\frac{1}{e} - \frac{1}{e_o} \right) + 1.32; \quad 25 \text{ g of water and } 0.1 \text{ g of } \text{CoCO}_3 \text{ in } 124 \text{ ml} \\ \ln(S) = 8.73 \left(\frac{1}{e} - \frac{1}{e_o} \right) + 2.05; \quad 30 \text{ g of water and } 0.1 \text{ g of } \text{CoCO}_3 \text{ in } 124 \text{ ml} \end{array} \right. \quad (5)$$

Other than the above empirical equations, equations (1) and (4) were also applied to correlating the experimental data. Neither equation (1) nor equation (4) can obtain a general correlation. It is presumed that carbon dioxide formed during the reaction may act as a cosolvent, thereby causing a change in acidity of water, which was not accounted for in equations (1) and (4). Studies on the effect of carbon dioxide on the solubility of carbonate near water's critical point are rare. Therefore, it is difficult to obtain a general correlation at this moment.

Table 1 The parameters of the chemical equilibrium constant in formation of complexes

<i>K</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
$\text{Co(OH)}_{2(\text{aq})}$	8.5	-3800	0.02	3000
Co(OH)_3	7.6	-9010	0.16	6350

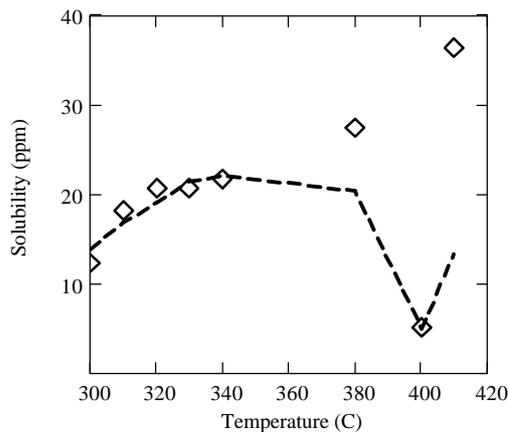


Figure 3 The solubility of Co(OH)_2 along isobaric path; 30 g of water and 0.1 g of Co(OH)_2 in 124 ml vessel.

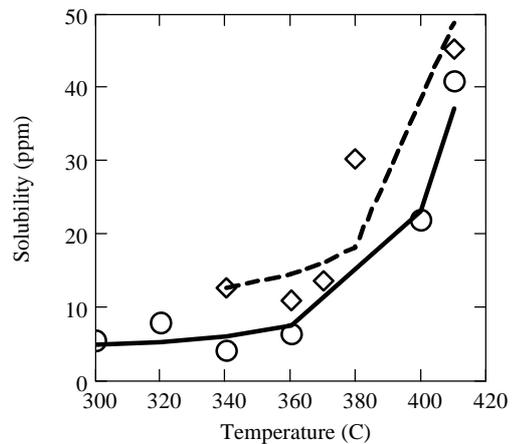


Figure 4 The solubility of CoCO_3 along isobaric path and their calculated results; ? : 25 g of H_2O and 0.1 g of CoCO_3 in vessel; ? : 25 g of H_2O and 0.1 g of CoCO_3 in vessel.

It is well known that the solubility of carbonate increases with decreasing pH. Instead of RO water, diluted HNO_3 aqueous solution (pH = 1.28) was used to study the solubility of CoCO_3 in acidic aqueous solution. The results are illustrated in Figure 5 with symbol \times . The diamonds shown in Figure 5 are those reproduced from Figure 4 for comparison. The

decrease of pH promotes the solubility when the temperature is below critical point and depresses that when, above critical temperature.

Table 2 The parameters of the equilibrium constant in formation of $\text{Co}(\text{OH})_2$ from CoO .

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
25 g of water	-7.0	1780	-0.4	3200
30 g of water	-9.5	3600	-0.6	2300

The Solubility of CoO

Since CoO might form $\text{Co}(\text{OH})_2$ in water, it is believed that the formation of cobaltous hydrate is the determining step. Accordingly, the experimental data of each isochoric path were fitted with equation (4), but no general correlation was found. The fitted results are shown in Figure 6 and the parameters used are listed in Table 2. Further studies that take into account the formation of complexes are undergoing.

CONCLUSION

In this work we have measured the solubility of $\text{Co}(\text{OH})_2$, CoO , and CoCO_3 in compressed hot water and correlated the experimental data with different model equations. The proposed empirical equations were determined and illustrated in Figures 1 - 6. Among them a general equation to predict the solubility of $\text{Co}(\text{OH})_2$ was obtained. It is presumed that a new model equation will be necessary to obtain general equations for CoCO_3 and CoO .

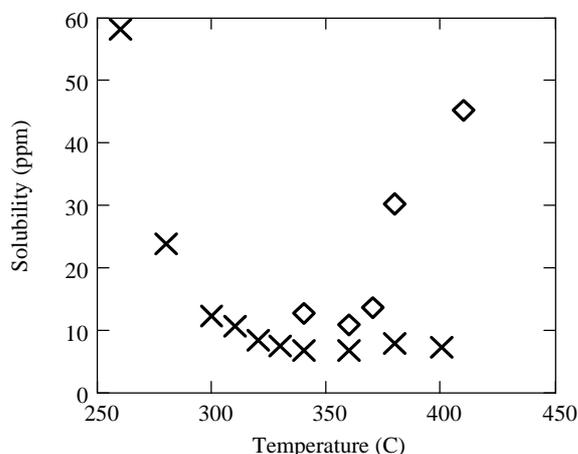


Figure 5 The Solubility of CoCO_3 in neutral and acidic water; ?: pH = 7; x: pH = 1.28.

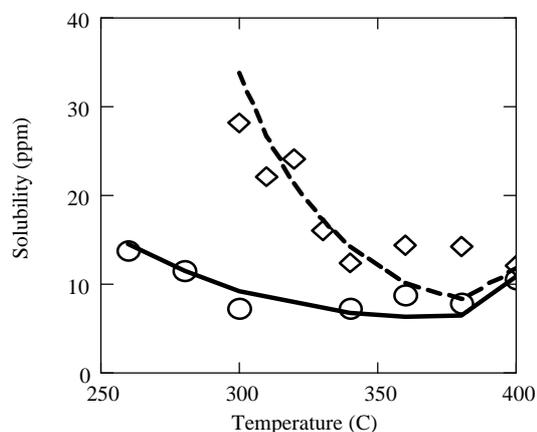


Figure 6 The solubility of CoO along isobaric path and their calculated results; ?: 25 g of water and 0.1 g of CoO in 124 ml; ?: 30 g of water and 0.1 g of CoO in 124 ml.

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