COPRECIPITATION OF Ca-Co SYSTEM AS CARBONATES

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Abstract:

Coprecipitation of Ca-Co system as carbonates has been studied experimentally as a function of molar concentration, pH and temperature. Quantitative precipitation can be obtained by carrying out coprecipitation at higher pH values and higher temperature. The results have been qualitatively explained in terms of the precipitation criteria based on conditional solubility product and side reaction coefficients.

Index terms- coprecipitation, Ca-Co system, conditional solubility product

I. INTRODUCTION

Complex metal oxides are traditionally prepared by repeated high temperature firing of the mixture of the component oxides or some decomposable salts with grinding at frequent intervals. The major drawback of this method is the formation of a multi-phased product due to imperfect mixing and very long diffusion times during sintering. One of the routes by which these materials can also be prepared involves coprecipitation followed by calcination under appropriate conditions. The use of the coprecipitation technique improves reactivity of the component oxides or salts.

The preparation of Ca-Mn carbonate solid solution precursor for the subsequent formation of Ca-Mn oxides have been studied by H.S. Horowitz et al (1978) and a phase diagram was set up. J.M. Longo et al (1980) have investigated the Ca-Mn carbonate system and have also studied the effect of isopropyl alcohol on the surface area of precipitates. K. Vidyasagar et al (1984) have studied the synthesis of Ca-Co and Ca-Fe complex oxides from the respective carbonate solid solution precursor and the method was also extended for the synthesis of oxalate solid solution precursors.

In this paper, coprecipitation of the carbonates of calcium and cobalt has been studied. The results have been explained in terms of the conditional solubility product. The effect of various parameters such as molar concentration, temperature, pH and additives on the coprecipitation have also been investigated.

II. EXPERIMENTAL SECTION

Reagents - Calcium chloride, Cobalt nitrate and sodium bicarbonate were of analytical grade. All the solutions were prepared in double distilled water.

Individual Precipitation: A series of individual precipitations as a function of pH were carried out. The chosen concentration was 1×10^{-2} M. An appropriate volume of the stock solution was diluted with double distilled water to give the desired concentration as mentioned above. To this, 1M sodium bicarbonate solution (30% excess of calculated amount) was added slowly and with constant stirring. After the addition of sodium bicarbonate, the solution was stirred for 15 minutes at 600 rpm at room temperature. The pH of the solution before and after the precipitation was noted. The pH of the solutions was controlled with dilute hydrochloric acid or ammonium hydroxide if necessary. The precipitates were filtered after 2 hours and washed with double distilled water to remove excess sodium bicarbonate. These were dried at 105°C (Dasgupta, 1992).

Coprecipitation: A series of coprecipitations were carried out as a function of pH. An appropriate volume of calcium chloride and cobalt nitrate were mixed and the solutions diluted with double distilled water so as to obtain a required molar ratios of Ca:Co. The precipitation method is similar to the one described above for individual precipitation.

The effect of temperature on the coprecipitation were studied at room temperature, 50°C, 75°C. 100°C and 125°C. Coprecipitation were also carried out in the presence of various alcohols. The specific surface area of these samples was then determined by solution absorption of p-nitrophenol (PNP) at room temperature (Giles et al, 1962).

Analysis: Titrimetric methods were selected for the analysis of the coprecipitates. Co was estimated by titration with 0.01M Ethylene diamine tetra acetic acid (EDTA) using xylenol orange as the indicator (Vogel, 1978) after separation as CoS. Ca was analyzed by titration with 0.01M EDTA using Patton and Reader's indicator (Vogel, 1978)

Characterization of coprecipitates: The carbonate precipitates were characterized using X-ray diffraction (XRD), Infra-Red Spectroscopy (IR), Thermogravimetry Analysis (TGA) and Differential Thermal Analysis (DTA).

The XRD was done on a Phillips diffractometer using CuK$_{\alpha}$ as the target.The XRD patterns of the carbonate samples has been shown in Fig. 1.
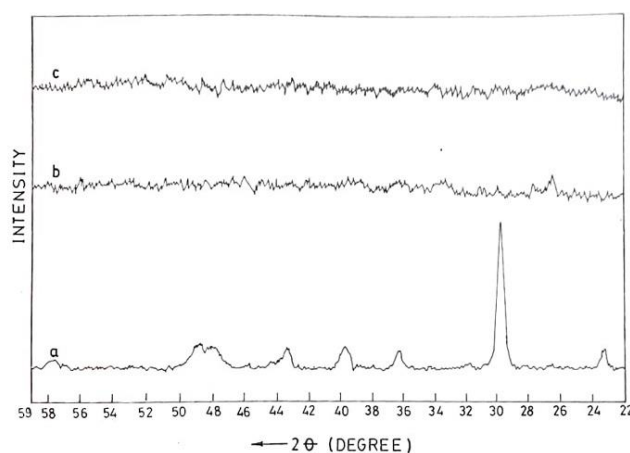

FIG. 1 : XRD PATTERN FOR COPRECIPITATED Ca-Co
CARBONATE SAMPLES (a) 0·1MCa:0·01M Co
(b) 0·1MCa:0·1M Co (c) 0·1MCa:0·2MCo

It is observed that only sample (a) is crystalline whereas the samples having a higher concentration of Co are amorphous in nature. The observed d-values in this case (3.03, 1.87, 3.85) were found to match with the standard d-values of $CaCO_3$ as calcite (Powder diffraction file, 1979).

The IR spectra was recorded using KBr pellets on a Perkin-Elmer 397 Infra-Red Spectrophotometer in the range 4000-400 cm^{-1}. The IR spectra has been given in Fig.2.
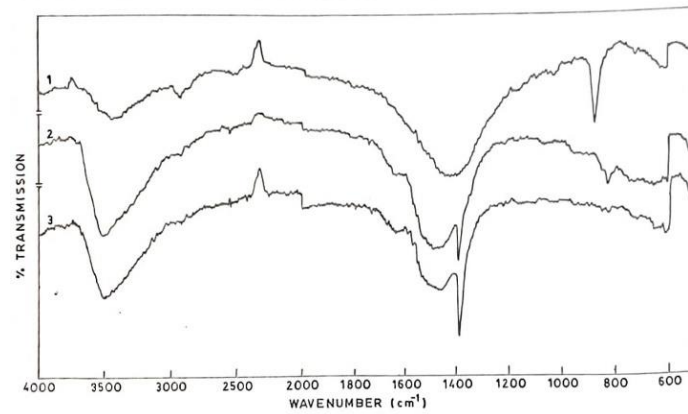
FIG. 2 : IR SPECTRA OF COPRECIPITATED Ca-Co CARBONATE SAMPLE –
(1) 0·1M Ca : 0·01M Co, (2) 0·1M Ca : 0·1M Co, (3) 0·1M Ca : 0·2M Co.

The carbonate sample having a concentration 0.1M Ca :0.01M Co show absorption bands around 1450, 1080, 870 and 720 cm^{-1} which are typical of the calcite structure (Nyquist et al, 1971).   The sharp peak around 1400 cm^{-1} may be due to the excess of NaHCO$_3$ remaining in the sample (Miller et al,1952). As the concentration of Co is increased, the prominent calcite peak at 870 cm^{-1} is not observed, instead CaCO$_3$ peak is observed around 740 cm^{-1} (Nyquist et al, 1971).

The TGA and DTA curves shown in Fig.3a and 3b respectively were recorded on a Du Pont 9900 Thermal Analysis System comprising of TGA 951 and DTA 1600.   Both the curves indicate the removal of combined water around 245°C.   The final decomposition of the coprecipitated carbonates take place around 965°C.
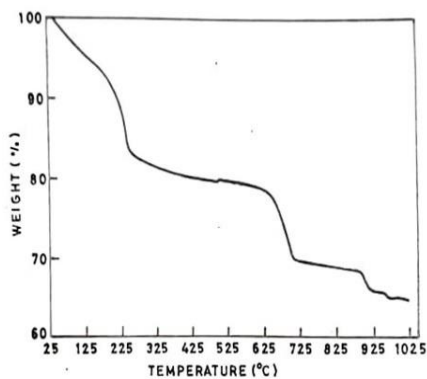

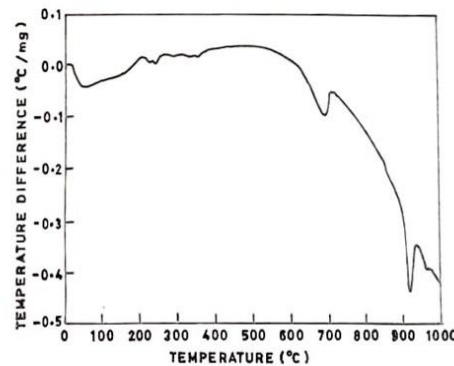FIG. 3a : THERMOGRAM OF COPRECIPITATED
CALCIUM AND COBALT CARBONATES

FIG. 3b : DTA CURVE FOR COPRECIPITATED Ca-Co
CARBONATES

III. RESULTS

Individual precipitation: The percentage precipitation of Ca and Co as a function of pH has been plotted in Fig.4.
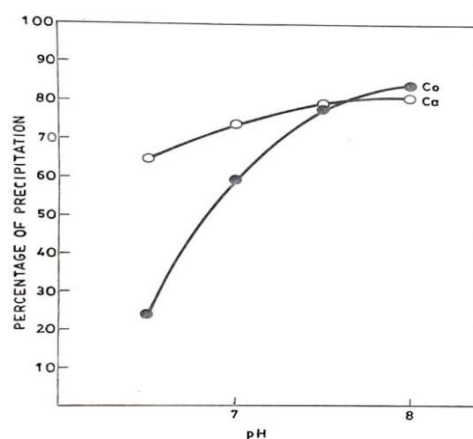

FIG. 4 : PRECIPITATION OF INDIVIDUAL
CARBONATES AS A FUNCTION OF pH

Both Ca and Co show a steady increase in precipitation with increasing pH giving a highest precipitation of 80% and 84% respectively at pH 8.0.

Coprecipitation: The percentage precipitation of Ca and Co as a function of molarity of Co has been shown in Fig.5.
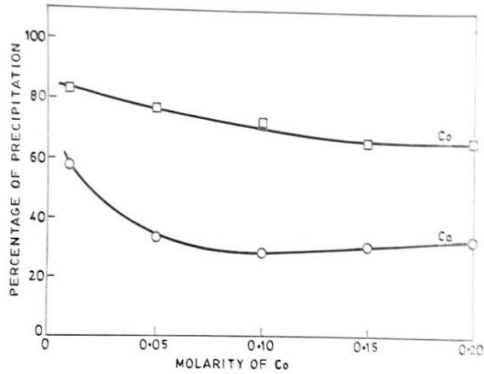

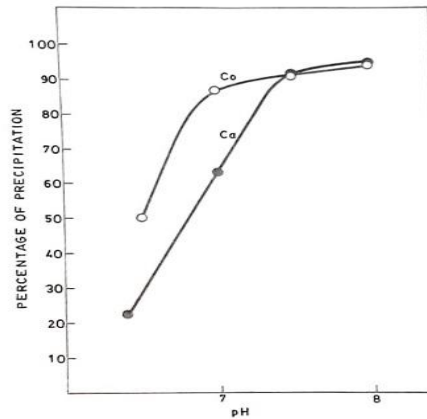FIG. 5 : COPRECIPITATION OF Ca AND Co CARBONATES AS A FUNCTION OF MOLARITY OF Co

FIG. 6 : COPRECIPITATION OF Ca AND Co CARBONATES FROM BINARY SOLUTION Ca : Co = 0·1M : 0·1M AS A FUNCTION OF pH

The percentage precipitation of Ca is highest at a molar ratio of 0.1M Ca:0.01M Co. The percentage precipitation of Ca and Co as a function of pH have been plotted in Fig.6 (0.1M Ca:0.1M Co), Fig.7 (0.1M Ca:0.2M Co), Fig.8 (0.1M Ca:0.3M Co).

FIG. 7 : COPRECIPITATION OF Ca AND Co CARBONATES FROM BINARY SOLUTION Ca : Co = 0·1M : 0·2M AS A FUNCTION OF pH

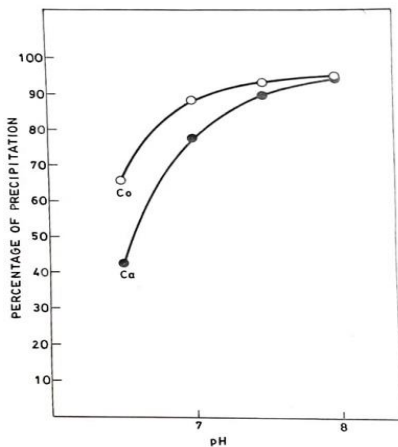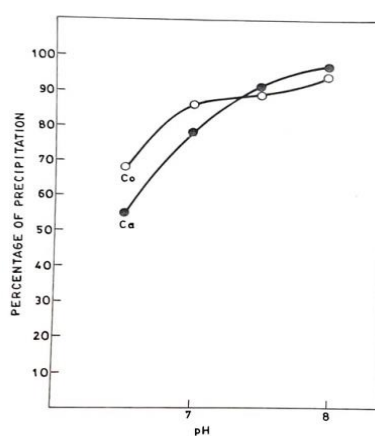
FIG. 8 : COPRECIPITATION OF Ca AND Co CARBONATES FROM BINARY SOLUTION Ca : Co = 0·1M : 0·3M AS A FUNCTION OF pH

Both Ca and Co show an increase in percentage precipitation with increasing pH giving almost quantitative precipitation at pH 8.0 in each case. The percentage precipitation of Ca and Co as a function of temperature (at pH 7.0) has been plotted in Fig.9.
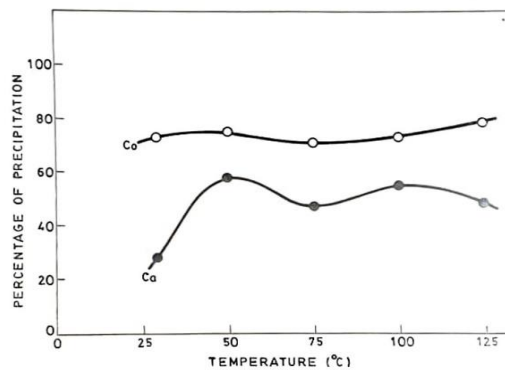
FIG. 9 : COPRECIPITATION OF Ca AND Co CARBONATES
FROM BINARY SOLUTION Ca : Co = 0·1M : 0·1M
AS A FUNCTION OF TEMPERATURE

Co shows a marginal increase in precipitation with increasing temperature. However, in case of Ca the percentage precipitation increases from 28% to 58% as the temperature is raised from room temperature to 50°C.

Effect of additives on coprecipitation: The effect of additives on the surface area of the coprecipitated samples was studied by carrying out coprecipitation in the presence of 5%, 15%, 20% v/v of methyl, ethyl, propyl and butyl alcohol.   The specific surface area determined by PNP absorption has been given in Table-1.

Table – 1 : Specific surface area of Ca-Co samples coprecipitated in the
presence of various additives

Additives v/v	Specific surface area m^2g^{-1}
Without alcohol	81.3
5% Methyl alcohol	108.3
10% Methyl alcohol	135.4
20% Methyl alcohol	81.3
5% Ethyl alcohol	94.8
15% Ethyl alcohol	94.8
20% Ethyl alcohol	67.7
5% Propyl alcohol	84.3
15% Propyl alcohol	94.8
5% Butyl alcohol	121.9
20% Butyl alcohol	94.8

It is observed that the coprecipitated samples in the absence of alcohol has a specific surface area of 81.3 m^2g^{-1}.   Precipitations carried out in the presence of 5-20 % alcohols give powders which are much finer in appearance and having higher surface area in general. Thus, an improvement in surface area can be achieved by the addition of 5-10% alcohol during the precipitation procedure.

Precipitation / Coprecipitation Criteria:

In the present investigation, an attempt has been made to understand coprecipitation in terms of the conditional solubility product (Schwarzenbach,1960, Ringbom,1963 and Dasgupta,1992). In the case of precipitation reactions, conditional solubility product is defined by the expression

$$S_{M'_j A'_i} = [M']^j \ [A']^i \ = \alpha^j_M \ \alpha^i_A \ S_{M_j A_i} \qquad \qquad ....(1)$$

where $S_{M'_j A'_i}$ is the conditional solubility product, $S_{M_j A_i}$ is the classical solubility product, $[M']$ denotes the total concentration of the metal, $[A']$ the total concentration of the precipitating agent in the solution and α coefficients are measures of extent of side reactions.

If several side reactions interfere, the overall α coefficients are practically equal to the sum of the individual values for each interfering reactant.

Thus, $\qquad \qquad \alpha_M = \alpha_M(A_I) \qquad + \alpha_M(A_{II}) \qquad + \ .... \qquad + (1-p) \qquad \qquad .... (2)$

and $\qquad \qquad \alpha_L = \alpha_L(B_I) \ + \ \alpha_L(B_{II}) \ + \ \ .... \ + (1-q) \qquad \qquad .... (3)$

α_M is the side reaction due to the metal and α_L is the side reaction due to the ligand. The various interfering components are designated by Roman numbers, p and q are the number of these components.

According to Ringbom (1963), the precipitation of 1:1 salt start when the value of the conditional solubility product is roughly $< 10^{-2}$. As the value decreases, more and more precipitate is formed and when the value is roughly $< 10^{-7}$ almost quantitative precipitation takes place. Thus, the value of $-\log S' > 2$ indicates the onset of precipitation and a value of $-\log S' > 7$ indicates complete precipitation. It may be noted that these are rough limits.

It is possible to calculate the conditional solubility product from the equations give above, provided the values of the equilibrium solubility product and the α coefficients are known. The solubility product values used in the present calculations are given in Table-2.

Table-2 : Solubility product values (Martell, 1977)

Metal Carbonate	Log S
Calcium carbonate	-8.0
Cobalt carbonate	-9.98

The value of log $\alpha_{L(H)}$ and log $\alpha_{M(L)}$ as a function of pH are given in Table-3 and 4 respectively.

Table-3 :   log $\alpha_{L(H)}$ values for ammonia and carbonate (Ringbom, 1963)

pH	Ammonia	Carbonate
0	9.4	16.3
1	8.4	14.3
2	7.4	12.3
3	6.4	10.3
4	5.4	8.3
5	4.4	6.3
6	3.4	4.5
7	2.4	3.1
8	1.4	2.0
9	0.8	1.0
10	0.1	0.3

Table-4 : Log $\alpha_{M(L)}$ values for various metals and ligands (Ringbom, 1963)

Metal and Ligand	pH						
	8	9	10	11	12	13	14
Calcium hydroxide						0.3	1.0
Cobalt hydroxide	0.1	0.4	1.1	2.2	4.2	7.2	10.2
Cobalt ammonia	0.2	1.0	1.8	2.9	4.9	7.2	10.2

Most of the α values used in the present calculations are at an ionic strength of 0.1. In the present calculations only the existence of mononuclear complexes has been taken into account. The specific equations for Ca and Co may be written as:

$$\log S_{Ca'CO'_3} = \log S_{CaCO_3} + \log \alpha_{Ca(OH)} + \log \alpha_{CO_3(H)} + \log \alpha_{NH_3(H)} + (1-p) \qquad ….(4)$$

$$\log S_{Co'CO_3'} = \log S_{CoCO_3} + \log \alpha_{Co(OH)} + \log \alpha_{Co(NH_3)} + \log \alpha_{CO_3(H)} + \log \alpha_{NH_3(H)} + (1-p) \quad …. (5)$$

Due to the addition of ammonia to control pH, the formation of hydroxides and ammonia complexes with the cations have been taken into account in the above equations.

In the case of coprecipitation for the Ca-Co system, the equations for Ca and Co may be written as:

$$\log S_{Ca'CO'_3} = \log S_{CaCO_3} + \log \alpha_{Ca(OH)} + \log \alpha_{Co(OH)} + \log \alpha_{Co(NH_3)} + \log \alpha_{CO_3(H)} + \log \alpha_{NH_3(H)} + (1-p) \quad ….(6)$$

$$\log S_{Co'CO'_3} = \log S_{CoCO_3} + \log \alpha_{Co(OH)} + \log \alpha_{Co(NH_3)} + \log \alpha_{Ca(OH)} + \log \alpha_{CO_3(H)} + \log \alpha_{NH_3(H)} + (1-p) \quad ….(7)$$

The above equations (6) and (7) takes into account the presence of other cations and their side reactions. It may be noted that $\alpha_{Ca(OH)}$ values are relevant only at pH values of 13 and above. Hence, in the pH range studied in the present work, the term $\log \alpha_{Ca(OH)}$ is not included in the calculations. Therefore, during coprecipitation the presence of the other cation marginally affect the precipitation of the cation under consideration.

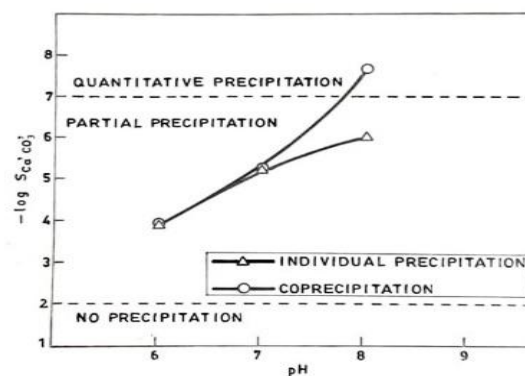The calculated values of –log S′ as a function of pH for Ca has been plotted in Fig.10.

FIG. 10 : CALCULATED CONDITIONAL SOLUBILITY PRODUCT FOR Ca CARBONATE AS A FUNCTION OF pH

Two curves have been shown, for individual as well as for coprecipitation. Both the curves match qualitatively with the experimental curves. The numerical value of –log S′ at pH 6.5 is around 4.5 which according to the precipitation criteria indicates partial precipitation. This was also found to be the case experimentally, both in the case of individual as well as coprecipitation. The value of –log S′ at pH 8.0 is around 6 for individual precipitation which indicates less than quantitative precipitation. Experimentally around 80% of Ca was found to precipitate at pH 8.0. However, the –log S′ value at pH 8.0 during coprecipitation is greater than 7 which indicates quantitative precipitation. Experimentally it was found that 95% of Ca coprecipitated at pH 8.0.

The calculated values of –log S′ as a function of pH for Co has been shown in Fig.11.
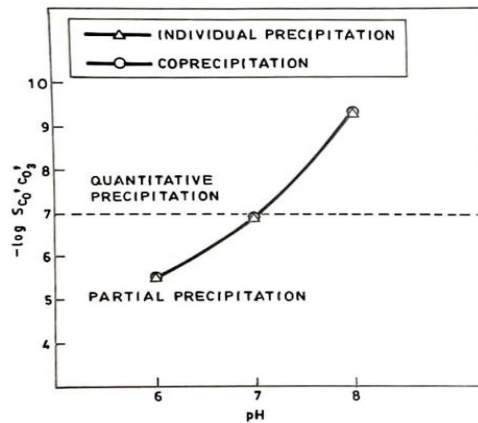

FIG. 11 : CALCULATED CONDITIONAL SOLUBILITY PRODUCT FOR Co CARBONATE AS A FUNCTION OF pH

The curves are in qualitative agreement with the experimental curves. The –log S′ value at pH 6.5 is around 6.0 which according to the precipitation criteria indicates partial precipitation. Experimentally also, only partial precipitation of Co was achieved at a pH of 6.5. At pH 8.0, the –log S′ value is greater than 7 indicating quantitative precipitation. Experimentally, it was noticed that around 84% of Co gets precipitated at pH 8.0 which increases to 94% during coprecipitation.

IV. CONCLUSION

Thus, it is observed that in order to maintain the desired ratio of the cations in the precipitate, it is necessary to control the pH during coprecipitation. In the present system, a higher pH value of about 8.0 and a higher temperature brings about almost comparative precipitation of both the cations. The coprecipitation/precipitation criteria based on conditional solubility products qualitatively explain the experimental results.

V. REFERENCES

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