STUDIES ON THE BASIC CARBONATES OF NICKEL

Part III: Potentiometric Study of Precipitation

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Abstract

The potentiometric method has been adopted to follow the precipitation of basic nickel carbonates during the addition of an alkali carbonate to a nickel salt in aqueous medium. The pH-titration curves obtained are found to correspond to the neutralization of carbonic acid. The results are interpreted on the basis of the hydrolysis of nickel carbonate, $NiCO_3$, to yield carbonic acid which is neutralized by the sodium hydroxide liberated during the hydrolysis of sodium carbonate. On this basis a method has been outlined for computing the compositions of precipitated basic salts from a knowledge of the amount of the metal precipitated under standard conditions at each molar ratio of the reactants and the corresponding pH of the medium.

Introduction

In an earlier communication[1] on the precipitation of nickel carbonates from aqueous solutions of nickel salts and alkali carbonates under standard condition, it was shown that upto a molar ratio (alkali carbonate/nickel salt) = 1.0, the amount of nickel precipitated was directly proportional to the amount of alkali carbonate added. However, at this stage only 84 % of the nickel content of the solution was thrown out. Nearly 2.5 moles of alkali carbonate had to be added per mole of nickel salt in order to completely precipitate the nickel. The precipitation of basic nickel carbonates from aqueous solutions of nickel sulphate, chloride and nitrate by the gradual addition of decinormal alkali carbonate solution has been followed potentiometrically using the glass electrode.[2,3] The changes in the pH of the medium during the potentiometric titration, have been correlated with the data on the amounts of nickel precipitated[1] and the compositions of the precipitates as determined by analytical methods.[4]

Experimental

Apparatus:—The apparatus used consisted of a Marconi glass electrode (Type TM 3888 A) along with a Tinsley electrometer (Type 3474 B) and a Tinsley Potentiometer (Type 3387 B). The set up was capable of reading glass electrode potentials precisely to within 0.0005 volts or 0.01 pH units.

Reagents Employed:—Exactly 0.05 molar solutions of nickel sulphate, chloride and nitrate and decinormal sodium and potassium carbonate solutions

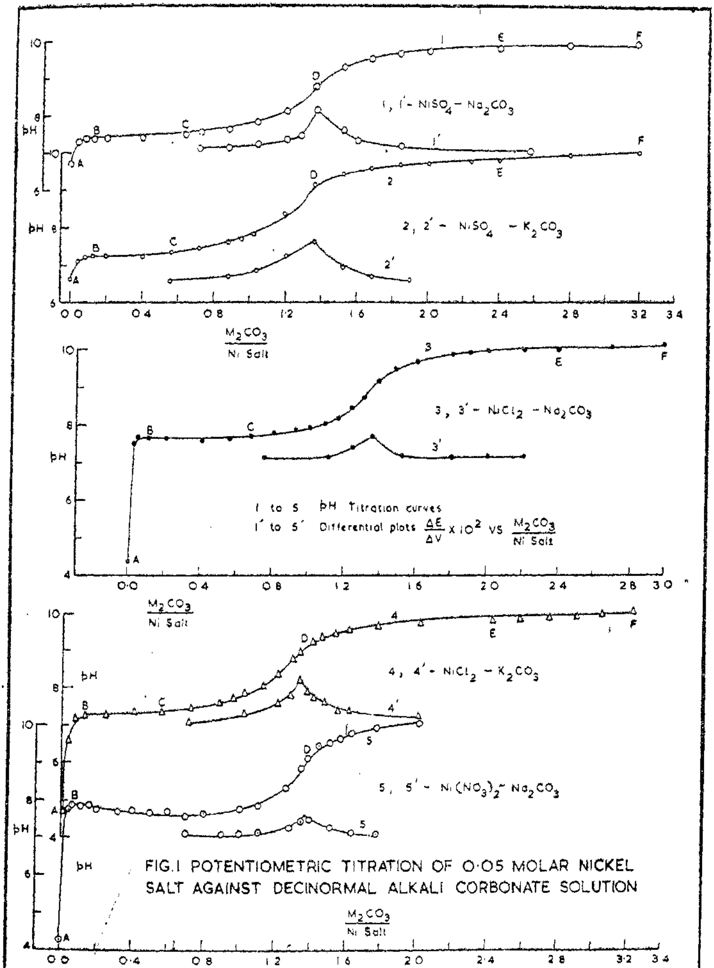

FIG. 1 POTENTIOMETRIC TITRATION OF 0·05 MOLAR NICKEL SALT AGAINST DECINORMAL ALKALI CORBONATE SOLUTION

TABLE I

Potentiometric Titration of Nickel Salts against Alkali Carbonates at Laboratory Temperature

System	Initial pH	Precipitation Beginning		Pptn. at const pH till M_2CO_3/Ni salt	Point of Inflexion		Curve Levels off		pH at M_2CO_3/Ni salt $=3.0$	Increase in pH for M_2CO_3/Ni salt $=2.4-3.0$
		pH	M_2CO_3/Ni salt		pH	M_2CO_3/Ni salt	pH	M_2CO_3/Ni salt		
1. $NiSO_4 - Na_2CO_3$	6.73	7.43	0.12	0.5	8.75	1.36	9.76	2.4	9.9	0.14
2. $NiSO_4 - K_2CO_3$	6.68	7.25	0.12	0.5	9.10	1.36	9.78	2.4	9.94	0.16
3. $NiCl_2 - Na_2CO_3$	4.38	7.67	0.08	0.68	8.91	1.36	9.99	2.4	10.15	0.16
4. $NiCl_2 - K_2CO_3$	4.64	7.28	0.12	0.56	8.8	1.34	9.81	2.36	9.95	0.16
5. $Ni(NO_3)_2 - Na_2CO_3$	4.31	7.88	0.08	……	8.90	1.36	……	……	……	……

were prepared and their strength checked up by analysis as described in an earlier communication.[1]

Procedure :—The glass electrode was calibrated over the pH range 2-11 using standard sodium acetate, acetic acid buffers for lower pH ranges and phosphate-sodium hydroxide buffers for higher ranges[5]. The calibration was checked up prior to each experiment.

An aliquot of 0.05 molar nickel salt solution was taken in a 250 ml. pyrex beaker. The glass electrode and the bridge of the calomel half cell were immersed in the solution. Exactly 0.1 Normal alkali carbonate solution was added dropwise from burette in increments of 0.5 to 1.0 ml. The solution was stirred mechanically during the addition of the precipitant and for a minute thereafter. The mechanical stirring was stopped and the glass electrode potential was measured. The titration was continued till an excess of alkali carbonate had been added even after the sharp rise in potential corresponding to the usual end-point was noticed. The titrations were carried out at laboratory temperature $(22 \pm 2^\circ C)$.

RESULTS

The pH-titration curves for the various systems of nickel salts and alkali carbonates and the corresponding differential plots are shown in Figure 1. The results of these titrations are summarised in Table I.

The initial pH value of nickel sulphate solution was nearly 6.7 whereas nickel chloride and nitrate solution had pH values around 4.4. It is seen in all the cases that the first few ml. of alkali carbonate solution added were utilized in raising the pH of the medium to that at which precipitation of the basic nickel carbonate occurred at the same (≈ 7.5) pH. The pH values at which precipitation started are different for different salts of nickel. Nearly 0.08 to 0.12 moles of alkali carbonate had to be added per mole of nickel salt in order to initiate precipitation of the basic nickel salts as was found out visually. Precipitation of nickel carbonate proceeded at constant pH till nearly 0.5 to 0.6 moles of alkali carbonate had been added per mole of nickel salt. Thereafter on further addition of alkali carbonate solution, the pH of the medium increased, at first gradually and later more rapidly to a point of inflexion. The inflexion in the pH-titration curve was obtained when 1.36 moles of alkali carbonate had been added per mole of nickel salt. The pH at the point of inflexion was about 8.8. When the potentiometric titration was continued the pH of the medium did not increase further to that of dilute sodium carbonate solutions, namely beyond pH 11. Instead, the pH-titration curve levelled off considerably and even when 2.4 moles of sodium carbonate solution had been added per mole of nickel salt, the pH of the medium was only about 9.8. Thereafter the pH-titration curve was a straight line with a small slope. Thus, between the molar ratios alkali carbonate added/nickel salt = 2.4 to 3.0, the increase in pH in the different experiments was only 0.15 units. When nearly 3 moles of alkali carbonate had been added per mole of nickel salt the pH of the medium was about 10.

Similar results were obtained when potassium carbonate was the precipitant.

DISCUSSION

The low initial pH of nickel salt solution is attributed to the hydrolysis of the salt formed by a weak base and a strong acid. Solutions of nickel chloride and nitrate have a lower pH value (around pH 4.4) than nickel sulphate solution (pH 6.7) of the corresponding concentration. This has been explained, in an earlier communication[6] to be due to the different coordinating tendencies of the anions and the effects of these groups in decreasing the attraction between the metal ion and oxygen of the hydroxyl group. So the alkali carbonate added in the initial stage (AB) of the potentiometric titration is consumed by the hydrogen ions formed due to the hydrolysis till the precipitation starts.

As already mentioned, during the initial stage of the precipitation (BC), the pH is maintained constant thereby indicating that the relative concentration of acidic and basic constituents responsible for the hydrogen ion concentration remains the same. It has been shown in an earlier communication[1] that up to a molar ratio of reactants, (alkali carbonate/nickel salt) = 1.0, the amount of nickel precipitated is directly proportional to the amount of alkali carbonate added. But it was also observed that at this ratio, the precipitation of nickel was incomplete and only about 84 per cent of the nickel content was precipitated at 25°C under the standard conditions specified. It was found by analysis[1] that at molar ratio of reactants, alkali carbonate/nickel salt, 1.0 to 1.5, corresponding to the second stage of precipitation in the pH titration, the addition of more of alkali carbonate does not substantially increase the amount of nickel precipitated. Meanwhile (CD), it causes a sharp rise in pH giving a point of inflexion at about pH 8.9 when 1.36 moles of alkali carbonate are added to a mole of nickel salt solution. In the next stage of the potentiometric titration (DE), after the end-point, the pH-curve levels off till the pH is nearly 9.8. The corresponding molar ratio of reactants (alkali carbonate/nickel salt) is 2.4 at this stage. This corresponds to the stage when almost all the nickel has been thrown out of solution. In the next stage (EF), even though the precipitation of nickel is complete, the pH-titration curve does not exhibit any sharp rise in spite of further addition of alkali carbonate. This implies that there is considerable buffering action in the medium. This effect is explained in terms of the hydrolysis of nickel carbonate to yield basic salts as shown below.

Hydrolysis of Metal Carbonates:—It is known that carbonates of metals undergo hydrolysis in aqueous solutions in accordance with the equation [*a*] giving rise to the metal hydroxide and carbonic acid. The carbonic acid liberated

$$M''CO_3 + 2H_2O \rightleftarrows M(OH)_2 + H_2CO_3 \qquad [a]$$

will be in equilibrium with its conjugate base, HCO_3^- according as

$$H_2CO_3 \rightleftarrows HCO_3 + H^+$$

When the metal M is a large cation with a comparatively low charge, (*e.g.* Na^+, K^+, etc.). It will have little attraction for the oxygen atom of the hydroxyl group.[7] The hydroxide will therefore dissociate into the metal cation and hydroxyl ions, *e.g.*

$$M(OH)_n \rightleftarrows M^{+n} + n(OH)^-$$

The abundant supply of hydroxyl ions would nuetralize the hydrogen ions liberated by the dissociation of carbonic acid resulting in the formation of bicarbonate ions, HCO_3^-.

For the first stage of ionization of carbonic acid, the ionization constant, K_{a_1}, has a value of 3×10^{-7}, the corresponding pK_a, value being 6.52[5]. The ionization constant K_{a_2}, for the second stage of neutralization, *viz.*,

$$HCO_3^- \rightleftarrows CO_3^{--} + H^+$$

has a value of 6×10^{-11} with pK_{a_2} equal to 10.22 at 20°C. In the neutralization of carbonic acid by a strong base, *e.g.*, sodium hydroxide, there is considerable hydrolisis of the salt produced. Consequently the pH values of neutralization for the fiirst and second stages do not coincide with the corresponding pKa Values. The first stage of neutralizatian of carbonic acid is complete only at pH 8.35 at 20°C. At the pK_{a_2} value of 10.2, the second stage of neutralization would have progressed only to 50 per cent. neutralization of bicarbonic acid, HCO_3^-, in decinormal solutions[5].

In the case of the hydroxides of aluminium and the transition elements, the larger charge and smaller size of the cation would increase the attraction between the metal and the oxygen atom of the hydroxyl. The lower electronegativity difference between the metal and oxygen (*viz.* 1.8 to 1.9 on Pauling's scale[8]) shows that the metal-oxygen bond has only about 55 per cent ionic character. Consequently, the tendencies of these metal hydroxides, to dissociate into hydroxyl ions are markedly lower. In addition, many of these hydroxides conglomerate and form complex net works and therefore become sparingly soluble. The solubility product of nickel hydroxide is considerably low. Gayer and Garrett[9] have determined the solubility of nickel hydroxide, $Ni(OH)_2$ in neutral, acid and alkaline media. The value for the solubility product of nickel hydroxide in water at 25°C is given as 6.5×10^{-18} and the water solubility as 1.0×10^{-4}. During the hydrolysis of nickel carbonate, therefore, nickel hydroxide is unable to furnish enough hydroxyl ions to neutralize the carbonic acid to bicarbonate stage. However, the hydrolysis of nickel carbonate is only partial in the first stage of the potentiometric titration. Therefore, the species present in the solution during the first stage of the potentiometric titration would be containing an excess of carbonic acid. In the later stages of the potentiometric titration, the precipitation of nickel would have progressed sufficiently so that there would be an excess of alkali carbonate which is not utilized for the precipitation of nickel. The hydroxyl ions furnished by the hydrolysis of the alkali carbonate would neutralise the liberated carbonic acid beyond its first stage of neutralization. The extent of this neutralization may be evaluated at various stages on the basis of the reactions taking place during the potentiometric titration as shown below.

REACTIONS OCCURRING DURING THE POTENTIOMETRIC TITARTION

In the potentiometric titration of nickel sulphate against sodium carbonate, the following reactions are expected to occur :

$$NiSO_4 + Na_2CO_3 \rightarrow NiCO_3 + Na_2SO_4 \tag{b}$$

$$NiCO_3 + 2H_2O \rightarrow Ni(OH)_2 + H_2CO_3 \tag{c}$$

In addition, there is some amount of unreacted sodium carbonate which also furnishes hydroxyl ions due to hydrolysis according to (*d*)

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH \tag{d}$$

As already pointed out, nickel hydroxide is unable to furnish hydroxyl ions easily. Therefore the carbonic acid liberated in (*c*) can only be neutralized by the sodium hydroxide formed according to (*d*). The net result is that, in the course of the precipitation process we have a continuous change in the amounts of (i) nickel carbonate formed and precipitated ; (ii) nickel carbonate hydrolysing to give insoluble nickel hydroxide (or basic carbonate) and free carbonic acid ; (iii) carbonic acid being neutralized in solution. The relative extents of these processess occurring simultaneously in solution, though probably at different rates, determine the pH of the medium. The pH for the first stage of neutralization of carbonic acid by a strong alkali like sodium hydroxide at 25°C is nearly 8.6. It is significant to point out that the pH values of the points of inflexion obtained in the potentiometric titrations are close to this value.

The pH titration curves obtained from the potentiometric studies with each system of nickel salt and alkali carbonate may therefore be interpreted on the basis of neutralization of carbonic acid by means of alkali hydroxide ; the amount of carbonic acid formed, however, being dependent on the amount of nickel precipitated and on the extent of hydrolysis of normal nickel carbonate in the medium.

On continuing the potentiometric titration beyond the point of inflexion, the pH of the medium increases only in small amounts, instead of increasing sharply to that of sodium carbonate solutions. In the region of molar ratio of reactants, (alkali carbonate/nickel salt) = 2.0 to 4.0, there is marked buffering of the medium. It has been shown in an earlier communication[1] that the following amounts of nickel are precipitated when different amounts of sodium carbonate are added to a solution containing 12.50×10^{-4}g. moles of nickel salt :

Na_2CO_3 added in 10^{-4}g. mole	12.50	18.75	25.00	37.50
Nickel precipitated in 10^{-4}g. mole	10.49	11.68	12.29	12.50
Percentage of Nickel precipitated	83.90	93.46	98.31	100

Even after adding to nickel salt, twice the amount of sodium carbonate solution, about 1.7% of the nickel still remains in solution. In order to completely throw out this remaining nickel from solution, it is necessary to add sodium carbonate which is nearly 60 times the amount of nickal to be precipitated. This fact and the considerable buffering of the medium as noticed from the potentiometric titration curves, points to the presence of bicarbonate ions out of all proportion to the amount of sodium carbonate added. This can only be explained on the basis of the hydrolysis of precipitated nickel carbonate in contact with alkali carbonate solutions above pH 9.8. This implies that nickel carbonate hydrolyses to different extents, the hydrolysis being only partial below pH 8.5. The rest of the nickel carbonate is therefore hydrolysable only at higher pH values. This accounts for the large formation of bicarbonate ions above molar ratio 2.0.

COMPOSITIONS OF PRECIPITATED BASIC NICKEL CARBONATES

Semi-quantitative Calculations.—From a knowledge of the pH-titration curve and of the amounts of nickel precipitated when reactants are mixed in different proportions, the extent of each of the processes (*b*), (*c*) and (*d*) taking place in the reaction system may be evaluated. From this, it should be possible to compute the compositions of the precipitates obtained in the course of the titration as indicated below.

Let the amounts of nickel salt taken and alkali carbonate added be a and b (in 10^{-4}g. moles.). Let the corresponding amount of nickel precipitated be c (in 10^{-4}g. moles.). It is presumed that nickel carbonate initially formed is c $NiCO_3$ and that a fraction, $(c-x)/c$, of this undergoes hydrolysis to nickel hydroxide. Since both nickel carbonate and hydroxide (or basic carbonate) are insoluble the pH of the medium is governed by the amount of unreacted sodium carbonate $(b-c)\,Na_2CO_3$, and the amount of carbonic acid formed by the hydrolysis of nickel carbonate *viz.* $(c-x)\ H_2CO_3$. The reactions occurring will be as follows :

$$a\mathrm{Ni}x_2 + b\mathrm{Na_2CO_3} \rightarrow c\mathrm{NiCO_3} + (a-c)\mathrm{Ni}x_2 + 2c\mathrm{Na}x + (b-c)\mathrm{Na_2CO_3} \qquad [\mathrm{i}]$$

$$(b-c)\mathrm{Na_2CO_3} + (b-c)\mathrm{H_2O} \rightarrow (b-c)\mathrm{NaHCO_3} + (b-c)\ \mathrm{NaOH} \qquad [\mathrm{ii}]$$

$$c\mathrm{NiCO_3} + 2(c-x)\mathrm{H_2O} \rightarrow x\mathrm{NiCO_3}.(c-x)\mathrm{Ni(OH)_2} + (c-x)\mathrm{H_2CO_3} \qquad [\mathrm{iii}]$$

where $x\mathrm{NiCO_3}(c-x)\mathrm{Ni(OH)_2}$ represents the composition of the insoluble basic carbonate.

The over all equation is therefore

$$aNix_2 + bNa_2CO_3 + (b+c-2x)H_2O \rightarrow xNiCO_3(c-x)Ni(OH)_2 + (a-c)Nix_2 + 2cNax + (c-x)H_2CO_3 + (b-c)NaHCO_3 + (b-c)NaOH \qquad [iv]$$

If there is formation of nickel bicarbonate, it is to be expected to be soluble. The soluble species $(c-x)H_2CO_3$, $(b-c)NaHCO_3$ and $(b-c)$ NaOH of the right hand side of equation (iv), determine the concentrations of the various ions in solution and hence the equilibrium.

It is possible to determine the pH of the medium at various molar ratios (b/a), of reactants from a knowledge of c, the amount of nickel precipitated and the corresponding value of x (as determined by analysis of the precipitate). Below pH 8.5,

$$[H^+] = \frac{[H_2CO_3] \times K_1}{[HCO_3^-]} \quad \text{or} \quad [OH^-] = \frac{K_w \times [HCO_3^-]}{K_1 \times [H_2CO_3]}$$

and above pH 8.5

$$[H^+] = \frac{[HCO_3^-] \times K_2}{[CO_3^{--}]} \quad \text{or} \quad [OH^-] = \frac{K_w \times [CO_3^{--}]}{K_2 \times [HCO_3^-]}$$

Conversely, from a knowledge of the amount, c, of nickel precipitated at various molar ratios and the corresponding pH of the medium it is possible to compute the compositions of the precipitates.

In the present work with carbonates it is not possible to find out how much of the carbonic acid formed exists as H_2CO_3 and how much as dissolved, but unhydrated CO_2. In the present work, since the partial pressure of carbon dioxide is low, it is likely that part of the carbondioxide escapes during the agitation of the solution. Even though the value of the equilibrium constant K′ is known, where

$$K' = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3 + CO_2]},$$

the loss of CO_2 was not prevented under the present experimental conditions. It is, therefore, not practicable to get precise values of pH from these results. The values of c and x were obtained in different experiments.[4] The pH value of the medium, calulated from these values, was compared with the value obtained during the potentiometric titration. These restrict the scope of the present set of calculations, which are consequently only of a semi-quantitative significance. The results of these calculations are presented graphically in Fig. 2 and show that although the two sets of values do not agree, especially at low pH values, yet the two curves are similar in nature. For these calculations, it is assumed that x has a value of $c/2$ upto a molar ratio of reactants (alkali carbonate/nickel salt) = 1.5. Above molar ratio 1.0, the precipitate has initially the composition

$NiCO_3 \cdot Ni(OH)_2$ but it rapidly hydrolysis to the more basic composition $NiCO_3 \cdot 2Ni(OH)_2$ as was found by analysis.[9] Above molar ratio $b/a = 2.5$, the value of $x = c/4$. It is also seen from Fig. 2 that in both cases the points of inflexion have nearly the same coordinates. Such calculations also indicate that at molar ratios $b/a > 4.0$, the precipitate becomes more basic (*i.e.* $x < c/8$) and possibly ultimately tends to the composition of nickel hydroxide. However, in the present work more precise measurements were not possible due to the inherent behaviour of the glass electrode in highly alkaline media.

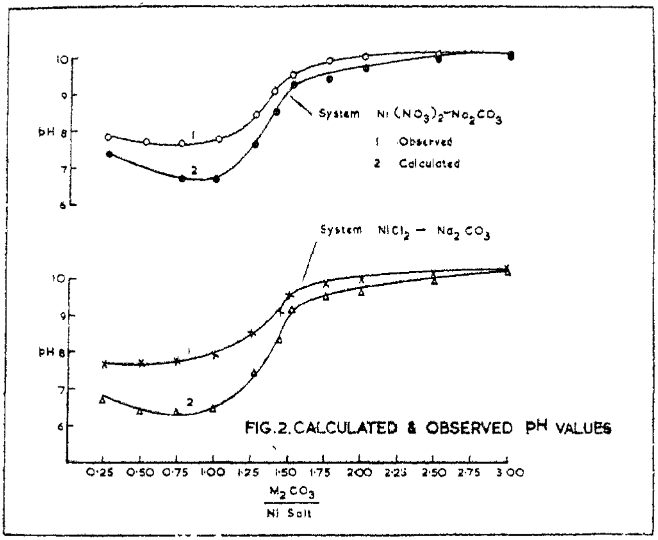

FIG.2. CALCULATED & OBSERVED PH VALUES

Attempts to determine the compositions of such precipitated basic carbonates have alao been made by Carriel and Singley.[10] They describe a method for the determination of the compositions of basic salts precipitated at constant pH. for the system nickel chloride, potassium carbonate, potassium hydroxide at room temperature they observe that above pH 10.5 the precipitated basic nickel carbonates approach the composition of pure nickel hydroxide. However, for the same system, Carriel and Singley state that in the pH range 8 to 10, the composition of the precipitate changes from $4NiCO_3 \cdot Ni(OH)_2$ to $3NiCO_3 \cdot Ni(OH)_2$ *i.e.* NiO/CO_2 changes from 1.25 to 1.33. In the present work, potentiometric and analytical methods show that the composition of the precipitate at pH 8 is $NiCO_3.Ni(OH)_2$ *i.e.* $NiO/CO_2 = 2.0$ and that at pH 9.5 it changes to $NiCO_3{\cdot}3Ni(OH)_2$ or $NiO/CO_2 = 4.0$. Both these compositions are more basic than the compositions reported by Carriel and Singley.[10] The formation of the basic nickel carbonate of composition $NiO/CO_2 = 2.0$ has been reported by Francois-Rossetti and coworkers.[11, 12] The composition $NiCO_3{\cdot}2Ni(OH)_2$ corresponding to the mineral zaratite, $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ has been reported by the above workers and also by Fenoglio,[13] Setterberg[14] and Stromholm.[15] These results are in agreement with the compositions obtained in the present work.

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