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Zinc Oxide Extraction from Pyrite Ashes Leaching Liquors

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Abstract

Recovery of zinc by alkaline precipitation from dilute pyrite leaching liquors is studied. The influence of pH, temperature, and mixing procedure on the recovery yield and product quality are analyzed. Chemical species in the precipitates are identified by x-ray analysis.

INTRODUCTION

Recovery of heavy metals from waste liquors is needed by today's chemical industry for ecological as well as for economical reasons.

Countries with pyrite resources produce sulfuric acid by roasting this mineral (*1*). The availability of sulfur from natural deposits as well as from petroleum refining processes makes pyrite noncompetitive when its use relies exclusively on sulfur (*2*).

Spain, with as much as 50% of the world pyrite resources, focuses its research interest in this field on the development of procedures capable of enhancing the value of this raw material (*3*).

The solid by-product resulting from pyrite roasting consists mainly of ferric oxide; it also contains some nonferrous metals in variable amounts. In order for this material to be used as a feedstock, reduction of the nonferrous metals to the limits imposed by factories is required (*4*).

When roasting is conducted in a multistep fluidized bed, leaching with aqueous solutions of HNO_3, HCl, and NaCl has been proposed as the most effective procedure for pyrite ashes conditioning because of the oxidant and complexing action of these solutions. Liquors containing Cu, Zn, Co, Fe,

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and some other metal ions are obtained from leaching. These liquors have a high chloride concentration, which allows for zinc separation by means of ion exchange with a strongly basic anion exchanger due to the high stability of the chloride complex formed. The rest of the metals are subsequently recovered by different procedures (*5*, *6*).

Water elution of the ion exchanger produces a liquor containing $ZnCl_2$, which cannot be electrolyzed directly for zinc production due to its low metal and high chloride concentration (11 and 12 g/L, respectively). The required zinc concentration for electrolysis is in the range of 110 to 215 g/L at commonly used operating current densities, and the chloride content is limited to a maximum of 50 mg/L because of the corrosive effect of this ion on the lead anodes.

However, recovery of zinc is needed due to the fact that its intrinsic value represents about 10% of the pyrite's, and in the case of Spain would cover nearly than 45% of the internal demand of this metal. An acceptable recovery must concentrate the feed solution and reduce their chloride content. The first objective can be achieved in an economic way by two procedures: solvent extration and alkaline precipitation followed by redissolution of the resulting solid product.

Yields higher than 98% cannot be achieved with solvent extraction even when a large number of stages is used. Furthermore, the volumetric ratio between aqueous and organic phases requires the use of large-size extractors which lead to higher investment costs than for chemical precipitation (*7–9*). Moreover, the last method has another important advantage in that zinc oxide is obtained under appropriate conditions. This is the most interesting zinc product for industrial uses (rubber, pigments, ceramics, catalysts, and electrolytic zinc) (*10*).

Precipitation of zinc from diluted liquors resulting from pyrite ash leaching is studied in this paper, the main objective being to establish the operating conditions for maximum recovery compatible with a suitable product purity for the required use. There are two main options. If the precipitate is going to be used as a final product, a low hydroxide content is required. If it is to be used for electrolytic zinc production, low chloride levels must be achieved (*11*).

The presence of chloride in the precipitates can be due to physical adsorption, favored by the high specific surface of colloidal zinc hydroxide, as well as to a chemical process leading to hydroxychloride formation.

Recovery of zinc by means of alkaline precipitation can be achieved, in principle, by different reagents. However, the desire for a high purity precipitate makes NaOH preferable.

The average composition of the liquors studied is as follows:

Zn	11 g/L
Cl	12 g/L
Fe(II)	0.33 g/L
Cd	0.8 mg/L
pH	1.5–2

With this composition it is necessary, before precipitation, to remove metals other than zinc. Cadmium is removered by cementation with powdered zinc. Ferrous ion is oxidized to ferric and then precipitated as ferric hydroxide at a low pH. About 5% of the total zinc in the solution coprecipitates with ferric ion, but it can be recovered subsequently by treating the precipitate with NaOH to redissolve the zinc as zincate which is incorporated back into the liquors (*12–14*).

EXPERIMENTAL

Simulated zinc-bearing solutions (11 g/L Zn) prepared from $ZnCl_2$ were used in the experimental runs. Precipitation was accomplished with NaOH solution (100 g/L). It is important to prevent carbonation of the alkali used because the formation of zinc basic carbonate in the precipitation process presents a serious problem because its subsequent transformation to the oxide requires severe thermal treatment (900°C).

Precipitation was conducted on a batch basis. Mixing of reactants was accomplished through two different methods that are identified as the direct method and the indirect method. In the first case the alkali was added to the stirred zinc solution; the opposite was done in the second. As will be seen later, the quantitative chemical composition of the precipitate is affected by the mixing procedure.

The experimental apparatus consisted of a 3-L glass spherical reactor with a paddle stirrer, pH electrode, thermometer, reflux condenser, feed inlet, and sampling line. The reaction system was immersed in a paraffin-coated salt-water thermostatic bath to maintain the temperature at a constant level.

Before mixing the reactants, they were preheated to the corresponding temperature and the mixture was stirred for 30 min and then filtered. Zinc analyses were carried out on the filtrate. The precipitate was water washed until no chloride occurred in the eluate, dried at 105°C, and analyzed for zinc and chloride. Zinc analyses were performed by the ammonium mercuric thiocyanate gravimetric method, and the Volhard method was used for chloride after dissolving the samples with H_2SO_4 (*15, 16*).

Chemical species were identified in the precipitates by means of x-ray analyses. A PW 1310 model Phillips apparatus was used with Kα copper radiation and nickel filter with the following operating conditions: Voltage, 40 kV; current intensity, 32 mA; sensitivity, 2×10^{-2}; and time constant, 2. The scanning was carried out in 0 to 50° range, equivalent to an inter-planar distance of 1.82 Å which is below the corresponding values for the characteristic lines of the crystalline compounds most probably present in the precipitates (*17*).

Selected Variables and Experiments Programming

The experimental design corresponds to the conventional sectioning procedure in which several values are checked for every selected variable, the rest being maintained at a constant level. Selected variables for the precipitation process, after a preliminary study, were chosen to be the following.

Temperature. Its influence on the chemical and physical properties of the precipitates was studied. Kinetic effects are less important due to the high precipitation rate of nonsoluble hydroxide.

pH. Zinc recovery yield is related to working pH through the hydroxide solubility product. However, experimental determination is required in practice because of the formation of other chemical species.

Mixing method. As pointed out before, the quantitative chemical composition of the precipitates is influenced by the way in which the reactants are mixed. As mentioned above, two methods were examined, the direct and indirect mixing procedures.

Table 1 shows the experimental design, indicating the values studied for every variable.

TABLE 1
Experimental Programming

Direct method		Indirect method	
Temperature (°C)	pH	Temperature (°C)	pH
25	7,8,9,10,11,12	25	7,8,9,10,11,12
45	7,8,9,10,11	45	7,8,9,10,11
75	6,7,8,9,10	75	6,7,8,9,10
98	6,7,8,9,10	98	6,7,8,9,10

RESULTS AND DISCUSSION

Zinc Recovery

Figures 1a and 1b show the effect on precipitation yield by the operating pH at different temperatures using the direct and indirect mixing methods.

Yields close to 100% are obtained over a wide pH range. This is a predictable result due to the low solubility of the precipitates.

At lower pH values, yield increases with increasing temperature. This can be explained as the result of an increase in the hydrolysis constant of zinc chloride. In effect, according to the reaction (*18*)

$$Zn^{2+} + 2H_2O = Zn(OH)_2 + 2H^+$$

the hydrolysis constant is given by the expression

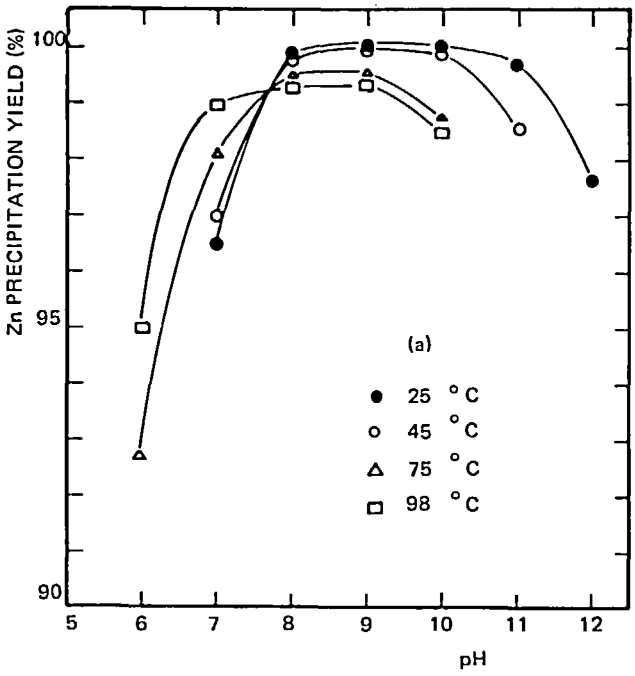

FIG. 1a. Zinc recovery versus pH: direct method.

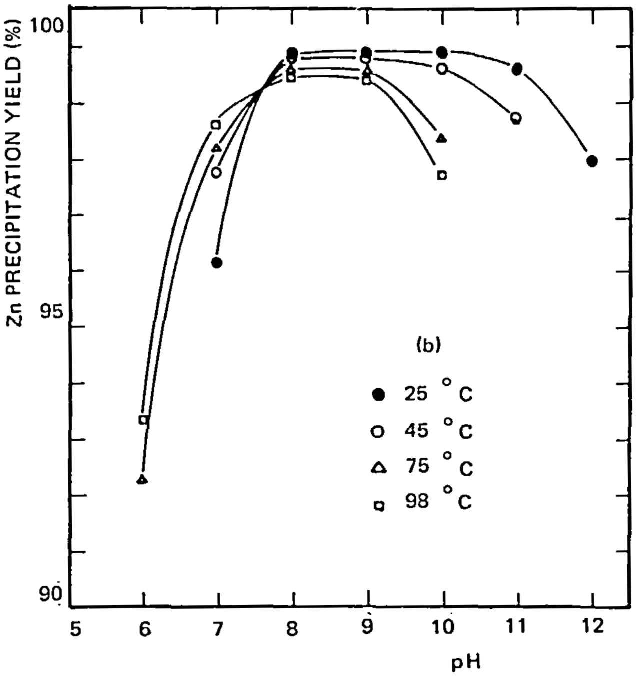

FIG. 1b. Zinc recovery versus pH: indirect method.

$$K_h = \frac{|H^+|^2}{|Zn^{2+}|} = \frac{K_w}{K_{sp}}$$

As the temperature increases, the ion product of water (K_w) increases faster than does the solubility product of the hydroxide (K_{ps}), and this leads to an increase in the hydrolysis constant and consequently a decrease in the residual zinc in the solution for a constant pH value.

At pH values higher than 9–10, depending on the operating temperature, a decrease in yield is observed, which is explained by the formation of soluble zincate according to the reaction

$$Zn(OH)_2 + 2OH^- = Zn(OH)_4^{2-}$$

In this range of higher pH values an increase of temperature leads to a decrease in the recovery of zinc. This can be explained by an increase of the stability of the complex ion and the solubility of zinc hydroxide as the temperature increases:

$$|Zn(OH)_4^{2-}| = K_{f(s)}|OH^-|^2$$

Zinc Content of the Precipitates

Figures 2a and 2b show the experimental results for the zinc content of the precipitates as a funtion of the working pH at different temperatures.

Although the curves for different temperatures exhibit different shapes, a common trend can be observed in the sense that an increase in operating pH leads to an increase in zinc in the solid product. At lower pH values this increase is slow and corresponds to the transformation of hydroxychloride to hydroxide (as will be seen later) which contains a higher percentage of zinc. At a pH value depending on the temperature, a sharp increase in zinc content is observed, corresponding to the spontaneous transformation of hydroxide to

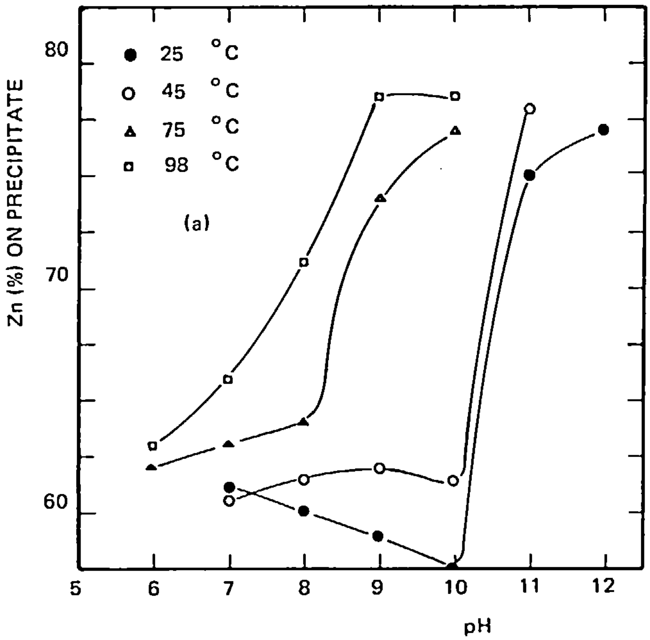

FIG. 2a. pH and temperature influences on the zinc content of precipitates: direct method.

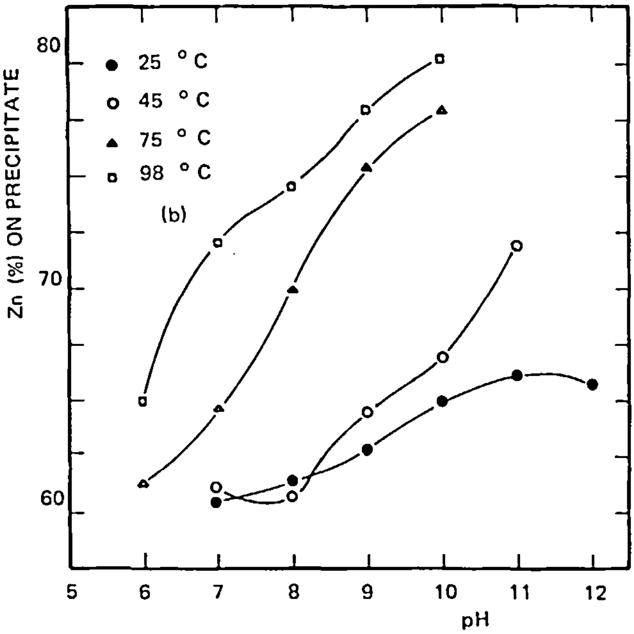

FIG. 2b. pH and temperature influences on the zinc content of precipitates: indirect method.

oxide, which is the richest zinc compound (80%). This transformation takes place at lower pH values as the temperature increases. One might carry out the precipitation process in an autoclave in order to obtain zinc oxide at lower pH values and consequently with less chemical consumption.

At 25°C, using the direct method, a small decrease in the zinc content of the precipitate is observed in the pH range between 7 and 10, which can be explained by a progressive increase in water and other ions in the precipitate due to higher adsorption capability of the solid particles.

Precipitates obtained by the indirect method show, in general, a higher zinc content than the corresponding precipitates prepared using the direct method to mix the reactants. That means that a higher ratio of zinc oxide occurs in precipitates prepared by the indirect method.

X-ray analyses confirm the presence of zinc oxide but do not show the characteristic peaks for crystalline zinc hydroxide. This doesn't necessarily mean the absence of this compound, which can be in an amorphous state. Figure 3a shows the x-ray analysis of a high purity zinc oxide crystalline precipitate, obtained by the indirect method at 98°C and pH 10. Figure 3b corresponds to a less pure precipitate as the decrease in the intensities of the

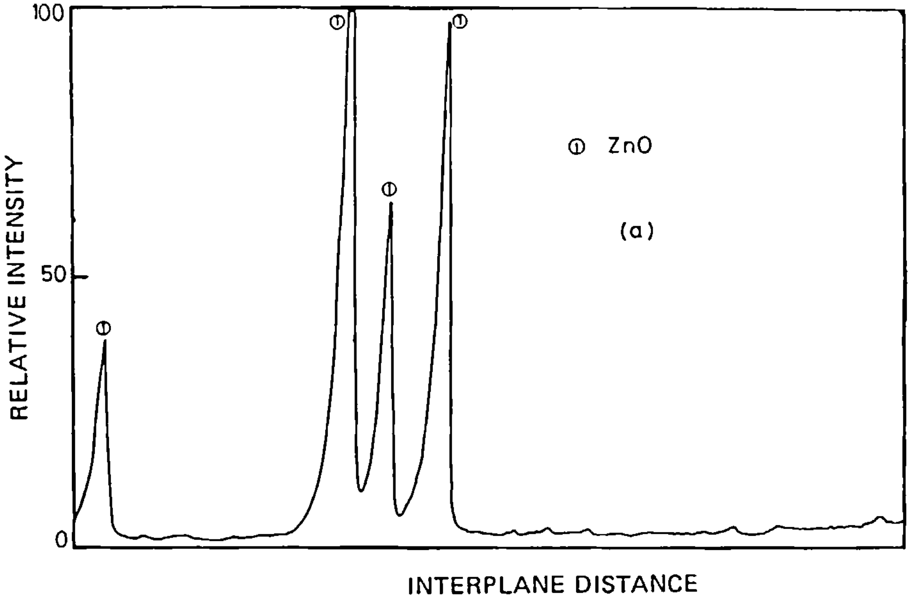

FIG. 3a. X-ray analyses of samples obtained at 98°C, pH = 10, indirect method.

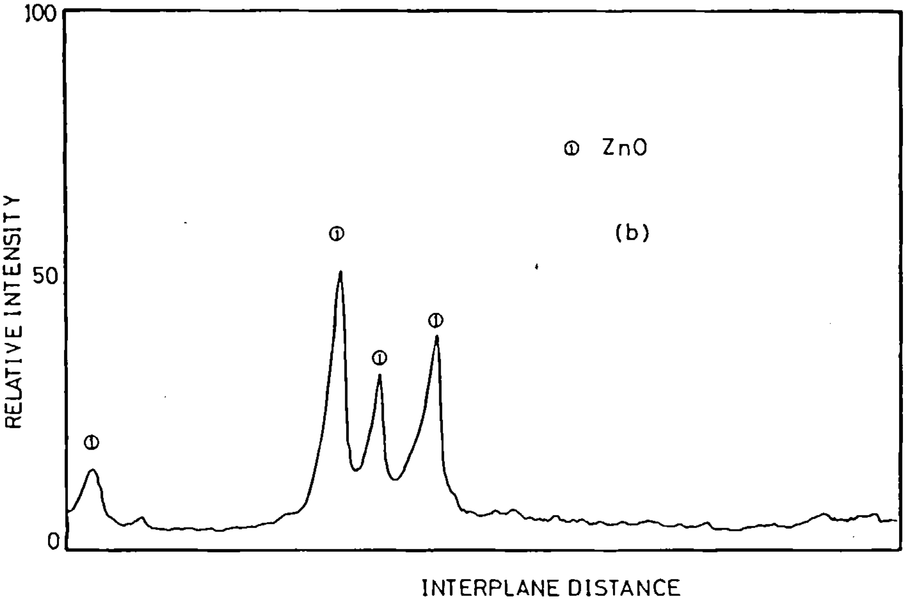

FIG. 3b. X-ray analyses of samples obtained at 98°C, pH = 7, indirect method.

zinc oxide peaks indicates. This precipitate was obtained under the same mixing and temperature conditions as the first one, and at a pH value of 7.

Chloride Content of Precipitates

The presence of chloride in the precipitates is a result of solid hydroxychloride formation. The literature (*19, 20*) refers to three different zinc hydroxychlorides: I, whose composition corresponds to the formula $Zn(OH)_2 \cdot ZnCl_2$; II, $4Zn(OH)_2 \cdot ZnCl_2$; and III, $7Zn(OH)_2 \cdot ZnCl_2$. The first compound is formed when the zinc chloride concentration in the initial solution is in the range of 7 to 0.04 *M*, the second in the range of 0.04 to 0.004 *M*, and the third when that concentration is below 0.004 *M*.

Hydroxychloride I can be rejected by taking account of the concentration of zinc chloride in the simulated liquors; according to this, hydroxychloride II is most probably formed.

Figures 4a and 4b shows the chloride content in the precipitates as a function of operating pH for different working temperatures. The general trend of the curves shows a decrease of chloride content as pH increases, which can be explained as the results of a progressive substitution of chloride ions by hydroxides into the crystal lattice due to a hydrolysis reaction:

$$4Zn(OH)_2 \cdot ZnCl_2 + 2OH^- = 5Zn(OH)_2 + 2Cl^-$$

However, in some of the curves the opposite trend is observed at some pH values. The reason may be due to physical adsorption of chloride ions into the precipitate because substantial amounts of colloidal and high surface area hydroxide are formed at these operating conditions.

The chloride contents of the precipitates decreases substantially as the operating temperature increases. This is reasonable because this increase enhances leaching of hydroxychloride according to

$$4Zn(OH)_2 \cdot ZnCl_2 = 4Zn(OH)_2 + Zn^{2+} + 2Cl^-$$

If curves corresponding to equal temperatures from Figs. 4a and 4b are compared, it can be clearly seen that the method of mixing reactants has a significant influence on the chloride content of the precipitates except for extreme pH values. Solid products with less chloride are obtained from the indirect method.

Hydroxychloride formation proceeds through two consecutive-competitive (*21*) reactions as follows:

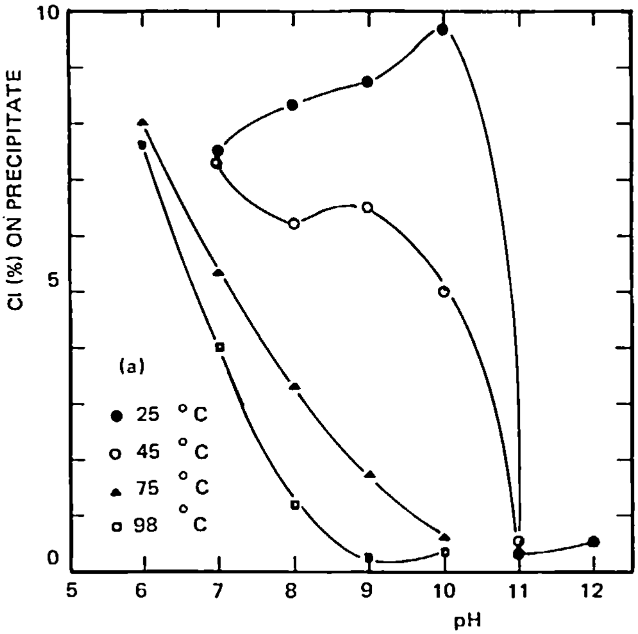

FIG. 4a. Chloride content of precipitates as a function of operating pH at different temperatures: direct method.

$Zn^{2+} + 2OH^- = Zn(OH)_2$	desired product
$4Zn(OH)_2 + Zn^{2+} + 2Cl^- = 4Zn(OH)_2 \cdot ZnCl_2$	nondesired product

Both take place at a high rate. The first one takes place at the contact surface between the reactants, where the $Zn(OH)_2$ concentration is higher. The reaction product diffuses immediately, and if it meets a hydroxide ion-rich medium (as in the indirect method), the second reaction will not take place. However, when the diffusion occurs in a zinc and chloride ion-rich medium (as in the direct method), the second reaction will occur and hydroxychloride will appear.

Figure 5 shows both situations schematically. The left part of the figure corresponds to the situation in the direct method, and the right to the situation in the indirect method.

The presence of crystalline zinc hydroxychloride II in the precipitates was confirmed by x-ray analysis. Figure 6 shows the results corresponding to a sample obtained by the direct method at pH 7 and 25°C. Zinc oxide and hydroxycholride peaks are cleariy observed.

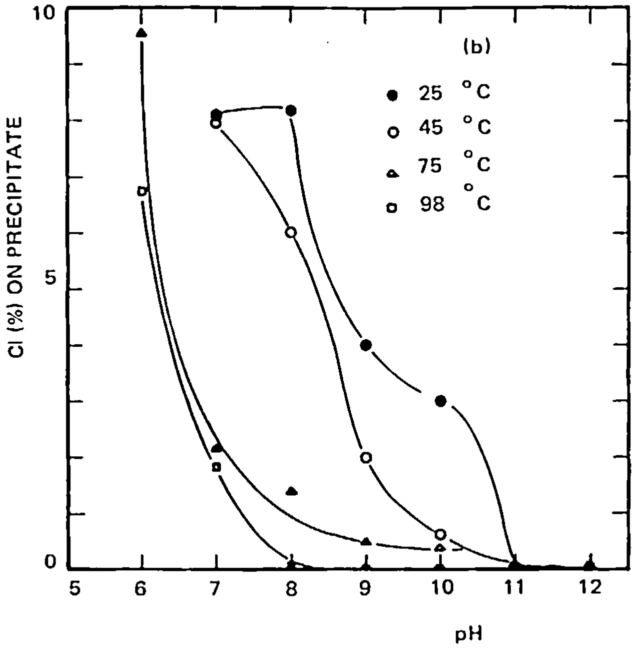

FIG. 4b. Chloride content of precipitates as a function of operating pH at different temperatures: indirect method.

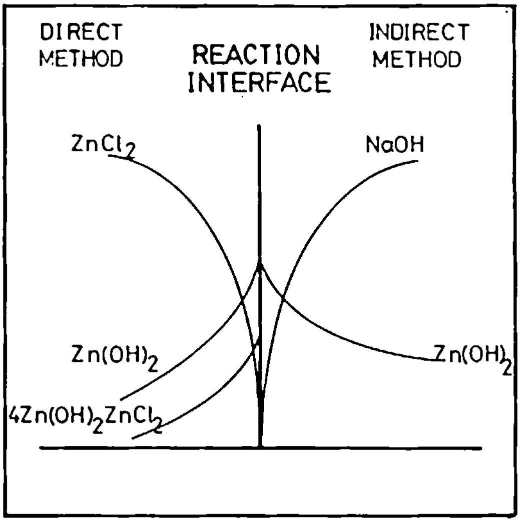

FIG. 5. X-ray analysis of a precipitate obtained at 25°C and pH = 7 by the direct method.

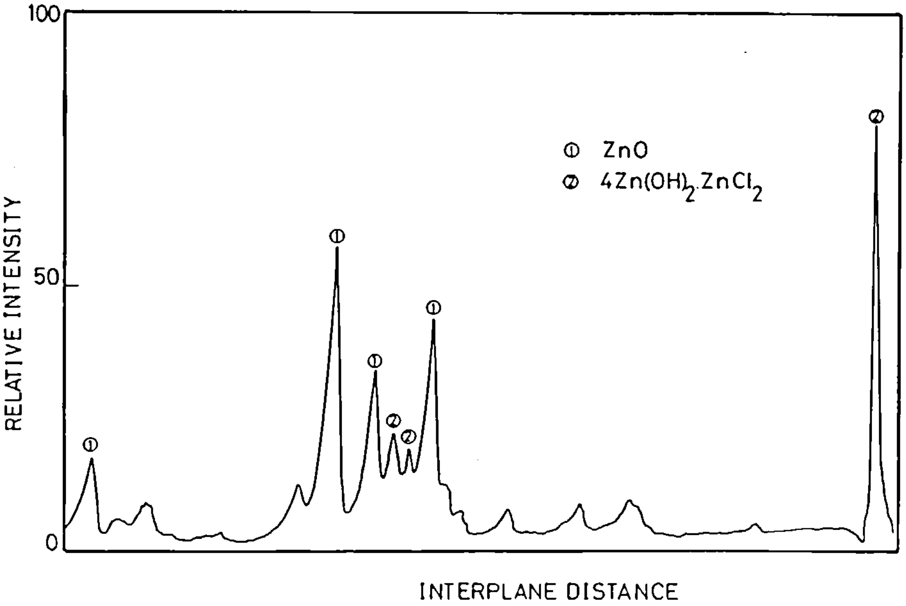

FIG. 6. Alkaline precipitation by the direct and indirect methods.

TABLE 2a
Chemical Species Percentages in Precipitates Obtained through the Direct Method

	Temperature (°C)											
	25			45			75			98		
pH	HC[a]	ZnO	H_2O	HC	ZnO	H_2O	HC	ZnO	H_2O	HC	ZnO	H_2O
6	—	—	—	—	—	—	61.9	30.7	7.4	57.5	35.5	7.0
7	57.1	34.4	8.5	55.7	34.3	10.0	40.6	48.3	10.1	30.5	57.0	12.5
8	63.4	30.6	6.0	47.8	42.2	10.0	26.9	63.0	10.1	9.5	76.5	13.8
9	67.0	24.6	8.4	50.0	40.1	9.9	14.2	70.6	15.2	2.1	95.3	2.6
10	75.2	17.3	7.5	38.9	50.6	10.5	4.8	95.7	—	3.7	96.3	—
11	0.8	91.6	7.6	1.1	96.7	2.2	—	—	—	—	—	—
12	1.2	88.1	10.7	—	—	—	—	—	—	—	—	—

[a] Zinc hydroxychloride.

TABLE 2b
Chemical Species Percentages in Precipitates Obtained through the Indirect Method

	Temperature (°C)											
	25			45			75			98		
pH	HC[a]	ZnO	H_2O	HC	ZnO	H_2O	HC	ZnO	H_2O	HC	ZnO	H_2O
6	—	—	—	—	—	—	75.0	22.3	2.7	52.5	39.9	7.6
7	62.1	31.2	6.7	61.2	31.5	7.3	17.8	68.8	13.4	13.2	78.2	8.6
8	63.7	29.5	6.8	47.2	43.6	9.2	11.7	80.2	8.1	2.1	90.6	7.3
9	31.4	60.3	8.3	17.1	77.1	5.8	5.4	91.5	3.1	0.9	98.7	0.4
10	24.2	68.4	7.4	5.2	87.1	7.7	3.9	95.1	1.0	0.0	99.8	0.2
11	0.5	94.6	4.9	0.9	96.9	2.2	—	—	—	—	—	—
12	0.2	93.4	6.4	—	—	—	—	—	—	—	—	—

[a] Zinc hydroxychloride.

In different precipitating conditions, imperfectly formed hydroxychloride was detected, showing one or two of the corresponding characteristic peaks in the diffraction pattern. At high pH and temperature, none appears (Fig. 3), which confirms the conclusions from Fig. 4.

With the results obtained in this work, the percentages of every chemical species in the precipitates have been calculated. X-ray analyses do not indicate the presence of crystalline zinc hydroxide, but this compound could be present in the amorphous state. Its percentage has been calculated as hydrated oxide. Results are reported in Tables 2a and 2b.

CONCLUSION

Alkaline precipitation allows one to recover zinc from dilute waste liquors with yields very close to 100% over a wide pH range. The precipitates obtained consist of zinc oxide, hydroxychloride, and probably hydroxide in percentages varying with operating conditions. An appropriate selection of these allows one to obtain a final product with the specified purity requirements to be used by industry.

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