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Sedimentation and Filtration of Zinc Oxi-hydroxychloride Suspensions

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Abstract

Sedimentation and filtration are studied and compared as feasible methods to carry out the separation of precipitates obtained from the alkaline precipitation of diluted zinc chloride liquors. The behavior of the suspensions in phase separation has been related to the chemical composition of the precipitate solids and the external morphology of their particles. According to the experimental results, sedimentation is the preferred method for primary separation when zinc oxide is the main product present in the solid phase.

INTRODUCTION

Efficient use of raw materials as well as pollution control are today's needs in the process industries. In that respect heavy metals have a special interest, due to their environmental impact and economic value. Effluents carrying them must be cleaned prior to disposal. Removal of heavy metals is in most cases accomplished by alkaline precipitation, which allows their recovery when economically feasible (*1–3*).

This is the situation for the zinc-bearing solutions resulting from water washing of the ion-exchange resins used to retain zinc, as a chloride complex, from pyrite ashes leaching liquors. Under adequate operating conditions, alkaline precipitation of these solutions results in zinc oxide of sufficient purity to be used as feed material in zinc electrolytes, as well as in the painting and ceramic industries.

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Alkaline precipitation of zinc is a simple operation from a technical point of view and gives recovery yields close to 100% when operated at a suitable pH. Nevertheless, it is not always easy to carry out the separation of the solid phase due to the colloidal nature of zinc hydroxide, which settles and filters with difficulty, as a result of the large specific surface of its particles (*4*).

This paper studies sedimentation and filtration as means to separate the precipitates obtained when treating diluted zinc chloride solutions with sodium hydroxide. The behavior of these suspensions in the phase separation step is related to their chemical constitution, which depends on the operating conditions in the precipitation stage as has been reported in detail previously (*5*).

EXPERIMENTAL

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The suspensions used in the sedimentation and filtration studies come from alkaline precipitation of zinc chloride acid solutions containing 11 g Zn/L (*6*). These solutions are similar to the zinc-bearing liquors referred to in the Introduction. A 100-g/L sodium hydroxide solution was used as the precipitation agent.

Precipitation was carried out at different temperatures and pHs; two procedures were used to mix the reactants, the direct and indirect methods. In the former, sodium hydroxide is added to the zinc chloride solution, and the zinc chloride is added to the sodium hydroxide in the second.

Study of the solid products obtained leads to the conclusion that they are mixtures of crystalline zinc oxide and zinc hydroxychloride in different percentages, depending on the operating conditions (*5*). In general, when precipitation is carried out at high pH and temperature, using the indirect method, solid products with a high zinc oxide content are obtained. Low pH and temperature lead to high zinc hydroxychloride content in the precipitates. The presence of noncrystalline zinc hydroxide in some precipitates is also possible and, as will be seen later, can be confirmed from sedimentation and filtration runs (*7*).

Table 1 shows the operating conditions used in the precipitation step leading to the suspensions used in the phase separation study. The chemical constitution of the corresponding solid products, as determined in previous work (*5*), is also indicated; amorphous zinc hydroxide is listed as hydrated oxide.

Sedimentation runs were carried out in graduated jacketed cylinders. Water from a thermostat was flowing continuously through the cylinder

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TABLE 1
Precipitation Conditions and Percentages of Chemical Species in the Solid Phase

		Temperature (°C)											
		25			45			75			98		
Method	pH	HC[a]	ZnO	H_2O	HC	ZnO	H_2O	HC	ZnO	H_2O	HC	ZnO	H_2O
Direct	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									
Indirect	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]HC = Zinc hydroxychloride.

jacket to maintain the temperature at the required level in each run. Homogenized samples of the suspensions to be tested were placed in the cylinders and allowed to settle. The height of the interface between the clear liquid and the sludge was taken at different times.

Settling velocity was determined by using the Kynch-Roberts method. The logarithm of $h_i - h_\infty$ is plotted versus time, h_i being the height at time t_i and h_∞ the ultimate height. From this curve the critical point is obtained (*8*), the corresponding height and time being h_c and t_c, respectively. The tangent to the settling curve at the critical point defines the height h_L, and the settling velocity is calculated using the expression (*9–11*)

$$v = \frac{h_L - h_c}{t_c} \tag{1}$$

The sedimentation area is calculated by means of the expression

$$A = \frac{Q_0 C_0}{v} \left(\frac{1}{C_L} - \frac{1}{C_S} \right) \tag{2}$$

where A = required sedimentation area
Q_0 = volumetric inlet flow rate of the suspension
v = settling velocity
C_0 = initial solids concentration
C_L = concentration corresponding to h_L
C_S = desired final concentration

The required height of the sedimentation tank is calculated by the expression

$$H = H_C + \frac{Q_0 C_0 t_s}{\rho_s A} + \frac{Q_0 C_0 \int_0^{t_s} \frac{1}{C}\, dt}{A} \tag{3}$$

where H = required height of settling tank
H_C = correction height due to the clarification zone and bottom inclination
ρ_s = density of the solid
t_s = time to reach a concentration C_S in the sludge

A value of 1.6 is commonly used for H_C. Solids concentrations of the initial and settled suspensions were determined by means of the standard dry matter test. A pycnometric method was used for solids densities.

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In the filtration study the Carman-Kozeny equation was applied to calculate the average specific resistance of the cake (*12–14*):

$$\frac{t - t'}{V - V'} = \frac{\alpha\mu\omega}{2A^2\Delta P}(V + V') + \frac{\mu\beta}{A\Delta P} \tag{4}$$

where t = time to collect a filtrate volume V
t' = time for the system to reach the steady state
V = filtrate volume
V' = filtrate volume at t'
α = specific cake resistance
β = filtering medium resistance
A = filtration area
ΔP = pressure drop in the liquid flowing through the cake
μ = viscosity of the liquid
ω = solid weight per filtrate volume unit

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Vacuum was used in the filtration runs. The system consisted of a Buchner funnel covered with filter paper, adapted to a graduated cylinder for filtrate collection. Pressure difference through the filter media was maintained at a constant level of 7882 kg/m^3 in all the runs by means of a vacuum regulator. The filtration area was 2.89×10^{-3} m^2.

A volume of 100 cm^3 of homogenized suspension was used in each run. Data on filtrate volume were taken at different times. Cakes obtained were dried and weighed; viscosities of the filtrates were also determined by means of a No. 75 Cannon-Fenske viscometer.

Experimental filtrate volume and time data were adjusted, and the specific resistance of the cake was calculated from the corresponding slope value.

The shape and size of the solid particles were determined by means of a conventional transmission electron microscope (Philips PW 6000) which has a high resolving power. A scanning electron microscope is not recommended in this case due to the small particle size and the presence of chloride in many of the precipitates (*15, 16*).

A carbon film was deposited over the 3-mm copper wire mesh used as the sample support. This carbon was obtained from graphite in a high vacuum evaporator (Japan Electron Optics, JEE 4B type). The samples were previously stirred in water suspension in order to obtain a solid phase consisting of individual particles. Ultrasonic stirring is not recommended because individual crystals can be destroyed.

RESULTS AND DISCUSSION

Sedimentation

Figures 1a and 1b show the settling curves of the suspensions obtained at 25°C for different pHs. As can be seen, there are two pH ranges in terms of settling velocity.

When precipitation is carried out at pH between 7 and 10, the resulting solid products settle at a low velocity and a highly concentrated sludge is not achieved (see C_S/C_0 values in Table 2). At pHs higher than 10, satisfactory sedimentation can be observed.

This can be explained as the result of a different chemical composition of the solid phase. At pH above 10, zinc oxide is the main product in the precipitate, and when the pH is lower than 10, the presence of zinc hydroxide becomes significant. Zinc oxide has a better settleability because its density and particle size are larger than those of the hydroxide, which is colloidal.

When the direct method of precipitation is used, Fig. 1a shows a decrease in settling velocity as pH increases in both ranges mentioned above. This can be explained as the result of an increase in the viscosity of the liquid phase with pH. Moreover, in the pH range 7 to 10, the zinc hydroxide content of the precipitates increases with pH because the transformation from zinc hydroxychloride to zinc hydroxide takes place according to the reaction

$$Zn_5Cl_2(OH)_8 + 2OH^- = 5Zn(OH)_2 + 2Cl^-$$

The former is a crystalline solid and its particle size is larger than that of $Zn(OH)_2$.

When the indirect method is used, some differences at pHs 9 and 10, with respect to the direct method, are noticed. As Fig. 1b shows, sedimentation is now a faster process. In this case the conversion from zinc hydroxide to oxide begins at lower pH, and the amount of oxide in the precipitates is already considerable.

Curves obtained at 45°C show the same habit (Figs. 1c and 1d), but a higher settling velocity is observed as the result of lower liquid viscosity (*17*) and the zinc oxide content increases.

The difference of settling velocity in the two pH ranges practically disappears at 75°C (Figs. 1e and 1f). This is due to physical as well as chemical reasons. There is a considerable decrease in the viscosity of the liquid phase with temperature (*18*), and there is a higher content of zinc oxide in the solid phase, also noted previously (5); when zinc hydroxide is present, the temperature increase leads to higher ionic mobility and a decrease of

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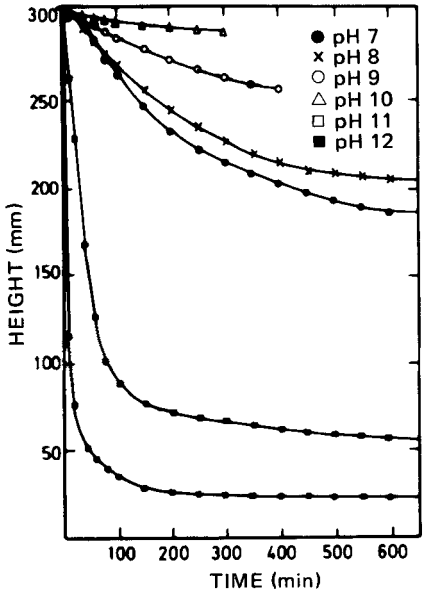

FIG. 1a. Settling curves corresponding to 25°C: direct method.

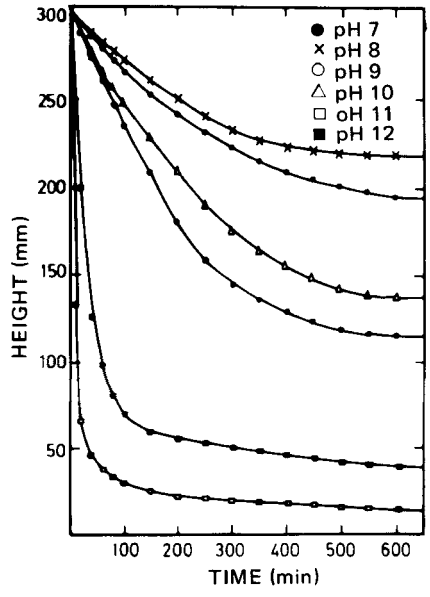

FIG. 1b. Settling curves corresponding to 25°: indirect method.

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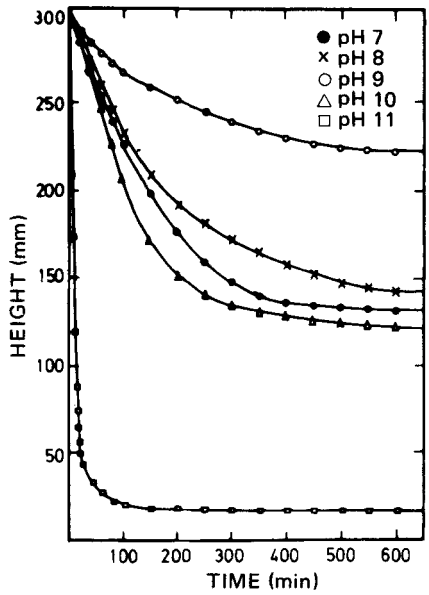

FIG. 1c. Settling curves corresponding to 45°C: direct method.

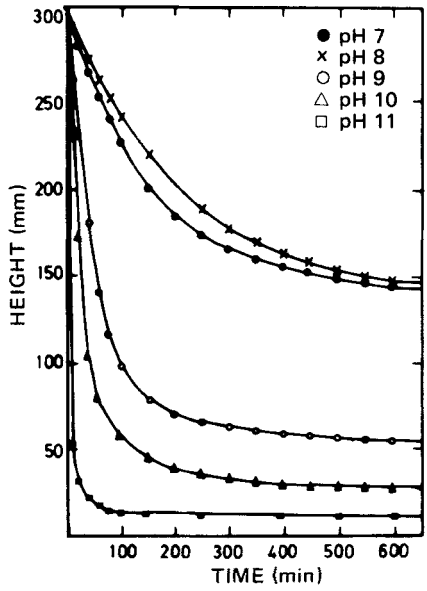

FIG. 1d. Settling curves corresponding to 45°C: indirect method.

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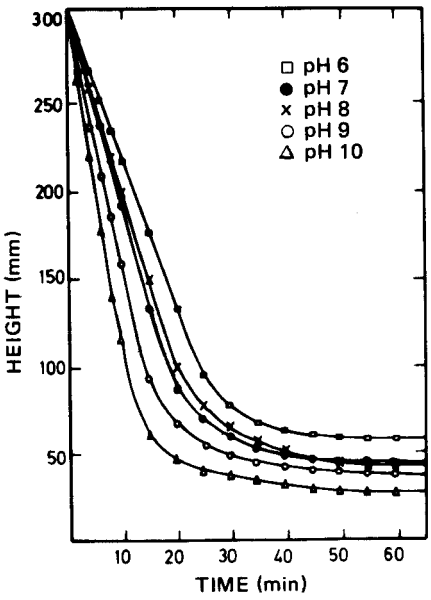

FIG. 1e. Settling curves corresponding to 75°C: direct method.

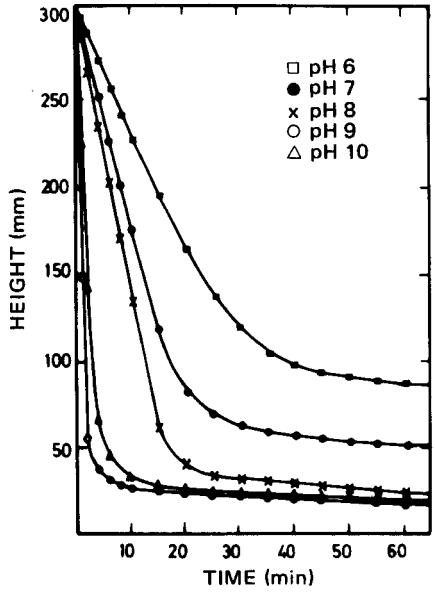

FIG. 1f. Settling curves corresponding to 75°C: indirect method.

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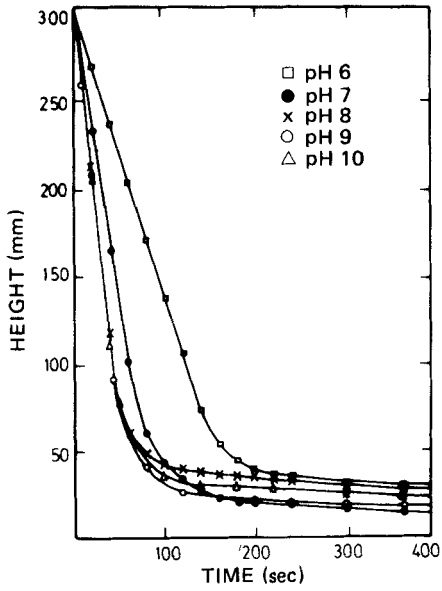

FIG. 1g. Settling curves corresponding to 98°C: direct method.

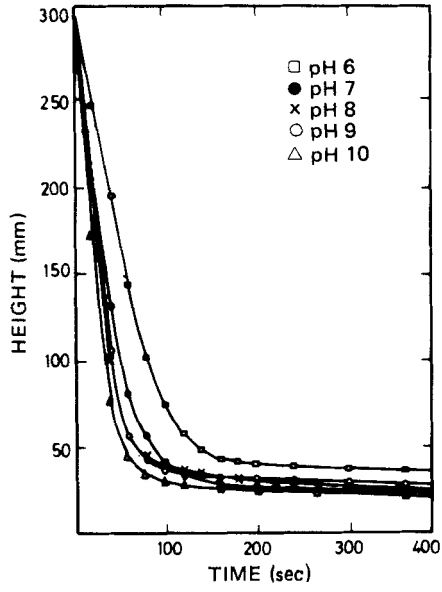

FIG. 1h. Settling curves corresponding to 98°C: indirect method.

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particle stability occurs because the double layer is more diffuse; flocculation becomes, then, more feasible.

When precipitation takes place at 98°C, all the precipitates consist mostly of zinc oxide, which settles readily (Figs. 1g and 1h).

Filtration

Specific resistance of cakes corresponding to different precipitation temperatures and pHs were calculated both from experimental filtrate volume and time data. Their values are plotted in Figs. 2a and 2b.

Conclusions of general validity are not obtainable from the experimental results shown in these figures, due to the interaction of opposing factors. Temperature and pH changes determine variations in the viscosity of the liquid phase as well as in the chemical constitution of the precipitates. The latter leads to changes in density, particle shape and size, specific surface area, and cake porosity which determine changes in filtration rate.

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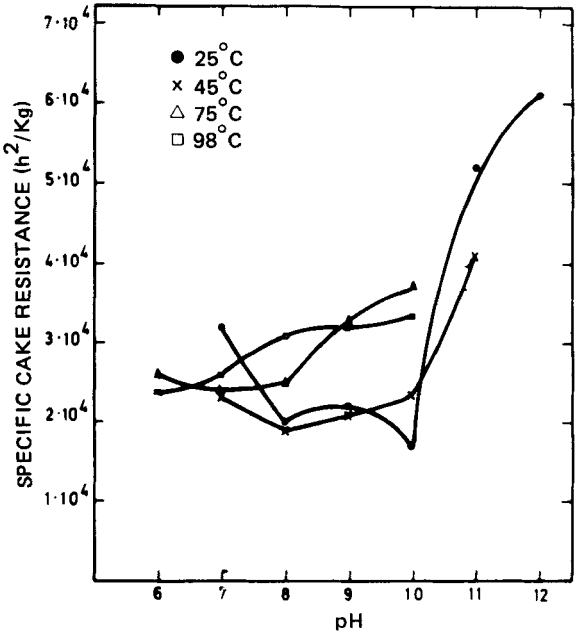

FIG. 2a. Specific cake resistance: direct method.

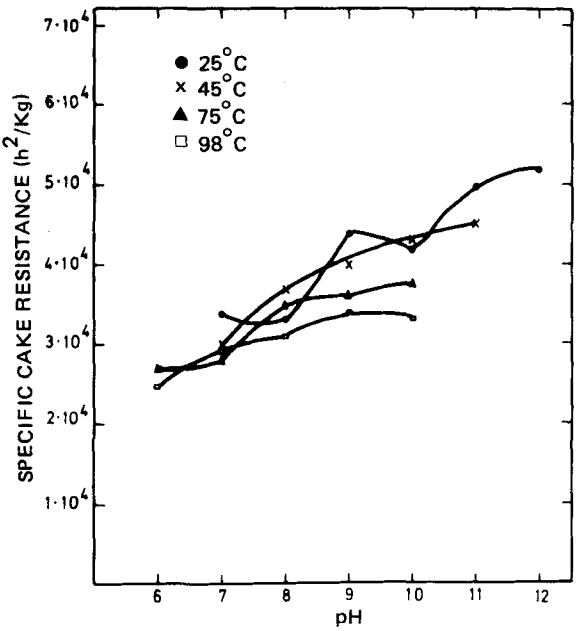

FIG. 2b. Specific cake resistance: indirect method.

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As a trend, it can be seen that at constant temperature a pH increase leads, in general, to a higher specific resistance of the cake. As indicated earlier, the viscosity of the liquid phase increases with pH and that could explain, in part, the decrease in filtration rate. The zinc oxide percentage is higher in the precipitates obtained at higher pHs. Its density is higher than that of the hydroxide, but the particle shape (sticklike) leads to a small porosity and this could be the cause of a higher specific cake resistance according to the expression

$$\alpha = \frac{K(1-\varepsilon)S_p^2}{\varepsilon^3 \rho_s} \tag{5}$$

where α = specific cake resistance
ρ_s = density of the solid
S_p = specific surface area of particles
K = Kozeny's constant
ε = porosity of the cake

Then the combination of physical and chemical factors leads to a decrease in filtration rate as the pH increases.

Temperature does not show a clear influence when the direct method is used to obtain the suspensions to be filtered. A clearer trend appears when the indirect method is employed. At constant pH the lower the temperature the higher the specific resistance of the cake, in general. An increase in liquid viscosity could be the main factor in this case.

With respect to the resistance of the filtering medium (β), it is important to point out that the values obtained adjusting the experimental filtration data were in some cases negative, which indicates that filtration of the suspensions studied does not fulfill rigorously the Carman-Kozeny hypothesis, which assumes a constant cake porosity, uniform particle size, and the absence of preferential channels (*19*). The precipitates obtained consist, in general, of a mixture of different chemical species and that leads to a nonuniform particle size, but the main reason for the process not following the Carman-Kozeny law seems to be the compressibility of the cakes obtained. These negative values were obtained at 25 and 45°C.

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Morphological Study of the Precipitates

Microphotographs presented in Figs. 3a to 3f show the morphologic characteristics of the precipitates obtained under different conditions. These characteristics are related to their behavior in sedimentation and filtration.

As can be seen, hexagonal as well as small nondefined shape particles are obtained when precipitation is carried out at low pH and temperature (Fig. 3a). At 25°C, hexagonal particles disappear as pH increases (Fig. 3b). At higher pH, stick-shaped particles are observed (Fig. 3c).

In the suspensions obtained at high pH and temperature, the stick-shaped particles are the only ones present (Fig. 3f).

Increasing temperature leads to solid products which are more crystalline and larger in size; this increase in particle size is especially noticeable in the hexagonal forms (Figs. 3a, 3d, and 3e). This increase in particle size with temperature can be explained as the result of the tendency of smaller particles to dissolve and diffuse from the suspensions to the larger particles, which grow.

According to the chemical composition of precipitates, as determined previously (*5*) by x-ray as well as chemical analyses (see Table 1), hexagonal forms can be attributed to zinc hydroxychloride particles and the stick-shaped particle are zinc oxide.

Particle diameters given in Figs. 3 have been calculated by measuring the length of the line which bisects the image of the particles (Martin's diameter (*20*)).

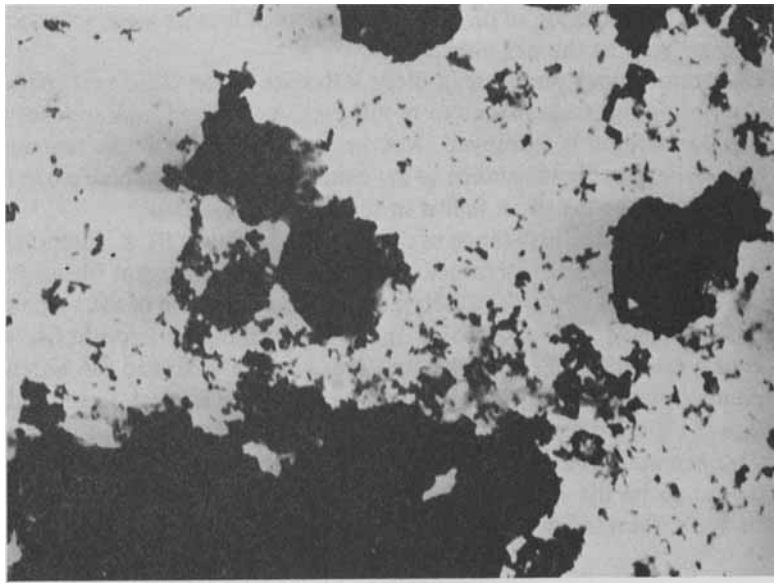

FIG. 3a. Microphotograph of the precipitate: $\bar{d}_p = 0.92$ μm, pH = 7, $t = 25$°C, and direct method.

FIG. 3b. Microphotograph of the precipitate: $\bar{d}_p < 0.10$ μm, pH = 10, $t = 25$°C, and direct method.

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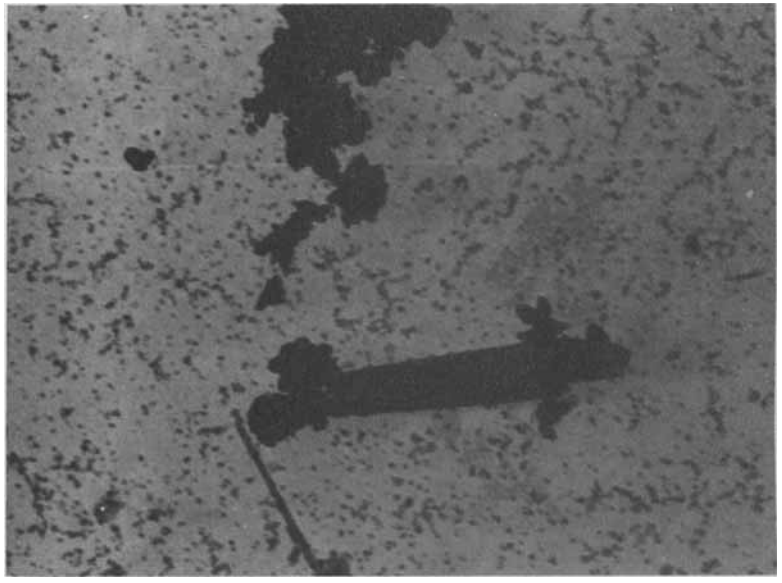

FIG. 3c. Microphotograph of the precipitate: $\bar{d}_p = 2.18$ μm, pH = 12, $t = 25°C$, and direct method.

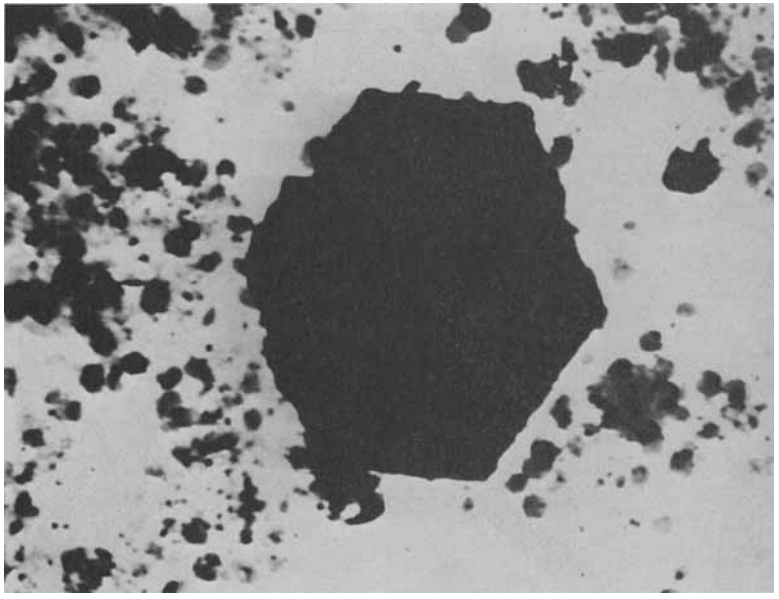

FIG. 3d. Microphotograph of the precipitate: $\bar{d}_p = 2.69$ μm, pH = 7, $t = 75°C$, and direct method.

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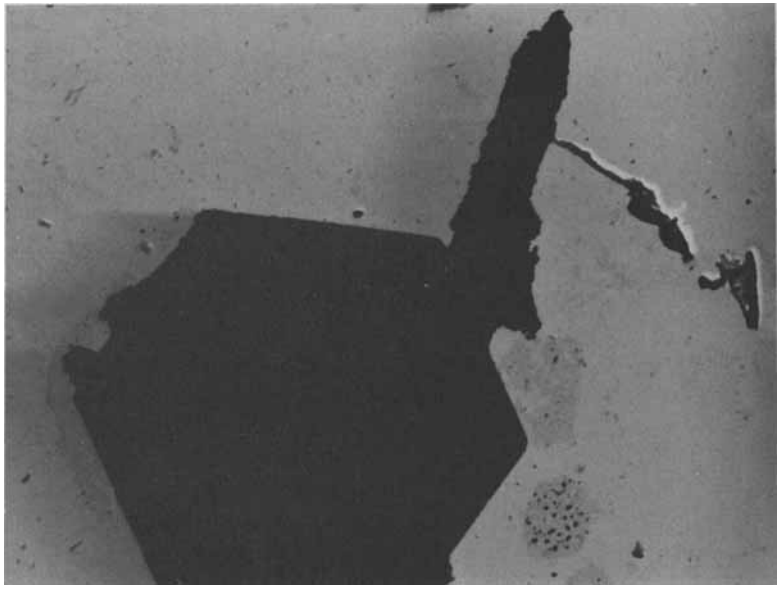

FIG. 3e. Microphotograph of the precipitate: $\bar{d}_p = 9.45$ μm, pH = 6, $t = 98°C$, and direct method.

FIG. 3f. Microphotograph of the precipitate: $\bar{d}_p = 2.11$ μm, pH = 9, $t = 98°C$, and indirect method.

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SEDIMENTATION VERSUS FILTRATION: COMPARATIVE STUDY

Both area and height of the required settling tanks have been calculated from Eqs. (2) and (3) for all the experimental operating conditions. Filter areas have also been determined from Eq. (4), which rearranges to the following expression:

$$A = \frac{2\mu\beta + \sqrt{(2\mu\beta)^2 + 8\theta\mu\alpha\Delta P}}{4\theta\Delta P}\frac{100}{\omega} \tag{6}$$

Tables 2 and 3 show the results obtained for an inlet mass flow rate of 100 kg sol/h.

As discussed earlier, increases in pH and temperature lead to an increase of zinc oxide in the precipitate and a more thickened sludge is obtained in sedimentation, as can be seen from the C_S/C_0 values. In these conditions a smaller settling tank is required to obtain the same degree of thickening.

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TABLE 2
Settling Tank Dimensions

Temperature (°C)	pH	C_S/C_0		A (m^2/100 kg sol/h)		H (m)	
		Direct method	Indirect method	Direct method	Indirect method	Direct method	Indirect method
25	7	1.38	1.28	264	119	1.80	1.91
	8	1.19	1.10	187	137	1.89	1.87
	9	—	1.83	—	188	—	1.91
	10	—	1.48	—	131	—	1.93
	11	5.26	12.00	118	155	1.92	1.91
	12	6.82	13.04	134	147	1.92	1.93
45	7	1.71	1.63	145	172	1.89	1.91
	8	1.63	1.53	173	190	1.91	1.88
	9	1.25	3.09	129	158	1.93	1.90
	10	1.16	3.90	155	184	1.91	1.89
	11	12.00	6.38	189	150	1.88	1.92
75	6	2.80	2.75	15	14	1.92	1.91
	7	3.66	5.00	14	13	1.91	1.93
	8	6.12	7.14	15	13	1.92	1.89
	9	12.00	9.68	19	14	1.88	1.91
	10	12.00	9.68	14	14	1.91	1.91
98	6	5.88	3.75	2	2	1.85	1.87
	7	4.92	6.52	2	1	1.85	1.87
	8	5.45	11.11	1	1	1.99	1.96
	9	7.50	9.38	1	0.6	1.99	1.93
	10	11.11	13.64	1	1	1.89	1.81

TABLE 3
Filtration Areas (m^2/100 kg sol/h).

Temperature (°C)	pH	Direct method	Indirect method
25	7	64	61
	8	50	66
	9	53	80
	10	47	80
	11	93	92
	12	101	95
45	7	49	55
	8	46	62
	9	49	69
	10	53	74
	11	76	77
75	6	50	47
	7	50	52
	8	52	61
	9	61	63
	10	67	65
98	6	42	44
	7	47	52
	8	50	56
	9	57	59
	10	58	63

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In filtration a higher area is required, in general, as pH increases. This seems to indicate that as zinc oxide in the precipitate increases, a lower filtration rate is obtained. However, at higher temperatures lower filtration areas are required, which can be explained as the result of a decrease in the viscosity of the liquid phase.

CONCLUSION

From an industrial point of view it is of interest to recover zinc from the studied liquors as zinc oxide. For this a high pH and temperature must be used in the precipitation step. In these conditions, sedimentation is the preferred method for primary separation of the precipitate. It provides a high sludge concentration with a relatively low settling tank size and allows one to use a final filtration dewatering step with a substantially reduced area requirement (*21*). The sequence settling tank-filter seems to be the most economical for the separation of the precipitates obtained from the liquors studied here.

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