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Filtration improvement of zinc sludge by using unconventional alkalization sequence

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Abstract: The novel ways for the filtration improvement of zinc hydroxide sludge precipitated from the zinc-containing solutions was investigated. It was found that, when the zinc-containing solutions were added to sodium hydroxide solution, the filtration of the obtained precipitates was improved to some extent, depending on the molar ratios of OH^-/Zn, in comparison with those obtained by conventional addition of hydroxide solution to zinc-containing solution, even the ratios were kept the same in these two alkalization methods. The experimental results showed that such an improvement may be contributed to the presence of muddy precipitates formed homogeneously in the sludge. It was suggested that it was zinc-containing solution that should be added into hydroxide solution, when the zinc was removed from aqueous solution by the precipitation of zinc hydroxides. As a result, the sludge obtained will be filtered and rinsed readily.

Key words: filtration; muddy zinc hydroxide; colloidal zinc hydroxide; wastewater of zinc

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Introduction

Zinc is one of the most important metals in modern industry and has been used widespreadly. Most of the zinc metals in the world is produced hydrometallurgically, i.e., by using the processes such as leaching, purification, electrowinning and electrorefinning (Morgan, 1977; Gill, 1981). As a result, zinc-containing solid wastes and wastewaters are generated in the courses of zinc metallurgy and applications (Brooks, 1991). Zinc is one of the heavy metals and should be removed from the wastes before these wastes can be disposed of safely. Conventionally, the zinc in solid wastes may be leached by mineral acids, and then precipitated by the addition of hydroxide solution to the leach solutions and wastewaters. The sludge obtained is colloidal and very difficult to be filtered (Schackmann, 1961). Currently, the zinc sludge is usually dewatered by frame-plate process (Philp, 1988). The resultant cake using this process can be hardly rinsed, which is quite unfavorable to the recovery of relatively pure zinc hydroxide.

In order to improve the filtration efficiency of colloidal sludge including zinc, chromium and other metals ions, filter aids such as diatomaceous silica and perlite may be mixed with the sludge to provide a great number of microscopic holes for the liquid to flow through (Zhao, 1995). When the metals in the cakes could be redissolved into the aqueous solution, the recycling of the filter aids may be possible. Nevertheless, in the most cases, the cakes may be discarded or treated by other processes other than redissolution with acidic solution, which may result to uneconomic consequence and much less practical significance.

Obviously, the most attractive ways to improve the filtration efficiency of zinc hydroxide sludge may lie in the improvement of the filterability of the sludge without help of any additional filter aids. Taking advantage of the facts that zinc hydroxide can be dissolved in both acidic and alkaline solutions and the precipitates formed homogeneously are usually muddy and readily to filter, the zinc-containing solutions are added into excessive sodium hydroxide solution in this

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research. Consequently, it was found that the filterability of zinc sludge could be improved to an extent, depending on the molar ratios of OH^-/Zn used. In this paper, the laboratory-scale experimental results are reported.

1 Experimental

All the chemicals were of analytical grade. Zinc nitrate and sodium hydroxide were used as the stock chemicals for the preparation of testing solutions. Zinc oxide and sodium chloride were used as the standards for the analysis of Pb, Zn and Na respectively, with ICP. The concentrations of zinc and NaOH were given in the texts in terms of apparent concentrations, i. e., the values of total amount of zinc and NaOH in the final solution divided by the total volume.

For the precipitation efficiencies tests (Fig. 1—3), 20 ml of 0.025—0.50 mol/L (1.63—32.70 g/L Zn) of zinc nitrate solution was added into 10 ml of 0—4 mol/L (0—160 g/L NaOH) sodium hydroxide solution, while stirred strongly with magnetic stirrers. An aliquot of 1 ml of the supernatant was taken out for analysis. The total volume was always kept at 30 ml. Typically, the apparent concentrations of zinc and NaOH in the final solid-liquid mixture solutions were 21.9 g/L (0.33 mol/L) and 53.2 g/L (1.33 mol/L), respectively, with a molar ratio of 4.0, unless otherwise indicated in the text. In comparison, a paralleling experiment was conducted by the addition of sodium hydroxide into zinc nitrate solutions, with the same concentrations shown above.

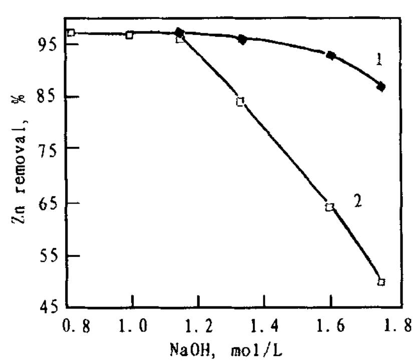

Fig. 1 Comparison of zinc precipitation by two alkalization sequences (Zn 18.9 g/L) Sequences of alkalization: 1. addition of zinc solution to NaOH solution; 2. addition of NaOH solution to zinc solution

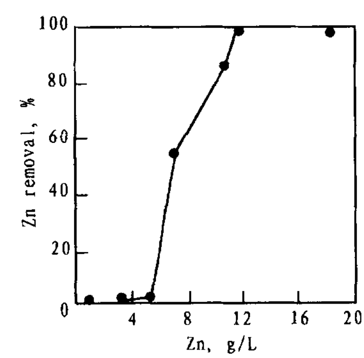

Fig. 2 Effect of the apparent concentration of zinc on the precipitation by the addition of zinc to NaOH solution NaOH: 10 ml of 4 mol/L; Zn: 20 ml

In the typical sludge filtration experiments, 460 ml of 0.4 mol/L (26 g/L Zn) zinc nitrate solution was added into 175 ml of 4 mol/L (160 g/L NaOH) sodium hydroxide solution, unless otherwise indicated in the text, while stirred strongly with magnetic stirrer. As a result, the apparent concentration of zinc in the solid-liquid mixture solution containing the precipitates was 0.29 mol/L (18.9 g/L Zn). It was observed that precipitate would not be seen until around 400 ml of zinc solution was added. Continued to stir for 15 minutes after all the given zinc solution was added. The white precipitate can be seen and will settle down to the bottom of the containers quickly. The change of the moist solid substance (the apparent concentration of zinc) in the filtered solution was realized by redispensing the cake into the given volume of filtrates. It was found that the filtration efficiency obtained in this way was nearly the same as that obtained from the newly prepared precipitate. A simple conventional vacuum filtration setup was used for the filtration tests of the sludge obtained. Glass microfibre filters were used as filter medium. The resistance of the filters was found to be negligible in comparison with that of the zinc sludge. During the filtration operation, the liquid was poured into the filtration funnel which was connected to a vacuum pump, while the time needed for the filtration of all the solution containing the precipitates was recorded. Stirred the precipitate to make it dispense homogeneously in the solution during it was filtered. The filtration capacity was calculated by the following formula:

$$FP = T - Zn/(t/A),$$

where FP is filtration capacity (kg, Zn/(h·m^2)); T-Zn is the total zinc in the cake (kg); t is the time needed for the filtration of the Zn precipitates in the given solutions (h); A is the filtration area of 0.00237 m^2 which was used in the experiments. The resistance of the filters was neglected.

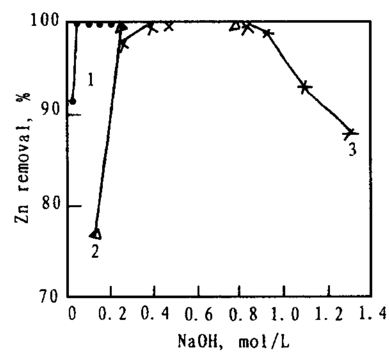

Fig.3 Effect of apparent concentration of NaOH on the precipitation at different apparent zinc concentrations by the addition of zinc to NaOH solution apparent zinc concentrations: 1. 1.1 g/L; 2. 5.5 g/L; 3. 10.9 g/L

2 Results and discussion

2.1 Parameters affecting the precipitation efficiency of zinc

The results are shown in Fig.1—3. For the comparison of the effect of alkalization sequences on the precipitation of zinc, 20 ml of 18.9 g/L zinc solution was mixed with 10 ml of different concentration of NaOH solution, and the results are shown in Fig.1. It can be seen that, for both two alkalization methods, zinc will be completely precipitated out from the solution, when the apparent concentration of NaOH (the total added NaOH divided by the final total volume) is lower than 1.35 mol/L (for alkalization method I, simplified as "zinc to NaOH method") or 1.15 mol/L (for alkalization method II, simplified as "NaOH to zinc method"), i.e., the corresponding molar ratios of NaOH/Zn are in the ranges of 2—4 or 2—3, respectively. When the apparent concentration of NaOH is increased further, part of the precipitates formed will be dissolved and the precipitation efficiencies of zinc will be decreased. Such decrease is more rapid for the case of addition of NaOH solution to zinc solution than the reverse alkalization order. For the zinc to NaOH method, zinc will be precipitated completely when the apparent zinc concentration is higher than 14 g/L, i.e., molar ratios of NaOH/Zn are lower than 4 (Fig.2), which can be further justified by the experimental results shown in Fig.3 in which the testing results using different NaOH and zinc concentrations are shown. Hence, a molar ratio of NaOH/Zn with lower than 4 should be used when the alkalization method of zinc to NaOH solution is practiced in industry.

2.2 Filtration improvement of the zinc sludge

The experimental results are shown in Fig.4—5. The precipitates were formed under the conditions of NaOH/Zn molar ratio at 4. The filtration capacity of the precipitates formed by zinc to NaOH method increased as the vacuum pressure was increased (Fig.4). The comparison of filtration capacity of the precipitates formed by zinc to NaOH and NaOH to zinc methods is shown in Fig.5. It can be found that the former (line I in Fig.5) is much higher than the latter (line II in Fig.5) at the vacuum pressures used. In addition, it was found that the higher the vacuum pressure was used, the higher the filtration capacity would be obtained.

When the NaOH/Zn molar ratios are further decreased, the filtration capacity will be reduced considerably, as shown in Table 1. However, the filtration capacity of the precipitates formed by the zinc to NaOH method is always higher than that by the other method.

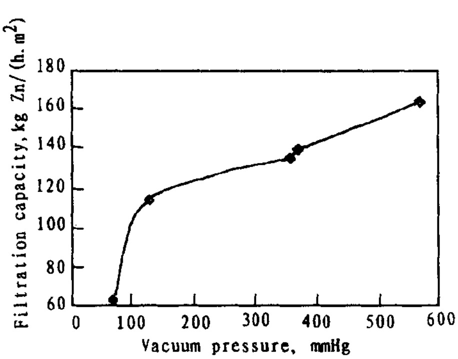

Fig. 4 Effect of vacuum pressure on the filtration capacity of zinc precipitates formed by the addition of zinc solution to NaOH solution
apparent Zn 18.9 g/L

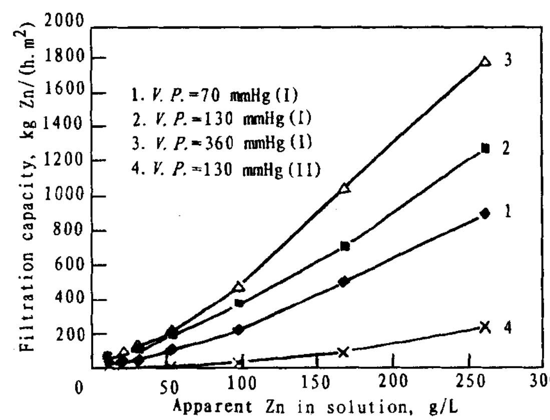

Fig. 5 Relationship between the apparent zinc concentration or alkalization sequences and the filtration capacity alkalization sequences: I. addition of zinc solution to NaOH solution; II. addition of NaOH solution to zinc solution

Table 1 The filterability comparison of the precipitates

No.	NaOH/Zn molar ratios	Filtration capacity, kg Zn/(h·m^2)	
		Zinc to NaOH solution method	NaOH to zinc solution method
1	4.0	74.4	9.0
2	3.55	26.7	6.5
3	2.46	24.7	5.9

Apparent Zn concentration: 20 g/dm^3

2.3 The comparison of physical properties of the precipitates

The detailed characterization of the precipitates was considered to be beyond the scope of the paper. However, it is rather readily to observe the precipitates by their appearance in the solutions. For the NaOH to zinc method, the precipitates formed will settle down very slowly, and is voluminous. It was well known that the precipitates formed in this way was colloidal, and very difficult to filter (Philip, 1988). In contrast, the precipitates formed homogeneously by the zinc to NaOH method was observed to be muddy, and could be filtered readily. In addition, the cake of colloidal precipitates will break when the filtration is finished or is dried. Nevertheless, the cake obtained by the zinc to NaOH method does not appear such phenomenon. The physical phenomena are summarized in Table 2.

Table 2 The comparison of the physical properties of zinc precipitates

Physical phenomena	Precipitation method used	
	Zinc to NaOH solution	NaOH to zinc solution
Settlement	Very quickly	Slowly
Filterability	Very good	Very poor
Typical filtration capacity at vacuum pressure of 130 mm Hg (apparent Zn: 98 g/L)	379.7 kg Zn/(h·m^2)	42.5 kg Zn/(h·m^2)
Rinsing	Very easily	Very difficult

3 Discussion

It is known that the properties of the precipitates formed homogeneously may be quite different from those formed heterogeneously. When zinc solution is added to NaOH solution, the alkalization is heterogeneous and the colloidal precipitates are obtained. However, when the mixing sequence of zinc and alkaline solutions is reversed, precipitates will not be formed until the molar ratios of NaOH/Zn are lower than around 4. If the ratios are decreased a little slightly, precipitates will be formed rapidly. Hence, the precipitates are formed homogeneously in this way and are muddy.

The chemical analysis results of the two types of precipitates show that the precipitates consist of zinc hydroxide and sodium zincate with various ratios, depending on the molar ratios of NaOH/Zn and alkalization sequences. When NaOH solution is added into zinc solution and the molar ratios of NaOH/Zn are kept at around 2, only zinc hydroxide will be formed. Nevertheless, the precipitates usually contain a large amount of sodium salts, which may not be rinsed out readily, if the frame-plate filtration process is used for dewatering of the voluminous precipitates.

The precipitates formed by the zinc to NaOH solution method are usually pure sodium zincates, if the molar ratios of NaOH/Zn are lower than around 4. That is the reason why the precipitates formed in this way can be filtered readily. Based on the following two alkalization reactions:

$$2NaOH + Zn(NO_3)_2 = Zn(OH)_2 + 2NaNO_3,$$

(for the NaOH to zinc solution method)

$$Zn(NO_3)_2 + 4NaOH = Na_2Zn(OH)_4 + 2NaNO_3,$$

(for the zinc to NaOH solution method)

the actual consumption of NaOH for the later method seems to be higher. It may be the disadvantage of using this alkalization method. But the economic-technical feasibility should be assessed based on a larger scale pilot experiments, when this method is attempted to be used in industry. Fortunately, as shown in Table 1, even the molar ratios are kept at lower level when the alkalization is carried out, the filtration capacity of the resulting precipitates will be also improved by using the zinc to NaOH method. Obviously, such an alkalization should be strongly recommended in practical applications.

It can be concluded that the filtration capacity and filterability will be increased to some extent when the conventional alkalization method for the pouring of alkaline solution into the zinc-containing solution is changed into the reverse alkalization sequence, i. e., the addition of zinc solution to NaOH or other alkaline solutions.

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