

Studies on Electrolytic Refining of Zinc. V

Removal of Lead from Zinc Sulfate Solution with Xanthate or Tetramethyl Thiuramdisulfide*

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Synopsis

Lead in zinc sulfate solution can be effectively removed with *K*-isoamyl xanthate or tetramethyl thiuramdisulfide. To obtain the desired results, these reagents of which concentrations are 0.5% aqueous solution of *K*-isoamyl xanthate or ammoniacal and 1% aqueous solution of tetramethyl thiuramdisulfide, must be added to the neutral zinc solution (pH 4.8), stirring vigorously at about 40°C. Resultant zinc sulfate solution under best conditions contains only lead of 0.1 mg/1 in the case of *K*-isoamyl xanthate and 0.2–0.3 mg/1 in the case of tetramethyl thiuramdisulfide, provided that reagents as ten times as the equivalence of lead are added.

I. Introduction

After going through the final purification process, the zinc sulfate solution treated in the commercial electrolytic zinc plant usually contains lead in the concentration of 1 mg/1 or so as one of the remaining impurities.

The trace of lead in an impure zinc solution produced in the leaching department is known only in part from the literature⁽¹⁾, in which the lead concentrations at the respective step in the purification process are described. The lead in zinc sulfate solution is partly removed by adsorbing it to a colloidal precipitate of ferric hydroxide, and nearly all the remaining lead is deposited on zinc-dust in successive treatments.

Under the equilibrium conditions, concentrations of lead and zinc in solution containing both cations which are in contact with zinc metal are prescribed by the following expressions, at 25°C: $[\text{Pb}^{++}]/[\text{Zn}^{++}] = 2.9 \times 10^{-22}$. If the solution contains zinc in concentration of 160 g/1, lead in zinc solution can be removed theoretically by zinc-dust treatment until the remaining lead reaches $[\text{Pb}^{++}] = 4.6 \times 10^{-17}$ mg/1, i. e., almost perfectly. In practical operation, however, lead as well as cobalt can scarcely be displaced from the neutral zinc solution by adding only the zinc-dust. The elimination of lead becomes more difficult as the lead concentration decreases, because the lead has less contact with the definite area of zinc metal. Usually, the concentration of lead in solution to be purified decreases up to 0.5 mg/1 or so, only when the excess of zinc-dust is repeatedly added.

* The 107th Report of the Research Institute of Mineral Dressing and Metallurgy.
(1) N. Matsuura, *Metal*, 23 (1953), 656.

The object of the present paper is to search for proper precipitant soluble in water for the lead in zinc solution in the hope that perfect combination of lead and precipitant might occur and more effective removal of lead from the zinc sulfate solution could be done. Many organic reagents which combine with lead and form insoluble lead compound were tested. It was found by many trials that xanthate and thiuramdisulfide showed a great promise. Then, these two organic reagents were examined in detail to obtain the most favorable conditions.

II. Experimental procedure

Reagents to be tested were dissolved in reasonable solvents and added to zinc sulfate solution containing a known quantity of lead, stirring vigorously at constant temperature. After stirring for an hour, the solution was filtered through Toyo Filter Paper No. 5C. With 10 ml of the filtrate thus obtained, the concentrations of lead were measured with Hitachi E.P.U.-2A type photoelectric spectrophotometer.⁽²⁾ The zinc sulfate solution used as a sample was a neutral solution containing 160 g per liter of zinc, and 100 ml of this solution was used in nearly all the experiments. Acidities of the solutions were measured with glass electrode pH meter.

Reagents shown the promise of being successful are listed in Table 1 together

Table 1. Reagents shown the great promise for removal of lead.

Reagent	Formula	Solvent	Formula of lead precipitate	Weight ratio of reagent to lead
Potassium isoamyl xanthate	$iso-C_5H_{11}O-C-SK$ $\quad \quad \quad \parallel$ $\quad \quad \quad S$	water	$(C_5H_{11}OCSS)_2Pb$	1.953
Tetramethyl thiuramdisulfide	$\begin{array}{c} CH_3 \\ \diagdown \\ N-C-S-S-C-N \\ \diagup \\ CH_3 \end{array}$ $\quad \quad \quad \parallel \quad \quad \quad \parallel$ $\quad \quad \quad S \quad \quad \quad S$	10%NH ₄ OH	$[(CH_3)_2NCSS]_2Pb$	1.160
Sodium isodiamyl aerofloat	$iso-C_5H_{11}O$ $\quad \quad \quad \diagdown$ $\quad \quad \quad P \begin{array}{l} \diagup S \\ \diagdown SNa \end{array}$ $iso-C_5H_{11}O$ $\quad \quad \quad \diagup$	water	$[(C_5H_{11}O)_2PSS]_2Pb$	2.822

with the solvent of their reagents and the form of lead compounds.

III. Experimental results and discussion

1. A number of organic reagents which were considered from chemical informations to be full of promise were selected and tested if their effectiveness were the same as others described in literature with the lead in the solution containing zinc of concentration. Test were conducted at 40°C, by using 100 ml of zinc sulfate solution containing lead of 9.68 mg/l. Reagents were added in various amounts to the sample solutions with various acidities.

The ratio, called the ratio of lead removal in the present paper, of lead concentration of filtered solution to that before the treatment was calculated from

(2) M. Watanabe and S. Fukushima, Sci. Rep. RITU, A8 (1956), 142.

the results of lead measurements. Fig. 1 shows the results of favorable reagents. A numeral with an arrow is the value of pH of the treated solution. Mercapto-benzothiazole, thionalid, picrolonic acid, and dipicryl amine, which would be used

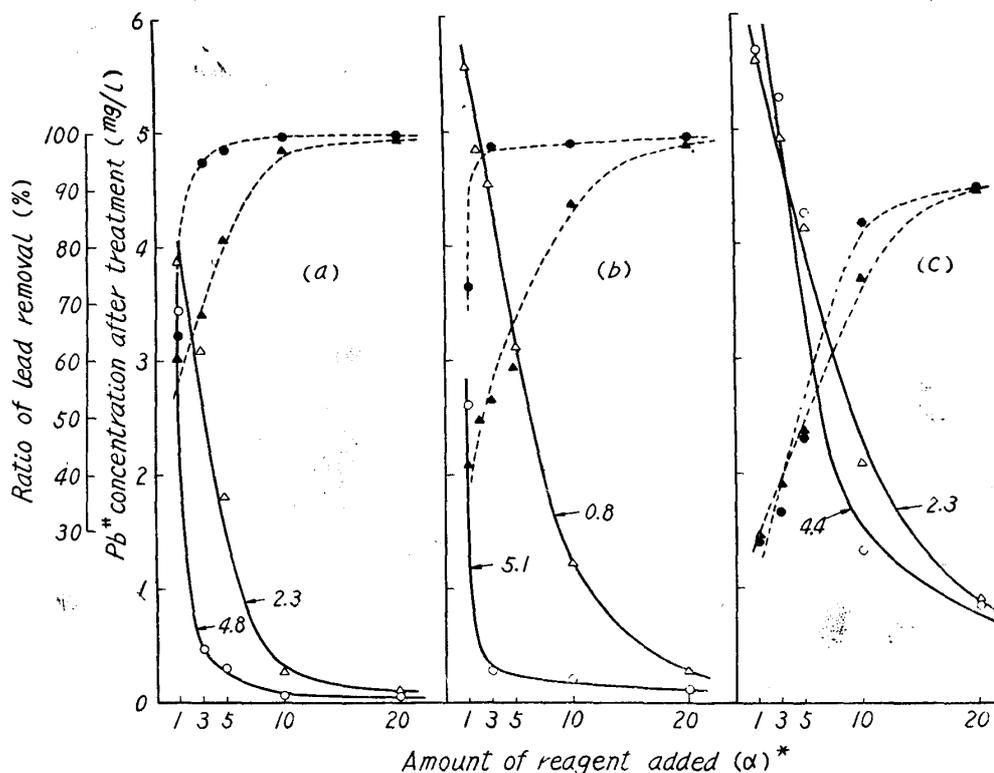


Fig. 1. Relation between the amount of reagent added and the lead concentration after treatment.

Tested solution: 160gZn/l, concentration of lead before treatment = 9.68mg/l,

Temperature: 40°C, Agitation time: 1hr,

(a) Potassium isoamyl xanthate

(b) Tetramethyl thiuramdisulfide

(c) Sodium isodiamyl aerofloat

* $\alpha = \frac{\text{Amount of reagent added practically}}{\text{Theoretical amount required for lead in solution}}$

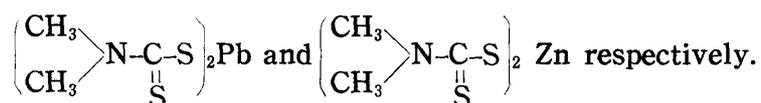
— Pb⁺ concentration

- - - - - Ratio of lead removal

in quantitative analysis for precipitating lead from solution, were also tried, but it was found that the all these reagents did not give any promise for the present purpose.

The reagents listed in Table 1 are collectors used in flotation of ores, and they form insoluble compounds, combining with various heavy metals. The heavy metal salts of aerofloat are usually less insoluble than the corresponding xanthates.⁽³⁾ Xanthate is also more effective under the present conditions. Tetramethyl thiuramdisulfide is an oxidation product of dithiocarbamic acid and is soluble in alkaline solution. This reagent forms water-insoluble compounds with lead and zinc and precipitates as

(3) A.F. Taggart, *Handbook of Mineral Dressing*, (1948), 12-09.



Thus, xanthate and tetramethyl thiuramdisulfide are the reagents with reasonable promise of being successful. These reagents, however, react not only with lead but also with zinc. To eliminate lead, therefore, they must be added in amount more than the equivalent amount of lead in solution. The ratio of the amount of reagent actually added to theoretical one varies widely with the degree of lead elimination and conditions of precipitation such as the acidity of the solution, as shown in Fig. 1. Hereafter, the values of this ratio are represented as α for convenience. Potassiumisoamyl xanthate and tetramethyl thiuramdisulfide are also designated in abridged form as K.A.X. or T.M.T. respectively.

Warren⁽⁴⁾ and Malatesta⁽⁵⁾ measured the order of solubilities of cupric, cobaltic, lead, ferric, and zinc xanthates, and found that these salts would be more soluble in the order named. The solubilities of these metal dithiocarbamate increase in the same order as named above except the replacement of iron with zinc. In consequence, the effective reagents, i.e., the reagents soluble in zinc sulfate solution are restricted within the solubilities of corresponding zinc salts. The remainder of the reagent precipitates. Van Heteren gave 5.3×10^{-9} for the solubility product of zinc ethyl xanthate, and 6.8×10^{-17} for that of lead ethyl xanthate.⁽⁶⁾ Equivalent concentration of xanthate in the present zinc solution is $[X^-] = 4.6 \times 10^{-5}$ mol/l, provided that activity of zinc takes up an analytical value as it is. From these data, it can be estimated that the corresponding solubility for lead is $[Pb^{++}] = 0.006$ mg/l. This value is sufficient to show that xanthate is of great promise.

2. Determination of agitation time

K.A.X. and T.M.T. were added to 500 ml of the zinc sulfate solution containing 9.95 mg per liter of lead. Two series of experiments were conducted at $\alpha = 3$ and 10, measuring lead concentration after a short interval and a long interval.

At an interval of fixed time, 20 ml of sample solution was filtered and analyzed. The results, summarized in Table 2, show that precipitation of lead within the first five minutes proceeds relatively rapidly, but slowly thereafter. In the case of K.A.X., the lead concentration in zinc solution reaches the minimum value after one-hour agitation, and with further agitation, precipitating lead xanthate is decomposed and the ratio of lead removal decreases. In the case of T.M.T., the precipitation of lead proceeds further, though gradually, in subsequent agitation, and no precipitate decomposes after 24 hours. From these results, one-hour agitation was adopted in all the experiments hereafter.

If the approximate quantity of soluble K.A.X. is calculated from the previous data on xanthate ion concentration concerning ethyl xanthate, about 9.3 mg/l of

(4) S. P. Warren, *Can. Min. Met. Bull.*, **26** (1933), 186.

(5) L. Malatesta, *Chimica e industria*, **23** (1941), 319.

(6) A. M. Gaudin, *Flotation*, 2nd Ed. (1957), 201-203.

Table 2. Relationship of agitation time and the concentration of lead after treatment or the ratio of lead removal.

Reagent	0.5% K.A.X. soln.				1% T.M.T. soln.			
	3		10		3		10	
Amount of reagent added (α)	Zn soln. concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)
Time								
5 (min)	2.80	71.9	0.44	95.6	1.82	81.7	0.41	95.9
10	1.31	86.8	0.27	97.4	0.96	90.4	0.28	97.2
30	0.92	90.8	0.24	97.6	0.46	95.4	0.25	97.5
1 (hr)	0.48	95.2	0.10	99.0	0.34	96.6	0.26	97.4
2	0.57	94.3	0.12	98.8	0.24	97.6	0.26	97.4
3	0.51	94.5	0.12	98.8	0.27	97.3	0.25	97.5
5	0.84	91.6	0.23	97.7	0.25	97.5	0.12	98.8
10	0.97	90.3	0.88	91.2	0.17	98.3	0.19	98.1
24	1.16	88.3	1.11	88.8	0.22	97.8	0.06	99.4

Tested solution : 160 g Zn/l, pH 4.8, concentration of lead before treatment = 9.95 mg/l, Temperature : 40°C,

K.A.X. is present in soluble form in the zinc solution. This value corresponds to one-sixth or one-twentieth of the reagents added in the present series ($\alpha=3$ and 10). On the other hand, the equivalent amount of K.A.X. combined with 9.95 mg per liter of lead is 19.4 mg per liter, i. e., twice the soluble K.A.X. The precipitation of lead, therefore, proceeds as the zinc xanthate precipitate dissolves again in solution and makes up a deficit of xanthate ion as lead precipitates. In actual operation, both K.A.X. and T.M.T. combine with zinc as soon as the reagent solution is added, and the zinc solution becomes white and muddy. With further agitating, some of the precipitate of zinc salts dissolves and the remainder glows in cluster. The zinc solution, in consequence, becomes somewhat clear, but as temperature lowers, zinc xanthate or zinc dithiocarbamate dissolved in filtered solution precipitates again. As mentioned above, the amount of reagent to be added, solution agitation, stabilities of reagent and precipitate, and etc. have great influence on the rate of lead removal, because the rate of lead precipitation is determined by the rate of dissolution of precipitating zinc salt. The amount of reagent has a greater influence in the case of K.A.X.

3. Acidity of zinc sulfate solution

Since xanthate is very unstable in acidic solution, the lead concentration after treatment varies naturally with the variation in acidity. For the sake of making clear the relation between effective range of pH of zinc sulfate solution and the amount of reagent, the following series of experiments were carried out.

Various conditions are summarized in Fig. 2. in which the lead concentration of treated solution and the ratio of lead removal in various acidities are shown.

Xanthate is available up to pH 3, but, in a less range than pH 3, it decomposes

rapidly. In case $\alpha=3$, the effective range is restricted in the neighborhood of pH causing hydrolysis of zinc, because xanthate must be also decomposed in a higher range than pH 3. When the addition of K.A.X. increases in the number of α to

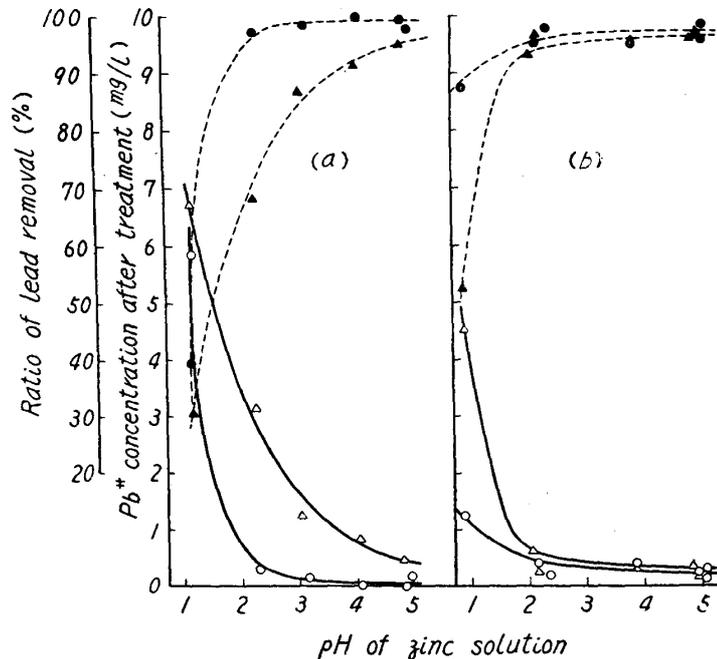


Fig. 2. Influence of acidity of zinc sulfate solution.

Tested solution: 160gZn/l, concentration of lead before treatment=9.68mg/l, Temperature: 40°C, Agitation time: 1hr, Amount of reagent added: \circ $\alpha=10$, \triangle $\alpha=3$, (a) K.A.X., (b) T.M.T.

Pb⁺ concentration is shown by the solid lines, and the ratio of lead removed by the dotted lines.

ten, xanthate is useful in the range of pH 3~5 and can remove lead to below 0.1 mg/l.

T.M.T. is more stable than K.A.X. and available to the solution of pH 2. With tenfold as much as the equivalent T.M.T., lead decreases in concentration to 0.2~0.3 mg/l. However, the difference in the results produced by the different amounts of T.M.T. is not so distinct as in K.A.X., that is, lead dithiocarbamate as well as T.M.T. itself is stable, though the removal of lead from zinc sulfate solution is somewhat unsatisfactory.

4. Influence of temperature

In some stages of purification process of leached solution, the zinc sulfate solution is frequently heated up to 80°C or higher. Like the acidity of zinc solution, the limitation in available temperature is one of the most important conditions that restricted this method from being in practical use. Table 3 shows results of experiments when the solution temperature varied from 20°C to 80°C. The ratio of lead removal decreased at high temperature. To find whether the decrease in this ratio came from the decomposition of added reagents or from the increase in solubilities of lead xanthate and lead dithiocarbamate, lead in the solution filtered after being cooled to room temperature was also measured. In

the case of K.A.X. ($\alpha=3$), the lead concentration after being cooled from 80°C to room temperature was 6.5 mg/l, and this value was larger than the result of $\alpha=1$, namely, 3.44 mg/l. (Fig. 1). This implies that at 80°C, added K.A.X. was

Table 3. Influence of temperature of the zinc solution treated on removal of lead.

Amount of reagent added (α)	Temperature (C°)	0.5% K.A.X. soln.			1% T.M.T. soln.		
		a (mg/l)*	b(mg/l)**	Ratio of Pb removal of a (%)	a (mg/l)	b (mg/l)	Ratio of Pb removal of a (%)
3	80	9.36	6.58	13.2	5.67	1.86	47.4
	60	1.39	1.04	87.1	0.40	0.17	96.3
	40	0.48	—	95.5	0.35	—	96.8
	20	0.50	—	95.4	0.00	—	100
10	80	7.42	1.70	31.2	4.86	0.04	54.9
	60	0.34	0.16	96.8	0.35	0.07	96.8
	40	0.07	—	99.4	0.27	—	97.5
	20	0.08	—	99.3	0.00	—	100

Tested solution : 160 gZn/l, pH 4.8, concentration of lead before treatment = 10.78 mg/l, Agitation time : 1 hr

* Results filtered at prescribed temperature

** Results filtered after being cooled to room temperature

almost decomposed. Furthermore, the lead xanthate was rather soluble at high temperature. Other examples of K.A.X. show that in case $\alpha=3$ lead could not be removed from the zinc sulfate solution at temperature higher than 40°C. Similarly, in case $\alpha=10$, it could not be removed at higher than 60°C. T.M.T. was more stable than K.A.X. at high temperature and was available up to 60°C in all experiments.

5. Influence of concentration of reagent solution

It is desirable that the reagent added to zinc solution is a concentrated solution, for example, powder as it is, because it is undesirable to have zinc solution diluted by the addition of the reagent. On the other hand, by using a concentrate solution, i. e., when a volume of reagent solution is small, the reagent combines with only zinc at the place where the reagent is added, and it takes time to spread uniformly in the zinc solution. There must be most suitable concentration. Experiments were conducted by varying the concentration of reagents. Results are shown in Table 4.

K.A.X. solution concentrated more than 1% was not favorable. Difference between K.A.X. concentrated more than 2% was not so much, about 30 and 60 per cent in lead removal being obtained at $\alpha=3$ and 10 respectively. On the contrary, when the reagent was added as a powder, the lead removal increased in ratio to 60 per cent ($\alpha=3$) and 80 per cent ($\alpha=10$). This may be due to the fact that the powder rather than a concentrate solution was dispersed by agitation before the K.A.X. combined with zinc.

Experiments with T.M.T. produced excellent results at all concentrations tested. The T.M.T., however, could be tested only up to 2% solution, because

the solubility of T.M.T. in 10 per cent aqueous ammonium solution is about 2%. Since the T.M.T. itself does not dissolve in the zinc solution, the addition of powder failed to give lead precipitate.

Table 4. Influence of concentration of the reagent solution on removal of lead.

Reagent	K. A. X.				T. M. T.				
	3		10		3		10		
Amount of reagent added (α)	Zn soln. Conc.	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)
powder			4.28	60.3	2.21	79.5	—	—	10.14
10% soln.		7.48	30.6	4.47	58.5	—	—	—	—
5% soln.		7.52	30.2	3.95	63.4	—	—	—	—
2% soln.		7.17	33.5	3.22	70.1	0.32	97.0	0.28	97.4
1% soln.		2.61	75.8	1.06	90.2	0.35	96.8	0.27	97.5
0.5% soln.		0.48	95.5	0.07	99.4	0.37	96.6	0.23	97.9

Tested solution : 160 gZn/l, pH 4.8, concentration of lead before treatment = 10.78 mg/l.,
Temperature : 40°C, Agitation time : 1 hr,

Reagents should be added at once at the beginning of treatment. If the addition of the reagent is divided by time, lead removal by a definite agitation time will decrease in the ratio, as is known from the mechanism of lead precipitation. Results obtained when the required amount of reagents was added by dividing in two are listed in Table 5 as an example.

Table 5. Example of adding the required reagent in twice.

Reagent	0.5% K.A.X. soln.		1% T.M.T. soln.		
	Solution after treatment	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)	Pb ⁺⁺ concentration (mg/l)	Ratio of Pb removal (%)
Method of addition					
Added at once		0.48	95.5	0.37	96.6
Added in twice, containing filtering*		2.55	76.3	—	—
Added in twice without filtering**		2.18	79.8	0.63	94.2

Tested solution : 160 gZn/l, pH 4.8, concentration of lead before treatment = 10.78 mg/l,
Temperature : 40°C, Agitation time : 1 hr, Reagent added : $\alpha=3$,

* After being agitated for 30 minutes at $\alpha=1.5$, the solution was filtered. Then, the reagent of $\alpha=1.5$ was added and agitated further for 30 minutes.

** After being agitated for 30 minutes at $\alpha=1.5$, the reagent of $\alpha=1.5$ was added without filtering and agitated further.

6. Influence of alkyl group of xanthate

The solubilities of the methyl, ethyl, and n-amyl lead xanthate in water were estimated by N. Mcleod⁽⁶⁾ to be 0.41, 0.15, and 0.04 mg Pb/l respectively at room temperature. Experiments concerning the influence of alkyl group were conducted with xanthates that could be obtained.

The tested xanthates, summarized in Table 6, were newly synthesized, and used as 0.5% solution. Results of experiments did not show any significant trend in spite of the fact that a number of carbons in alkyl radical differ from one

Table 6. The lead concentration treated by various kind of xanthate.

Kind of xanthate	Number of carbon in alkyl radical	Amount of xanthate added (α)	
		3	10
Methyl xanthate	1	0.23	0.09
Ethyl xanthate	2	0.33	0.12
Isopropyl xanthate	3	0.24	0.18
Isoamyl xanthate	5	0.48	0.07

Tested solution : 160 gZn/l, pH4.8, concentration of lead before treatment = 10.78 mg/l, Temperature : 40°C, Agitation time : 1hr,

another, and that the difference of the lead concentration in treated solutions is not so great.

As already described the xanthate ion to combine with lead is supplied from dissolution of zinc precipitate. The present experiments, therefore, could not be free from variations more or less in effective xanthate by the conditions of zinc precipitate. Thus, it is perhaps due to the above-mentioned reasons that the experimental results did not show any difference in respective lead xanthate.

Summary

Many organic reagents were tested to remove lead from the zinc sulfate solution, and it was found that xanthate and tetramethyl thiuramdisulfide hold great promise. These two reagents were further tested in detail to obtain the best conditions. The results are summarized as follows:

(1) The rate of the lead removal is principally controlled by the rate of dissolution of precipitating zinc xanthate or zinc dithiocarbamate. Lead precipitation occurs rapidly within the first five minutes, after which time it goes on gradually. After one or two hours, the lead concentration in treated solution reaches the lowest value. With further agitation, the xanthate decomposes and the removal of lead decreases in ratio. On the addition of T.M.T., the lead concentration is lowered during 24 hours of agitation.

(2) Reagents are most effective at about pH 5 in all the cases, and decrease in their effect with decreasing pH of zinc solution. However, the extent of decrease in their capacity depends upon the amount of reagents added and the stabilities of reagents and precipitates. When K.A.X. was added ten times the equivalent amount, the effective limit of pH of zinc solution was 3. On the other hand, T.M.T was effective up to pH 2, even when the reagent was added three times the equivalent amount.

(3) When temperature of the zinc sulfate solution reached 80°C, the removal of lead was impossible, because not only the reagents and lead precipitates de-

composed, but also the lead salts of respective reagent increased in their solubilities. On the addition of reagents three times the equivalent amount, the effective limit of temperature was 40°C in the case of K.A.X. and 60°C in the case of T.M.T. respectively. When the addition of reagent was increased ten times, even the K.A.X. preserved its effect up to 60°C.

(4) The K.A.X. should be used in solution whose concentration is below 0.5%, because at higher concentration its capacity becomes much less. The T.M.T. may be used at any concentration.

(5) The alkyl group of xanthate does not affect the removal of lead from the zinc sulfate solution.

Thus, lead is very effectively removed from the zinc sulfate solution by adding the K.A.X. or the T.M.T., but the attainable concentration of lead after treatment are below 0.1 mg/l and 0.2~0.3 mg/l under the conditions in which reagents are added ten times the theoretically required amount of K.A.X. and T.M.T. respectively. The T.M.T. is in general more stable than the K.A.X. under any conditions.

In conclusion, the author wishes to express his thanks to Prof. M. Watanabe of the Institute for his kind guidance and Asst. Prof. T. Yamasaki for his useful suggestions and many reagents used in the present investigation.