

# COPRECIPITATION - FLOTATION REMOVAL OF HEAVY METAL IONS

## *AĞIR METAL İYONLARININ ORTAMDAN AUNMASI İÇİN ÇÖKTÜRME - FLOTASYON YÖNTEMİ*

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### ÖZET

Sulu çözeltilerdeki çeşitli ağır metallerin ortamdan uzaklaştırılması için çöktürme-flotasyon yöntemi geliştirilmiştir. Bunun için demir-klorür ve potasyum oleat çöktürücü olarak kullanılmış, çöken bu bileşikleri yüzdürmek için de potasyum etilksantat toplaya olarak kullanılmıştır. Deney sonuçları ortamdaki bakır, kurşun ve çinkonun hemen hemen hepsinin ortamdaki uzaklaştırıldığını göstermiştir.

### ABSTRACT

A precipitate and adsorbing colloid flotation procedure is developed for the removal of various heavy metals from aqueous solutions. The study is carried out for the coprecipitation and removal of metal ions with ferric chloride as a coprecipitant and potassium oleate and potassium ethyl xantogenate as extra coprecipitants and collectors.

It is found that copper, lead and zinc can be removed almost quantitatively from aqueous solutions.

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## 1. INTRODUCTION

Numerous Methods exist for the removal of heavy metal ions from dilute aqueous solutions. The precipitation flotation method refers to the formation and flotation of an insoluble precipitate and the adsorbing colloid flotation method to the removal of a solute by adsorption on (or possibly, coprecipitation with) a carrier floc which is then floated. A detailed review of laboratory scale work in precipitate flotation and adsorbing colloid flotation was written by (Clarke and Wilson, 1983). Lemlich provides a detailed discussion of the theory, models and experimental results of precipitate flotation and its relations to the other foam separations (Lemlich, 1972). Currin et al investigated the compatibility of the adsorbing colloid flotation of copper, sodium lauryl sulphate and ferric hydroxide with a number of precipitation reagents (Currin, et al. 1979). The study of Mukai and co-worker on adsorbing colloid flotation using ferric hydroxide, sodium oleate and a pine oil frother includes work on copper (Mukai, et al. 1979).

Many industrial wastes contain several different metal ions so we sought to the simultaneous removal of copper, lead and zinc from aqueous solutions by precipitation and adsorbing colloid flotation.

## 2. EXPERIMENTAL

The aqueous solutions studied contain 25 mg/l copper, zinc and lead ions. They are obtained by dissolution of the respective metals (over 99.9 % pure) in dilute nitric acid. Ferric chloride in concentrations of 70 mg/l, 80 mg/l, 90 mg/l and 100 mg/l is used as coprecipitant. Potassium oleate (KOL) in concentrations of  $5 \cdot 10^{-5}$ ,  $1 \cdot 10^{-4}$ ,  $5 \cdot 10^{-4}$ ,  $1 \cdot 10^{-3}$  and  $5 \cdot 10^{-4}$  M is used as coprecipitant and collector, while extra coprecipitation of the ions still remaining in solution is

carried out with potassium ethyl xantogenate (KEtX). The ionic strength is varied by means of Na<sub>2</sub>SO<sub>4</sub>. All chemicals used are of analytical reagent grade quality. Adjustment of pH from 4 to 6.5 is made with sodium hydroxide using a pH - meter and a glass electrode .

Prior to the flotation tests for the removal of heavy metal ions from aqueous solutions, the detailed conditions of coprecipitation of ions such as copper, lead and zinc with ferric hydroxide are studied. In the precipitation tests the desired amount of ferric chloride is added to the test solutions containing 25 mg/l of each heavy metal ion. After pH adjustment to the desired value, the mixed solutions are agitated for 5 min by means of a magnetic stirrer at 150 rpm. Then the required amount of sodium sulphate is added and stirring is continued for 5 more min. The mixed solutions are left undisturbed and kept at 25 C for 30 min. Then the precipitate is centrifugally separated at 12000 rpm for 15 min by means of a T-24 Yanetzki centrifuge.

The concentration of each heavy metal ion in the supernatant liquid is measured by ICP optical emission spectrometry.

Coprecipitation experiments are carried out using sodium oleate and potassium ethyl xantogenate as extra coprecipitants.

Flotation experiments with heavy metal ions coprecipitated with ferric chloride as coprecipitant and potassium oleate as coprecipitant and surfactant are carried out in a 300 cm flotation column with sintered glass bottom (height 60cm, diameter 3 cm ), air flow rate - 60 ml/min.

After coprecipitation with the precipitant and pH adjustment of the test solutions containing 25 mg/l of each heavy metal ion, sodium oleate and potassium ethyl xantogenate are added with continuous agitation (magnetic stirrer). Finally pH of the solution is exactly adjusted again. The flotation time is 5 min.

### 3. RESULTS AND DISCUSSION

#### 3.1. Coprecipitation Of Heavy Metal Ions Uith Ferric Hydroxide.

##### 3.1.1. Effects of pH setting and Fe (3+) addition on the coprecipitation of heavy metal ions.

Table 1. Effect of Settling pH on residual concentration of each heavy metal ion in supernatant liquid after coprecipitation.

pH	Fe<3* ) mg/1	R E S I D U A L		
		Cu<2*>, mg/1	Pb(2 <sup>+</sup> ),mg/1	Zn<2 <sup>+</sup> >mg/1
4	100	18,35	4,87	20,16
4,5	100	17,47	4,79	21,39
5	100	13,32	2,61	20,58
5,5	100	9,08	1,32	21,64
6	100	4,08	0,69	19,98
6,5	100	0,03	< 0,02	8,06

Table 1. Shows the effect of pH setting on the coprecipitation of Cu ( 2+), Pb (2+) and Zn (2+) with ferric hydroxide. The test solutions contain 25 mg/1 of each heavy metal ion and 100 mg/1 Fe <3+).It is seen that treatment with ferric hydroxide at pH = 6,5 results in the complete removal of Cu (2+) and Pb (2+) from the solutions studied, while the removal of Zn (2+) requires the application of other reagents.

The effect of the Fe <3 ) amount on the coprecipitation of each heavy metal ion is determined at optimal pH • 6.5. The results in table 2 suggest that the coprecipitation of Cu (2+ > and Pb (2+) is complete by the addition of 100 mg/1 Fe

<3+), in contrast to Zn (2+) coprecipitation.

Table 2. Effects of the Fe (3 ) addition on residual concentration of each heavy metal ion.

pH	Fe<3 <sup>+</sup> > mg/1	R E S I D U A L		
		Cu(2 ), mg/1	Pb<2 <sup>+</sup> >,mg/1	Zn(2 <sup>+</sup> )mg/1
6,5	70	0,326	0,045	17,36
6,5	80	0,061	0,042	14,20
6,5	90	0,050	0,030	12,48
6,5	100	0,030	< 0,020	8,06

3.1.2. Effects of added salt (Na<sub>2</sub>SO<sub>4</sub>) and collector concentration (KOL and KEtX) on the coprecipitation of heavy metal ions.

concentration (KOL and KEtX) on the coprecipitation of heavy metal ions.

One of the factors affecting the efficiency of the adsorbing colloid flotation is the extent to which other ions are adsorbed onto the primary layer of the floe (Currin et al., 1979). Very large changes in surface potential and in surface concentration of surfactant result from varying the salt concentration. Here the effect of the concentration of the salt added (Na<sup>+</sup>SO<sub>4</sub><sup>-</sup>) on the coprecipitation with 100 mg/l Fe (3+) at pH \* 6,5 is studied. In all experiments a possibly interfering substance <Na<sub>2</sub>SO<sub>4</sub>> is added to the solution after ferric hydroxide is precipitated to avoid the eventual loss of the interfering ion by coprecipitation.

The results, shown in Table 3 , indicate that only Cu <2+> and Pb<2+> are removed from the starting solutions.

KOL is usually applied as a cationic collector in adsorbing colloid flotation of copper ions with a ferric hydroxide carrier, but KOL is also used to improve precipitation (Miloshev, 1991).

Table 3. Effect of added salt on residual concentration of each heavy metal ion.

pH	C Na <sub>2</sub> SO <sub>4</sub>	RESIDUAL		
		Cu(2 <sup>+</sup> )mg/l	Pb(2 <sup>+</sup> )mg/l	Zn(2 <sup>+</sup> )mg/l
6,5	2,0.10 <sup>-2</sup>	0,55	0,23	17,95
6,5	2,5.10 <sup>-2</sup>	0,24	0,22	16,18
6,5	5,0.10 <sup>-2</sup>	0,18	0,33	11,80
6,5	1,0.10 <sup>-1</sup>	1,06	0,36	17,15

Coprecipitation is carried out at 5.10<sup>-2</sup>mal/l Na<sub>2</sub>SO<sub>4</sub>, 100 rog/l Fe (3+) , pH\* 6.5 and different concentrations of potassium oleate collector.

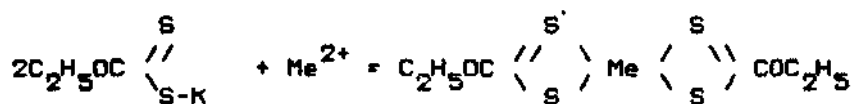
Data on the effect of collector concentration are shown in Table 4. It is seen that KOL does not act as extra coprecipitant.

Table 4. Results of coprecipitation of Cu (2<sup>+</sup>), Pb(2<sup>+</sup>) and Zn(2<sup>+</sup>) with Fe(OH)<sub>3</sub> and KOL at 5.10<sup>-2</sup>Na<sub>2</sub>SO<sub>4</sub>.

pH	C <sub>KOL</sub> ,M	RESIDUAL		
		Cu(2 <sup>+</sup> ),mg/l	Pb(2 <sup>+</sup> ),mg/l	Zn(2 <sup>+</sup> )mg/l
6,5	5.10 <sup>-6</sup>	0,11	0,22	15,08
6,5	1.10 <sup>-5</sup>	0,11	0,25	13,93
6,5	5.10 <sup>-5</sup>	1,26	0,72	24,92
6,5	1.10 <sup>-4</sup>	0,56	0,22	16,74
6,5	5.10 <sup>-4</sup>	0,60	0,84	13,88

Okamoto and Chou and others have shown the advantages of using chelating surfactants in ion flotation and it seemed

likely that such surfactants would also be useful in precipitate and adsorbing colloid flotation (Okamoto, 1978). Potassium ethyl xantogenate is used as extra coprecipitant of Zn <2+> remaining in the solution, since this substance forms chelate complexes of low solubility product and inherently high hydrophobicity;



KEtX consumption is stoichiometrically related to the initial metal content of 25 mg/l.

It is established that the optimal conditions under which the content of Cu < 2+ > , Pb (2+) and Zn <2+> in the solutions studied decreases below the detectable limits <Cu (2+) < 0,002 mg/l, Pb (2+) < 0,002 mg/l and Zn (2+) < 0,67 mg/l) are as follows: pH=6,5 % 100 mg/l Fe(3+), 5.10 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> 1.10<sup>-4</sup>M KOL and KEtX in an amount of 70 % of the stoichiometric one required for the initial metal content of 25 mg/l.

### 3.2. Precipitate Flotation And Adsorbing Colloid Flotation Procedure.

On the basis of the coprecipitation results described in 3.1, experiments are carried out for the coprecipitation and removal of metal ions with ferric hydroxide as coprecipitant and potassium oleate and KEtX as extra coprecipitants and collectors.

Direct flotation experiments are carried out with solutions containing 25 mg/l of each heavy metal ion.

Fig. 1. shows the effect of the concentration of potassium oleate on the recovery of Cu <2+>, Pb <2+> and Zn <2+>. The removal of Zn <2+> by flotation with potassium oleate as collector is unsatisfactory, (about 20% Zn (2+)

recovery)» while Cu (2+) and Pb (2+) recovery is about 90%. This result is, however, insatisfactory.

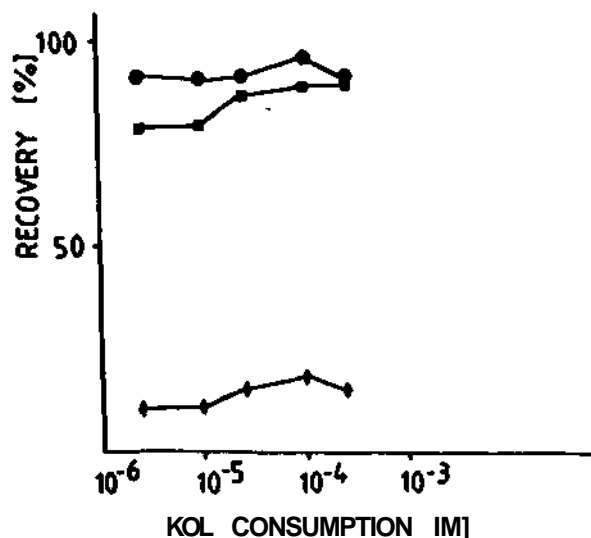


Fig.1. Effects of KOL consumption on the recovery of Cu (■), Pb (●) and Zn (◆).

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At KOL concentrations of above  $1.10 \text{ mol/l}$ , the flotation efficiency decreases. This decrease in flotation efficiency with the rise of the collector concentration can be explained in terms of two possible models (Sheimon, 1967):

1) as the collector concentration increases, its surface concentration at the air-water interface becomes sufficiently large so that hydrophobic particles are no longer able to attach to the bubbles.

2) it becomes possible for a second layer of surfactant ions to adsorb on the particle, thus making the particle hydrophilic again.

In order to check the mechanism type in our case the surface tension of the starting and those of the purified aqueous solutions studied are measured. Fig.2 shows that up to  $1.10^{-4} \text{ M KOL}$  the oleate ions adsorb mainly onto the colloid particles while at  $5.10^{-4} \text{ M KOL}$  adsorption of oleate



ions at the liquid - gas interface has already started.

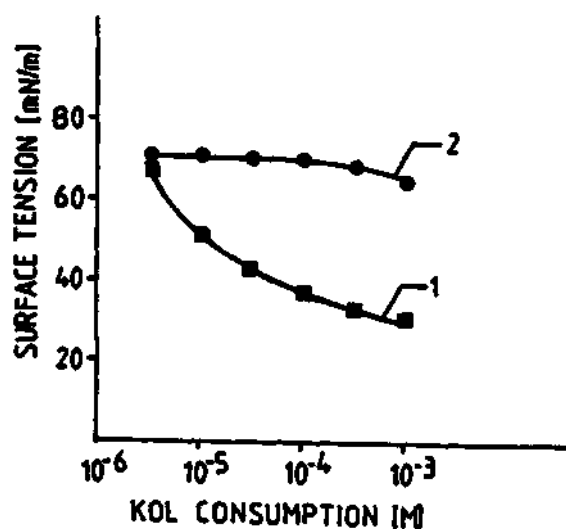


Fig.2. Change of surface tension  $\sigma^*$  starting aqueous solution (■) and purified aqueous solution (●) depending on KQL consumption.

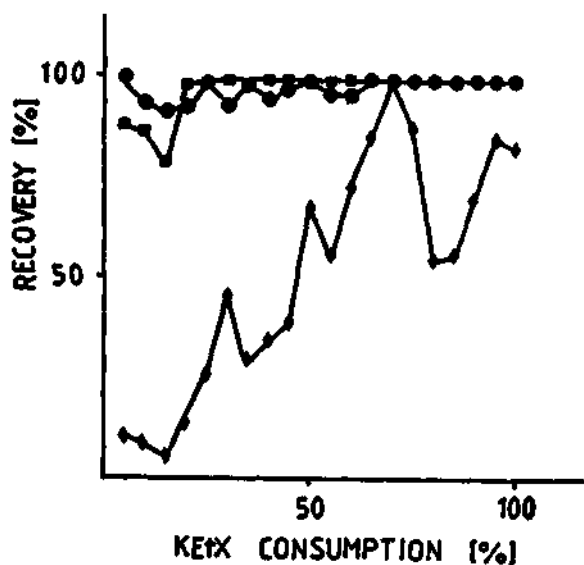


Fig.3. Cu (■), Pb (●) and Zn (◆) recoveries as a function of KetX consumption relevant in percent to stoichiometrical metal content.

Fig.3 shows the effect of the combined use of KOL and KETX on the removal of heavy metal ions.

The Cu (2+) , Pb (2+) and Zn (2+) recovery is about 98% with potassium ethyl xantogenate in an amount of 70% of the stoichiometric one with respect to the initial metal content of 25 mg/l.

It is found that Zn(2+) can be removed almost quantitatively from aqueous solution using this chelating surfactant (KETX).

### 3.3. DISCUSSION

There has been some question as to the mode of removal of ions by adsorbing colloid flotation. Separation could be effected by coprecipitation or post - adsorption on the floc. Some of the work on copper indicates that actually coprecipitation is the most important step in the scavenging of an ion from solution by ferric hydroxide flocs. A concept exists in the literature that the removal of ions such as Cu (2+), Pb (2+) and Zn (2 ) from aqueous solutions by coprecipitation with Fe(3+) is probably due to the metal ion uptake of ferric hydroxide precipitate through adsorption, inclusion, and mixed crystallization processes(Mukai et al, 1979).

The adsorption of oleate ions on colloid particles containing the precipitated metal ions is checked by measuring the surface tension at the liquid/gas interfaces of the starting and purified aqueous solutions according to the method of Uihelmy.

Curve 2 <fig.2> shows that oleate ions adsorb predominantly onto colloid particles containing precipitated metal ions. In this way, KOL (due to the effect of oleate groups) has an additional purification effect by increasing the recovery of some ions (Cu <2 ) and Pb (2 ).

Potassium ethyl xantogenate improves slightly the Cu(2 ) and Pb(2 ) recovery and drastically that of Zn <2 ) due to

its ability to form chelate complexes with these metal ions with low solubility and high hydrophobicity.

#### 4. CONCLUSION

The recovery of heavy metal ions such as copper, lead and zinc from aqueous solutions is possible by the application of a combination of precipitate and adsorbing colloid flotation.

It is shown that such metal ions as copper and lead are completely coprecipitated and then floated successfully by setting pH and Fe addition to optimum conditions. On the other hand, the addition of potassium oleate and potassium ethyl xantogenate together with Fe in the coprecipitation stage leads to the complete elimination of zinc ions and to the improvement of the recovery and increase in the degree of removal of heavy metal ions.

It is experimentally established that oleate ions are adsorbed mainly on the surface of the colloid particles containing the precipitated metal ions. \*

#### 5. ACKNOWLEDGMENTS

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## 6. REFERENCE&

Clarke, A.N., D.J.Uilson, 1983; "Foam Flotation - Theory and Applications", Morsel Dekker, New York.

Currin B.L., R.M. Kennedy, A.N.Clarke and D.J.Uilson, 1979;"Electrical Aspects of Adsorbing Colloid Flotation. X. Pretreatments, Multiple Removals, Interferences» and Specific Adsorption", Separ. Sei. Technol., volume 14, S. 669 - £87.

Lemlich, R., Ed., 1972; "Adsorbitive Bubble Separation Techniques", New York.

Miloshev, S. and I.Nishkov, 1991 ; "Environmental controls in metallurgical industries ond scrap metal recycling", In:Proc. of the Int. Symp. on Env. Contr. in Metallurgical Industries, <ed. by M.Cholkle and A.Oliver), S. 243 - 253.

Mukai S., T.Wokamatsu and Y.Nakahiro, 1979; "Study on the removal of heavy metal ions in waste water by the precipitation - flotation method", Rec. Dev. Separ. Sei, volume 5 , S. 67 - 78.

Okamoto Y. and E.J.Chou, 1975; "Faom Separation of Mercury Ion with Chelating Surfactant! The Selectivity of the Removal of Cadmium and Mercury Ions with 4-Dodecyldiethylenetriamine", Separ. Sei., volume 10, S. 741 - 753.

Sheimon I., Ph. D. Thesis, 1967; Univ. of the Witwatersland, Yohonesburg, South Africa.