

# Studies of extractive removal of silver(I) from chloride solutions

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**Abstract.** For efficient recovery of silver(I) from chloride solutions, amine extractants were used. The effect of the type of diluent, extractant and chloride concentration, contact time and reextraction were studied. It was found that the best diluent for this process was xylene. Extraction of silver depended on concentration of hydrochloric acid, sodium chloride and extractant and additionally on the contact time. Reextraction of Ag(I) ions from the loaded organic phase showed that it can be removed only little using  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , NaOH,  $\text{NH}_4\text{NO}_3$ , and  $\text{NaNO}_3$  as the stripping agents.

## 1 Introduction

Silver has many physical properties which are very difficult to substitute using other metals. It responds greatly to light. It does not corrode. It is a very unusual electricity conductor and has antibacterial properties. Because of these properties many electronics and solar cell manufacturers as well as clothing and pharmaceutical industries have taken an interest in silver. The increased use of this element in production processes has raised its demand. Unfortunately, the amount of available silver is reduced due to irreparable wear. Hence development of an efficient method of obtaining silver is a very important. The most interesting and practical method seems to be hydrometallurgy [1, 2].

Interest in hydrometallurgical methods based on chloride solution leaching of copper sulphide concentrates is due to obvious advantages of these approaches [3-5]. A high solubility of chlorides in comparison to sulphates allows for operation with more concentrated solutions (reduction of liquid volume) and a simultaneous recovery of associated metals like silver, gold and lead. The highly corrosive activity of chloride solutions is no longer a risk due to availability of new construction materials (metals, plastics and ceramics). In addition, chloride leaching is better than other leaching media such as thiourea, cyanide and thiosulphate, due to its low toxicity, low costs and the level of technical "maturity" [6].

Chloride leaching of copper sulphide concentrate under oxidizing conditions changes  $\text{Ag}_2\text{S}$  form of silver into the solution containing chlorocomplexes of silver(I) e.g.  $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{2-}$ ,  $\text{AgCl}_4^{3-}$ , and in some cases (such as low concentration of hydrochloric acid or high metal concentration, presence of iron and increased temperature) silver precipitates as  $\text{AgCl}$  [7].

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A low content of silver, a noble metal, in the leach solution makes the process efficient and effective, without losses in solid residues. In addition, all production industries involving silver require purified metals containing as little impurities as possible. One of the best methods of separation is solvent extraction.

Separation of silver(I) ions from the chloride solutions by solvent extraction has been tested and described in several reports [8, 9]. Commonly, the use of Lewis base rule (hard and soft bases and acids) is a guide, where the ligands of the sulphur atoms are considered to be „soft base” and are applied to extract Ag(I) deemed as „soft acids” [10, 11]. For extraction of Ag(I) various organic compounds containing sulphur and phosphorus are used, including Cyanex 471X (triisobutylphosphine sulphide, TIBPS) [10], TBPS (tri-*n*-butylphosphine sulphide), TOPS (tri-*n*-octylphosphine sulphide) [12] and bis-*O,O*-diisobutylphosphorodithioester derivatives [9]. High extraction recoveries of Ag(I) and high selectivity for Fe(III) and Cu(II) were obtained. It was shown that selective extraction of individual metals increases with the length of the alkyl chain between two groups P=S(S), and it had a positive effect on the regeneration process of the loaded organic phase.

Commercial acid extractants such as Cyanex 302 (bis-(2,4,4-trimethylpentyl)-monothiophosphinic acid) and Cyanex 301 (bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid) [13, 14] also showed a high Ag(I) extraction efficiency. However, neither showed selective extraction of Ag(I) with the co-existing Cu(II) ions in solution and for other noble metals such as Pd(II), Au(III) and Pt(IV).

Ligands containing sulphur and nitrogen (thiourea derivatives) were also checked as effective extractants towards silver(I) ions in concentrated acid and chloride solutions i.e. dodecylthiourea, tetraethylthiuram disulphide, dibutyl- and diphenylthiourea, DPHT and DBT, respectively, as well as other derivatives of thiourea. Dodecyl thiourea was an efficient extractant and allowed for the selective release of Ag(I) from Fe(III) and Cu(II) in strongly acidic chloride solutions [15, 16].

Diphenyl- and di-*n*-butylthiourea (DPHT and DBT) extractants provided the best extraction efficiency of Ag(I) from the chloride solution containing 2 M HCl and 3 M NaCl at low selectivity ratios in relation to other non-noble metals [16]. When testing the selectivity of Ag(I) extraction from Cu(II) and Fe(III), the separation coefficients of  $\text{Ag}^+/\text{Fe}^{3+}$  and  $\text{Ag}^+/\text{Cu}^{2+}$  were approximately 3 and 1. In addition, ineffective extraction of the loaded organic phase using sodium thiosulphate was achieved [9].

Extraction of Ag(I) was also conducted using compounds with more complex structure, such as amide derivatives of monomeric calix[4]arene and the compound trialkylthiophosphonate. These extractants systems were well characterized in terms of Ag(I) extraction, but no data are provided in relation to selectivity of Ag(I) extraction to other metals. The resulting extraction recoveries were at low levels, only calix[4]arene obtained an Ag(I) extraction degree of 60% at low acid concentrations [17, 18].

Selectivity was not examined using salts of tri- and tetra alkylammonium, which were used for extraction of Ag(I) to provide a high degree of recovery of Ag(I). These salts caused lower Ag(I) extraction recovery when the concentration of chloride ions in the aqueous solution increased [17].

Despite widespread use in industrial hydrometallurgical processes, phosphorus-containing compounds are considered less environmentally friendly than extractants which have hetero atoms such as either oxygen, nitrogen or sulphur in their structures. For this reason, this study tested the extraction of Ag(I) chloride solutions with amines. This work considers the environmental protection point of view and the lack of reports in the literature about the use of amines. The objective of this study was to examine the process of silver(I) ions extraction from the chloride solutions. The effect of type of diluent, hydrochloric acid concentration, sodium chloride concentration, contact time, extractant concentration and stripping on silver(I) recovery was investigated. Additionally, the process of silver(I) ions extraction was tested from the chloride pregnant leach solutions (PLS), received from atmospheric leaching of the copper flotation concentrate from Lubin Plant of KGHM Polska Miedz S.A..

## 2 Experimental

### 2.1 Reagents

Amine extractants were used as organic solvents without further purification. Detailed information on extractants used is presented in Table 1. Xylene (Avantor) and toluene (Avantor) were used as the diluent.

**Table 1.** Characteristics of amine extractants.

Amine	Sign	Concentration [%]	Supplier
Triethylenetetramine	TETA	97	Sigma-Aldrich
Tris(2-aminoethyl)amine	TAEA	96	Sigma-Aldrich
Diethylenetriamine	DETA	99	Huntsman

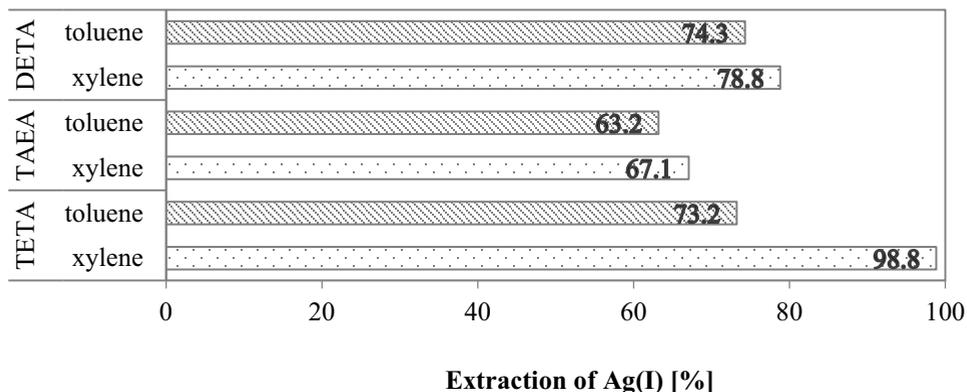
### 2.2 General extraction procedure

Synthetic solutions of silver(I) ions were prepared by dissolving a known amount of silver nitrate ( $\text{AgNO}_3$ ) in distilled water with hydrochloric acid and sodium chloride ( $0.4 - 73.0 \text{ g/dm}^3$  of  $\text{HCl}$ ,  $58.5 - 234.0 \text{ g/dm}^3$  of  $\text{NaCl}$ ). The initial  $\text{Ag(I)}$  concentration for synthetic solutions was  $50 \text{ mg/dm}^3$ . Chloride leach solutions were generated in atmosphere chloride leaching of a solid residue after sulphate leaching of the commercial flotation sulphide concentrate produced at the Lubin Concentrator (KGHM Polska Miedz S.A.). The solutions after chloride leaching contained  $\sim 0.05 \text{ g/dm}^3$  of  $\text{Ag(I)}$ ,  $\sim 0.50 \text{ g/dm}^3$  of  $\text{Pb(II)}$ ,  $\sim 0.36 \text{ g/dm}^3$  of  $\text{Cu(II)}$ ,  $\sim 0.02 \text{ g/dm}^3$  of  $\text{Co(II)}$ ,  $\sim 0.02 \text{ g/dm}^3$  of  $\text{Ni(II)}$ , and  $\sim 0.01 \text{ g/dm}^3$  of  $\text{Zn(II)}$ . The organic phase contained one of three extractants and xylene or toluene as a diluent. Different solutions were used as a stripping agent:  $\text{NaOH}$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The aqueous and organic phases were shaken at 325 rpm and ambient temperature ( $25 \pm 1^\circ\text{C}$ ) using a mechanical shaker ELPAN 357. The concentration of  $\text{Ag(I)}$  in the aqueous phase before and after extraction and reextraction was determined by means of flame atomic absorption spectrometry (FAAS) using a Varian SpectrAA 20 Plus instrument.

## 3 Results and discussion

### 3.1 Effect of type of diluent

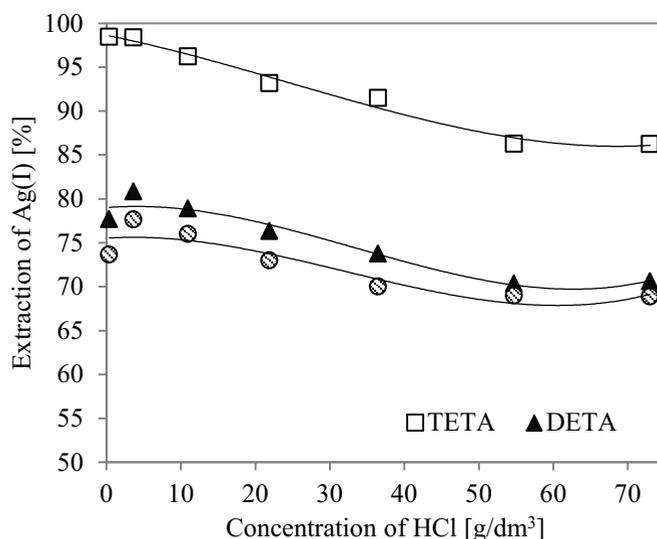
The effect of varying diluents such as toluene and xylene in the organic phase (extractant – TETA, DETA, TAEA with concentration 10% (v/v)) on extraction of  $\text{Ag(I)}$  was studied. The solutions containing  $0.05 \text{ g/dm}^3$  of  $\text{Ag(I)}$ ,  $3.7 \text{ g/dm}^3$  of  $\text{HCl}$ ,  $234 \text{ g/dm}^3$  of  $\text{NaCl}$  were used as the aqueous phase. The results are given in Fig. 1. The best  $\text{Ag(I)}$  extraction can be observed for TETA extractant, and it can be seen that the extraction percentage is higher when xylene was used as the diluent. Therefore, in the further studies only xylene, as the diluent, was used.



**Figure 1.** Silver(I) extraction using amine extractants from chloride solutions (extractant: 10% (v/v)).

### 3.2 Influence of HCl and NaCl concentration on silver(I) extraction

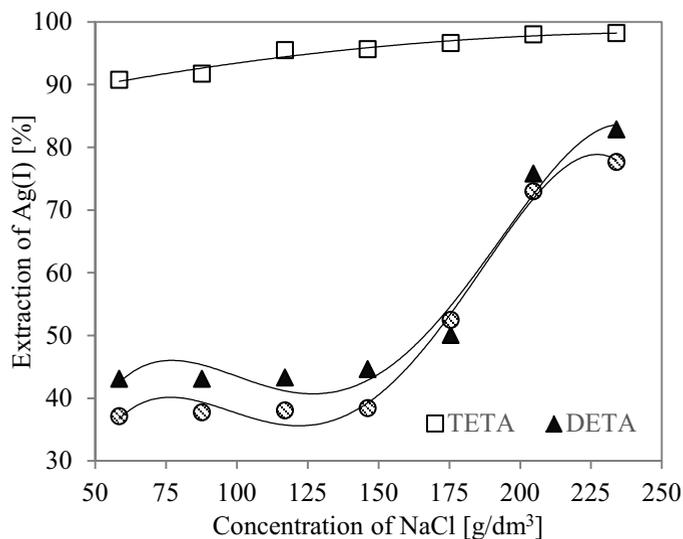
The effect of hydrochloric acid concentration on silver(I) extraction was checked for selected extractants (TETA, TEPA and TAEA) diluted with xylene. The concentration of extractants in the organic phase was equal to 10% (v/v). The solutions containing 0.05 g/dm<sup>3</sup> of Ag(I), 0.4 – 73.0 g/dm<sup>3</sup> of HCl, 58.5 – 234 g/dm<sup>3</sup> of NaCl were used as the aqueous phase. Extraction was performed at ambient temperature. Aqueous (A) and organic phases (O) were contacted for 60 minutes at the phase ratio equal to 1. Figure 2 presents the effect of HCl concentration on extraction of silver with the studied extractants. Extraction of Ag for all extractants decreased with increasing the hydrochloric acid solution concentration. Similar conclusions can be found in [10], where the influence of hydrochloric acid in aqueous phase on silver(I) extraction by using CYANEX 471X was investigated. It was also shown that silver extraction decreased with increasing hydrochloric acid concentration of the aqueous phase. This decrease was attributed to formation of non-extractable anionic silver species in the aqueous phase, which could not be extracted by the organic system.



**Figure 2.** Ag(I) extraction as a function of HCl concentration (extractant: 10% (v/v)).

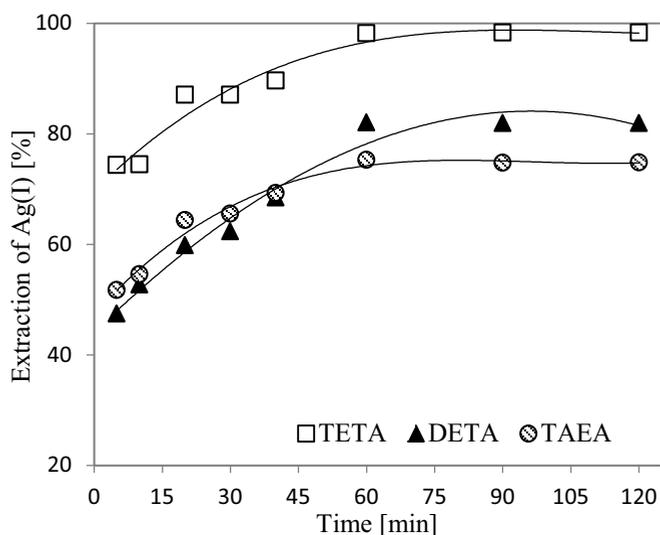
Figure 3 presents the effect of NaCl concentration on extraction of silver with studied extractants. The extraction efficiency of Ag(I) increased with increasing sodium chloride solution concentration. The highest efficiency of the process for TETA (98%), DETA (83%) and TAEA (78%) was obtained at NaCl concentration of 234 g/dm<sup>3</sup>.

The results presented in Figure 2 show that the best Ag(I) extraction efficiency was observed from the solution containing 3.7 g/dm<sup>3</sup> of HCl and 234 g/dm<sup>3</sup> of NaCl in the aqueous phase. The further studies were performed using this composition of the aqueous phase.



**Figure 3.** Ag(I) extraction as a function of HCl concentration (extractant: 10% (v/v)).

### 3.3 Effect of contact time on silver(I) extraction



**Figure 4.** Effect of contact time on silver(I) extraction using TETA, DETA and TAEA as extractants from the chloride solution (extractant: 10% (v/v)).

The effect of contact time on silver extraction is presented in Figure 4, where the extraction efficiency of silver(I) was plotted vs. time. The process was carried out at ambient temperature and the contact time varied in the range of 5 – 120 minutes. The concentration of the extractants (TETA, DETA, TAEA) was equal to 10% (v/v). The phase ratio A/O (aqueous/organic) was equal to 1.

The results show that for extractants tested, the silver(I) ions were removed after 60 min of shaking (Figure 4). The extraction efficiency was equals to 98, 82 and 75% for TETA, DETA and TAEA, respectively. Therefore, the contact time of 60 min was recommended as the time, which enables to achieve the equilibrium of the silver extraction.

### 3.4 Effect of extractant concentration

To study the effect of extractant concentration the content of TETA, DETA and TAEA in the organic phase varied in the range of 2.5 – 20% (v/v) (Table 2). The aqueous (A) and organic phases (O) were contacted for 60 minutes at the phase ratio A/O equal to 1. Extraction was performed at ambient temperature. It was observed that the extraction efficiency increased with increase of the extractant concentration. The maximum extraction efficiency of silver(I) (96.9, 96.7 and 84.5%, for DETA, TETA and TAEA respectively) was obtained at the highest concentration of extractant equal to 20% (v/v).

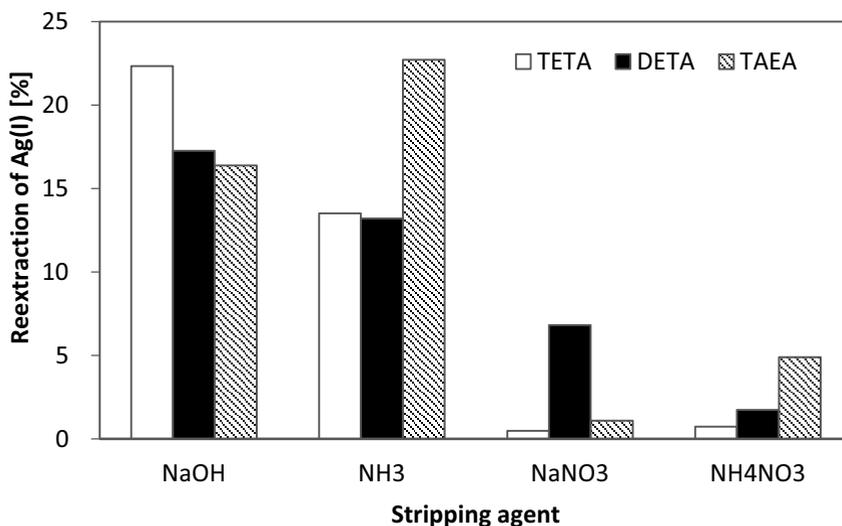
This result can be explained in light of increasing number of extractant molecules which leads to the increase of recovery. Applying too high concentration of extractant in the organic phase, while silver concentration in solutions is low, may be unprofitable. Therefore, it was assumed that optimum extractant concentration was 20% (v/v).

**Table 2.** Silver(I) extraction using amine extractants (TETA, DETA, TAEA) from chloride solutions.

Extractant concentration [% (v/v)]	TETA		TAEA		DETA	
	<i>E</i> [%]	<i>D</i>	<i>E</i> [%]	<i>D</i>	<i>E</i> [%]	<i>D</i>
2.5	10.3	0.1	4.4	0.1	3.6	0.04
5	16.9	0.2	43.6	0.8	11.8	0.1
7.5	81.0	4.3	69.8	2.3	59.3	1.5
10	96.5	29.1	75.4	3.1	80.7	4.2
15	96.7	29.0	80.9	4.2	90.6	9.6
20	96.7	27.6	84.5	5.4	96.9	31.8

### 3.5 Reextraction

A stripping test was performed using freshly loaded and pre-filtered organic phases containing 0.07 g/dm<sup>3</sup> of Ag(I) ions and 0.5 mol/dm<sup>3</sup> of stripping agents (NH<sub>3</sub>·H<sub>2</sub>O, NaOH, NH<sub>4</sub>NO<sub>3</sub>, and NaNO<sub>3</sub>) in the aqueous phase. Stripping of loaded organic was carried out at one-to-one volume ratios of loaded organic and stripping solutions. After 60 min contact, the phases were allowed to disengage. The aqueous phases were separated and analysed. The results obtained are presented in Figure 6. For all tested extractants low reextraction efficiency of Ag(I) was obtained. The best stripping of Ag(I) ions from the loaded organic phase in the case of TETA and DETA was observed by using 20 g/dm<sup>3</sup> NaOH and the reextraction efficiency was consecutively 22 and 17%. In case of TAEA, the results showed that the metal can be stripped at only 23% efficiency in the one-stage process. Very poor stripping efficiency was obtained using NH<sub>4</sub>NO<sub>3</sub>, and NaNO<sub>3</sub> as the stripping agents. The value of reextraction was not higher than 7%.



**Figure 5.** Reextraction of silver(I) for amine extractants (TETA, DETA, TAEA).

### 3.6 Extraction of silver(I) from multicomponent solutions after chloride leaching

Silver(I) ions were also extracted from the chloride leaching solutions containing lead, copper, cobalt, nickel and zinc. Metals extraction were determined with the organic solution consisting of 10% of extractants (TETA, DETA, TAEA), the A/O ratio of 1:1 and ambient temperature. During extraction, no third phase formation was observed. The extraction efficiency of particular metals and separation factors for silver(I) are shown in Table 3. It can be seen that the metal extraction order was Ag>>Cu>Zn>Ni>Pb>Co for TETA, Ag>>Cu>Co>Zn>Ni>Pb for DETA and Ag>>Cu>Ni>Co>Zn>Pb for TAEA. The highest co-extraction was observed for copper(II), where separation factors (S) were the lowest. In relation to other metals, the most selective extractant for silver(I) was TETA.

**Table 3.** Silver(I) extraction using amine extractants (TETA, DETA, TAEA) from multicomponent solutions after atmosphere chloride leaching.

Metal	C <sub>initial</sub> [mg/L]	TETA		DETA		TAEA	
		E [%]	S <sub>Ag/Me</sub>	E [%]	S <sub>Ag/Me</sub>	E [%]	S <sub>Ag/Me</sub>
Ag(I)	46.2	96.6	-	96.8	-	79.5	-
Pb(II)	501.2	0.9	3039.6	0.3	9387.8	1.2	308.7
Cu(II)	364.2	9.7	264.0	20.84	114.9	31.1	8.6
Zn(II)	12.4	2.4	1138.0	4.43	652.7	11.3	30.4
Ni(II)	15.3	1.8	1557.0	3.26	897.1	17.3	18.5
Co(II)	23.7	0.7	4286.2	14.32	181.0	15.1	21.8

## 4 Conclusions

TETA, DETA and TAEA were used as extractants in solvent extraction of silver(I) ions from the synthetic chloride solutions, and solutions resulting from atmosphere leaching of the copper flotation

concentrate. The experimental results showed that Ag(I) can be efficiently extracted from the solutions using amine as an extractant. The best results were obtained by using xylene as a diluent. Additionally, extraction of silver(I) was efficient for 60 minutes of contact time. The process significantly depended on the hydrochloric acid, and sodium chloride concentrations for DETA and TAEA in the aqueous phase, but for TETA the influence of increasing sodium chloride concentration was very small. The most effective results were obtained for the solution containing 3.7 g/dm<sup>3</sup> of HCl and 234 g/dm<sup>3</sup> of NaCl in the aqueous phase. Extraction from the chloride leaching solution showed high Ag(I) ions recovery for all used extractants, and also co-extraction of Cu(II) ions to a small degree. Stripping of Ag(I) ions from the loaded organic phase in the case of TETA, DETA and TAEA was not efficient. The best results for TETA and DETA was observed by using 20 g/dm<sup>3</sup> NaOH (22 and 17% respectively), and for TAEA silver(I) can be stripped with only 23% extraction efficiency.

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