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Ion exchange recovery of silver from concentrated base metal-chloride solutions

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Abstract

Ion exchange has not been extensively studied nor industrially used for recovering small amounts of silver from concentrated base metal-chloride solutions. A novel multistep process utilizing a weak anion exchanger with polyamine functionality is proposed and its performance investigated experimentally. Suitability of a silica based polyamine functional resin WP-1 to the task was demonstrated by comparing Ag uptake and selectivity of several ion exchange resins and adsorbents using batch equilibrium experiments. HCl was found to be the best choice for washing impurities, especially Cu, from the bed after the loading step. Tetrasodium salt of EDTA was found suitable especially for selective desorption of lead from the loaded bed, but also other impurities were scrubbed if still present after the wash. Both thiosulfate and thiourea were shown to be effective for elution of Ag from the WP-1 bed, but thiourea is preferred because of the slight affinity of thiosulfate towards the resin. Stability of the performance of the process was shown in several consecutive adsorption-elution cycles containing all the needed washing and scrubbing steps. With the developed process, 72% pure silver product was obtained. As the washing step can be designed such that no silver is lost, the recovery yield for Ag depends only on the length of the loading step, and even 100% recovery can thus be achieved for the whole process.

Keywords:

Silver; Chloride solution; Weak anion exchanger; EDTA; Thiosulfate; Thiourea

1. Introduction

In earth's crust Ag is most commonly associated with ores of Au, Cu, Pb and Zn (United States Geological Survey, 2014). Chloride-leaching for these kinds of ores and their concentrates has been stated to be feasible method in the future due to its energy efficiency and higher solubility of metals compared to conventional sulfate-leaching (Flett, 2002; Hyvärinen and Hämäläinen, 2005). Thus chloride solutions containing small amounts of Ag are created (Paiva and Abrantes, 1994). Ag may be recovered from these solutions by precipitation as AgCl (Asano and Terao, 1999), but purity of the product is low and the method is not applicable in high chloride concentrations due to increasing solubility of AgCl (Gammons and Yu, 1997). Ag may be cemented by Cu powder, but the purity of the product is low, and also Ag is not totally recovered if there is Cu(I) in the solution (Hyvärinen and Jyrälä, 2004; Peters and Kazel, 1978). Solvent extraction has been extensively studied as a substitute for previously described techniques, but yet it has not been used widely in industrial scale. Variety of mainly solvating extractants have been used, from which tri-isobutylphosphine sulfide (TIBPS) has been observed to be the most promising one especially because its selectivity over base metals, especially Cu (Paiva, 2001). Recently Ono and Hatano (2013) patented a method for recovering Ag from Cu bearing chloride solutions with tributylphosphate (TBP).

Despite the fact that ion exchange is generally seen as a potential method for recovering minor metals at small concentrations, it has not been extensively studied for recovering Ag from concentrated base metal-chloride solutions. Hiai and Abe (2012) have patented a method, in which Ag is recovered from chloride leachates of CuS or CuO ores, or their concentrates, with strong anion exchangers. Drawbacks of the method are that it is applicable only in Ag concentrations below 30 mg/L and Cu concentration needs to be reduced from typical 20-30 g/L by solvent extraction.

Yurtsever and Şengil (2012) have recently reviewed natural and synthetic Ag adsorbents. Their functional groups contain mainly different kinds of N- and S-donor atoms and/or chelating properties. To give an example, triethylenetetramine and N,N-dimethylaminopropylamine functionalized acrylic copolymers were found to have a capacity of approximately 100 mg/g, but they were selective for Cu over Ag even at relatively low excess of Cu (equilibrium concentrations Cu = 10 mg/L, Ag = 1 mg/L) (Buhaceanu et al., 2009). While some materials have been reported to exhibit good selectivity for Ag over base metals in certain conditions such as dilute solutions in nitrate medium (Zhang et al., 2012), good selectivity in highly concentrated chloride solutions has not been reported with any commercial or experimental adsorbents or ion exchangers.

Besides selectivity, another aspect that deserves attention is elution of Ag from the bed if the separation process is operated in loading-elution mode. Thiosulfate is known to form strong complexes with Ag and thus it has been used in photography as a fixing agent for Ag. From that application it has been adopted as eluent in solvent extraction of Ag (Rickelton and Robertson, 1987), which makes it attractive eluent also for ion exchange. Also thiourea is known to associate strongly with Ag (Gherrou et al., 2002), and it has been found to enhance desorption of Ag from cation exchanger by Yurtsever and Şengil (2012).

Therefore, the aim of this work was to develop an ion exchange method for recovering Ag in presence of a large excess of base-metals in concentrated chloride solutions. Several ion exchange resins and other adsorbents were first tested in batch experiments. After that a single column ion exchange process was developed for a polyamine functional weak anion exchanger WP-1. In particular the issue of selecting the eluent was addressed. The process was also run for several cycles to study its stability and accumulation of impurities.

2. Experimental

2.1 Materials and reagents

All the separation materials tested are introduced in Table 1. They include three weak anion exchangers, two strong anion exchangers, one weak cation exchanger, two strong cation exchangers, two chelating resins, one polymer adsorbent, two activated carbons and one fiber adsorbent.

In addition to the separation materials the following chemicals were used: AgCl (supplier VWR International), $CaCl_2 \cdot 2\ H_2O$ (Sigma-Aldrich), $CuCl_2 \cdot 2\ H_2O$ (VWR International), EDTA tetrasodium salt (Acros Organics), $FeCl_3 \cdot 6\ H_2O$ (Riedel-de Haën), 37% HCl (Merck), $MgCl_2 \cdot 6\ H_2O$ (Merck), NaBr (VWR International), NaCl (VWR International), $Na_2S_2O_3$ (Merck), Na_2SO_3 (Riedel-de Haën), $NiCl_2 \cdot 6\ H_2O$ (Merck), nitrilotriacetic acid (Acros Organics), $PbCl_2$ (Sigma-Aldrich), $SC(NH_2)_2$ (Sigma-Aldrich), $ZnCl_2$ (VWR International). All the chemicals were of analytical grade, except NaCl in feed solutions was of technical grade.

Table 1 Characteristics of the separation materials used in the experiments for recovery of Ag from base metal-chloride solutions. Acronyms: WBA = Weak anion exchanger, SBA = strong anion exchanger, WAC = weak cation exchanger, SAC = strong cation exchanger, DEAE = diethylaminoethyl.

Name	Supplier or manufacturer	Type	Physical structure	Functional group
WP-1	Purity Systems Inc.	WBA	Macroporous silica	Polyamine
Purolite A830	Purolite	WBA	Macroporous acryl	Tertiary amine
IRA-67	Sigma-Aldrich	WBA	Acrylic gel	Tertiary amine
Purolite A860	Purolite	SBA	Macroporous acryl	Quaternary ammonium
IRA-410	Fluka	SBA	PS-DVB gel	Quaternary ammonium
Purolite C104	Purolite	WAC	Acrylic gel	Carboxylic acid
Dowex 50	Fluka	SAC	PS-DVB gel	Sulfonic acid
Purolite C160	Purolite	SAC	Macroporous PS-DVB	Sulfonic acid
Dowex M4195	Supelco	Chelating	Macroporous PS-DVB	Bis-picolylamine
IRA-743	Sigma-Aldrich	Chelating	Macroporous PS-DVB	N-methyl-D-glucamine
XAD-7	Sigma-Aldrich	Polymer adsorbent	Macroporous PS-DVB	-
Norit pk 1-3	Norit Americas Inc.	Activated carbon	-	-
Univar	Univar	Activated carbon	-	-
DEAE-cellulose	Sigma-Aldrich	Fiber adsorbent	Cellulose fiber	DEAE

2.2 Phase equilibrium measurements

Ag uptake characteristics of the separation materials were investigated by equilibrating them in shaker at 25 °C for 2-3 days with what represents a typical feed solution in chloride based hydrometallurgical processes (see Table 2), except that c_{Ag} was 40 mg/L. The amounts of phases in shaken test tubes were 10 mL of solution and 0.5 of g dry separation material.

The feed solutions were synthetic, and they were prepared by mixing the metal chloride salts with NaCl and HCl containing aqueous solution overnight. The Cl^- and Br^- concentrations were increased to the desired level with NaCl and NaBr. The obtained solution was filtered to remove possible undissolved traces of the metal chlorides, and analyzed with ICP. The E_h of the solution is over 1.0 V in the working pH range and thus the Cu and Fe are present exclusively as Cu(II) and Fe(III). This was verified by calculations with Medusa software (*KTH - Chemistry / Chemical Equilibrium Diagrams*, n.d.).

The separation materials were used as received without any pretreatment (dry materials). The adsorbed amounts of metals were calculated from liquid phase ICP analyses (see Section 2.4) with material balance:

$$[\mathrm{Ag}]_\mathrm{S} = \frac{\left([\mathrm{Ag}]_\mathrm{L}^0 - [\mathrm{Ag}]_\mathrm{L} \right) V_\mathrm{L}}{m} \quad (1)$$

, where S and L stand for solid and liquid phase respectively, V_L is volume of the liquid phase and *m* is the dry mass of the adsorbent or ion exchanger. Thus units are mg/L for liquid phase and mg/(g dry material) for solid phase.

2.3 Column experiments

Dynamic column separation experiments were done in 15 mm diameter Kronlab columns at room temperature (22-23 °C). The volume of the resin (WP-1) bed was approximately 20 mL and flowrate 2.0 mL/min (6.0 BV/h). Both acid and base form beds were used depending on the process configuration. The bed was treated 2-3 times either by 1 M HCl- – 1 M NaOH – H_2O or 1 M NaOH – 1 M HCl – H_2O sequences, depending on the desired form of the bed.

Details of the individual column experiments are given in Table 3. Some relevant additional information, like length of some individual steps, is also given in connection with the discussion of the results. The runs began with loading step of 4-11 BV, which was followed by set of washing, scrubbing and elution steps with varying chemicals, lengths and sequences. In some runs several sequences were done to study the stability of resin and behavior of the system. The resin was protonated with HCl before the loading of the following sequence if needed. From each step several samples were collected if the purpose was to record the full breakthrough curves and study the behavior of the particular step. Otherwise collective sample was taken.

Table 2 Typical feed solution both in batch and column experiments for recovery of Ag from base metal-chloride solutions.

Ag	**Ca**	**Cu(II)**	**Fe(III)**	**Mg**	**Ni**	**Pb**	**Zn**	**Br**	**HCl**	**Cl_{total}**
25 mg/L	56 g/L	18 g/L	150 mg/L	1000 mg/L	20 mg/L	400 mg/L	350 mg/L	20 g/L	10 g/L	230 g/L

Table 3 Features of the column experiments for studying recovery of Ag from base metal-chloride solutions. Deviations from feed solution presented in Table 2 have been given in column "Other information".

Run	**Resin form**	**V_{bed}, ml**	**T, °C**	**Wash – scrub – elution**	**Other information**
1	Free base	19.4	22.0	4 M NaCl – 1 M $Na_2S_2O_3$ + 0.1 M Na_2SO_3 – 4 M NaCl	c_{Ag} = 212 mg/L, c_{Br} = 80 g/L
2	Free base	19.4	23.0	0.25 M EDTA – 4 M NaCl – 1.5 M $Na_2S_2O_3$ + 0.75 M Na_2SO_3	c_{Ag} = 212 mg/L, c_{Br} = 80 g/L Washed resin bed from run 1
3	Free base	19.4	23.0	0.5 M NaCl – 0.25 M EDTA – 0.5 M $Na_2S_2O_3$ + 1 M Na_2SO_3	c_{Cu} = 70 g/L
4	Protonated	20.0	22.0	0.5 M NaCl – 0.25 M EDTA – 1.5 M $Na_2S_2O_3$ + 0.75 M Na_2SO_3	
5	Protonated	19.8	22.0	1 M NaCl pH 2 – 0.25 M EDTA – 1 % $SC(NH_2)_2$ in 1 M HCl – 1 M NaCl pH 2	
6	Protonated	20.3	23.0	1 M NaCl – 0.25 M EDTA – 1.5 M $Na_2S_2O_3$ + 0.75 M Na_2SO_3 – 1 M NaCl – 2 M HCl	5 repeated cycles
7	Protonated	20.0	20.5	1 M HCl – water – 0.25 M EDTA – 1 % $SC(NH_2)_2$ in 1 M HCl – water	4 repeated cycles

2.4 Analytical techniques

All metal analyses of aqueous samples were done from 1 M HCl, 1 M NaCl -media with inductively coupled plasma atomic emission spectroscopy (ICP-AES). Standard solutions used were Ag 1000 mg/L in 0.5 M HNO_3 (supplier Romil), Ca 10 000 mg/L in 0.5 M HNO_3 (Romil), Cu 10 000 mg/L in 0.5 M HNO_3 (Romil), Fe, Mg, Ni, Pb and Zn 100 mg/L as multi standard in 2-5% HNO_3 (AccuStandard), Pb 10 000 mg/L in 0.5 M HNO_3 (Romil), and Zn 10 000 mg/L in 0.5 M HNO_3 (Romil).

3. Results and discussion

3.1 Silver recovery efficiencies and selectivities of the separation materials

Initial screening of separation materials was done with batch experiments using the solution described in Table 2. None of the screened separation materials bound over 50% of the Ag from the studied base metal-chloride solution (Fig. 1a). The recovery yield was approximately 40% or higher with five materials, including two weak anion exchangers (WP-1, Purolite A830), one chelating resin (Dowex M4195) and both activated carbons (Norit pk 1-3, Univar).

For the five above mentioned promising materials separation factors for Ag over the impurities, α (−), were calculated based on the distribution coefficients, D_g (L/g dry material), as follows (“Recommendations on ion-exchange nomenclature,” 1972):

$$\alpha_{\text{Ag/M}} = \frac{D_{\text{g,Ag}}}{D_{\text{g,M}}} = \frac{[\text{Ag}]_{\text{S}} / [\text{Ag}]_{\text{L}}}{[\text{M}]_{\text{S}} / [\text{M}]_{\text{L}}} \tag{2}$$

Ag/Ca, Ag/Mg and Ag/Ni selectivities were extremely high for all the studied materials (Fig. 1b). As these impurities will thus not cause problems in the separation process, the ordinate in Fig. 1b is scaled such that the selectivity for Ag over the more strongly bound base metals is better seen. Purolite A830 resin and Univar activated carbon had low Ag/Pb and Ag/Zn selectivities, while Dowex M4195 had low Ag/Zn and especially Ag/Fe selectivity. For Norit activated carbon the Ag/Fe selectivity was low. Considering the composition of the feed solution (Table 2), high selectivity over Cu is perhaps the most important property of the materials. As observed in Fig. 1b, the Ag/Cu separation factor was not over 10 for any material. The highest value ($\alpha = 3.4$) was obtained for WP-1, which also had very high selectivities for Ag over the other impurities except Pb. Thus WP-1 was chosen a primary separation material for dynamic column separation experiments.

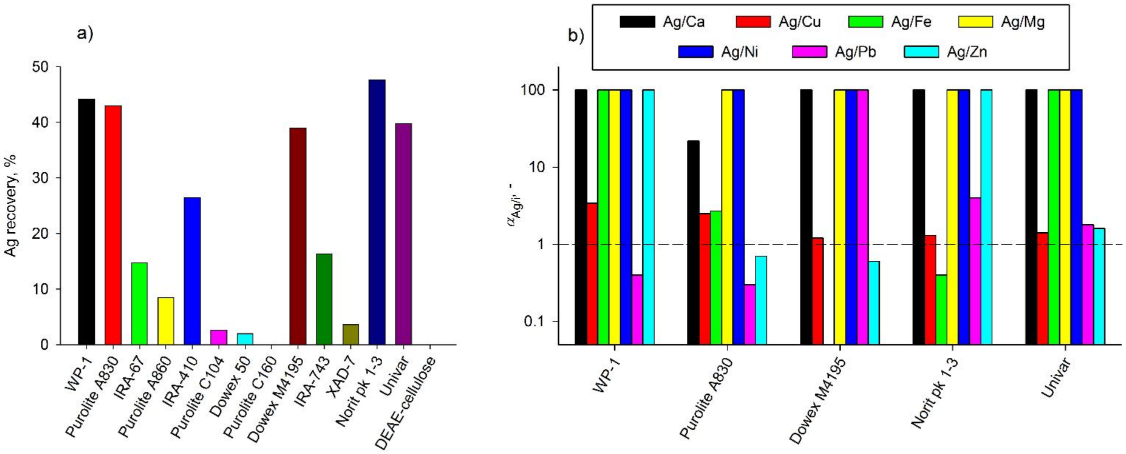

Fig. 1 a) Silver recovery efficiencies and b) separation factors Ag/M of the screened separation materials in recovery of Ag from base metal chloride solutions.

3.2 Construction of process sequence for separation column operation

Because of the complexity of the feed solution (Table 2) and low concentration of the target metal, there are many options how to perform the ion exchange recovery process of Ag. The chosen process sequence depends especially on the desired recovery yield and purity of the product solution.

Our proposed process consists of five steps:

1. *Loading of the separation column for 4-11 BV*.
2. *NaCl or HCl wash*.
3. *0.25 M EDTA scrubbing*.
4. *Elution either by thiosulfate or thiourea solution*.
5. *Protonation if needed*.

In Fig. 2 are presented typical breakthrough curves in the loading step with base (Run 3) and acid form (Run 4) resin beds of WP-1. Affinity order of the metals with both beds was: Pb > Ag > Zn > Cu > Fe > Ni > Mg. The chloride complex formation plays a big role. Speciation plots for the metals were calculated with Medusa software (*KTH - Chemistry / Chemical Equilibrium Diagrams*, n.d.), though they are only discussed here in writing to save space. Pb forms strongly anionic complexes as does Ag. Presence of anionic Ag complexes has been verified from formation constants given in NIST database (Smith and Martell, 2004). Fraction of anionic Zn chloride complexes is also dominant and Cu also forms a significant amount of anionic chloride complexes. The selectivity of Pb and Ag over Zn and Cu can be explained by the affinity of the polyamine functional group of the resin towards more hydrophobic Pb and Ag species. Though the Pb and Ag atoms are large, the hydration of those large ions is generally weaker compared to the smaller ones (Shannon, 1976). Fe(III) complexates fairly strong with the chloride, but the amount of $FeCl_4^-$ is low. Ni, Mg and Ca do not form anionic complexes.

In runs 1, 2 and 3, where free base form resin beds were used, some Fe precipitate was locally observed in the beginning of the loading step. This phenomenon is verified by the fact that the pH increases to over 3, because the resin absorbs acid, but then quickly decreases as the feed contains 10 g/L HCl (Table 2) and the precipitate is removed. Although it does not affect much to the flow in the column, it clearly affects the adsorption of the metals. With the free base form bed, breakthrough of Ag occurred at void volume of the column, i.e. right after the start of the run. Moreover, Ag and Pb fronts were very broad with low gradients, which indicates that the Fe precipitate might cause some kinetic problems. With the acid form bed of WP-1 (Run 4), the breakthroughs of Zn, Ag and Pb occurred much later. The concentration fronts were steeper and more regular shaped, which indicated much better Ag recovery performance compared to the free base form bed. In the experiments displayed in Fig. 2, the dynamic Ag capacity of the acid form bed at practically 0% loss of Ag (i.e., approximately 4% breakthrough) was 0.15 mg/(mL bed). With free base form bed, however, breakthrough occurred almost immediately and even at 40% breakthrough the amount of Ag bound to the ion exchanger was only 0.06 mg/(mL bed).

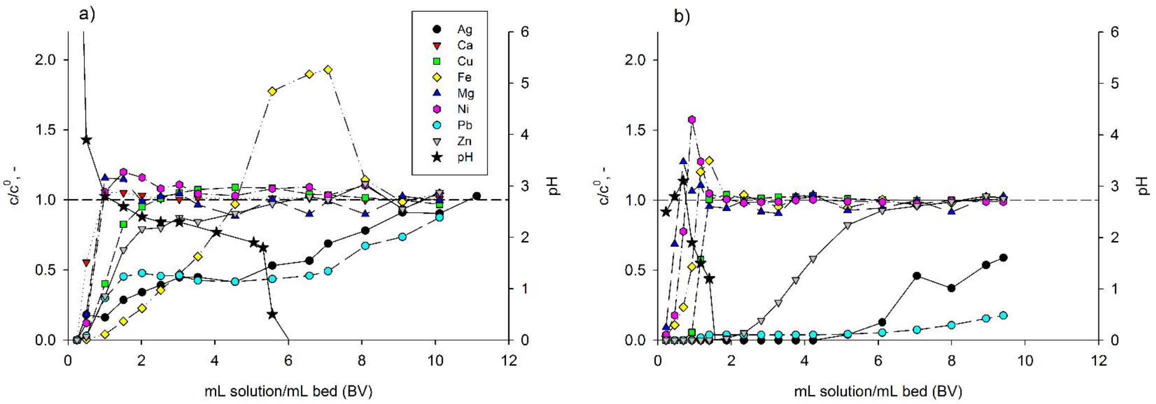

Fig. 2 Loading step in recovery of Ag from base metal-chloride solutions with weak anion exchanger WP-1. Breakthrough curves for a) free base form (Run 3) and b) acid form resin beds (Run 4).

The purpose of the step 2 (washing) was to remove impurities, especially Cu and Zn, from the resin bed. Other metals successfully washed from the bed included Fe, Mg and Ni, but Pb remained in the bed. 2.3 BV of 0.5 M NaCl in Run 3 was found to be effective solution for the task (Fig. 3a). If a lower amount of NaCl was used for washing, the level of Zn removal was not sufficiently high. If a larger volume and/or a more concentrated salt was used (Run 1), small Ag losses were observed (Fig. 3b).

Efficiency of the washing (step 2) has a significant meaning to the latter steps. Because the amount of Cu in the feed is such high, in some runs small amount of Cu migrated to the elution step and a precipitate was formed with thiourea. In the reaction Cu(II) is reduced to Cu(I), which then forms a sparingly soluble complex with formamidine disulfide, an oxidation product of thiourea (Ratajczak et al., 1975). Thus with the process configuration with the thiourea elution in step 4 the washing in step 2 should be acidic, since above pH 4 Cu forms a solid $CuCl_2{:}3Cu(OH)_2$ compound reducing the solubility of Cu to non-acidic chloride solutions (*KTH - Chemistry / Chemical Equilibrium Diagrams*, n.d.). In practice, such precipitates were indeed observed during the thiourea elution with even 2.0 BV washing pulse of 1.0 M NaCl in pH 2.0 (Run 5), but not with 2.0 BV pulse of 1.0 M HCl (Run 7). After the wash the acid in the void fraction of the bed needs to be removed by additional water rinse, because the acid form of EDTA, if formed in the step 3, is sparingly-soluble.

In scrubbing step 3, tetrasodium salt of EDTA was used for desorbing of strongly bound Pb, and the rest of the other impurities remaining after step 2, especially Zn, from the resin bed. It can be seen from Figs. 3c and d (Runs 3 and 2) that the scrubbing is really selective for all the impurities over Ag. Pure Pb solution was obtained if the bed was first washed with NaCl, and Pb enriched mixture of all the impurities was obtained if the scrubbing was done directly after the loading step. EDTA is known to be a strong complexation agent for various metals, and the selectivity of the scrubbing for the impurities over Ag is readily explained by the difference in the stabilities of the metal-EDTA complexes. From the impurities Cu, Fe, Ni, Pb and Zn have much higher metal-EDTA stability constants than Ag (Table 4). Mg has a value closer to that of Ag, but still it was selectively desorbed in this step if it was conducted directly after loading (Fig. 3d).

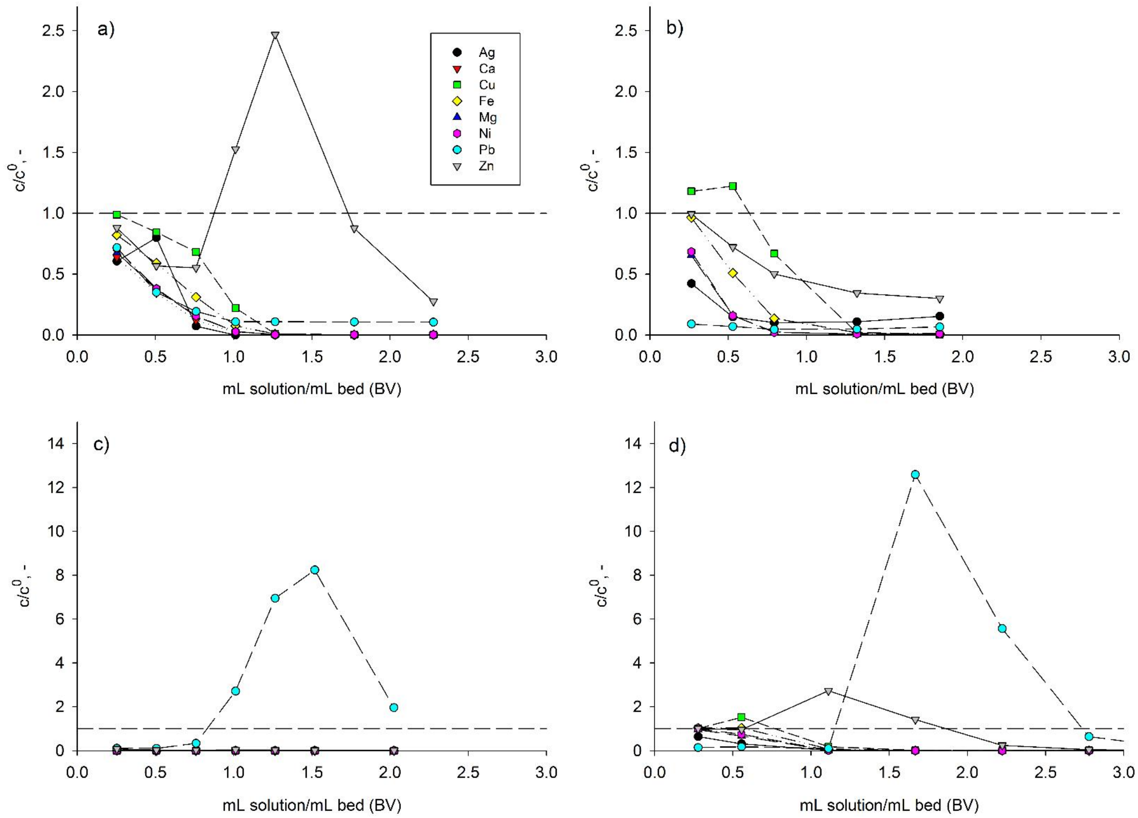

Fig. 3 Washing (step 2) and EDTA-scrubbing (step 3) curves after recovering Ag from base metal-chloride solution. a) 2.3 BV wash with 0.5 M NaCl (Run 3), b) 1.9 BV wash with 4.0 M NaCl (Run 1), c) 2.0 BV scrubbing with 0.25 M EDTA after NaCl wash (Run 3), d) direct scrubbing with 0.25 M EDTA after loading (Run 2). See Table 3 for details about the experimental runs.

Table 4 Stability constants (log *K*) of EDTA-complexes with metals in the feed solution for recovery of Ag from base metal-chloride solutions (Ivanov and Tsakova, 2005; Martell et al., 1974).

Ag	**Ca**	**Cu(II)**	**Fe(III)**	**Mg**	**Ni**	**Pb**	**Zn**
7.3	10.7	18.8	25.1	8.8	18.6	18.0	16.5

First choice as an eluent in step 4 was thiosulfate, since it is known to be a strong complexing agent for Ag forming $Ag(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)_3^{5-}$ compounds in wide Eh-pH range (Aylmore and Muir, 2001). The composition of the solution used (1.50 M $Na_2S_2O_3$ + 0.75 M Na_2SO_3) was adopted from patent of Fyson (1993), which introduced an Ag fixing agent for photography. Purpose of the Na_2SO_3 is to stabilize the solution, because $S_2O_3^{2-}$ is known to decompose forming SO_3^{2-} and elemental sulfur. The elution peak of Ag from WP-1 bed with the thiosulfate eluent (Run 4) was sharp (Fig. 4). The maximum c/c^0 was 9.3 and no Ag was observed after 2.5 BV. The problem was the affinity of thiosulfate itself to the resin bed, from which it was hard to strip. Consequently the remaining thiosulfate reacted with the protonation acid in the step 5 forming SO_2 gas and elemental sulfur:

$$S_2O_3^{2-}(aq)+2H^+ \rightarrow SO_2(g)+S(s)+H_2O \tag{3}$$

Thiourea was identified as an alternative eluent. It associates strongly with heavy metals and also with Ag, because it is a strong Lewis base having free electron pairs in both sulfur and nitrogen atoms. The Lewis base properties also make the complexes more stable at low pH, which is why the thiourea eluent should be acidic (Gherrou et al., 2002). Also with thiourea (Run 5), the elution peak was sharp having maximum c/c^0 of 7.7 and after 1.9 BV there was no Ag at the eluate (Fig. 4).

Full elution curves were recorded in Runs 4 and 5 (see Table 3), and are presented in Fig. 4. In Run 6, where the resin bed was washed for 1.0 BV with 1.0 M NaCl and scrubbed for 3.5 BV with 0.25 EDTA, 75% pure Ag-thiosulfate eluate was collected. Cu was the only impurity. In the otherwise similar Run 5, where the resin bed was washed for 2.0 BV with 1.0 M NaCl (pH 2) and scrubbed for 3.5 BV with 0.25 EDTA, a 27% pure Ag-thiourea eluate was collected. The amounts of the impurities were: Ca 4%, Cu 64%, Pb 3% and Zn 1%. Thus it can be concluded that the purity of Ag in the eluate is higher with thiosulfate compared to the case of thiourea elution. The first explanation to this behavior is affinity of Cu to the thiourea eluent used. In literature, values of 10.2, 13.0, 15.9, 18.1 are given for stability constants of 1:1, 1:2, 1:3 and 1:4 Cu(II)-thiourea complexes respectively (Krzewska et al., 1980), while no values for Cu(II)-thiosulfate complexes were found. The other factor is that the acidity of the eluent (1 M HCl) increases the affinity of the eluent towards Cu.

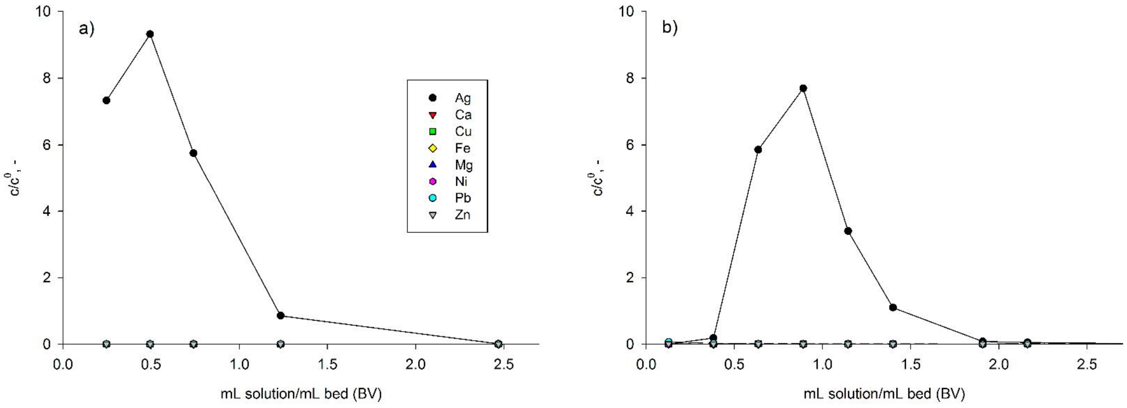

Fig. 4 Concentration profiles in elution of Ag recovery process from base metal-chloride solutions. Elution with a) 1.50 M $Na_2S_2O_3$ + 0.75 M Na_2SO_3 (Run 4) and b) 1 wt.% $SC(NH_2)_2$ in 1 M HCl (Run 5).

Because the Cu is not eluted from the bed with thiosulfate, there is a serious risk of its accumulation in the long term. On the other hand, even if it is not completely eluted with thiosulfate, it could possibly be desorbed in the protonation stage by HCl especially if that step was long enough. It is also possible that with both eluents, the purity could be increased with longer washing and scrubbing steps, but this would lead to increased chemical consumption and effluent amounts. In addition, the obtained eluate might still need further purification and concentration before producing the final product.

Despite the better Ag/Cu selectivity with the thiosulfate elution, thiourea is the preferred reagent because thiosulfate is too strongly bound to the resin bed. In continuous operation this could cause a need for periodical regeneration of the bed.

If thiosulfate is used in elution, the resin is preferably protonated prior to the next loading step, so that the pH cannot increase in an uncontrolled manner during loading, and thus local Fe precipitates cannot form. 1.0 BV of 1.0 HCl was found to effectively protonate the WP-1 bed. Here, another benefit of the thiourea elution is seen; separate protonation of the bed is not needed because the eluent by itself is acidic.

3.3 Stability of the process during several process cycles

The stability of the performance of two alternative processes (thiosulfate and thiourea eluents) was investigated with two continuous runs with four and five full loading-elution cycles including appropriate washing, scrubbing and preconditioning steps. The results and sequences are shown in Table 5. Though using different eluents was the main origin of the variation in the sequences, the runs differed from each other in many features. Thus the purpose was not just to compare the eluents, but to gain information about effect of the different steps to operating the suggested Ag recovery process.

According to the ICP analyses, the loaded amounts of some metals at some cycles were lower than the sum of the desorbed amounts in different steps. The experimental uncertainty in the loaded amounts can be assumed to be larger than that of the desorbed amounts because it has been calculated indirectly from the difference between measured concentrations in the feed and the concentration profiles in the column outlet. Nevertheless, some trends over the cycles can be clearly seen and are discussed below. All the purities discussed in the text have been calculated based only on those metals shown in the Table 5.

In Run 6 the behavior of the process was not stable over the five cycles (Table 5). The loaded and eluted amounts of Ag became lower after each cycle. Yields for Ag in loading decreased from 96 to 84% within the five cycles. Also the loaded amounts of impurities became smaller. This implies that Cu and the thiosulfate eluent itself were accumulating to the bed as discussed in the previous section. Also the eluted amounts of Ag decreased significantly, by 59%, indicating that part of the eluent was consumed by the impurities. As a result, Ag purities in the eluate decreased from 75 to 11% during the 5 process cycles.

After each cycle more and more Cu was observed in the samples of EDTA scrubbing and thiosulfate eluate instead of the desired NaCl wash. In the 3rd cycle there was more Cu in the eluent than Ag, and in 5th cycle the amount of Cu was almost eight times higher. The longer NaCl wash and HCl regeneration after the elution did probably not remove the accumulated Cu because the conditions were alkaline and the regeneration acid was spent to the protonation.

A similar trend as with Cu was observed also with Pb, the amount of which increased in the eluate during the Run. However, due to the smaller concentrations of Pb, the absolute amount was not as significant to the Ag purity as that of Cu.

In Run 7, over the four cycles, the process was much more stable than in Run 6 (Table 5). In fact, the purity of Ag in the eluate even increased from 61% to 72%. The loaded amount of Ag remained exactly the same, with 0% losses during loading, and the eluted amount decreased by 6%. In this process, Cu was clearly better washed with a 2.0 BV pulse of

1.0 M HCl after loading than with a short pulse of 1.0 BV NaCl in Run 6. Zn was washed partly with the HCl and mostly in the subsequent 1.0 BV water rinse. Pb was scrubbed practically completely with the EDTA, and its high purity (96%) is also noteworthy.

Table 5 Multicycle runs (6 and 7) for recovery of Ag from base-metal chloride solutions. For loading step the adsorbed amounts of metals are given, and for other steps the washed, scrubbed or eluted amounts are given. In addition to the presented sequences, run 6 had 3.0 BV long 1.0 M NaCl wash and 1.0 BV long 2.0 M HCl regeneration, and run 7 had 2.0 BV long water washes, after the elution.

Run 6: Thiosulfate elution			*Material balances (as mg)*			
Cycle	**Step**	**Duration**	**Ag**	**Cu**	**Pb**	**Zn**
1	Loading	5.0 BV	3.5	338	44.1	36.0
	NaCl wash	1.0 BV	0.0	356	0.0	5.8
	EDTA scrub	3.5 BV	0.2	2.3	48.2	32.8
	Thiosulfate elution	2.5 BV	2.7	0.9	0.0	0.0
2	Loading	5.0 BV	3.3	214	44.1	34.0
	NaCl wash	1.0 BV	0.0	314	0.0	6.2
	EDTA Scrub	3.5 BV	0.2	11.0	46.4	29.5
	Thiosulfate elution	2.5 BV	3.2	2.1	0.3	0.2
3	Loading	5.0 BV	3.3	203	44.1	33.2
	NaCl wash	1.0 BV	0.0	301	0.0	6.6
	EDTA scrub	3.5 BV	0.6	8.3	46.3	27.8
	Thiosulfate elution	2.5 BV	2.5	2.9	0.3	0.0
4	Loading	5.0 BV	3.1	234	44.0	31.7
	NaCl wash	1.0 BV	0.0	280	0.0	7.8
	EDTA scrub	3.5 BV	0.9	22.4	47.1	24.9
	Thiosulfate elution	2.5 BV	1.8	5.9	0.5	0.4
5	Loading	5.0 BV	2.9	156	43.8	28.1
	NaCl wash	1.0 BV	0.0	256	0.1	8.4
	EDTA scrub	3.5 BV	1.2	29.0	46.6	20.6
	Thiosulfate elution	2.5 BV	1.1	8.0	0.6	0.4

Table 5 Continued.

Run 7: Thiourea elution			*Material balances (as mg)*			
Cycle	**Step**	**Duration**	**Ag**	**Cu**	**Pb**	**Zn**
1	Loading	5.0 BV	2.8	330	46.8	37.1
	HCl wash	2.0 BV	0.0	384	0.0	14.3
	Water rinse	1.0 BV	0.0	0.5	0.0	27.4
	EDTA scrub	3.5 BV	0.0	1.3	48.6	0.6
	Thiourea elution	2.0 BV	3.3	1.7	0.4	0.0
2	Loading	5.0 BV	2.8	355	46.0	36.5
	HCl wash	2.0 BV	0.0	381	0.1	14.1
	Water rinse	1.0 BV	0.0	0.3	0.0	28.1
	EDTA scrub	3.5 BV	0.0	1.6	53.6	0.7
	Thiourea elution	2.0 BV	3.2	1.2	0.4	0.0
3	Loading	5.0 BV	2.8	284	45.9	36.2
	HCl wash	2.0 BV	0.0	386	0.2	14.3
	Water rinse	1.0 BV	0.0	0.3	0.0	24.5
	EDTA scrub	3.5 BV	0.0	1.5	50.3	0.7
	Thiourea elution	2.0 BV	3.3	0.9	0.4	0.0
4	Loading	5.0 BV	2.8	305	45.9	36.4
	HCl wash	2.0 BV	0.0	393	0.2	14.4
	Water rinse	1.0 BV	0.0	0.3	0.0	26.9
	EDTA scrub	3.5 BV	0.0	1.3	44.7	0.6
	Thiourea elution	2.0 BV	3.1	0.8	0.4	0.0

4. Conclusions

Recovery of silver from concentrated base metal-chloride solutions was studied. Based on batch screening experiments, in which several different adsorbents and ion exchangers were compared, polyamine functional weak anion exchanger WP-1 was chosen for dynamic column studies. Protonated form of the resin was observed to have better dynamic capacity for silver, and also with free base resin there was some Fe precipitate observed. Affinity order of the metals to the resin was Pb > Ag > Zn > Cu > Fe > Ni > Mg, which can be explained by the tendencies of the metals to form anionic chloride complexes, and by the affinity of the resin towards the less hydrated Pb and Ag. Adsorbed impurities besides lead were satisfactory washed with water or NaCl, but HCl is preferred because it was able to remove also small traces of copper from the bed, which is essential for the elution step. Since EDTA forms strong complexes with base and heavy metals, it effectively scrubbed lead but also other impurities if present after the previous wash.

Thiosulfate and thiourea both have strong affinities to silver and thus may be used for elution, though thiourea is preferred because thiosulfate was observed to have some affinity to the resin. Also due to the chemical nature of the eluents, thiosulfate solution should be slightly alkaline meaning that additional protonation step is needed while thiourea solution should be acidic thus leaving the resin readily in protonated form. Presence of even minor amounts of copper was found to be a problem with the both studies eluents. With thiourea it forms precipitate, and with thiosulfate it is not eluted and thus accumulates to the process.

The optimized process with thiourea elution was steadily operated for four full cycles. No metals or chemicals were accumulated to the bed, yield and purity (61-72%) of silver did not decrease, and no silver was lost in the washing or scrubbing steps.

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