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 was 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.

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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 a 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 it has not yet been used widely on an industrial scale. A 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 of 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.

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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 the eluent in solvent extraction of Ag (Rickelton and Robertson, 1987), which makes it an 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 the 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), and $ZnCl_2$ (VWR International). All the chemicals were of analytical grade, except NaCl in feed solutions which was of technical grade.

2.2. Phase equilibrium measurements

Ag uptake characteristics of the separation materials were investigated by equilibrating them in a 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 pre-treatment (dry materials). The adsorbed amounts of metals were calculated from liquid phase ICP analyses (see Section 2.4) with material balance:

$$[Ag]_S = \frac{\left([Ag]_L^0 - [Ag]_L\right)V_L}{m}, \tag{1}$$

where S and L stand for solid and liquid phase respectively, V_L is the 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 flow rate was 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 the 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.

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

Table 1
Characteristics of the separation materials used in the experiments for the 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