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E-waste management through silver recovery from scrap of plasma TV monitors

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***Abstract*—The method of extraction of silver from scrap of plasma TV monitors using noncyanide reagents – sodium thiosulphate and acidothiourea – were investigated. Recovery of silver from silver-containing acidothiourea leach solutions was also examined. It was found that sodium thiosulphate did not offer an efficient silver extraction while dilute acidothiourea solutions provided almost complete extraction of silver from scrap of plasma TV monitors. The recovery of silver through coagulation-precipitation from acidothiourea leach solutions was carried out with a natural biodegradable material (persimmon tannin extract) and a cationic cellulose (Catinal HC/LC). Persimmon tannin extract, dissolved at pH 13.8, was proved to be a promising material for complete silver recovery. Besides, precipitative recovery of silver with sodium sulfide was conducted and a complete recovery of silver was achieved, which indicated that the sulfide precipitation could be a viable technology too in hydrometallurgical processing to remove complexed silver from acidothiourea leach solutions.**

INTRODUCTION

Silver, a precious metal, is one of the widely used elements in industry for various processing and in jewelry for ornament. The majority of this element is consumed in film processing (40-50%), electrical and electronic industries (20-30%) and ornament and jewelry (10%) [1]. An annual demand for silver in Japan alone is reported to be 2597 ton, of which 567 t is demanded for electrical and electronic products [2]. Broad application and growing demand for silver are the two key reasons for its recovery. Although, silver is mostly recovered from scraps of X-ray films, photographic films and jewelry [3], very recently electronic equipments such as, personal computers were examined to estimate the amount of potentially recoverable metals, which includes precious metals (silver, gold, palladium) and other metals too [4].

Owing to rapid developments in technology as well as tech-savvy customers' demand to accept new commodities, electronic products are being replaced by newer models at a much faster rate e.g. the continuous replacement of CRT monitors by LCD displays and/or plasma monitors and, very lately, by high-definition TV sets. Predictions indicate that a huge numbers of televisions will need to be disposed of in the coming years [5]. However, a new law on the treatment of waste home appliances already came into effect in Japan on 1 April 2001, enforcing the commencement of full-fledged recycling of waste home appliances including television sets, air conditioners, refrigerators and washing machines [6]. Scrap of plasma TV monitors, an emerging e-waste, is thus thought to create an environmental problem due to its massive disposal. Hence recovery of silver from scrap of plasma TV monitors is of great concern.

Conventional cyanidation is considered as the mainstream method for the leaching of silver from ores and has been practiced over the years. The advantages of cyanidation process over other extraction methods include its simplicity, fast leaching kinetics, and ease of recovery. Considering a deadly environmental impact of using cyanide, it seems to be essential to establish an economic and environmentally viable option for recovery of silver by using non-toxic reagents. A suitable replacement for cyanide may be the use of thiosulfate [7] due to the fact that thiosulphate is substantially less expensive than cyanide, and it facilitates the leaching of complex materials through matrix degradation [8]. Another potential candidate for using as lixiviant is thiourea [9] because thiourea in acidic media can readily dissolve precious metals (e.g. gold) as a stable complex [10], which eventually facilitates leaching of metals from complex ores, concentrates and other potential sources of precious metals. Hence the purpose of this study is to investigate a hydrometallurgical method to recover silver from the scrap of plasma TV monitors by using sodium thiosulphate and acidic thiourea solutions.

MATERIALS AND METHODS

Analysis of Sample

Scrap of plasma TV monitors in powdered form was kindly provided by Nishinihon Kaden Recycle Corporation, Kitakyushu, Japan and was stored in desiccators at room temperature until used. The average moisture content of the as-received sample was determined by heating a measured amount of scrap to 105°C for 24 h. Total dissolution tests were individually carried out by using concentrated HCl, aqua regia and acidic thiourea at their boiling temperatures. The digestion liquid was diluted with deionized water and filtered using 1 µm filter paper. Finally, the silver content of the filtrate was determined.

The particle size distribution of the powdered scrap was determined by using a particle size separator consisting of four sieves, which separated a measured amount of scrap of plasma TV monitors (10 g) into five particle size ranges (<53, 53-75, 75-150, 150-300 and >300 µm).

Leaching tests

The scrap of plasma TV monitors was leached in thermostated glass reactor using sodium thiosulphate solution and acidothiourea solutions by varying parameters such as pH, liquid-to-solid (L/S) ratio and concentration. The leaching process continued for 24 h and 4 h, respectively, for thiosulfate and acidothiourea to ensure complete leaching. The silver contents in all solutions were determined by using ICPS-8100 ICP/AES spectrometer. All reagents used during the experiments were of analytical grade and no further purification was done. All measurements were carried out in triplicate and average values were taken.

Silver recovery by coagulation-precipitation

After a successful extraction of silver from scrap of plasma TV monitors by using acidothiourea solutions, coagulation-precipitation tests were conducted by using a natural biodegradable material (persimmon tannin extract) and a cationic cellulose. Besides, precipitation of silver with sodium sulfide was accomplished.

Results And Discussion

Characterization

The moisture content and specific gravity of the scrap of plasma TV monitors were determined to be 7.24% and 1.88, respectively. From total dissolution experiments, the maximum content of silver was obtained to be 2.2 mg/g in case of dissolution with acidic thiourea. The presence of silver in the scrap was further confirmed by X-ray diffractogram (XRD) with 30 mA, 40 kV and 2 deg/min continuous scanning speed. The particle size distribution showed that 43.2% and 30.7% of the scrap belong to 53-75 µm and <53 µm fractions, respectively, while the amount of the largest particle size fraction (>300 µm) was very insignificant. However, the 53-75 µm and <53 µm particle size fractions of the scrap were mixed together to carry out further experiments.

Thiosulphate leaching

Silver ion is known to form complexes with thiosulfate. The application of thiosulfate solutions for silver leaching from natural materials was well documented by [11] who first determined the optimal conditions for silver dissolution by using ammonia-thiosulfate solution. The complexing ability of thiosulfate solutions of different concentration is not great enough to extract silver from silver sulfide concentrates. Since the main parameters for such dissolution process are the concentration and pH, the effects of pH at varying thiosulfate concentration and at a constant L/S ratio, as shown in Fig. 1, were investigated. The pH was maintained by using $CH_3COOH/NaCH_3COO$ buffer with a buffering capacity of 0.01 M. However from Fig. 1, it is found that silver extraction has not reached even 50% at a pH ranging from 1 to 5. The experiments were restricted to this pH range to avoid thiosulfate decomposition. The sudden drop of extraction at pH higher than 4 is attributed to the decomposition of thiosulphate.

However, to obtain a clear view on silver extraction by thiosulphate, further experiments were carried out at pH 3. The effect of L/S ratio and thiosulfate concentration on silver extraction was illustrated in Fig 2, which showed that extraction of silver did not go beyond 50% even at increasing leachate concentration.

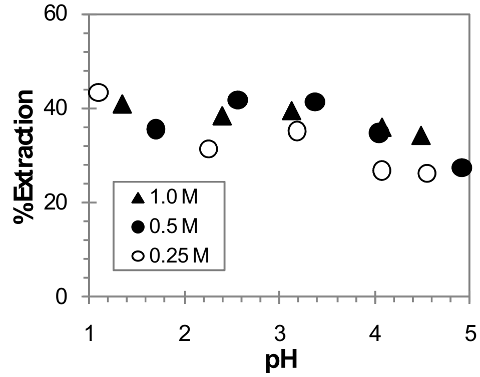

Fig. 1. Extraction of silver from using sodium thiosulfate at varying pH.

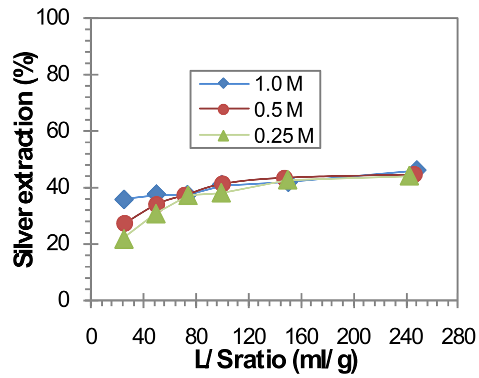

Fig. 2. Effect of L/S ratio on silver extraction at pH 3.

Acidothiourea leaching

Since thiourea forms a strong cationic complex with silver ($Ag[CS(NH_2)_2]_3^+$), it represents an attractive leaching alternative. Even though thiourea alone was unable to extract silver and H_2SO_4 could extract only a small amount (<10%) of silver from scrap of plasma TV monitors, a high extent (>99%) of silver extraction was achieved by using a mixture of 0.05 M thiourea and 0.05 M H_2SO_4 solution. This indicated a clear advantage over other methods where ferric ions are reported to be a requirement along with acidic thiourea solution [12]. This result can be explained by the fact that low concentration sulfuric acid facilitates complexation between silver and thiourea while high concentration acid impedes the complexation rather protonates thiourea, which results low extraction in the end.

Coagulation-precipitation of silver with persimmon tannin solution (PTS) and Catinal HC/LC

Coagulation and precipitation is recognized as a useful tool for recovery of elements. A nonconventional coagulant, obtained from powdery persimmon tannin extract, as well as a cationic cellulose (Catinal HC/LC) was used for silver recovery. The coagulant named persimmon tannin solution (PTS) was prepared by dissolving a measured amount of persimmon tannin extract (containing 18% tannin) in distilled water at pH 7 and 13.8, which were termed as PTS-1 and PTS-2, respectively. PTS-2 was found to be very efficient with 100% recovery of silver at and above 0.3 coagulant dosages while PTS-1 could only recover 40% of silver from acidothiourea leachate solutions even at high coagulant dose. This is attributed to the fact that persimmon tannin extract being completely dissolved at pH 13.8 (PTS-2) ensured all polyphenolic groups to be entered into water and thus enabling coagulation with silver thiourea complex. On the other hand, persimmon tannin extract was only partially dissolved at pH 7 (PTS-1) and did not enhance silver recovery through coagulation beyond 40%. Nevertheless, a reduction of silver was postulated since metallic silver was observed from digital microphotograph at the surface of the precipitation cake. Since the reductive mechanism involves many parameters and is complicated, a detailed study is necessary to fully understand it. However, Catinal HC/LC was found to be not so effective in silver recovery from silver-containing acidothiourea solution since it provided <60% recovery even at high dose.

Precipitation of silver with sodium sulfide

An innovative approach of silver recovery was tested by employing precipitation technique with sodium sulfide solution. It provides a practical route to recovery of silver after its extraction from scrap of plasma TV monitors. A varying concentrations of sodium sulfide ($Na_2S{\cdot}9H_2O$) were added to 10 ml of silver-containing acidothiourea leach solution and shaken for a while. The suspension was allowed to settle for 24 h. After that the supernatant was collected and the concentration of silver was measured. As shown in Fig. 3, a very small dose (0.5 ml) of both 20 mM and 50 mM of sodium sulfide can provide 100% silver recovery through precipitation. Such a high degree of precipitation suggests a possible recovery route for silver from silver-containing acidothiourea leach solutions.

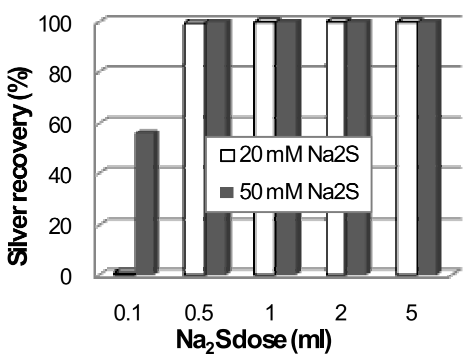

Fig. 3. Recovery of silver through precipitation with sodium sulfide at room temperature.

CONCLUSION

Laboratory scale experiment showed that silver could be extracted almost completely from scrap of plasma TV monitors by means of acidothiourea leaching. Coagulation-precipitaion with a natural biodegradable material, persimmon tannin extract, and sulfide precipitation of silver put forward a very useful recovery method. This process offered an advantage in hydrometallurgical processing by solving both silver extraction and its recovery problems.

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