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A NON-POLLUTING METHOD OF SILVER RECLAMATION

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Introduction

Pure silver is a brilliant, lustrous, white transition metal occupying the copper subgroup of the periodic table. This metal has been known since antiquity, having been mentioned in Genesis and in pre-dynastic Egypt (5) where it was originally used for coinage and decorative purposes.

This uncommon element comprises about 10⁻⁸ percent of the earth's crust (13) and occurs primarily as ores of argenite (Ag₂S) and horn silver (AgCl). Silver ores are also associated with as many as 55 other minerals (2), the chief forms being compounds of lead, copper and zinc. About 66 percent of the primary supply of silver is obtained as a by-product of copper, lead and zinc mining (15).

Silver has the highest electrical and thermal conductivity of all metals. However, its use in electrical circuitry is largely supplanted by copper because of costs considerations. In addition to its major use in photography, silver is used in various types of reflective surfaces, such as front-surface mirrors.

Silver has had a venerable history as a key element in atomic-weight determinations since the time of Stas (8). It is also used as an operational standard for chemical analysis and in defining the quantity of the Faraday (8). A high degree of measurement accuracy is attainable because of the high purity (99.999%) of commercial silver. As a result, silver has found widespread use in the laboratory in many types of chemical analyses and in the photographic industry which uses over 28 percent of all the industrial silver consumed.

Why Reclaim Silver?

The National Security Council has estimated that only a 10-15 year supply of silver bearing ore remains (14). Strategically, silver is extremely important in any war effort for photographic and electrical applications (2) and it is necessary that a large supply be available for national emergencies. Forecasts of the United States demand for silver between the years 1985 and 2000 range from 240 million to 505 million troy ounces (2). Current annual demand is approximately 174 million troy ounces (14). In 1964, the consumption of silver, which did not include coinage, amounted to 347.4 million troy ounces. New production totaled only 215 million ounces. Demand in the photographic industry is projected to remain heavy, since little substitution of a silverless photo-

graphic process is foreseen. All trends project an increasing demand and a shortening supply forcing the price of silver to extremely high levels.

It has been found that some laboratories may be discarding from \$500 to \$600 or more of silver per year because of the lack of a convenient and economical method of recovery. Such a practice is not only wasteful, but also environmentally dangerous. Silver chloride, when discarded in any conventional waste disposal system, is toxic to beneficial bacteria in concentrations of 5-10 pp. (1). From both the economic and environmental points of view, reclamation of silver is desirable.

Problems of Reclamation

There are currently many processes used in the recovery of silver. Basically, these fall under three categories (3) which may be used in the recovery of silver from photographic solutions and other silver bearing materials: (a) metallic replacement, (b) electrolytic plating and (c) chemical precipitation. More recently, ion-exchange and reverse osmosis have been investigated as possible techniques for recovering silver from dilute solutions (3). Each process has its own advantages and disadvantages in particular applications.

One of the problems associated with the recovery and precipitation of silver from halide salts (with the exception of silver fluoride) is their insolubility in aqueous solutions. Silver in the +1 state forms many complex ions, one of which is ammonia (5, 9, 13). Since ammonium hydroxide is readily available in the laboratory, it is a convenient source of ammonia which forms a linear complex with silver as indicated in the following equation:



Since the dissolution of AgCl and AgBr in concentrated NH_4OH is nearly complete and these silver-halides are the most prevalent silver salts, this was used as a convenient starting point in the recovery process. The problem is to carry out the silver reduction in an efficient and rapid manner.

In an attempt to reclaim silver, electrolysis experiments were carried out using various types of metal electrodes such as might readily be found in many laboratories. Aluminum, copper, zinc and carbon electrodes were used but metal contamination of the solutions and of the plated silver were too severe to be acceptable. In addition, plating was slow and incomplete, and the recovery of silver from the undissolved electrodes was difficult. Had more expensive platinum or gold electrodes been used better results may have been obtained.

Many chemical methods for the precipitation of silver from various types of waste materials have been discovered (1, 12, 17). Sodium sulfide is often used to precipitate silver from black and white fixing solutions in photography.

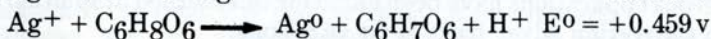
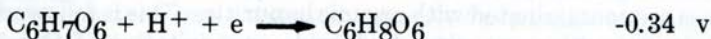
In another attempt at reclaiming silver, the formation of silver sulfide from silver halide accomplished nothing since this necessitated other recovery procedures and the method was abandoned. Another procedure involved the reduction of silver by the addition of zinc powder. The addition of zinc was difficult to control and led to a considerable contamination of the precipitated silver by undissolved zinc powder, making this method also undesirable.

In 1943, a team of University of Chicago chemists (1) developed a powerful reducing agent called sodium borohydride. Only within the last few years has the potential of this chemical been realized. Sodium borohydride is a highly efficient reducing agent. One mole is capable of reducing eight moles of silver. However, sodium borohydride has some major disadvantages. It is expensive and produces toxic boron compounds that would cause pollution problems. In addition, the reagent cannot be used in any acidic solution since the evolution of explosive hydrogen would result.

Other reducing agents were explored but found ineffective for a variety of reasons. Many produce silver particles that clogged the filtering system. What was needed was a reducing agent that would be capable of reducing the silver to the free metal form, yet be inexpensive, non-toxic and easy to handle.

A New Process

During this period of research it was learned that ascorbic acid (vitamin C) is a very powerful reducing agent, especially in very basic conditions. The electrode potential of ascorbic acid for the first state (ascorbic acid may furnish two electrons for reduction) is -0.127 volts at a pH of 5 and -0.34 volts at a pH of 7(4). It may also be greater at a higher pH. Since the reduction potential of silver is +0.799 volts (16), an overall cell reaction at the unit activity of the Ag⁺ ion, may be written as follows:



Since E⁰ is positive, the reaction is thermodynamically spontaneous as written, and silver will precipitate from the solution. The equilibrium constant of this cell reaction can be calculated from the Gibbs free-energy change by the equation:

$$- \Delta G^0 = RT \text{Ln}k = nFE^0$$

or simplifying

$$\log k = n \frac{(E^{\circ} \text{ right} - E^{\circ} \text{ left})}{0.0591}$$

The equilibrium constant, at unit activity of the Ag⁺ ion, is calculated to be 19.3. This large value indicates that the chemical equilibrium lies to the right as written and the reaction goes essentially to completion.

Experimentation showed that in ammonical solutions, AgCl and AgBr could be recovered in high yields using ascorbic acid as a reductant. In solutions prepared with pure silver halides, no problem was encountered with the formation of a silver metal precipitate of adequate size and no clogging of filters occurred. However, many typical silver chloride residues were contaminated with silver dichromate indicator, fats, proteins and other organic materials. The presence of these compounds in solution prevented the formation of a silver particle of a size convenient for filtration. In addition, the size was so small that no settling occurred.

In order to circumvent the problems encountered with impurities found in silver halide residues, a number of pre-treatment steps before complexation with NH₄OH were necessary. Excess silver dichromate indicator, red in color, could be converted to the yellow sodium form by the addition of a small amount of chloride ion, usually hydrochloric acid. With continued experimentation it was found that the organic impurities could be effectively oxidized using a combination of nitric acid and potassium permanganate (10). Effective pre-treatment digestion eliminated all problems associated with particle size and settling created by the complex organic matrix.

Conclusion

This process for the recovery of silver from silver-halides, which has recently been patented (U.S. Patent 4.078.918), consists of a pre-treatment digestion phase which is necessary when the silver chloride residues are contaminated with organic impurities. This is followed by a complexation with ammonium hydroxide, precipitation of the silver with ascorbic acid, filtration and washing of the free silver metal. Numerous applications have been found for this method in addition to its use in recovering silver from Mohr titrations.

The silver from dated films and photographic papers may be recovered by complexing with NH₄OH, thereby eliminating the need for burning papers, a usual step in the recovery of silver from such sources. The silver from photographic solutions may be precipitated by making the solutions basic with NH₄OH before addition of ascorbic acid. However, the amount of silver usually found in these solutions is very small compared with the amount of NH₄OH needed for pH adjustment. Based on \$5.00 per ounce of silver this process for recovering silver from black and white photographic solutions is not economical compared with more established procedures.

In addition to its use for the reclamation of silver, this process has also been extended to the precipitation of other metals, such as gold, palladium and mercury. The recovery of palladium and mercury may be desirable for laboratories that use these metals as catalysts. Although platinum metal is theoretically recoverable with ascorbic acid as the reductant, *i.e.* positive cell potential, successful recovery has yet to be achieved and additional work remains to be done in this area.

The advantages offered by this method are numerous. It is a simple process using inexpensive equipment commonly found in most chemical laboratories. All waste effluents remaining from the recovery process are biodegradable or recyclable. The ammonia is oxidized to nitrites by *Nitrosomonas* and *Nitrobacter*, bacteria indigenous to waste disposal facilities (16). This reduced form of nitrogen is more acceptable for discharge into lakes and rivers.

In conclusion, this patented process will offer many advantages not found in other types of recovery processes. It is simple and economically feasible for any laboratory to utilize the process in an effort to reduce the expense and pollution hazards associated with using silver compounds.

Literature Cited

1. Anon. 1974. A cleanup agent that recovers precious metal. *Business Week* (Nov. 2; p. 80 F).
2. Clarke, T.G. 1975. *Silver* (Bull. 667). U.S. Dept. of Interior, Bureau of Mines.
3. Eastman Kodak. 1972. Recovering silver from photographic materials. *Kodak Pub. No. J-10*. Eastman Kodak Co.
4. Everling, F.B. 1969. (From abstract). *Physiol. Chem.* 350(7):886.
5. Foster, W. 1936. *Inorganic chemistry for colleges* (2nd ed.). Van Nostrand and Co., Inc.
6. Gebhardt, L.P. and D.A. Anderson. 1959. *Microbiology* (2nd ed.) C.V. Mosby Co.
7. Handy and Harman. 1964. *Silver market in 1964* (49th annual review). Handy and Harman.
8. Laitinen, H.A. and W.E. Harris. 1975. *Chemical analysis* (2nd ed.) McGraw-Hill Book Co.
9. Parks, G.D. 1945. *Modern inorganic chemistry*. Van Nostrand and Co.
10. Perman, C.A., A new, efficient chemical method for the recovery of silver from silver chloride residues, *Talanta*, Manuscript in print.
11. Schack, C.H. and B.H. Clemmons, 1965. *Review and evaluation of silver production techniques* (Cir. 8266). U.S. Dept. of Interior, Bureau of Mines.
12. Schreiber, M.L. 1965. Present status of silver recovery in motion-picture laboratories. *J. of SMPTE* 74:505.
13. Sienko, M.J. and R.A. Plane. 1966. *Chemistry* (3rd ed.). McGraw-Hill Book Co.
14. Standard and Poor's Corporation. 1977. *Standard and Poor's Quarterly* (p.m. 185).
15. U.S. Dept. of Interior. 1977. *Mineral industry survey* (annual report).
16. Weast, R.C. (Ed.). 1970-71. *Handbook of chemistry and physics* (51st ed.). The Chemical Rubber Co.
17. Willbanks, O.L. 1953, Reclaiming silver from AgCl residues. *J. Chem. Educ.* 30:347.