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Radiological Waste Processing for the Recovery of Silver through Cementation with Zinc Powder

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Abstract: The recovery of silver from silver-thiosulphate-fixer solutions of radiological wastes has been studied by cementation in batch-stirred reactors using zinc powder as the cementing agent. Silver is efficiently recovered from the solutions. The silver recovery rate and the total silver recovery increased with pH. Metallic silver was the product for cementation in deoxygenated solutions at all pH studied. With non-deoxygenated solutions and at low pH values, metallic silver cemented first, followed by silver sulfide. At high pH values, metallic silver was the cementation product. Electrochemical reactions are proposed for the cementation process in the presence and absence of oxygen.

Keywords: Radiological waste, silver recovery, thiosulphate, water remediation, zinc powder

INTRODUCTION

In radiological plate processing, a fixer solution, developer solution, and rising water are produced as wastes. The fixer solution has a high concentration of silver ranging from 8 to 12 g/l as silver-thiosulphate complexes (1). It is considered to be extremely toxic (2). The developer solution is

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very corrosive due to its high content of thiosulphate, while the rinsing water is considered to have low toxicity.

Because of its high silver concentration and high toxicity, the fixer solution requires a treatment to reduce its content of silver below 0.5 mg/l, before it can be dumped to the sewage system. The scope of this treatment has been to recover the silver due to its high economic value (3). There are various schemes to recover this metal such as cementation with metallic iron, which is used for low volumes of effluents. However, this process produces a low quality precipitate due to co-precipitation of iron hydroxides. This implies an additional cost to refine the silver (4). The possibilities of carrying out ion exchange exist using either resins or liquid membranes (5). Electrolysis (3,6–8) or silver sludge precipitation followed by thermal decomposition (9) can also be practiced. The use of bio-adsorbents has been proposed (10) as well as modified activated carbon (11). Of all these processes, cementation with iron is generally followed (12), due to the high investment cost of the others (4).

Zinc powder has been proposed as the cementing agent of silver in silver-thiosulphate solutions, which are recovered from leaching of silver ores in the minerals industry (13,14). In this field, copper scrap is the common material used to cement the silver. However, zinc presents the advantage of being cheaper than copper and is readily available as a powder. Since the zinc powder posseses a large surface area, a high silver cementation rate should be attained. In fact, zinc powder is extensively used to cement silver from silver-cyanide solutions in the leaching of silver ores with cyanide (15,16). Before contacting the zinc with the silver-cyanide solution, this needs to be deoxygenated for an efficient silver cementation as dictated by the process known as Merril-Crowe (17). It appears that in the case of the silver-thiosulphate solutions deoxygenation is not necessary to efficiently cement the silver with zinc (14).

This work aims at the recovery of silver from radiological fixer solutions by cementation employing zinc powder. The effect of both the pH and oxygen in the cementation process has been studied. The cementation products have been characterized by scanning electron microscopy to define the forming silver compounds and the chemical reactions occurring in the process.

EXPERIMENTAL PROCEDURE

The fixer solution used in this work was collected from a radiological laboratory in Colima, México. This solution was analyzed for thiosulphate, sulphite, and silver and their concentration was determined to be 0.1, 0.01, and 0.043 mol/l, respectively.

Dilute solutions of sulphuric acid and sodium hydroxide were used for adjusting the pH in the cementation tests. Zinc powder from Sigma Aldrich with a purity of 99.99% was used as the cementing agent. The size of the zinc powder was reported to be 50% below 20 μm.

The cementation tests were carried out in a 2 liter sealed stirred reactor with openings for a Pt-saturated KCl Ag/AgCl combined electrode, a pH electrode, a nitrogen dispersion tube and a thermometer. The stirring speed was kept constant at $52.4\,s^{-1}$. For the experiments in the absence of oxygen, the fixer solutions were first purged during 10 minutes with nitrogen gas, which was passed through a pyrogalol solution to remove traces of oxygen. Then, the zinc powder was added. An Orion 920 potentiometer was used to monitor the ORP and pH in solutions. The oxidation-reduction potential (ORP) was measured with a flat platinum electrode and Ag/AgCl reference electrode. These ORP values were referred to the Standard Hydrogen Electrode to obtain the redox potential, Eh, using 0.197 volts as the potential value of the reference electrode. The temperature in the cementation tests was maintained constant at 30°C by employing a Cole Palmer 1095-00 isothermal bath. For experiments carried out in the presence of oxygen, the solutions were not purged with nitrogen.

Cementation was initiated with one liter of fixer solution to which the given amount of zinc powder was added. An aliquot of 10 ml was withdrawn from the solution at regular time intervals for analysis of zinc and silver, which was done by atomic absorption spectrometry using a Varian spectrometer model 300. The silver recovery was then determined by subtracting the silver concentration at time t to the initial silver concentration. The cementation products were characterized by scanning electron microscopy using a Phillips XL30 equipment coupled with a Dx4i model X-ray fluorescent spectrometer for performing the particle microanalysis.

RESULTS AND DISCUSSION

Silver recovery through cementation with zinc powder was first studied in deoxygenated fixer solutions at different pH values, namely 4.5, 6, 7.5, and 9. The amount of zinc powder, that was added, corresponded to a zinc/silver mol ratio of 1 with 0.043 mol as the initial mass of silver in the fixer solution. Figure 1 presents the silver recovery as a function of time. It is noted that the silver recovery rate and the amount of recovered silver increased with the pH. The same behavior has been reported elsewhere (8). This is an indication that OH^- ions are involved in the cementation reaction of silver ions with zinc.

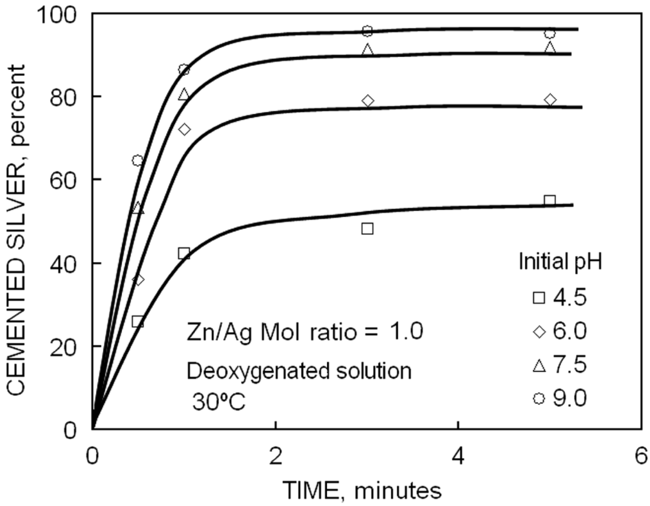


Figure 1. Silver recovery as a function of time in cementation of silver from deoxygenated silver-thiosulfate fixer solutions with 0.043 mol of silver at various pH values, using a Zn/Ag mol ratio of 1.0.

At pH 4.5, the cementation product was found to be metallic silver, as observed in Fig. 2. This silver is botroidal in shape coating the zinc particles. The same type of product was identified at the other pH values. In order to correlate the consumption of zinc to the mass of cemented

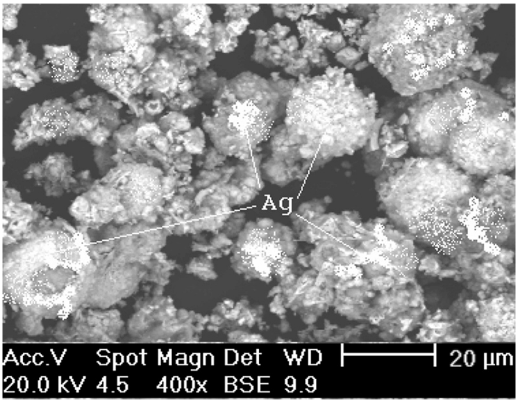


Figure 2. SEM microphotograph of cement product in recovery of silver from deoxygenated silver-thiosulfate fixer solutions with 0.043 mol of silver, at pH 4.5 and a Zn/Ag mol ratio of 1.

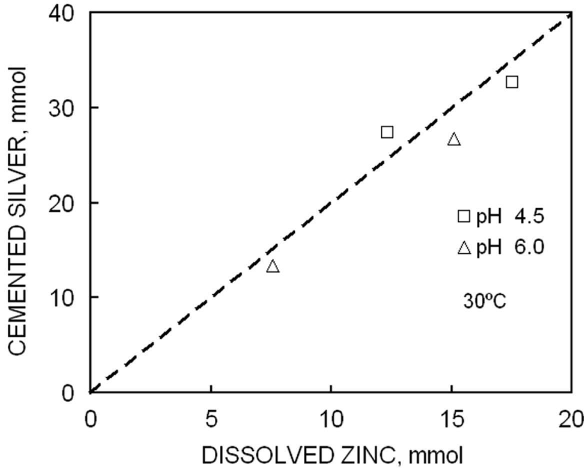


Figure 3. Cemented silver as a function of dissolved zinc in recovery of silver from deoxygenated silver-thiosulfate fixer solutions with 0.043 mol of silver, at pH 4.5 and 6.0 and a Zn/Ag mol ratio of 1.0.

silver, the amount of zinc released to the solution was plotted as a function of the amount of silver cemented. Figure 3 shows this relationship for the pH values of 4.5 and 6. It is noted that the amount of dissolved zinc is linearly proportional to the amount of cemented silver. The value of the slope of the line indicates the molar relationship between cemented silver and dissolved zinc. This value was found to be nearly 2.0, which means that one mol of zinc cements two mols of silver. To ascertain the soluble zinc species formed in the cementation process, an Eh-pH diagram for the Zn-$S_2O_3^{2-}$ system was built using the HSC software. This Eh-pH diagram is depicted in Fig. 4, wherein the Eh values at the end of the cementation tests are presented as the open squares. It is seen that for pH values lower than 6.2, the $ZnOH^+$ ions are the stable species and above this pH value $Zn(OH)_2(s)$ is predominant.

Based on the aforementioned discussion, it may be that silver cementation takes place according to the following electrochemical reactions at pH below 6.2:

$$Ag(S_2O_3)_2^{3-} + e^- = Ag + 2S_2O_3^{2-} \qquad \Delta G^\circ = 25.40\,kJ/mol \tag{1}$$

$$Zn = Zn^{2+} + 2e^- \qquad \Delta G^\circ = -147.07\,kJ/mol \tag{2}$$

$$Zn^{2+} + OH^- = ZnOH^+ \qquad \Delta G^\circ = -35.00\,kJ/mol \tag{3}$$

where the values of ΔG° for the above equations were determined from the ΔG° values of each species reported by (18).

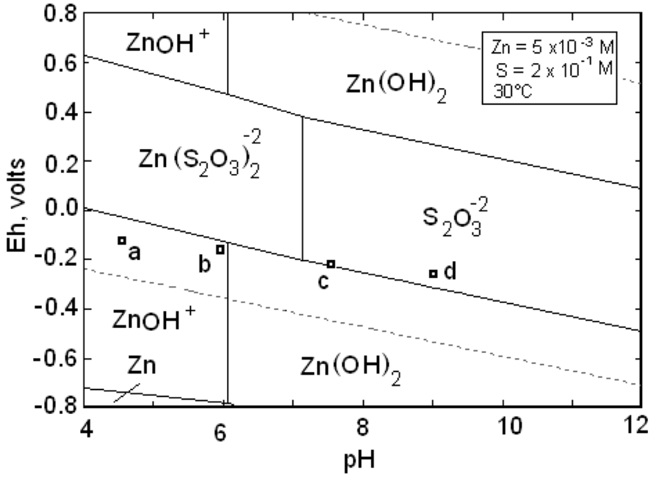


Figure 4. Eh-pH diagram for the Zn-$S_2O_3^{2-}$-H_2O system for 5×10^{-3} mol/l zinc and 2×10^{-1} mol/l sulfur. The open squares in the diagram represent Eh values at the end of the cementation tests for a Zn/Ag mol ratio of 1.2 at different pH values: (a) pH 4.5, (b) pH 6.0, (c) pH 7.5, and d) pH 9.

The overall electrochemical reaction for the cementation reaction is then given by:

$$2Ag(S_2O_3)_2^{3-} + Zn + OH^- = ZnOH^+ + 4S_2O_3^{2-} + 2Ag \qquad \Delta G^\circ = -109.35\,\text{kJ/mol} \tag{4}$$

Eq. (4) indicates that increasing the pH promotes the cementation reaction until equilibrium is reached.

Above pH 6.2, $Zn(OH)_2(s)$ forms, then the overall electrochemical reaction may be expressed as follows:

$$2Ag(S_2O_3)_2^{3-} + Zn + 2OH^- = Zn(OH)_2(s) + 4S_2O_3^{2-} + 2Ag \qquad \Delta G^\circ = -11.26\,\text{kJ/mol} \tag{5}$$

Silver cementation with zinc powder in solutions to which oxygen was not eliminated were carried out at different pH values, namely 4.5, 7.5, and 9.0, using an amount of zinc corresponding to a zinc/silver mol ratio of 1.2. At pH 4.5, these studies were also carried out using a zinc/silver mol ratio of 1.8. In all these tests, the initial mass of silver in solution was 0.043 mol. The recovery of silver is given in Fig. 5.

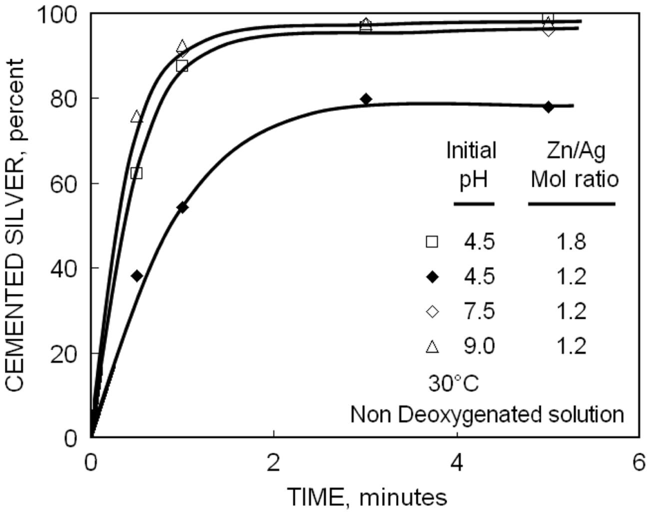


Figure 5. Silver recovery as a function of time in cementation of silver from non deoxygenated silver-thiosulfate fixer solutions with 0.043 mol of silver, at various pH values and Zn/Ag mol ratios of 1.2 and 1.8.

When the zinc/silver mol ratio was increased from 1.2 to 1.8, the silver recovery rate and the total recovery of silver was higher at pH 4.5. This is due to a larger surface area of zinc for the cementation of silver. It is well known that cementation of metals ions is directly proportional to the surface area of the cementing agent (17).

With the zinc/silver mol ratio of 1.2, the silver recovery rate increased as the pH was raised from 4.5 to 7.5. This behavior was similar to that in the cementation tests performed with deoxygenated solutions. Raising the pH from 7.5 to 9 did not further increase the silver recovery rate.

As in the cementation with deoxygenated solutions, the molar relationship between cemented silver and dissolved zinc was determined, at pH 4.5 and for the Zn/Ag mol ratios of 1.2 and 1.8. This molar relationship is plotted in Fig. 6. It was found to be nearly one, meaning that one mol of silver is cemented by one mol of zinc. Accordingly, a higher amount of zinc was required for silver cementation in the presence of oxygen than in the absence of oxygen.

The one-to-one molar relationship between dissolved zinc and cemented silver is found in the chemical cementation reaction proposed by Wan et al. (14) for the cementation of silver in silver-thiosulphate solutions, which contained NH_3. In order to delineate the possible cementation

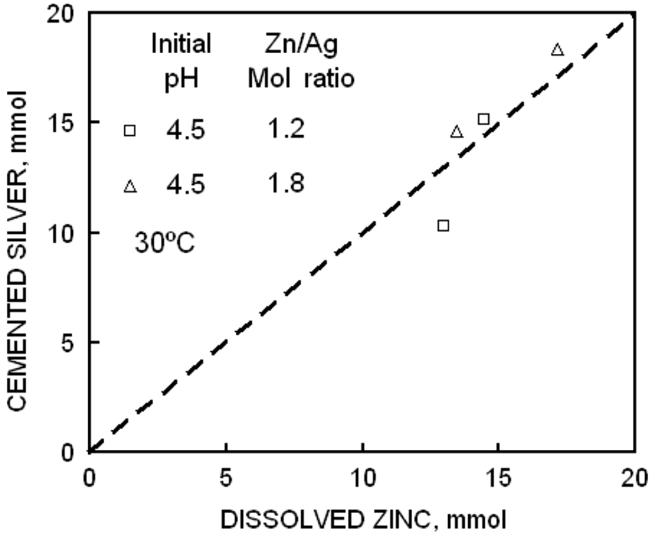


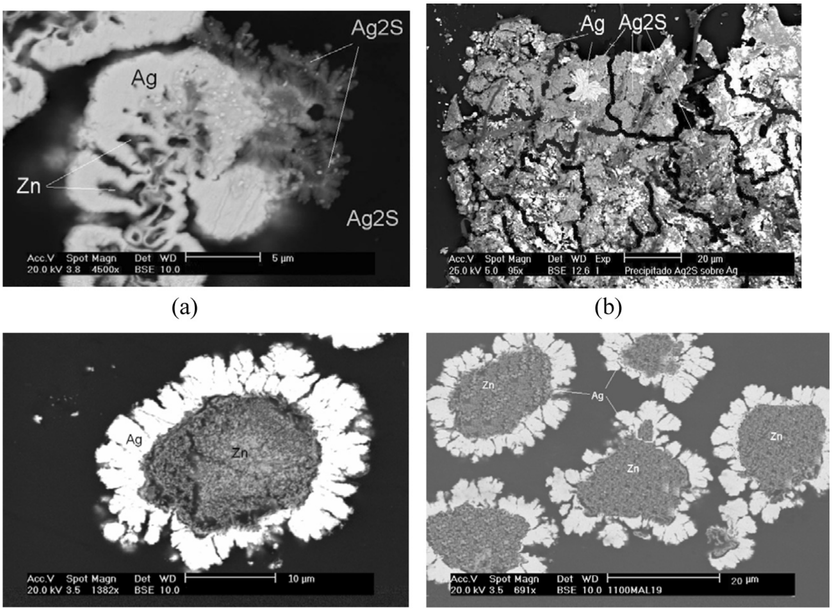
Figure 6. Cemented silver as a function of dissolved zinc in recovery of silver from non deoxygenated silver-thiosulfate fixer solutions with 0.043 mol of silver, at pH 4.5 and Zn/Ag mol ratios of 1.2 and 1.8.

reactions, the products of cementation were identified. Figures 7a and 7b show microphotographs of the products at pH 4.5 using the zinc/silver mol ratio of 1.8 and 1.2, respectively. Figures 7c and 7d depict the microphotographs corresponding to the cementation products at pH 7.5 and 9.0, respectively, with a zinc/silver mol ratio of 1.2.

At pH 4.5, the microphotographs show that cemented silver coats the cementing zinc particle, and crystals of silver sulphide (Ag_2S) are deposited on the cemented silver. This morphology suggests that silver ions cemented as Ag at the beginning of the cementation, then as Ag_2S.

The formation of Ag_2S can be accounted for by the redox conditions in the silver-thiosulphate solutions. Figure 8 depicts an Eh-pH diagram for the Ag-S-$S_2O_3^{2-}$ system wherein the final Eh values in the cementation tests are given by the open squares. It is noted that conditions existed for the formation of Ag_2S. This likely results by the formation of S^{2-} from the reduction of S^{4+} in the $S_2O_3^{2-}$ of the $Ag(S_2O_3)_2^{3-}$ complex. Then, Ag_2S may form by the cathodic reaction given by:

$$2Ag(S_2O_3)_2^{3-} + 3H^+ + 4e^- = Ag_2S + 3.5S_2O_3^{2-} + 1.5H_2O \qquad \Delta G^\circ = -798.68\,\text{kJ/mol} \tag{6}$$



(a) (b)

(c) (d)

Figure 7. SEM microphotographs of cement products in recovery of silver from non deoxygenated silver-thiosulfate fixer solutions with 0.043 mol of silver. (a) pH 4.5 and a Zn/Ag mol ratio of 1.2, (b) at pH 4.5 and a Zn/Ag mol ratio of 1.8, (c) pH 7.5, Zn/Ag mol ratio of 1.2, and (d) pH 9.0, Zn/Ag mol ratio of 1.2.

Eq. (7) is coupled to the anodic reaction (2), and taking into account Eq. (3), the overall electrochemical reaction for the formation of Ag_2S may be given by:

$$2Ag(S_2O_3)_2^{3-} + 2Zn + H^+ = Ag_2S + 2ZnOH^+ + 3.5S_2O_3^{2-} + 1.5H_2O$$
$$\Delta G^\circ = -798.68\,\mathrm{kJ/mol} \qquad (7)$$

As noted, Eq. (7) supports the one molar ratio between cemented silver and dissolved zinc, which is given in Fig. 6.

Figures 7c and 7d show that the cementation product was metallic silver at pH 7.5 and 9. This is because the redox conditions in the solutions were in the stability region of Ag, as shown in the Eh-pH diagram given in Fig. 8. In this figure the final Eh values in the cementation tests are shown by the open squares. Under these conditions the formation of Ag can be accounted for by Eq. (5).

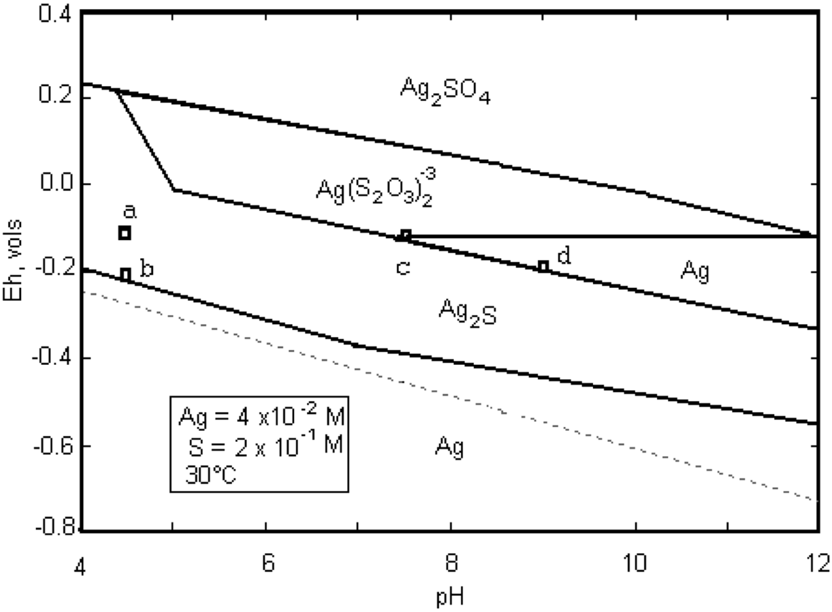


Figure 8. Eh-pH diagram for the Ag-$S_2O_3^{2-}$-H_2O system for 4×10^{-2} mol/l of silver and 2×10^{-1} mol/l sulfur. The open squares in the diagram represent Eh values at the end of the cementation tests: (a) pH 4.5 and Zn/Ag mol ratio of 1.2, (b) pH 4.5 and Zn/Ag mol ratio of 1.8, (c) pH 7.5 and Zn/Ag mol ratio of 1.2 and (d) pH 9 and Zn/Ag mol ratio of 1.2.

CONCLUSIONS

1. The silver as thiosulphate complex species in the fixer solutions of radiological waste can be efficiently recovered through cementation with zinc powder.
2. Oxygen in the fixer solution and the pH determined the type of silver product recovered from the cementation process.
3. In the absence of oxygen, metallic silver formed at all pH values. While in the presence of oxygen, metallic silver and silver sulfide are the cementation products at pH values below 7.5. Above this pH value, metallic silver was the product.

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