Nature of the silver precipitation obtained by cementation from thiosulphate solutions

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Abstract: The morphology and composition of the deposits formed on the surface of magnesium disk during cementation from thiosulphate solutions (0.0025 – 0.1M) [Ag(S2O3)2]3– + 0.5M S2O32– have been studied. A porous deposit with low adhesion is formed on the surface of the magnesium metal substrate. Within a wide range of [Ag(S2O3)2]3– ion concentrations, sulfur as well as silver are constituents of the deposit at the initial stages of cementation and at the end of the reaction. This is attributed to the electrochemical behaviour of magnesium in thiosulphate solutions resulting in the exceeding of current limit on cathode for pure silver reduction. Hence, parallel electrochemical reactions take place that are very close in their values to the standard redox potentials of reduction of [Ag(S2O3)2]3– ions to Ag0 and S2O32– ions to S2–. Sulfur content in the cement deposits increases with the decrease in [Ag(S2O3)2]3– ion concentration and increase in cementation time. This tendency is also observed with the decreasing solution temperature.

Keywords: Cementation • Silver • Magnesium disk • Thiosulphate • SEM images

1. Introduction

The chemical method of leaching silver by thiosulphate solutions from Ag2S was suggested almost three decades ago [1]. Subsequent publications have demonstrated the efficiency of thiosulphate solutions as an alternative to cyanide solutions in hydrometallurgy of gold [2–4], and of gold and silver [5]. Cementation has also been examined in the literature as a cheap and technologically simple method for recovery of metals. Thus, cementation by copper [6] or zinc [7,8] was studied for the thiosulphate solutions of gold and/or silver. When zinc is used the difference (ΔE°) between standard electrode potentials on anode (1) and cathode (2) is greater than 0.7 V. This fact should guarantee the high rate of silver cementation and completeness of its recovery from the solutions:

(anode) \[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}, \quad E = 0.76 \text{ V} \]  \hspace{1cm} (1)

(cathode) \[ [\text{Ag(S}_2\text{O}_3\text{)}_2]^{3–} + \text{e} \rightarrow \text{Ag}^{0} + 2 \text{S}_2\text{O}_3^{2–}, \quad E = 0.01 \text{ V} \]  \hspace{1cm} (2)

At a pH above 6.2, Zn2+ ions form Zn(OH)2 on the surface of zinc [8]. The insoluble zinc hydroxide blocks the anode surface resulting in a decrease in the rate of cementation [9]. A similar deactivation of zinc surface takes place in the [Ag(CN)2]2––CN––OH– system [10]. Thus, due to the formation of Zn(OH)2 compact film, the metals recovery from thiosulphate solutions via zinc cementation is a problem. The same passivation layer was formed in case of ZnSO4 water solutions made by interaction CdSO4 solutions with zinc powder surface [11]. Therefore, periodic activation of the substrate is necessary for the reactivation of anode operation.

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Examples of effective methods of substrate activation include mechanical activation during silver deposition in thiosulphate solutions [9], exposure to ultrasonic field as seen during cadmium deposition in sulphate solutions (in CdSO₄ solutions, the film diffusion control is stipulated by the formation of basic zinc sulfate which retards the process by forming a passivating layer on the zinc powder surface) [11] and the use of excess CN⁻ ligands during silver deposition in cyanide solutions [10].

Literature reports the possibility of using non-ferrous and precious metal deposition by magnesium as an alternative for zinc and other well known substrates (e.g. iron, aluminum) [12–14]. It was shown that silver may be completely recovered from thiosulphate solutions via magnesium cementation [15]. The main features of magnesium cementation that helps its use in hydrometallurgy are: (i) low value of standard electrode potential (E°Mg²⁺/Mg = −2.36 V) which ensures the high cementation rate and completeness of metal recovery from the solution; (ii) Mg²⁺ ions do not form complexes with ligands – the main components of leaching solutions; (iii) Mg²⁺ ions are non-toxic, favoring the environment friendly technology of metal recovery via cementation.

The principal aim of the present work is the investigation of the possibility of using magnesium as a substrate for recovery of silver from thiosulphate solutions.

2. Experimental Procedure

Silver cementation was carried out with a working solution volume of 200 cm³, on magnesium disk of a diameter of 30 mm rotating at 1000 min⁻¹ within the temperature range of 20–40°C in thermostat glass vessel. Before the experiment was started, the disk surface was ground by fine-grained emery paper and then chemically polished in the solution of following composition (mass %): 7–79 phosphoric acid (ρ = 1.7 kg dm⁻³) and 23–21 potassium nitrate. For the cementation process, solutions of (0.0025–0.1) М Na₃[Ag(S₂O₃)₂] + 0.5 М Na₂S₂O₃ were prepared from sodium thiosulphate and silver nitrate. The solution acidity was maintained within the pH range of 6.0–6.5 by adding sulphuric acid. The qualitative end point of cementation was determined by the reaction of silver in the solution with sulphide-ions. After the experiment the magnesium disk with the deposit was washed with water, acetone and dried in air at 60°C.

The surface of the disk was analyzed by ZEISS EVO 40XVP scanning electron microscope and “ULTRA 55” analyzer “EDAX” in secondary (SE) and backscattered electron (BSE) regimes. Elemental analysis of the surface with an Oxford INCA Energy 350 detector equipped with Energy dispersive X-ray spectroscopy (EDX) was carried out at the different distances from the edge to the centre of magnesium disk (A, B, C positions) as shown in Fig. 1.

The deposits were removed from the surface of magnesium disk and were analyzed by X-ray diffraction (XRD). In order to identify the compounds in the samples, phase analysis was performed on the patterns obtained on the powder diffractometer DRON-3M (Cu-Kα; Ni –β filter). The patterns were received in the scan regime in step intensities of 0.05º and 15 s per point. Calculations were carried out on CSD program complex for structural analysis [16].

3. Results and Discussion

Table 1. Content of silver and sulfur in cemented deposits at A, B and C positions of magnesium disk after total silver cementation (≥99 %)

| Concentration [Ag(S₂O₃)₂]³⁻, mol L⁻¹ | t, °C | Ag, at% | S, at% | Ag, at% | S, at% | Ag, at% | S, at% |
|------------------------------------|------|---------|--------|---------|--------|---------|--------|
| 0.0025                             | 20   | 52.94   | 47.06  | 50.21   | 49.79  | 41.16   | 58.84  |
| 0.005                              | 20   | 55.22   | 46.82  | 53.18   | 46.82  | 38.72   | 61.28  |
| 0.01                               | 20   | 68.76   | 31.24  | 73.17   | 26.83  | 53.88   | 46.12  |
| 0.005                              | 30   | 61.44   | 38.56  | 60.72   | 39.28  | 48.65   | 51.35  |
| 0.005                              | 40   | 59.11   | 40.89  | 60.68   | 39.32  | 51.93   | 48.07  |

Figure 1. Scheme of magnesium disk microlocal parts for SEM micrographs investigation. A, B, C positions were the distances from the disc edge: 1 – 2; 6 – 7 and 11 – 12 mm, correspondently.
due to the large $\Delta E^0$ value between Reactions 1 and 2 and considerable cathode polarization caused by the high stability of $[\text{Ag(S}_2\text{O}_3\text{)}_2\text{]}^{3-}$ complex ($\text{pK} = 14.15$). The spongy nature of the cement deposit favors its easy crumbling out from the support surface providing the activation of the magnesium anode surface:

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e} \quad E^0 = -2.36\text{V} \quad (3)$$

Influence of $[\text{Ag(S}_2\text{O}_3\text{)}_2\text{]}^{3-}$ ions concentration and temperature on the morphology of deposits was not evident (Fig. 2). All products of cementation were very similar under SEM observation.

The cement deposit includes silver, as well as sulfur, which is determined by the the Reactions 4 and 5 at the cathode. The redox potentials of Reactions 4 and 5 being comparable to the redox potential of the Reaction 2.

$$\text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} + 8\text{e} \rightarrow 2\text{S}^{2-} + 6\text{OH}^- \quad (4)$$

$$\text{S}_2\text{O}_3^{2-} + 2\text{e} \rightarrow \text{S}^{2-} + \text{SO}_3^{2-} \quad (5)$$

The relative content of silver and sulfur in the cement deposited on the magnesium surface depends upon the distance from the disk edge to the center; concentration of $[\text{Ag(S}_2\text{O}_3\text{)}_2\text{]}^{3-}$ ions and temperature. The larger the distance from the edge, the higher the sulfur content (Fig. 3, Table 1). This is caused by the decrease of linear velocity in A→C direction which accordingly reduces $[\text{Ag(S}_2\text{O}_3\text{)}_2\text{]}^{3-}$ ion diffusion to the surface of magnesium disk. As a result, the sulfide deposition due to Reaction 4 increases on the cathode surface. The same regularity is observed with the increase in solution temperature (Table 1), and is also explained by enhancement in diffusion. A similar effect occurs at the local level. Thus, at the top, where the solution has...
the most favorable access to the cathodic areas of the deposit, the silver content is much higher than that in the cavities (Fig. 4).

The silver content in the deposit increases with the increase in $[\text{Ag(S}_2\text{O}_3\text{)}_2]^{3-}$ ion concentration both after the cementation (Table 1) and at its initial stages (Table 2)

| [Ag(S2O3)2]3– concentration, mol L–1 | Ag, at% | S, at% |
|-------------------------------------|---------|--------|
| 0.0025                              | 69.52   | 30.48  |
| 0.005                               | 69.82   | 30.18  |
| 0.01                                | 74.83   | 25.17  |
| 0.1                                 | 90.65   | 9.35   |

Table 3. Miller indexes, experimental and calculated values for Bragg angle of main phase (Ag (Cu-type structure, space group Fm3m, $a = 0.41198(9)$ nm)) of deposit after 1 min cementation on magnesium disk from solution of 0.1 M Na$_3$[Ag(S2O3)$_2$] + 0.5 M Na$_2$S$_2$O$_3$.

| Miller index | $2\theta_{\text{exp.}}$ | $2\theta_{\text{calc.}}$ |
|--------------|-------------------------|---------------------------|
| 1 1 1        | 37.092                  | 37.109                    |
| 0 0 2        | 43.271                  | 43.246                    |
| 0 2 2        | 63.217                  | 63.230                    |
| 1 1 3        | 76.072                  | 76.066                    |

and should correlate with the cathode depolarization concentration. However, even in 0.1 M $[\text{Ag(S}_2\text{O}_3\text{)}_2]^{3-}$ the pure silver does not deposit. This gives an indirect confirmation that current density at cathodic area exceeds its boundary value to form silver films.

When solution attenuates in $[\text{Ag(S}_2\text{O}_3\text{)}_2]^{3-}$ ions, i.e., cementation tends to the end point, the intensity of the Reactions 4 and 5 increases. This is apparent from the increase in sulfur content in the cement deposit due to Ag$_2$S formation (Reactions 6–8):

$$2[\text{Ag(S}_2\text{O}_3\text{)}_2]^{3-} + \text{S}^2- \rightarrow \text{Ag}_2\text{S} + 4\text{S}_2\text{O}_3^{2-} \quad (6)$$

$$\text{S}^2- + 2\text{H}_2\text{O} \leftrightarrow \text{H}_2\text{S} + 2\text{OH}^- \quad (7)$$

$$2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + 2\text{H}^+ + 2\text{e} \quad (8)$$

Thus, with the initial concentration of 0.005 mol dm$^{-3}$ and after 3 min. of cementation, the integral content of silver and sulfur on the disk (at position ‘A’ in Fig. 4) equals 81.12 and 18.88 at.%; while after 5 min the content is 52.22 and 46.82 at.%, correspondingly. The silver content in the cement deposit may increase also due to the disproportionation Reaction 9 that takes place during silver cementation by zinc in thiosulphate solution [8]:

$$3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 4\text{S}^2- + 2\text{SO}_4^{2-} + 2\text{OH}^- \quad (9)$$

XRD analysis was performed for all samples studied and all the patterns were very similar. As an example, the X-ray diffraction pattern for the deposit after 1 min cementation from solutions of 0.1 M Na$_3$[Ag(S2O3)$_2$] + 0.5 M Na$_2$S$_2$O$_3$ (Fig. 5) is shown. Since Ag$_2$S and S phases should be amorphous they, will not be detected.

**Figure 3.** SEM micrographs of magnesium disk surface after cementation in 0.0025 M $[\text{Ag(S}_2\text{O}_3\text{)}_2]^{3-}$ solutions at 20 °C and content of silver and sulfur at positions A, B and C.
by X-ray diffraction. Using XRD analysis we concluded that the main phase for our samples was Ag in Cu-type structure with space group \(Fm\overline{3}m\), \(a = 0.41198(9)\) nm while a small quantity (about 5–7%) of secondary phases were also seen. The results of identification of the main phase is shown in Table 3, where \(2\theta_{\exp}\) and \(2\theta_{\text{calc}}\) are experimental and calculated values, respectively, for Bragg angles.

4. Conclusions

In general, the complete cementation process can be written by the following electrochemical reaction:

\[
\text{Mg}^2+ + 2[\text{Ag}(_2\text{S}_2\text{O}_3)_3]^{3-} = \text{Mg}^{2+} + 2\text{Ag}^0 + 4 [\text{S}_2\text{O}_3]^{2-} \tag{10}
\]

where, the consumption of Mg and \([\text{Ag}(_2\text{S}_2\text{O}_3)_3]^{3-}\) per 1 mol of Ag are 0.5 and 1 mol, respectively.

A porous deposit composed of silver and sulfur formed on magnesium over a wide range of silver thiosulphate concentrations is due to the reduction of silver ions and oxidation of thiosulphate species.

The silver and sulfur content in the cement deposit is a function of \([\text{Ag}(_2\text{S}_2\text{O}_3)_3]^{3-}\) ion concentration and temperature. The decrease of \([\text{Ag}(_2\text{S}_2\text{O}_3)_3]^{3-}\) ion concentration and temperature increases the reaction leading to higher sulphide-ion formation.

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