# INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

# Silver Cementation with Magnesium in Cyanide Solutions

O. I. Kuntyi, G. I. Zozulya, and O. G. Kurilets

Lvivska Politekhnika National University, Lviv, Ukraine

Received July 29, 2006

**Abstract**—Contact precipitation of silver with a magnesium powder from 0.0025–0.01 M solutions of the system  $[Ag(CN)_2]^--CN^-$  in the hydrodynamic mode was studied. The dependence of the silver cementation rate in the initial stage on the concentration of the  $[Ag(CN)_2]^-$  complex and on the surface area of the cementing agent was examined, and the relationship of the temperature factor with the depolarization of silver reduction on microcathodes and acceleration of magnesium dissolution on microcanodes was analyzed.

#### DOI: 10.1134/S1070427207020048

A number of techniques for recovery of gold and silver from ores and secondary raw materials are based on hydrometallurgical processes [1-3]. Analysis of publications devoted to this issue [3] shows that the cyanide method is the most widespread in the world practice of leaching-out of these metals. Further, metallic gold and silver (M) are precipitated from the resulting solutions by cementation with zinc [1, 2] by the reaction

$$2[M(CN)_2]^- + Zn \rightarrow 2M + [Zn(CN)_4]^{2-}$$
. (1)

The formation of the cyanide complex  $[Zn(CN)_4]^{2-}$  by the main reaction results in binding of free cyanide ions CN<sup>-</sup>. Side reactions (2) and (3), whose share exceeds that of the main reaction, also lead to binding of CN<sup>-</sup> anions:

$$Zn + 4CN^{-} + 2H_2O \rightarrow [Zn(CN)_4]^{2-} + H_2 + 2OH^{-},$$
 (2)

$$2Zn + 8CN^{-} + O_2 + 2H_2O \rightarrow 2[Zn(CN)_4]^{2-} + 4OH^{-}.$$
 (3)

In view of the fact that the actual consumption of zinc is tens of times that theoretically calculated for cementation [2], its use as a cementing metal makes difficult the technological cycle of leaching, cementation, leaching, etc. Furthermore, it is necessary to recover zinc from spent solutions after the reduced metals are isolated and  $CN^-$  ions are neutralized. Because the concentration of zinc is low, this process is not economically feasible.

Similar complications arise if zinc is used as a cementing metal in noncyanide leaching solutions, with thiosulfate or thiocarbamide. Therefore, cementation with metals whose ions do not form complexes with ligands, the main components of leaching solutions, aluminum [4-6] and magnesium [7-9], have become more intensive in the last decade.

The aim of this study was to examine the possibility of using magnesium for contact precipitation of silver from cyanide solutions that model solutions for leaching of ores, scrap metal, and spent electrolytes and washing water formed in silver plating. This study proceeds with systematic examination of the recovery of nonferrous and precious metals from solutions by cementation with magnesium [7-9].

## **EXPERIMENTAL**

Contact precipitation of silver was carried out in the system  $[Ag(CN)_2]^--CN^-$ . Solutions for cyanide leaching of ores and secondary raw materials were modeled and kinetic and electrochemical features of the process, as well as the morphology of the reduced metal, were analyzed. Solutions containing equimolar amounts of [Ag(CN)<sub>2</sub>]<sup>-</sup> complexes and free cyanide ions CN<sup>-</sup> were prepared from AgNO<sub>3</sub> and NaCN. The cementation was carried out in a thermostated glass container with a solution volume of 0.1 l in the atmosphere nitrogen at  $20-40^{\circ}$ C, with vigorous mechanical stirring. A magnesium powder with average particle size of  $0.42 \times 0.15 \times 0.04$  mm, scrap metal of the 1.0-1.1-mm fraction, and a magnesium disk 30 mm in diameter were used for the experiments. Before each experiment, the disc was trimmed with a fine emery paper, degreased with alcohol, and its



**Fig. 1.** Variation of the silver concentration c with time  $\tau$  in cementation with a magnesium powder in solutions of the system  $[Ag(CN)_2]^--CN^-$  in relation to (a) initial content of silver cyanide complex  $c_0(Ag)$ , (b) magnesium powder weight m(Mg), and (c) temperature. (a)  $T = 20^{\circ}C$ , m(Mg) = 0.10 g.  $c_0(Ag)$  (M): (1) 0.01, (2) 0.005, (3) 0.0025. (b)  $T = 20^{\circ}C$ ,  $c_0(Ag) = 0.005$  M. m(Mg) (g): (1) 0.05, (2) 0.10, (3) 0.15. (c)  $c_0(Ag) = 0.005$  M, m(Mg) = 0.10 g. T (°C): (1) 20, (2) 30, (3) 40.

lateral surface was insulated with a Teflon tape. During the cementation, samples of a solution were periodically taken and analyzed for the silver content by atomic-adsorption spectroscopy (AAS-IN atomic-absorption spectrophotometer in an air-propane-butane flame at a wavelength of 328.1 nm).

After the cementation was complete, the powders, scrap metal, and disc were washed with water and acetone, dried in air at 80°C, weighed, and examined with an optical microscope equipped with a digital camera. On separating the precipitate, the content of magnesium ions in solution was determined by titration with Trilon B.

It was found that the rate of cementation with powdered magnesium in solutions of the system  $[Ag(CN)_2]^--CN^-$  is directly proportional to the content of the complex. For example, the cementation rate in 0.0025, 0.005, and 0.01 M solutions of the  $[Ag(CN)_2]^-$  complex at 20°C is 0.00044, 0.00077, and 0.00186 mol min<sup>-1</sup>, respectively, during the initial 2 min, when a virtually linear time dependence of the silver concentration is observed (Fig. 1a). Thus, the contact precipitation of silver with magnesium in cyanide solutions can be considered a first-order pseudoreaction ?(pseudo-first-order reaction)? in the initial stage.

The cementation rate is also virtually directlyproportional to the surface area of the magnesium powder in the initial stage (Fig. 1b). For example, the cementation rate in a 0.005 M  $[Ag(CN)_2]^-$  solution is, during the first 2 min, 0.00040, 0.00077 and 0.00121 mol min<sup>-1</sup>, respectively, for a magnesium powder weight of 0.05, 0.10, and 0.15 g. This agrees with the general dependence of the contact precipitation rate of a metal on the surface area of a cementing agent in contact with a solution [10].

The temperature factor is of no importance for acceleration of the silver cementation (Fig. 1c). For example, the cementation rate increases by about 15% in the initial stage for 0.005 M solutions in the range  $20-30^{\circ}$ C and by about 25% in the range  $30-40^{\circ}$ C. This behavior can be accounted for by acceleration of electrode processes associated with depolarization of process (4) at microcathodes [11], and also by acceleration of reaction (5) at microanodes; in addition, heating promotes diffusion:

$$[Ag(CN)_2]^- + e \rightarrow Ag + 2CN^-, \qquad (4)$$

$$Mg \rightarrow Mg^{2+} + 2e.$$
 (5)

In a wide range of concentrations of the cyanide complex  $[Ag(CN)_2]^-$ , silver films (Figs. 2a-2d) or compact metal formations (Figs. 2e-2i) appear on the smooth magnesium surface. This is primarily attributable to a strong cathodic polarization of silver in cyanide electrolytes [11]. Silver films are not homogeneous, which is caused by the electrochemical nonuniformity of the magnesium surface. For example, outgrowths, which are known to have an increased energy [12], are formed in prolonged cementation at crystallite boundaries on smooth magnesium samples (discs) (Figs. 2a, 2b). The heterogeneity of the silver precipitate is considerably more pronounced on the surface of magnesium scrap (Figs. 2c, 2d) and especially on powder particles (Figs. 2e, 2f). In the last case, the corrugated surface and internal stresses are reasons for the increased electrochemical (energy-related) heterogeneity, which leads to a high current density on microcathode and microanode parts and,



**Fig. 2.** Micrographs of the surface of (a, b) magnesium discs, (c, d) scrap, (e, f) powder, and (g-i) silver formations upon contact precipitation at 20°C from a 0.005 M [Ag(CN)<sub>2</sub>]<sup>-</sup> + 0.005 M CN<sup>-</sup> solution. Magnification: (a, g-i) 100; (b, e, f) 200; (c, d) 50.

accordingly, to a high cementation rate. Furthermore, the corrugated surface of magnesium powder particles precludes formation of solid silver films, which is characteristic of the contact precipitation from solutions of complex salts [10] and is observed on the magnesium disc (Figs. 2a, 2b). Therefore, the microanode parts are not blocked by a bulk silver precipitate reduced on microcathodes. These latter are formed as outgrowths during cementation (Fig. 2f), which are agglomerated in anodic dissolution of magnesium. After the cementing agent is completely consumed, the silver particles formed reproduce particles of magnesium powder or their fragments (Fig. 2g–2i).

Thus, the contact precipitation of silver with a magnesium powder from cyanide solutions enables complete utilization of magnesium as a cementing metal. The specific expenditure of magnesium is only determined by microcathod?ic reactions of silver reduction (4) and side reaction (6), because reactions similar to (2) and (3) do not occur:

$$2H_2O + 2e \rightarrow H_2 + 2OH^-.$$
(6)

As demonstrated by the experimental results, the practical expenditure of magnesium on reaching a 99% extraction of silver is 150-300% of the theo-

retical value, i.e., 0.17–0.34 g per gram of reduced silver.

No precipitation of magnesium hydroxide was observed during the cementation and a long time after its completion, which is due to the low concentration of  $Mg^{2+}$  formed by microanod?ic reaction (5) and to a comparatively low alkalinity of the medium. The precipitation of  $Mg(OH)_2$  from a 0.01 M solution begins at pH 10.4 and is complete at pH 12.4 [13]. In the model solutions under study, this value does not exceed 10.5. Thus, the precipitation of silver from cyanide solutions with a magnesium powder makes it possible to obtain a pure reduced metal, with cyanide ions not bound by ions of the cementing agent.

#### CONCLUSIONS

(1) Compact silver films are deposited from solutions of the system  $[Ag(CN)_2]^--CN^-$  on a smooth magnesium surface, and monolithic silver particles are formed on a corrugated surface.

(2) The rate of silver cementation with a magnesium powder is directly proportional to the concentration of the complex  $[Ag(CN)_2]^-$  and to the surface area of the cementing agent in the initial stage of the process. The temperature factor is associated with

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the depolarization of silver reduction on microcathodes and with the acceleration of magnesium dissolution on microanodes.

3. The specific expenditure of magnesium for a 99% extraction of silver is 0.17-0.34 g per gram of reduced silver, which corresponds to a 150-300%dissolution of the cementing agent relative to the theoretical value. No magnesium hydroxide is formed during the cementation and a long time after its completion, which makes it possible to obtain pure silver precipitates.

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