

Silver Recovery from Spent Photographic Solutions by Natural Magnetite: Attempts to Estimate the Process Mechanism and Optimal Process Conditions

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Abstract – Spent solutions from classic photographic processes have been used for cementation of silver onto natural magnetite sand. The effects of the solid phase content, initial pH of the solution, modified by sulphur acid, on the amount of silver recovered have been studied. Some ad hoc experiments were performed by treatment with 76% selenic acid as well as telluric acid. The silver deposits depend on the pH of solution (sulphur acid treatment) and the type of acid used. The sulphur acid treated solutions allow silver deposits mainly close to the magnetite surface as thin flat deposits, while those treated by selenic and telluric acids results in enormous amounts of star-like dendrites. **Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.**

Keywords: Silver Recovery, Spent Photographic Solutions, Deposit Shape, Cementation, Magnetite

I. Introduction

Noble metal recovery of spent and cyanate leach solutions is of great economic and ecological importance. The present article addresses silver recovery from spent thiosulphate solutions from photographic processes by natural magnetite (sand). The magnetite exhibits almost semiconductor surface behavior and relatively low specific surface area but its use in the silver recovery is not investigated yet taking into account the large use of adsorption process performed by various adsorbents [1],[2],[3],[4],[5]. The sorption processes can employ a variety of inorganic [6] and organic adsorbents [2], [6]. In this context, we have to mention the electrolysis as one of the principle process of silver recovery and refining [7], [8], and [9].

The cementation of silver by iron [10], zinc [11], [12], [13] or copper [10], [14], [15] is among the oldest one [14], [16], [17]. Its is widely used in the mining industry [18] for precipitating copper from solution by scrap iron and then applied to gold solutions, iron being replaced by zinc. It is still under strong academic interest [15], [17], [19], and [20] but despite the developments in the engineering application of the process the theory is under detailed investigation and lagging behind [10], [14], [15], and [19]. In the context of development of low-cost processes for silver recovery from waste solutions the present work deal with magnetite induced process by two main reasons:

- 1) The magnetite is a low-cost material of either natural or artificial (chemically precipitated) origin.
- 2) The magnetite can be used for adsorption from aqueous solutions for a variety of substances and

hazardous species [21].

- 3) The magnetite can be separated from the process solution remotely by magnetic devices, which avoids any mechanical operations like sedimentation, filtration or centrifugal treatment leading to lost of the target material.

The main questions about the silver recovery by natural magnetite developed by our group at the initial stage of the development of the program are:

- a) Estimation of the mechanism of the recovery process: adsorption or cementation (by ion containing sites on the magnetite surface).
- b) The form of the deposits and tendencies in their time-evolution
- c) The effect of the pH and the type of the acid used in the initial solution pre-condition treatment.

The answers reported in the next section of the article give enough information about the process mechanism, the type of the deposits and the effect of the preconditioning of the treated silver-containing solutions.

II. Experimental

II.1. Materials

The magnetite sand was delivered from natural deposits near the Iskar River (near Sofia, Bulgaria) and classified by sieving. A narrow fraction of 125–200 μm (sieve diameter) was used. The fraction was preliminary treated in an air-fluidized bed to clean the surface from any contaminants on its surface: the intensive friction between the particles and the collisions in the fluidized allow removing mainly SiO_2 deposited on the magnetite

surface and giving a brown color of the magnetite. As a results of this preliminary decontamination process the magnetite becomes black-metallic in color. Then the magnetite was rinsed by distilled water and dried at room temperature. The particles are almost round with a sphericity factor 0.8 (see Fig. 1) and a density of 5140 kg/m^3 . The spent thiosulphate solution (light-brown in color) was delivered from various sources of the movie making industry and contains about 0.7% mass silver. The data of the element analysis are summarized in Table I.

TABLE I
CONTENT OF THE ORIGINAL SPENT PHOTOGRAPHIC SOLUTION
PH = 6.4

Element	Ag	Fe	Al	Cu	Ca
Content mg/L	665.7	29.75	4.858	0.405	16.95

II.2. Procedures

The magnetite of different amount (5g or 10g) was charged in 50mL flasks shaken on a laboratory shaking machine for 60min at 220rpm. The preliminary treatment and pH adjustments were made by addition to the thiosulphate solution 1mL of H_2SO_4 (0.1M, 1M, 2M, 1%, 2% and 5%). The pH was adjusted in the range from 2.5 up to 6.4 and controlled by pH-meter (model *pHep+* of Hanna instruments).

After each treatment the solutions were separated from the solids (magnetite + deposits) by filtration and forwarded to elemental analysis and microscope observations of the deposits, respectively.

II.3. Methods

The elemental analysis of the thiosulphate solution was performed by ICP device (model High dispersion ICP-OES "Prodigy" of Teledune Leeman Labs). The photos of both the magnetite particles and the silver deposits were taken by OLYMPUS BX53 microscope equipped by a digital camera.

III. Results and Discussion

III.1. Experimental Result: the Process of Recovery

The results are illustrated in the best way the photos (see Figs. 2, 3, 4, 6, 7) strongly indicating formation of large silver deposits in cavities of the magnetite surface.

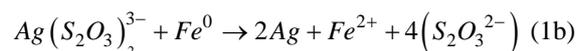
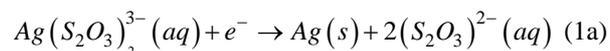
The deposit shapes and thicknesses as well as the increase in the iron ions in the solutions (see in Table II the dotted data about the Fe content) clearly reveal that process of recovery is a cementation at iron ion – containing sites on the magnetite surface. The preliminary treatments by sulphuric acids reveal that weakest action by 0.1M and 1% H_2SO_4 provide the largest silver recovery (see Table III) at $\text{pH} \approx 6.4$.

The decrease in the pH (see Table II) reduces the amount of the silver recovered even though the amount of iron in the treated solution increases (see Fig. 5). From Fig. 5 it is evident that the two-fold increase in the amount of the magnetite increase almost twice the amount of the silver deposited but the tendency with the variation in pH remains. The treatment with sulphuric acid when the solution pH remains in the range 5.7 – 6.4 is the optimal under the experimental conditions created in this study and confirm the abovementioned comments.

TABLE II
EFFECT OF THE MAGNETITE LOAD AND THE SULPHURIC ACID
TREATMENT ON THE SILVER RECOVERY.
TIME OF EXPOSURE = 60 MIN

Sample	Fe_3O_4 Load (g)	H_2SO_4 treatment (1 mL to the Thiosulphate solution)	pH	H_2SO_4	
				Ag (mg/L)	Ag Yield %
S0		-	6.4	665.7	
S1	5	0.1M	6.4	605.9	8.98
S2	5	1M	4.0	618.9	7.03
S3	5	2M	3.2	625.8	5.99
S4	10	0.1M	6.3	598.4	10.10
S5	10	1M	3.8	615.0	7.6
S6	10	2M	2.9	619.5	6.94
S7	5	1%	6.1	604.0	9.26
S8	5	2%	6.1	611.4	8.15
S9	5	5%	5.9	604.5	9.26
S10	10	1%	6.0	587.9	11.82
S11	10	2%	6.0	586.9	11.87
S12	10	5%	5.7	588.5	11.59

Therefore the silver cementation by iron in the sites on the magnetite surface can be expressed as



The successful performance of the process is possible in the pH range $\text{pH} \approx 5 - 7.6$ which matches the experimentally determined conditions providing the maximum silver yield with the cementation by natural magnetite. Moreover, this range of Ph is too close to the Point of Zero Charge (PZC) of the magnetite (see [21] for large comments on this subject relevant to adsorption processes).

III.2. Experimental Result: Shape of the Deposits

The deposits are mainly as thick pieces of bright silver at the magnetite surface separating it from the solution or as almost round "bullets" in the cavities. The smooth shapes of the deposits indicate that process of the cementation was performed near the iron-containing sites. This is due the limitation of 60 min of the experiments performed which does not allow the process

to be developed towards the bulk of the thiosulphate solution and resulting in formation of dendrites [10],[14], [22]. Formation of dendrites, however, was observed in some experiments with H_2SO_4 (see Figs. 4(c) and 6(b)) and in the ad hoc treatment of the thiosulphate solution by concentrated selenic and telluric acids (see further in this work Figs. 7(a), (b)).

The kinetic of the process strongly affects the shape of the deposits. For example, Sulk and Jaskula [10] reported formation of dendrites in solutions treated with 0.5M H_2SO_4 in 60 min exposure experiments. These experiments are between ours performed with 0.1M and 1M H_2SO_4 where smooth deposits were observed. Some explanation about these differences can be attributed to the fact that during the shaking of the flask the solution is oxygenated to some extent due to surface caption of air.

The oxygenation of the solution leads to granular shape of the deposits (see for example Figs. 3(a), (b)). Following Sulk and Jaskula [10], [14], [22] further increase in the concentration of the copper ions up to $0.5M Cu^{2+}$ yields total disappearance of dendrites from the surface (the cementation was performed on copper surfaces).

TABLE III
ELEMENTAL CONTENT OF THE THIOSULPHATE SOLUTION TREATED
BY MAGNETITE AFTER 60 MIN EXPOSURES

S	Fe ₃ O ₄ (g)	SA 1mL	Ag mg/L	Fe%	Al	Cu	Ca
S0	-	-	665.7	29.75	4.858	0.405	16.95
S1	5	0.1M	605.9	47.75	3.270	1.605	34.91
S2	5	1M	618.9	73.14	14.030	1.625	36.76
S3	5	2M	625.8	98.05	24.08	1.515	39.39
S4	10	0.1M	598.4	67.89	3.735	1.415	44.24
S5	10	1M	615.0	120.6	15.92	2.465	48.96
S6	10	2M	619.5	168.0	28.92	3.015	52.16
S7	5	1%	604.0	51.60	4.035	0.760	39.39
S8	5	2%	611.4	49.56	4.135	0.500	33.41
S9	5	5%	604.5	54.52	5.170	0.350	32.91
S10	10	1%	587.9	74.41	3.785	1.555	47.72
S11	10	2%	586.9	83.87	3.760	1.370	43.70
S12	10	5%	588.5	91.47	4.530	2.040	46.45

SA: Sulphuric Acid ; S – sample

The data summarized in Table II show the amount of Cu^{2+} in the experiments performed. Dendrites were observed in experiments denoted as S2, S6, S9 and S12, facts that confirm the statement of Sulk and Jaskula [10], [14], and [22]. We have to take into account, that in the process reported here, the magnetite emits ions in to the solution instead copper ones as in the process commented above [10], [14], and [22]. The formation of large amounts of dendrites in the solutions treated with concentrated selenic (Fig. 7(a)) and telluric (Fig. 7(b)) acids indicates that they are formed as cathodic sites (formed on small protrusions magnetite surface) and promotes formation of anodic sites in the close neighborhood [15].

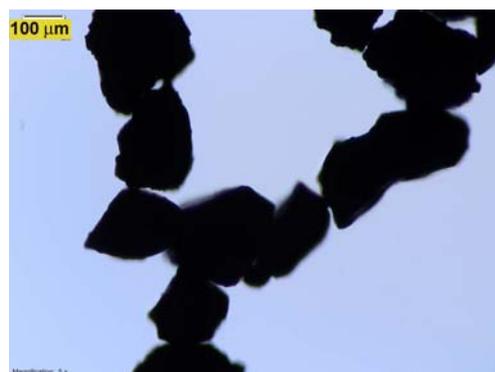
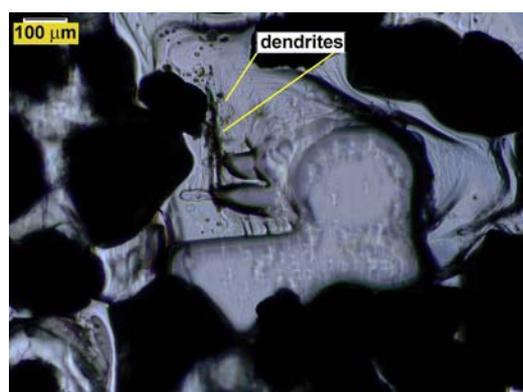
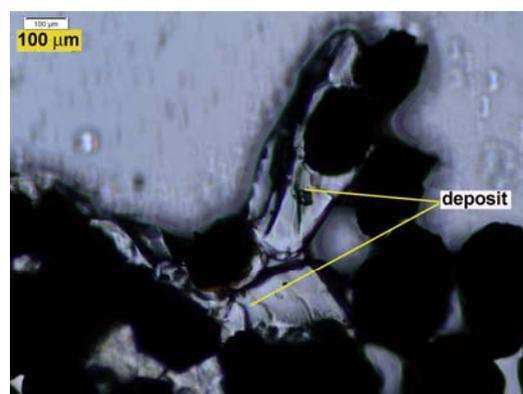


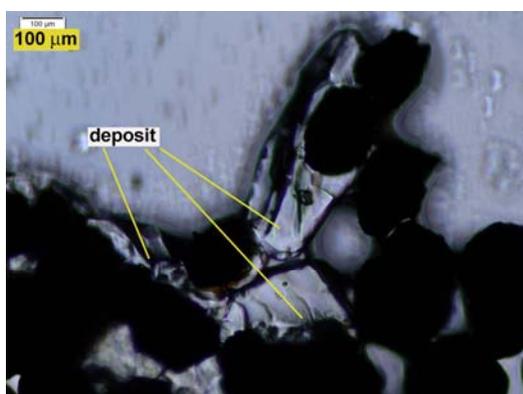
Fig. 1. Virgin magnetite particles. Magnification: 5x



(a) Magnification: 5x

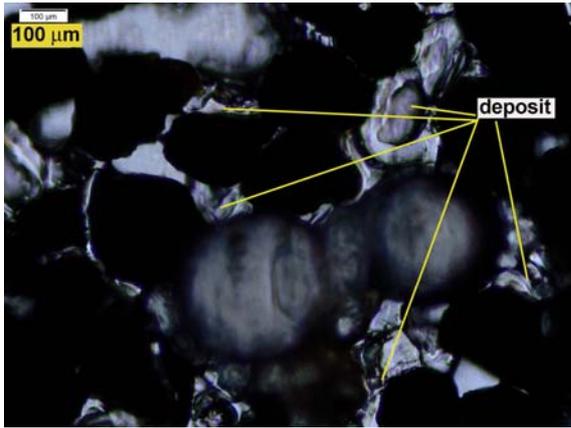


(b) Magnification: 5x

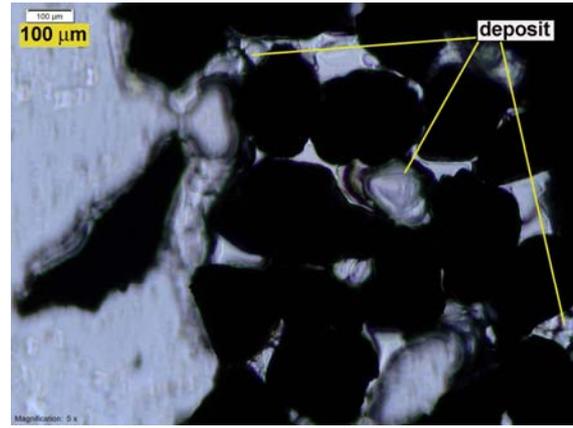


(c) Magnification: 5x

Figs. 2. Magnetite particles with smooth silver deposits developed by addition of 1 ML of 0.1M H_2SO_4 to the solution

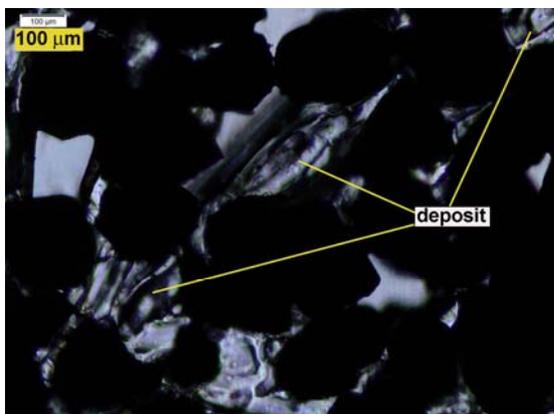


(a) Magnification: 5x

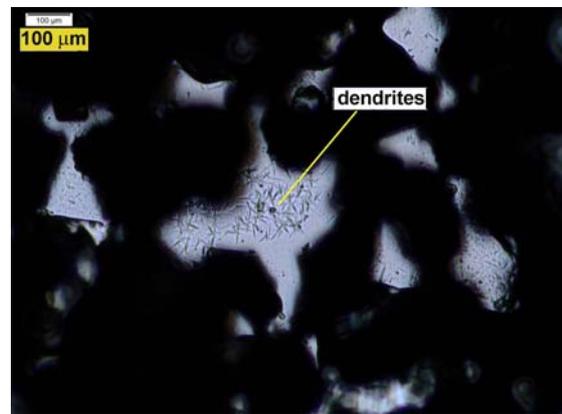


(b) Magnification: 5x

Figs. 3 Magnetite particles with smooth silver deposits developed by addition of 1 mL 1M H_2SO_4 to the solution



(a) Magnification: 5x



(b) Magnification: 5x

Figs. 4. Silver deposits performed by magnetite in a thiosulphate solution treated with 2M sulphuric acid

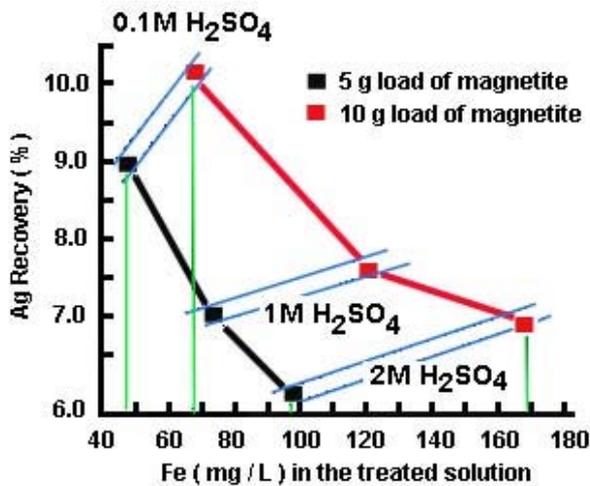


Fig. 5. Effects of the iron release into the thiosulphate solution and the amount of the magnetite load on the silver recovery

These experiments are only the beginning of a program addressing initial treatment of thiosulphate solutions with respect to optimal silver recovery.

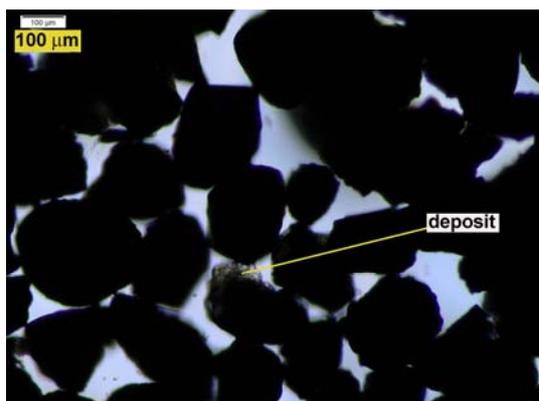
Further detailed experiments on the dosage of the acid to solution have to be performed, that is a subject of further scientific reports.

IV. Conclusion

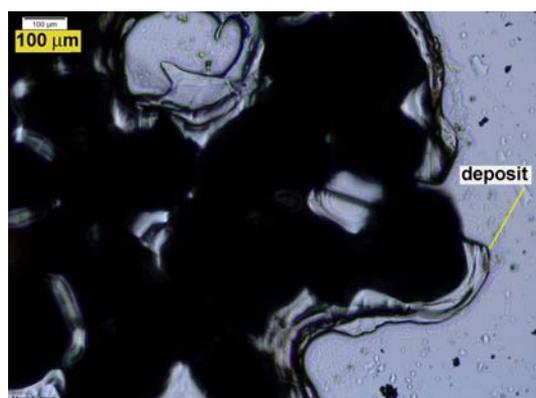
The work presents initial experimental data on silver cementation onto natural magnetite from spent photographic solutions.

The experiments provided some results guiding the further experiments in this direction, among them:

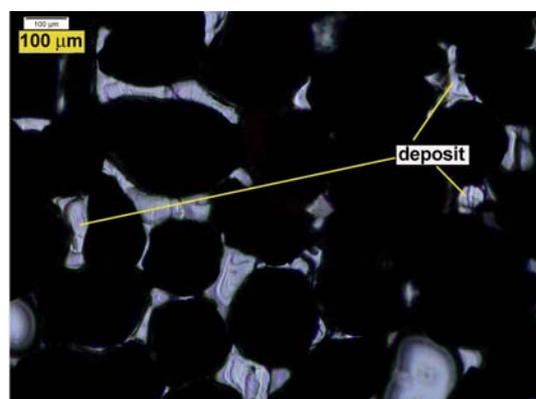
- 1) The treatment with 0.1M and 1% H_2SO_4 results in maximum yield of silver deposited onto the magnetite surface. These experiments were performed at pH (see Table II) close to the point of zero charge of the magnetite.
- 2) The weak treatment with 5% H_2SO_4 and 2M H_2SO_4 leads to formation of small amounts of dendrites in the bulk on the solution, not on the magnetite surface.
- 3) The magnetite has not been used so far for precious metal deposition (cementation) unlike iron, copper and zinc. However, we may suggest that existing of some sites on the magnetite surface allowing replacement of the iron ions by silver ones, makes the process at issue close to that performed by iron scrap.



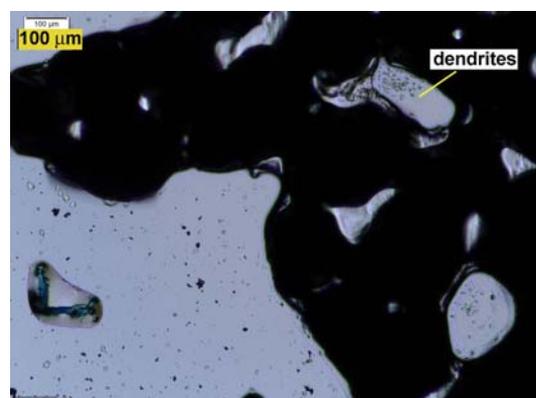
(a) Magnification: 5x



(b) Magnification: 5x

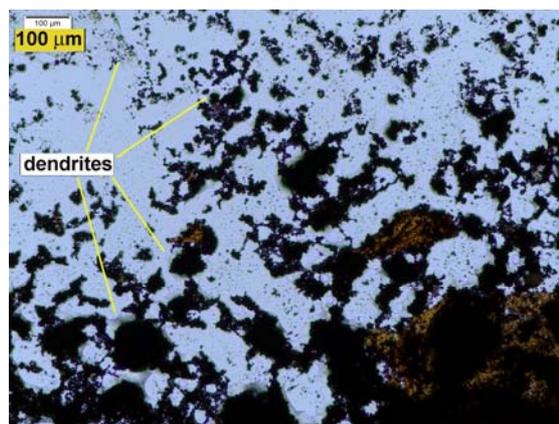


(c) Magnification: 5x

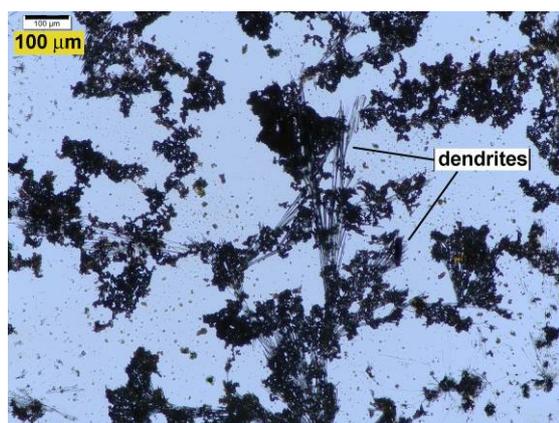


(d) Magnification: 5x

Figs. 6. Silver deposits performed by magnetite in a thiosulphate solution treated with sulphuric acid : A) 1% ; B 2% ; C,D) 5%



(a) Magnification: 5x



(b) Magnification: 5x

Figs. 7. Silver deposits performed by magnetite in a thiosulphate solution treated by selenic and telluric acids: (a) 76 % selenic (H_2SeO_4) acid and (b) telluric $Te(OH)_6$ acid

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