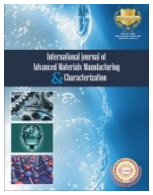

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Metallic Silver from Leach Liquor: A New Approach for Silver Nano Metal Synthesis

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ABSTRACT

The leach liquor of a low grade silver ore containing 0.5% Ag is used to produce two varieties of metallic silver following two routes. Route-I leading to silver mould by precipitating out silver chloride with 1.62g/L NaCl and later on roasting the silver chloride with Na_2CO_3 in 2:1 ratio at 1000°C for 2h. Route-II leading to silver nano metals by treating the leach liquor with 5% (v/v) hydrazine hydrate as reductant and 10mL of 0.01M sodium lauryl sulfate in 100mL of leach liquor as surfactant. The paper first time reports the production of silver nano metal from impure leach liquor. This is a new dimension to the conventional nano metal preparation.

Introduction

Silver is obtained in nature in its native form. Apart from coin making (ancient eras) and jeweler making, silver has its uses in various fields like electrical, thermal and pharmaceuticals due to its high electrical and thermal conductance's and for its proficient antibacterial activity respectively. Extraction of silver deals with the leaching with different reagents like ferricyanide,[1-3] cyanide,[4-5] thiosulfate,[6-8] thiourea,[9-11] ferric ion,[12] sulfate,[13] nitric acid[14-15] and chloride/hypochlorite.[16] Ultrasound assisted leachings[17-18] are also one of the recent trends. Silver is extracted from the leach liquor through electrochemical deposition, [19] electroseparation[20] and precipitation.[21]

Synthesis of silver nano metal is one of the most up-to-date investigations in today's world due to its high applicability. Nano metals show amazing properties due to high surface to volume ratio. Nano clusters provide a potential platform to study atoms as well as bulk and looking towards both the sides being in the middle.[22] Nano metallic particles have many such unique properties as compared to the bulk.

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Investigations so far have reported the preparation of silver nano particle synthetically from silver nitrate,[23-26] silver diamine[27-28] and silver thiosulfate.[23] One thing to be noted here that all those silver nano particles are produced from high grade pure salts. This paper first time reports the preparation of metallic silver from a leach liquor of low grade silver ore containing 0.5% silver which would never be used for industrial silver production. Nano metal synthesis from a pure salt is in ease due to its purity and assurance of the absence of other ions. But synthesizing pure metal nano particles from a solution having varieties of ions is a challenging task. The advantages of producing silver nano metal from impure leach liquor are 1) it may suggest another method of metal extraction from the leach liquor apart from the conventional ones, 2) it would give a process to produce nano silver from leach liquor of various kind of silver ores and the secondary silver materials and 3) it will substitute the electrode position and electro separation thereby reducing the electrical energy. Moreover this paper also reports the production of metallic silver mould from route-I via precipitation of silver chloride followed by roasting and metallic silver nano powder via reduction method.
(Chemical bonds between primary particles) state, since their

Experimental Method

The low grade ore was leached with 3% nitric acid with 10% pulp density (w/v) and 80°C for 3h. The silver in the leach liquor was analyzed in ICP-OES. The rest other impurities were analyzed through AAS. The follow up procedures with the

leach liquor is divided into two routes where both the route leads to the production of metallic silver in normal form and in nano powder form.

Route-I: To 1L of silver leach liquor; 1.62g/L NaCl was added to get a curdy white precipitate of AgCl. The precipitate was collected, washed and dried. The precipitate was mixed with Na_2CO_3 with 2:1 (0.5g AgCl+ 0.25g Na_2CO_3) ratio and calcined at 1000°C for 2h. Metallic silver obtained in a solidified melt. The XRD of the silver metal is given in Fig.1. It is matched perfectly with the standard pattern of silver (JCPDS-41-1402).

Route-II: Addition of 5% (v/v) hydrazine hydrate as reductant and 10mL of 0.01M sodium lauryl sulfate in 100mL leach liquor as surfactant so as to produce silver nano metals.

Characterization

All the phase determination of the low grade ore and metallic silver obtained from both the routes were carried out in Analytical X'pert PRO PW-3040/60 X-ray diffract meter. The morphology, particle size and EDX were determined by transmission electron microscope (TEM) FEI-Tecnai G^2 using a carbon coated Ni-grid.

Results and discussion

The total chemical composition of the low grade ore is given here in Table-1. It shows 0.5% silver and 0.31% Copper as major contents. Rest other metals are in traces.

Leaching

The ore was leached in 3% nitric acid and 10% pulp density (w/v) at room temperature (300K) to liberate metal values from the matrix. Along with silver most of the copper comes into the solution. Table-2 describes the leach liquor composition showing 0.49g/L silver and 0.29g/L copper. Sathaiyan et al.[21] have reported the leaching of silver button cells at 50°C as optimum temperature.

$$Ag + HNO_3 \rightarrow AgNO_3 \quad \ldots\ldots\ldots (1)$$

Metal formation

Metallic silver was obtained from the leach liquor through two different routes given below.

Route-I: Silver was extracted from the solution as AgCl when 1.458g NaCl was added to 900mL (1.62g/L) of leach liquor. The weight of the precipitate was 0.601g from 900mL leach liquor indicates complete extraction of silver from the leach liquor as silver chloride. The equation is-

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3 \quad \ldots\ldots\ldots (2)$$

Out of the 0.601g silver chloride 0.5g was taken and thoroughly mixed with sodium carbonate in 2:1 ratio and roasted at 1000°C for 2h where silver metallic mould was formed. The weight of the silver metal after washing and drying was found to be 0.37g showing complete silver extraction from the AgCl powder. The equation is written as-

$$AgCl + Na_2CO_3 \rightarrow Ag + CO_2 + NaCl \quad \ldots\ldots\ldots (3)$$

At the end of the whole process complete extraction of silver noticed showing significant effectiveness of the process.

The XRD of the obtained silver mould is presented in Fig.1(b) showing clear and well defined peaks of silver matched perfectly with the standard pattern of silver (JCPDS-41-1402). The grain diameter (D) was calculated from the Scherrer's formula-

$$D = K\lambda/2\beta \cos\theta \quad \ldots\ldots\ldots (4)$$

K= Shape factor (Calculated as 0.94)

λ= Wave length of the incident light

β= Line broadening at half of the full intensity in radians

θ= Bragg's angle

With the application of the aforesaid equation the grain diameter of the smelted silver obtained from route-I was found to be 16.26 nm.

Route-II: The primary reaction involves the reduction of Ag^+ through hydrazine hydrate to metallic silver. Sodium lauryl sulfate was used as the surfactant so as to inhibit the aggregation of the particles. Silver nano metals are formed within 10 minutes as shown in Fig.2. (a to d). The diffraction patterns and the shinning lustrous surface obtained in dark field are also presented here (Fig.2.d). At the time period of 10 min the particles are spherical in shape. Silver nano particles formed at 10min show average particle diameter of 50 nm. Size distribution ranges in 50±10 nm in most of the cases whereas there is also the presence of petit spheres with size of around 10nm. The clear and defined SAED patterns of silver nano particles also provide the evidence of the above mentioned facts. Silver nano metal synthesis from various investigations shows multiple shapes and sizes in different conditions. Panacek et al.[27] have produced silver nano particles with average size of 50 nm from silver amine complex at pH 11.5-13. Shankar et al.[24] have produced ultra small silver nano particles of 4nm diameter by digestive ripening route. Sun and Xia[26] have produced monodispersed silver nano cubes at 160°C from silver nitrate and ethyl alcohol. In these aspects the nano silver obtained through our route is quite comparable in terms of size, shape and the process also.

With increase in the time the particles start growing into bigger particles. The TEM images of Fig.3 (a-d) show the silver nano particles of 1h. The particle diameter was caculated to be around 150nm. A keen observation to the particle reveals the shape change from spherical to somewhat hexagonal which is clear in Fig.3.b.

Further increase in time from 1h to 4h prominently shows the growth of the tiny particle towards defined hexagonal as shown in Fig.4.(a-d). The particle size was measured and found to be around 350nm.

The EDX of the sample (Fig.5) showing prominetly the presence of silver. The other major elemental peaks like Ni and carbon should be subtracted as the grid of TEM was made up of Ni coated with a thin film of carbon. Minor impurities like Si and Cu were also detected and did not taken into account due to very negligible peak size.

Analyzing the TEM images the rate of crystal growth was calculated by measuring the diameter and presented as a bar diagram in Fig.6. It was found that in the first 30 min the rate of crystal growth was 2nm/min. For the next 30min the rate of crystal growth increased to 3nm/min. After that it was slowed down to 1nm/min.

Cause of the selective reduction

The reason behind the selective precipitation of the silver metal alone from a solution having the presence of varieties of other metals may be attributed to the respective reduction potential values. The reduction potential of Ag is 0.8V which is greater than that of Cu (0.34V) described in Table-3. This is the single parameter that rules over the selective precipitation.

The valance shell configuration of silver is $3s^1\ 4d^{10}$ and that of copper is $2s^1\ 3d^{10}$. Rest other metals present in the leach liquor are having even partially filled d-orbitals. The aforementioned trend of metal formation is quite general and it's all due to the energy of the d-band centre relative to the Fermi energy.[23] The higher the energy of the d-bands, higher is the electron accepting capacity and more is the ease of reduction and metal formation. Following the relative energy of the orbital's 3d<4d<5d, it is only silver precipitated as nano metal particle leaving behind rest other metals.

Flow sheet

The flow sheet gives the total operating steps to produce silver metallic mould and silver nano metals from the low grade silver ore. This is a unique flow sheet which shows the preparation of silver nano metals from low grade silver ore containing0.5%silver.

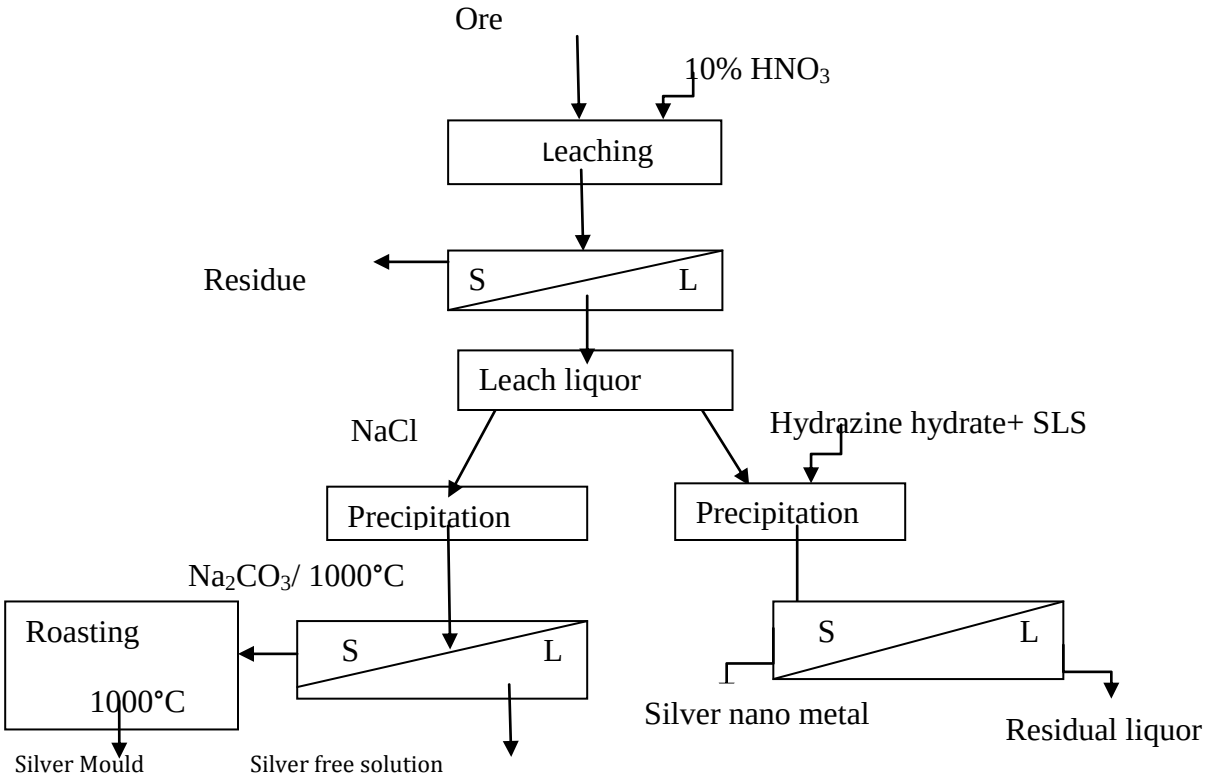

Fig. 6Flow sheet for silver metal production

Conclusions

Metallic silver was produced from the leach liquor of a low grade silver ore having 0.5% silver. Silver metal was produced from two different routes generating two kinds of silver metal. Route-I produces silver mould by precipitating silver chloride with addition of 1.62g/L NaCl to silver leach liquor followed by mixing with Na_2CO_3 in 2:1 ratio and roasting at 1000°C for 2h. Route-II produces silver nano metal by addition of 5% (v/v) hydrazine hydrate and 0.01M SLS as dispersant in room temperature (300K). The nano metal thus produced could be placed in the same regime with various other nanometals produced from different conditions available in the literatures and is comparable in size, shape and process also. The whole process is summarized as a process flow sheet.

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Stick Pattern

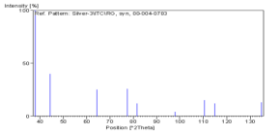

Fig-1 stick XRD pattern of silver nano metal

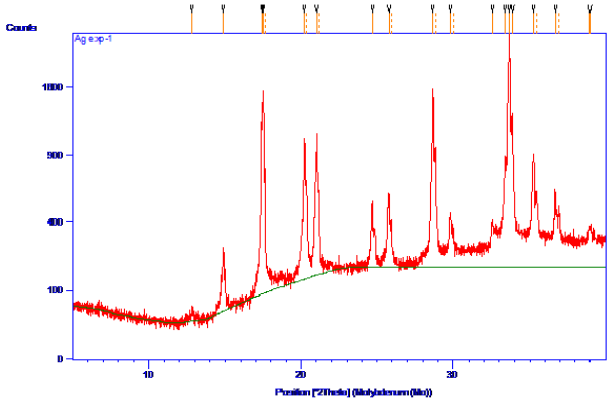

Fig1(b) XRD pattern of silver nano metal

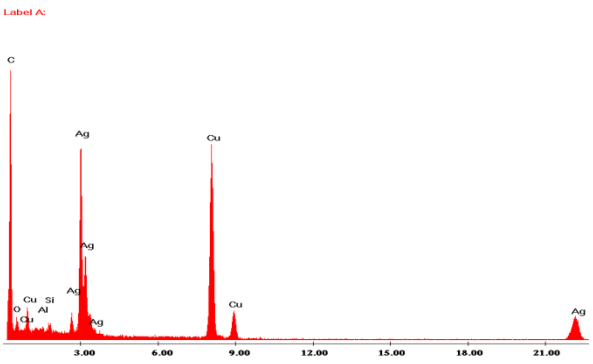

Fig 5 EDX image of the leach liquor

Name and formula

Reference code:	00-004-0783
Mineral name:	Silver-3*C*, syn
PDF index name:	Silver
Empirical formula:	Ag
Chemical formula:	Ag

Crystallographic parameters

Crystal system:	Cubic
Space group:	Fm3m
Space group number:	225
a (Å):	4.0862
b (Å):	4.0862
c (Å):	4.0862
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm^3):	10.50
Measured density (g/cm^3):	10.50
Volume of cell (10^6 pm^3):	68.23
Z:	4.00
RIR:	5.20

Subfiles and Quality

Subfiles:	Inorganic Mineral Alloy, metal or intermetallic Common Phase Educational pattern Forensic NBS pattern
Quality:	Indexed (I)

Comments

Color:	Light gray metallic
General comments:	Purity >99.999%. Opaque mineral optical data on specimen from Great Bear Lake, Canada: RR_2R_e=94.1, Disp.=16, VHN_{100}=55-63, Color values .314, .321, 94.2, Ref.: IMA Commission on Ore Microscopy QDF.
Sample source:	Sample obtained from Johnson Matthey Company, Ltd.
Analysis:	Spectrographic analysis indicated faint traces of Ca, Fe and Cu.
Optical data:	B=0.181
Melting point:	960.6°
Temperature:	Pattern taken at 27 C.

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Primary reference:	Swanson, Tatge., *Natl. Bur. Stand. (U.S.), Circ. 539*, **1**, 23, (1953)
Optical data:	Winchell., *Elements of Optical Mineralogy*, **II**, 17

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	2.35900	38.117	100.0
2	2	0	0	2.04400	44.279	40.0
3	2	2	0	1.44500	64.428	25.0
4	3	1	1	1.23100	77.475	26.0
5	2	2	2	1.17960	81.539	12.0
6	4	0	0	1.02150	97.891	4.0
7	3	3	1	0.93750	110.501	15.0
8	4	2	0	0.91370	114.928	12.0
9	4	2	2	0.83410	134.890	13.0

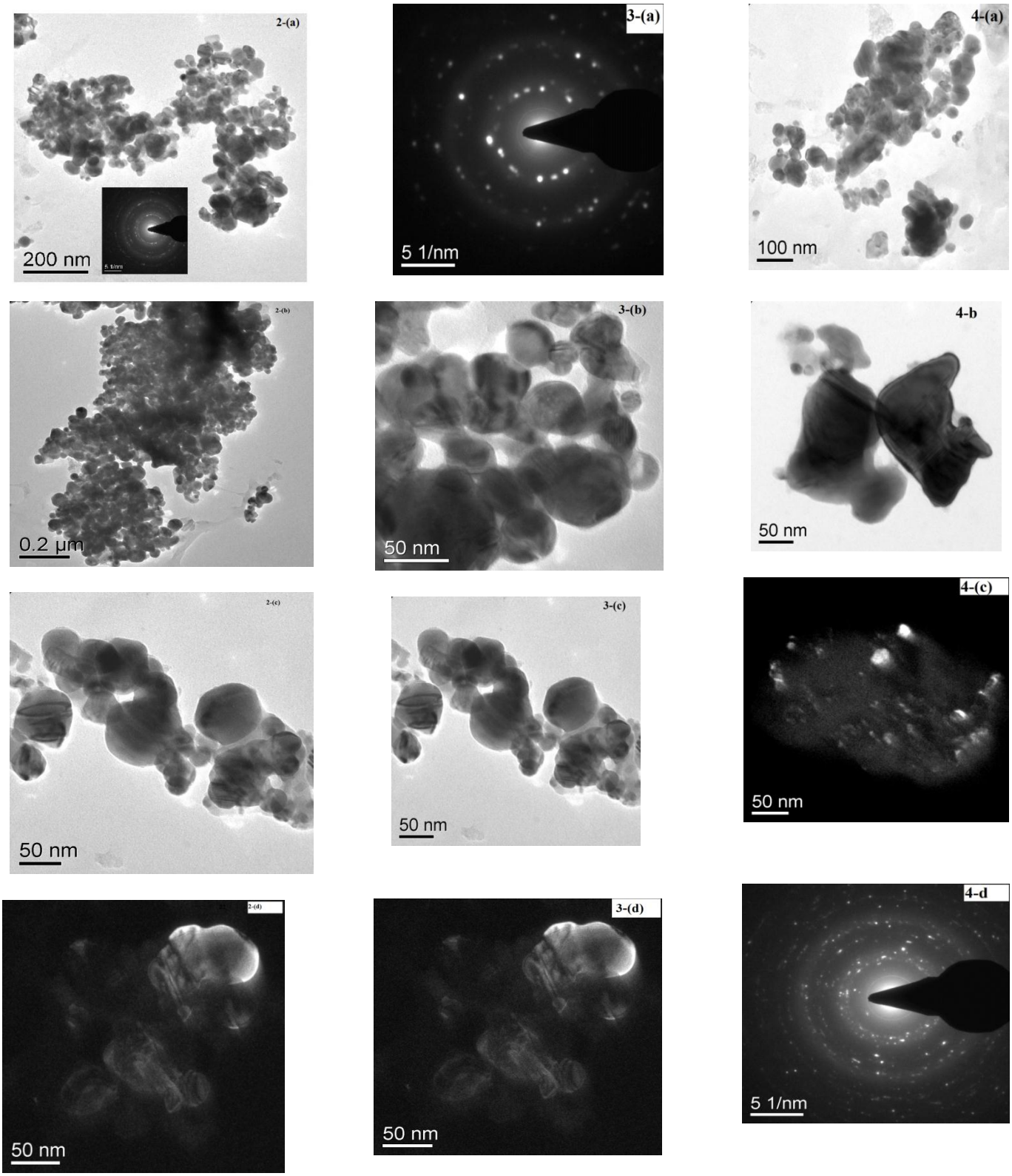

Fig 2-4 Showing TEM images

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