

A NEW PROCESS TO RECOVER SILVER AS SILVER METAL POWDER FROM SECONDARY SOURCES: THERMODYNAMIC AND KINETIC STUDY

Maricela Villicaña Méndez^{1,2}, Juan Francisco Pérez Robles², Alejandro Manzano Ramírez² Luz Ma. Reyna Avilés² and Jesús González Hernández²

¹Engineering Posgraduate Student from Querétaro Autonomous University-México

²Research and Advanced Studies Center IPN-Unidad Querétaro-Libramiento Norponiente 2000, Frac. Real de Juriquilla-Querétaro-Qro.-México-jfperez@ahoo.com

ABSTRACT

In this work a new process to recover silver from secondary sources (like a recycled material or a slag) is proposed. Silver is recovered from minerals by the cyanidation process where it is solubilised by an alkali cyanide, potassium or sodium. Cyanide process involves the producción of the complex specie, $\text{Ag}(\text{CN})_2^-$ in the presence of oxygen. The concentrates obtained from minerals by a gravimetric or flotation process have been treated by cyanidation for a long time. In many works kinetics and mechanisms of dissolution of silver and gold by cyanide have been extensively studied [Contreras-1960, Hedley-1968, Schlitt-1981]. Silver precipitation is carried out out by a cementation process with zinc powder.

From secondary sources, first the silver is solubilized using a diluted nitric acid solution and then recovered normally by an electrolysis process. Silver also can be recovered by a new cementation process using an iron electrode and a catalyst agent, as it is described in this paper. From this process colloidal dispersions are produced by grinding the obtained clusters in the presence of a tensoactive agent.

In this study, thermodynamics and kinetics parameters of the new process to recover silver from secondary sources are determined and discussed. From the technical point of view the process is feasible and gives results that in practice can be applied to obtain bulk metal from secondary sources. In addition, if it is preferred, nano and micrometric particles could be obtained in this new process. Production of colloidal particles micrometric or submicrometric has been extensively studied in others papers; but in this new process could be easily obtained by redispersion the clusters in a high energy mill. In addition this process it is feasible to recover

the by-products to prevent environment pollution. Some details of the process are not mentioned here.

INTRODUCTION

A novel process to recover silver from primary or secondary sources is described in this work. First silver is solubilized from a roasted mineral or a waste material as a scrap.

Silver is recovered from minerals by the cyanidation process where is solubilized by an alkali cyanide, potassium or sodium. Cyanidation process involves the production of the complex specie, $\text{Ag}(\text{CN})_2^-$ in the presence of oxygen. In many works kinetics and mechanisms of dissolution of silver and gold by cyanide have been extensively studied [Contreras-1960, Hedley-1968, Schlitt-1981].

Precipitation of silver and gold from cyanide solution is carried out by metallic powder zinc, after deaeration of the solution to prevent zinc oxidation, as in the Merrill-Crowe process. Silver precipitation by zinc is a cementation process [Szczygiel-1984].

Silver also is solubilized from secondary sources by a diluted nitric acid solution and then recovered by an electrolysis process. In this new process, silver is recovered by a cementation process with an iron electrode and fluoride ion as a catalyst agent. In this way, clusters of silver metal are obtained. By grinding the clusters in a ball or a high energy mill, nanometric or micrometric silver particles can be obtained in both organic or aqueous solution (using a tensoactive agent).

In this work thermodynamics and kinetics parameters for the new process to recover silver are determined and discussed. From the technical view the process is feasible and gives results that in practice can be applied. By this

process it is feasible to recover the by-products to prevent environment pollution.

EXPERIMENTAL PROCEDURE

For the tests, AgNO_3 solution 0.2679 M was prepared and transferred to a plastic vessel where the reaction is carried out. A solution with a different concentration can be used if it is preferred. For this solution a ratio of 0.4433 mole of fluoride ion per mole of silver ion is added and after this an iron electrode is introduced into the solution. At this stage, silver particles start to be generated. Small aliquots of solution are extracted time to time to evaluate the concentration of the silver ion and hence the conversion to metal. Silver powder is separated from the reaction products by sedimentation, rinsed with enough water to eliminate the excess of catalyst and hydrated iron oxide. Iron oxide is produced when the pH of the solution is increased beyond 5.0. When the silver powder is on the bottom of the reaction reactor, the excess of water is withdrawn by decantation, the powder is dried and then characterised by X-ray diffraction.

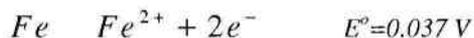
RESULTS AND DISCUSSION

Thermodynamics aspects

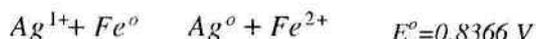
As discussed previously, the process is based in the cementation of silver ion by an iron electrode. Half cell reaction of the Ag^+/Ag system is:



Since the reaction is carried out in the presence of an iron electrode, the half cell reaction for the system Fe/Fe^{3+} is:



and the complete cell reaction [Chang-1992]:



It is assumed that the reaction is completed until 99.0 % of the silver ion is transformed to silver metal and therefore the concentration of the iron ion Fe^{3+} is 0.088 M. With this final concentration the potential for the redox reaction is calculated from the Nernst equation as follows:

$$E = E^0 - \frac{0.0591}{n} \log Q \quad (1)$$

where Q is the ratio of products/reactants.

$$\Delta G = -nFE \quad (2)$$

For three temperatures the experimental results are shown in Table I.

Table I Q, ΔG and ΔH values from the Nernst equation for the conversion of silver ion into silver metal.

T(°K)	Q x 10 ⁻⁴²	$\Delta G(\text{J})$	$\Delta H(\text{J})$
303	0.5290	-201,678.88	-83,454.52
313	0.0250	-194,919.72	-72,793.57
323	0.0014	-214,245.25	-88,217.31

It can be seen from Table I, that ΔH values are negative, this means that the reaction is exothermic and some quantity of heat may be dissipated. Also it was observed for all the cases a positive potential and thus the Gibbs Free Energy has a negative value, which means that the reaction is spontaneous. For the 99.0 % of conversion high values of the Q ratio can be obtained. This means that there is a very high tendency to obtain silver metal. In practice the reaction has a slow rate and no metal was observed without the presence of a catalyst agent. To accelerate the reaction rate it is necessary to add a small quantity of a catalyst agent and thus scale the process at an industrial level. The reaction is strongly accelerated if an oxidising agent as the fluoride ion in small concentrations is used. This ion attack the iron and consequently FeF_2 and/or FeF_3 are formed as it can be observed from the Eh-pH diagrams [Peters-1970]. From Fig. 1, FeF_3 is the stable specie in the water stability region and at concentrations of the fluoride ion used in this work.

In fact, for the concentrations of the fluoride ion used in this work, FeF_3 is formed, which has a solubility of 0.091 parts in 100 parts of water. This means that all the FeF_3 formed is solubilized for the conditions used in this work. This explains the positive influence that small concentrations of fluoride ion has on the kinetic of the redox process, the conversion of silver ion into silver powder.

In practice the reaction stops until the concentration of the silver ion is small enough to give a 99.0 % of conversion or more. This suggests that FeF_3 dissolves and gives the necessary ion fluoride for the corrosion of the electrode and a new quantity of FeF_3 . This gives the necessary electrons for the conversion of silver ion to silver metal.

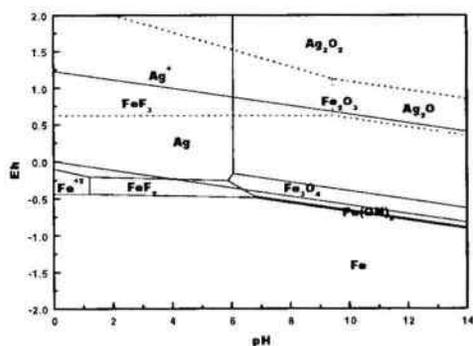


Figure 1- Eh-pH potential for the system Ag/Fe in aqueous media

Kinetic of the process

In Figure 2 the data for the conversion of silver ion to metal silver are represented at three temperatures.

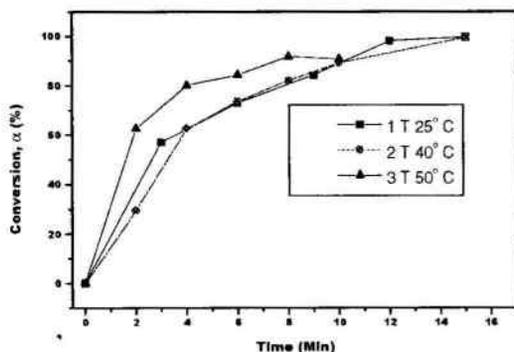


Figure 2-Graphical representation for silver ion conversion into silver metal at three different temperatures.

From the figure, the time for a maximum conversion is 15 minutes using an electrode area of 11.01 cm² for 40 ml of solution.

As it was discussed earlier from the thermodynamics results, the conversion from ion silver to metal silver is possible in the presence of fluoride ion as a catalyst agent. Although it is necessary to determine the rate conversion to know if the process is technically feasible. From the literature the reaction could be seen as an homogenous one. According with the Law Action Mass, reaction rate is proportional to the reactant concentration and can be expressed by the following equations [Habashi-1970]:

$$r = dC_A/dt \quad r = KC_A \quad (3)$$

where C_A is the concentration of the silver ion at time t . From these equations:

$$\frac{dC_A}{dt} = KC_A \quad (4)$$

Rearranging this equation and by integration:

$$K = \frac{1}{t} \ln \frac{C_{A0}}{C_A} \quad (5)$$

where K is the specific constant of reaction.

From the model, a graphical representation of $\ln C_{A0}/C_A$ versus time, t , must be a straight line if the proposed model is correct. Experimental results at three temperatures are represented graphically in Figure 3.

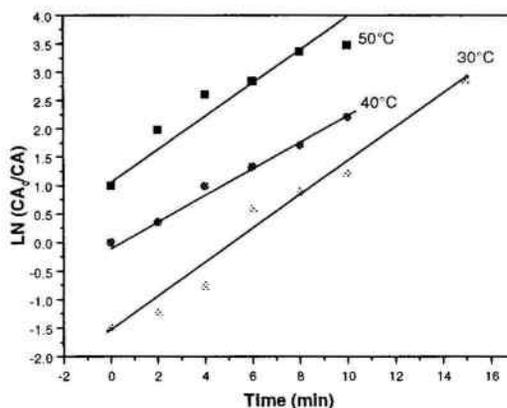


Figure 3-Graphical representation for a first order reaction of silver ion to silver metal conversion.

The experimental results shown in this figure fit to a straight line, which means that the consideration is correct.

From the equation (5) values for the rate constant can be determined as a function of the temperature. By using the Arrhenius equation, the activation energy of the process can be determined. In Figure 4 are represented the values of K versus $1/T$.

The data are fitted to an straight line and here the inclination of the line is $-E_A/R = m$. The activation energy is calculated as [Habashi-1970]:

$$E_A = 33.36 \text{ KJ/mol}$$

According to Habashi, this activation energy is typical value for a process controlled by a chemical reaction in the interface.

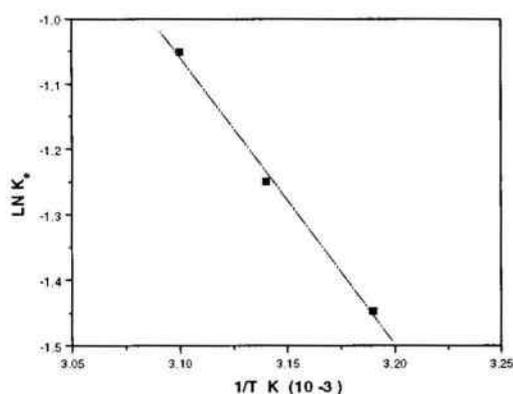


Figure 4. Graphical representation for rate constants at three different temperatures (30, 40 and 50 °C) .

In this case the produced silver metal is initially deposited on the surface of the electrode. Once big clusters are formed, due to the weight, the material is withdrawn from the surface to the solution and then sediments on the lower part of the reaction vessel where is recovered by decantation. Then it is rinsed with enough water to eliminate the residual iron oxide produced from the electrode.

X-ray diffraction of the powders

Silver metal is stable in an aqueous medium at room temperature, as can be seen from the Eh-pH diagram. In figure 5 is represented an X-ray diffraction patterns for the powders obtained from this process.

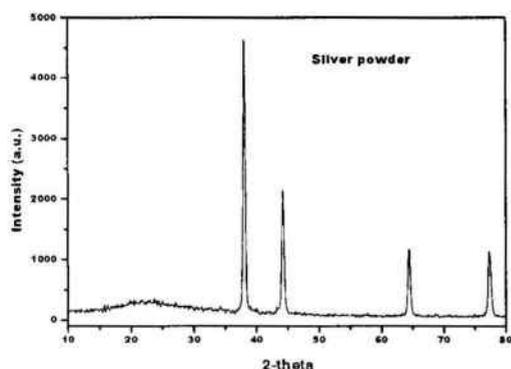


Figure 5. X-ray diffraction for the powder obtained from the process.

By comparing the pattern for the silver powder only silver metal is present in the final product of the reaction. This agree with the information obtained from the Eh-pH diagram.

Considerations about the proposed process.

When the iron electrode is introduced into the solution, silver metal is precipitated in the form of a a spongy mass. If colloidal particles of the metal are preferred, a tensoactive agent may be added to the mass to partially coat the metal particles and then redispersed by ball or high energy mill or other type.

Also, when metal particles are formed these may be recovered from the bottom of the vessel, dried and then pressed to obtain metal bars. When the purity of the metal is very important, it is necessary to melt the metal powder, taking into account the difference in temperature to melt the formed iron oxide. The flowsheet proposed for the process using a secondary source of silver is shown in Figure 6.

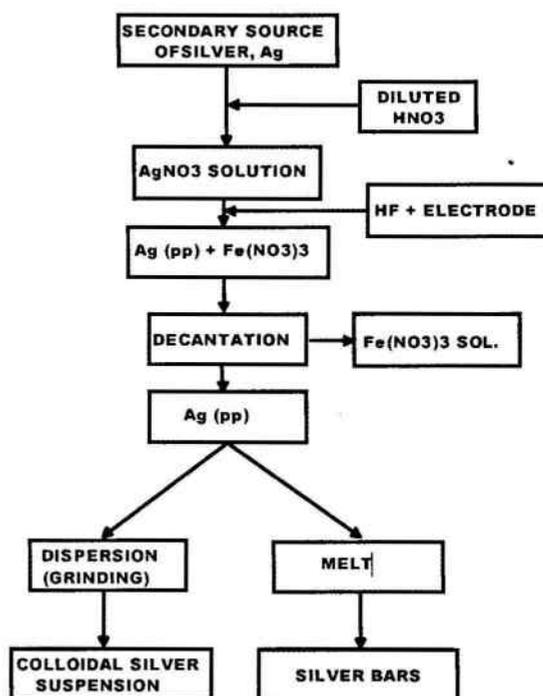


Figure 6. Solubilization and silver recover as a colloidal particles and bulk metal from the proposed process.

By-products may be recovered according to the flowsheet presented in the Figure 7.

From the flowsheet, an stoichiometric quantity of Ca(OH)_2 is necessary to precipitate the fluoride ion and hence, prevent environment pollution. From this way ion fluoride is withdrawn as CaF_2 .

This compound has a very low solubility constant, 2×10^{-6} . An additional quantity of Ca(OH)_2 will be necessary to obtain $\text{Ca(NO}_3)_2$ and hydrated iron oxide. Calcium nitrate has a variety of uses. Iron oxide with a high purity may be recovered and utilized as a pigment agent in the production of paints and in the magnet manufacture.

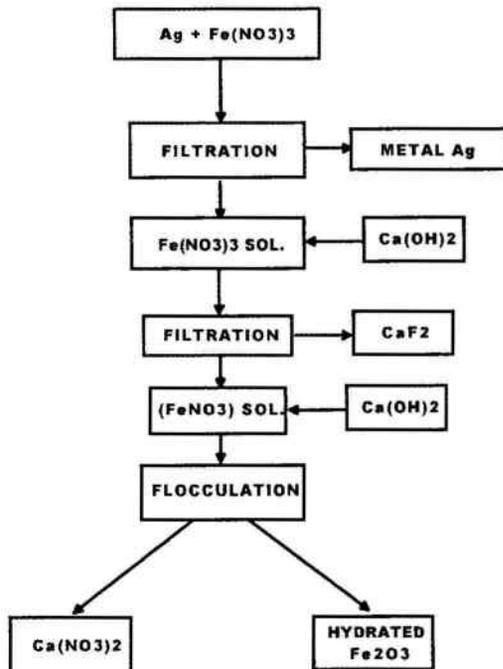


Fig 7. Flowsheet to recover waste materials from the proposed process.

CONCLUSIONS

- ✓ A new process to recover silver from a secondary source is described. The process include the solubilization of silver and cementation with an iron electrode in the presence of a small quantity of fluoride ion as a catalyst agent.
- ✓ The catalyst enhances the corrosion of the electrode and hence the liberation of the electrons to reduce the silver ion to silver metal. Also, the material of the electrode is not a special one and then the conversion is possible by using sheets or iron from waste.
- ✓ For the reaction there is no a considerable temperature dependence. Then the process can be carried out at room temperature resulting in a considerable energy saving.
- ✓ Silver deposition on the electrode is not a problem, clusters are separated by itself weight. This fact, facilitates the chemical-control reaction
- ✓ Thermodynamic and kinetic study of the process show that the process is technically feasible and that it is strongly dependent from the presence of a catalyst agent.

✓ Contamination of the product can be significantly reduced, by rinsing the obtained silver powder with destilated water.

ACKNOWLEDGEMENTS

The authors want to acknowledge Consejo Nacional de Ciencia y Tecnología (CONACYT), for their economic support, project number 28269-U

REFERENCES

- Chang R., Química. Primera edición en Español, Mc Graw Hill, 1992.
- Contreras Castro D., Experimentación de Minerales de Oro y Plata por el Proceso de Cianuración, Comisión de Fomento Minero, Boletín No. 8, México D.F., 1960.
- Habashi F., Principles of extractive Metallurgy Kinetics of Heterogeneous Reactions., Vol 2, Science Publishers, Paris.
- Hedley N., Tabachnik H., Chemistry of Cyanidation, Mineral Dressing Notes, American Cyanamid Company, No. 23, 1968.
- S.M.E. Short Course Bio-extractive Mining, Denver Colorado, February 1970.
- Schlitt W.J., Larson W.C., Hishey J.B. Editors, Gold and Silver Leaching, Recovery and Economics, Proceedings from 110th AIME Meeting, Chicago, 1981.
- Szczygiel Jordens Z., Torres Reyes A., Metalurgia no Ferrosa, Ed. Limusa Wiley México, 1984, 321-323.