

THIOUREA LEACHING OF GOLD-BEARING MINE WASTES FROM THE MADJAROVO PROCESSING PLANT IN THE SOUTH EAST OF BULGARIA

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ABSTRACT

The study presented in this paper deals with the issues concerned with the utilisation of floatation tailings produced in the past by plants in which complex sulphide gold-bearing ore was processed. The concentration of gold and silver in the tailings is found to be sufficiently high to justify starting a research programme for their recovery. A number of studies have shown that thiourea has potential for such treatment — treatment which is not amenable to cyanidation of ores or where environmental concerns make the use of cyanide compounds problematic.

The choice of thiourea in this research was motivated both by environmental and technological considerations. The region in question is environmentally sensitive because it is a border region of Bulgaria, and also because the *Arda* River, which is a major source of water supply, runs through the region. The impetus for the research was provided by the fact that the relatively high content of sulphides as a potential cyanide-consuming mineral is considered a major technological drawback necessitating the use of an alternative lixiviant such as thiourea.

A technical flow-sheet, developed for the recovery of gold and silver from mine tailings, is presented. It consists of the following operations: magnetic separation, floatation, hydrochloric leaching, and thiourea leaching. The purpose of hydrochloric leaching is to provide the oxidant required for the next stage of thiourea leaching and to expose the surfaces of the gold particles for further processing.

The method presented is typical of how suitable technologies could be developed for recovering valuable materials from potentially harmful wastes for reuse and/or recycling. It is argued that due attention should be paid to such technologies for reinforcing efforts at sustainable solid waste management.

Keywords: Bulgaria; mine; tailings; solid; waste; thiourea; gold; silver; environment; recycling.

1. INTRODUCTION

Continuing efforts are being made to identify lixivants that are effective for leaching gold out of gold-bearing materials, but excluding cyanide mainly because conventional cyanidation processes are not effective for treating ores that are refractory in character. Moreover, cyanide compounds are very toxic to both humans and animals. They are also known to have serious and adverse environmental impacts.

Bulgaria is a relatively small country where in the past gold-bearing mine wastes had been generated in large quantities close to the sources supplying water to the urban

areas. This emphasises the need for developing an alternative to the use of cyanide for leaching gold out of gold-bearing mine wastes.

Thiourea is known to possess properties that make it potentially a good substitute for cyanide for leaching gold out of gold-bearing materials. However, despite its faster kinetics than cyanide, so far its use in industrial operations of this kind has been limited. This is because a number of factors preclude its application on a wider scale, notably the high cost of the lixiviant and the fact that the route for the effective removal of precious metals from the solution is not yet well established. Clearly, further research and development is needed to address these persistent problems that could have significant implications for the environment.

During leaching gold is anodically oxidised to the aurous state. Subsequently it is presumed that gold stays in the solution only as an aurothiourea compound. However, for the acidic thiourea solutions, it is generally accepted that oxidising agents such as FeCl_3 , H_2O_2 , etc. oxidise not only the gold but also the thiourea to form formamidine disulphide (FDDS). Thus the mechanism of gold dissolution is directly linked to the automatic reduction process in which thiourea is spontaneously oxidised to FDDS in the process of forming gold. However, in spite of the considerable amount of work done so far, the precise role of FDDS in the process is not yet clear. Also, information is not available on the thiourea/FDDS ratio that has to be maintained in the system or on their synergistic effects. In an earlier study Gaydardjiev and Spassova (1992) have shown theoretically that FDDS is the most important compound for the leaching and separation of gold.

2. EXPERIMENTAL WORK AND RESULTS

2.1 *Experimental procedure*

In this work the material under investigation was tailings from the lead-zinc floatation of sulphide ore. To begin with, the entire waste pond containing the tailings was examined thoroughly. Single core drill samples containing varying amounts of precious metals, as well as representative samples, were then analysed. The purpose of this exercise was twofold: to arrive at realistic conclusions on the process itself, and to develop suitable technology for the treatment of such mineral resources.

Mineralogical, chemical and phase analyses of the samples were carried out, and the results showed that the only elements of interest were silver and gold. The silver and gold contents recovered were 5.6 and 1.2 g/tonne respectively. Also, mineralogical analysis suggested that the predominant rock mass consisted of quartz sand which, after proper treatment, could be rendered suitable for reuse in the glass manufacturing industry. Accordingly, the design of a combined process, with which all the valuable components of the waste could be recovered, was undertaken.

Flotation was performed in a pneumo-mechanical machine, called the 'Mechanobr', using 31 cells. The flotation collectors of the AERO Cyanamid series were used. Magnetic separation was carried out using the High Intensity Wet Magnetic Separator (HIMS), and leaching was performed in an agitator vessel using a mechanical stirrer. The solid/liquid ratio was kept at 1:1 under gravity filtration, and the agitation speed was kept constant. The elemental assay for both solid and liquid phases was accomplished by using ICPAES.

The precious metals contained in the tailings were first concentrated by froth flotation. The recovery of precious metals, which was less than 30 percent, was not satisfactory, however. Nevertheless, it was clear that this product could be realised as a mixture along with the concentrate produced in the plant as at present. It is also to be noted that the main objective of flotation is not to obtain a standard concentrate, but to separate the non-ferrous metals present in the flotation concentrate in order to prevent undesirable reagent consumption. The relatively high iron content of the ore (2.8 percent of Fe) is also a factor thought to be responsible for the low recovery rates of the precious metals. It was concluded therefore that, when the ferrous minerals were separated out, better results could be expected in terms of the recovery of the precious metals contained in the waste.

2.2 Removal of the iron-bearing components

The method employed for the removal of the iron-bearing components consisted of two stages. The first was that of using high-intensity magnetic separation, and the second that of salt-acid leaching. Samples representing flotation tails from the pre-flotation of the waste were subjected to magnetic separation. The non-magnetic fraction resulting from magnetic separation was then subjected to salt-acid leaching. The aim of this operation was to unwrap the gold particles; that is, to release them from the covered hydroxy-ferrous coatings by dissolving them, and, by so doing to expose the surfaces of the free gold particles for the next stage of thiourea leaching. Another purpose of salt-acid leaching was to provide in-situ FeCl_3 , which is an oxidant essential for thiourea leaching.

Salt-acid leaching was performed according to the methods of mathematical planning. Two different samples were subjected to leaching — the non-magnetic fraction resulting from the magnetic separation of tailings, and flotation tailings that were not subjected to magnetic separation. Three factors were examined: X1 denoting the concentration (degree of dilution) of HCl; X2 denoting the leaching time; and X3 denoting the pulp temperature. The parameter subjected to optimisation was Y (Y1 and Y2), which represented the minimum iron content present in the solid cake obtained after leaching. Normal regression analysis was carried out using results obtained from experiments.

The optimal values of the input and target parameters for the leaching of the non-magnetic fraction were found to be:

X1 = 1:19; X2 = 60 min; X3 = 59°C; and Y1 = 0.20%

The corresponding values for the leaching of the flotation tailings, that were not subjected to magnetic separation, were found to be:

X1 = 1:22; X2 = 62.5 min; X3 = 77°C; and Y2 = 0.43%

An analysis of the results obtained from these studies indicate that:

- (a) Due to the fact that the precious metal particles are very loosely connected to the magnetic iron minerals, the amount of these metals lost in the magnetic fraction is negligible.
- (b) By far the greater part of the precious metals tends to remain in the non-magnetic fraction which itself is subject to further treatment.
- (c) The quartz particles are also slightly recovered in the magnetic fraction, while the recovery rate for the ferrous minerals is in the neighbourhood of 50 percent.
- (d) Minimum iron content in the material was achieved when salt-acid leaching was preceded by magnetic separation.

2.3 Thiourea leaching — thermodynamic considerations

A detailed thermodynamic analysis of the leaching system was carried out before embarking on the experimental tests. The entire range of possible reactions for gold, silver and electrum were considered in the analysis by taking into account the effects of FeCl_3 , thiourea and its oxidised compounds (formamidine disulphide). A careful analysis of the thermodynamic parameters (free Gibbs energy, reaction constants, etc.) indicated that the compounds of disulphide performed a key role in the leaching system, because they were found to be in the most stable thermodynamic state.

2.4 Thiourea leaching at ambient temperature

Experiments for estimating the optimal leaching parameters at room temperature were conducted in accordance with the methods of the 'Latin quadrant' with simple 'pass' via the following stages: flotation, magnetic separation, and salt-acid leaching. The subjects of optimisation were concentrations of gold and silver in the post-leaching solution. Considering that salt-acid and thiourea leaching were performed separately, it could be presumed that the greater part of the iron ions had been removed with the liquor from the salt-acid leaching, and, accordingly, a lack of oxidants could be expected. In order to prevent this, it was decided to conduct thiourea leaching with an

additional supply of iron ions in the form of FeCl_3 . And, therefore, the consumption of FeCl_3 had to be considered in the factorial design.

According to the model obtained from the processed experimental data, the following values for the input parameters were estimated for both gold and silver:

pH = 2.0; thiourea consumption = 3 kg/t; FeCl_3 consumption = 650 g/t; and leaching time = 102 min.

It was concluded from the results of the experiments that the degree of silver dissolution was fairly insufficient, in fact much smaller than that of gold which reached 87 percent. The results also suggested that the consumption of thiourea should be considered a key factor especially for the silver leaching system. Also, the relatively low value of FeCl_3 consumption indicated that the additional supply of iron ions in the pulp was not significant. In other words, the remaining amount of iron ions in the filtrate after salt-acid leaching should be sufficient as an oxidant for the optimum performance of thiourea in the system. This was the reason why it was decided to test the possibility of combining the two operations, namely those of salt-acid leaching and thiourea leaching, into a single operation.

2.5 Combined salt-acid and thiourea leaching at higher temperatures

The optimal conditions, estimated for salt-acid leaching, showed that the maximum amount of ferrous ions in the filtrate after leaching (and therefore the maximum efficiency of the iron-removal operation) was achieved under higher temperatures. On the other hand, it is a well-established fact that such an environment facilitates thiourea oxidation in a number of steps, of which the first is that of disulphide formation. Also, thermodynamic studies of the system revealed that compounds containing disulphide were key to the functioning of the leaching system. Accordingly, it could be expected that higher temperatures, which maintained a favourable environment for disulphide formation, should have a catalytic effect on leaching kinetics. In order to test this hypothesis, a series of combined salt-acid and thiourea leaching experiments were performed at higher temperatures to study the influence of pulp pH on leaching kinetics. These experiments were carried out with the following parameters: pulp temperature = 60°C ; thiourea consumption = 3 kg/t, and degree of salt-acid dilution = 1:19. Results showed that maximum gold recovery rate was achieved when pH was maintained close to 3.5. The recovery rate for silver with this value of pH was found to be about 60 percent.

When we consider the practical aspects of thiourea technology in the context of its possible commercialisation, a major economic concern is that of high reagent consumption. An analysis of the test data suggests that the maximum leaching recovery rate for both gold and silver is achieved with a thiourea consumption of 1.3 kg/t and pH = 3.5. These findings vindicate our assumption that higher temperatures facilitate leaching processes and, at the same time, reduce the amount of reagent consumed.

Indeed, conclusions drawn from the thermodynamic analysis of the disulphide compounds that are key factors in leaching, are also in line with these findings.

3. CONCLUDING REMARKS

The following conclusions emerged from the study reported in this paper:

- (a) Within the temperature range studied, thiourea is found to behave favourably as a leaching agent for the recovery of gold, with a recovery rate of approximately 90 percent. However, a comparable recovery rate could be achieved for silver only under even higher temperatures.
- (b) It is possible to combine the processes of salt-acid and thiourea leaching into a single process. But this is contingent upon the development and solution of mathematical equations for estimating the optimal system parameters.
- (c) Operation at higher temperature facilitates the reduction of reagent consumption from 3 kg/t to 1.4 kg/t, accelerates leaching kinetics from 102 min. to 28 min, and lowers pulp acidity from pH = 2.0 to pH = 3.5.
- (d) The assumption made in the thermodynamic analysis of the system is validated by experimental results, namely that the disulphide compounds have a key role to play in the process, especially in the recovery of silver. Also, there is evidence to show that disulphide formation is facilitated at higher temperatures (Oudenne and de Cuyper, 1986).
- (e) Salt-acid leaching, either as a separate operation or combined with thiourea leaching, is essential for removing iron and also for exposing the surfaces of the gold particles by dissolving the hydroxy-ferrous compounds to form FeCl_3 which acts as an oxidising agent in the subsequent leaching of thiourea.
- (f) Thiourea would appear to have much potential for application in treatments that are not amenable to the cyanidation of ores, or when cyanidation could have serious environmental impacts. Further studies should be undertaken to develop further the use of thiourea in such treatments.
- (g) In Bulgaria there are far too many instances of improper treatment and disposal of mining and mineral solid waste of the kind described in this paper, and they are a persistent source of growing and potentially serious health and environmental impacts. However, due mainly to the unavailability of necessary skills and especially finance, rendering these wastes harmless is proving to be very difficult indeed. Ideally, strategies and economically viable technologies should be developed whereby valuable and/or useful materials could be recovered from such

wastes for reuse or recycling. If this could be done, it would contribute in good measure to the efforts that are currently being made for achieving at least a degree of sustainability in solid waste management.

The research, on which this paper is based, is a typical example of what can be done in this respect — in this particular case the recovery of precious metals from a potentially harmful waste, and, at the same time, rendering the residue of that waste harmless or at least less harmful.

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