Acquirement of Gold from Concentrate (Pezinok, Slovakia) with Utilization of Algae in Mechanochemical Processes

Jana Ficeriová¹, Erika Dutková¹, Zdenka Lukáčová¹, Jarmila Harvanová²

¹Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia
²University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 04181 Košice, Slovakia
ficeri@saske.sk

Abstract. The deficiency of primary raw materials and the difficult processing of sulphide concentrates with low gold content, as well as the long-time use of the dangerous cyanide method, instigated to the search a more effective and environmentally conscious method of acquirement this noble metal. For this reason, this work was focused on gold obtaining from a refractory sulphide complex concentrate (Pezinok, Slovakia) with the application of the non-cyanide mechanochemico-biological process. Gold in this complex concentrate occurs physically enclosed in the intercrystalline space of sulphide minerals, and is also isomorphic and fills structure defects in sulphides. The exclusion of gold from such complex mineral matrices of the concentrate can be achieved by using a mechanochemico-biological process. This innovative process makes possible obtaining of gold using an application of a thiourea solution, which is a convenient alternative opposite to the toxic cyanidation method. The utilized of the biological process with the application of algae has shown that algae with siliceous structures make it possible to obtain of gold from a complex concentrate (Pezinok, Slovakia) with dimension in the nano range. These algae are part of aquatic ecosystems and, in addition, are being food for other animals, utilizing for fuel production and, more recently, they are the important raw material for the production of hydrogen, methane and some types of biofuels. Limnetic algae (diatoms, golden algae) have unique properties, they create the largest mass of biomass of all plants on Earth and at the same time they are able to move. The mechanochemico-biological process is a method that enables to obtain gold nanoparticles 100 nm from the refractory sulphide concentrate (Pezinok, Slovakia). Mechanochemical activation of this concentrate and silica shells of the limnetic algae of tribes (Dinobryon, Surirella) in thiourea solution caused changes in physico-chemical properties of the minerals of gold as well as in the constituents of the algae minerals. These structural changes had under specific conditions a decisive influence on the exclusion of gold nanoparticles to the thiourea solution. The gold nanoparticles had subsequently fixed in the cellular matrix on mechanochemically activated alga shells. The reason for the fixation of gold nanoparticles was the action of biomolecules that algal cells during activation secreted while they defend against the chemical effect of metal ions present in the solution. Nanoparticles of gold were acquirement from the concentrate after less than two hours by described mechanochemico-biological process. In the case of mechanochemical activation of the concentrate, but without the activation of defined algae, the exclusion of gold nanoparticles was not confirmed even after a triple activation time.
(six hours). Owing to, the algae had to be activated to recover of gold from this sulphide concentrate. It follows, the entire mechanochemico-biological process had to be followed.

1. Introduction

The obtaining of gold from a refractory sulphide concentrates in Slovakia and abroad, stimulates many scientists and private companies to find solutions focused on the processing of these secondary sources with the aim of the acquirement of gold to the next of using for society in practice.

The problem of processing secondary sources with low gold content is in the center of attention of all the advanced economies of the world, with a strong emphasis on environmental protection. Obtaining this noble metal from secondary raw materials and reducing the environmental load by recycling requires a versatile strategy and, in particular, the use of cyanide-free methods. The cyanide leaching process is indeed highly toxic and also and substantially disadvantageous because the gold in the secondary sources is finely dispersed and cannot come into contact with the cyanide solutions. A very serious problem is also of liquidation of cyanide solutions and the handling of this substance. These justified reasons should be global avoided the use of cyanide technologies in obtaining gold.

However, the release of gold from complex mineral matrixes of sulphide concentrates is possible to achieve by the application of mechanochemico-biological processes [1]. The non-cyanide hydrometallurgical process of obtaining gold from concentrates by thiourea solutions is a preferred alternative to the toxic cyanidation method [2]. The thiourea compared to cyanide represents an ecologically acceptable leaching agent with exceptional kinetics and selectivity. Mechanochemical processes utilize high-energy milling and intensify processes through the formation of various surface and volume defects in solids. The main advantage of mechanochemical processes compared to traditional technologies is the smaller number of technological operations, the considerably shorter time required to obtain the desired product at favorable ambient temperatures, as well as the formation of nanostructures [3].

The biological method by using of freshwater algae with silicate shells in mechanochemical processes is considered to be a more environmentally friendly and efficient method than toxic cyanidation to recover gold from refractory sulphide of gold-bearing concentrates [4]. Presented innovative study is focused on the application of mechanochemico-biological process enables to obtain gold nanoparticles from the refractory sulphide concentrate (Pezinok, Slovakia). Mechanochemical activation of this concentrate and silica algae shells in thiourea solution increases the number of fine particles with a large specific surface area and some degree of disruption of the mineral components.

Currently present it is a direct necessity to deal with non-cyanide technologies of gold extraction in terms of his high value and specific properties as well as his irreplaceability in the fields of banking, healthcare, computer technology, rocketry, and aerospace and also in the production of goldsmiths products.

2. Experiments

2.1. Methodology

The chemical analysis of the samples was measured on a 240FS/240Z atomic absorption spectrometer (Varian, Australia). The specific surface area SA was determined by the low-temperature nitrogen BET adsorption method using a Gemini 2360 sorption apparatus (Micromeritics, USA). The morphology of the samples was monitored by scanning electron microscopy using EDX-FE method SEM Mira 3 (Tescan, Czech Republic). The particle size distribution was measured by photon cross-correlation spectroscopy using a Nanophox particle size analyzer (Sympatec, Germany). The amorphization of the samples was evaluated by the X-ray diffractometry method.
2.2. Mechanochemico-biological activation

Mechanochemico-biological activation was performed in a stirring ball mill Attritor Molinex PE 075 (Netzsch, Germany) with the volume of the milling chamber 500 ml. Sample of sulphide concentrate (Pezinok, Slovakia) 50 g, thiourea as the leaching medium 2 g and siliceous shells of limnetic algae of genera Dinobryon/Surirella (Třeboň, Czech Republic) 2 g together with sulphuric acid (to maintain the pH of the solution = 1) was milled with 200 ml of destilled water and 2000 g steel balls of diameter 2 mm as the milling media. The mill was operated at revolutions of milling shaft 600 min$^{-1}$ for milling time 120 min at ambient temperature.

3. Results and discussions

Complex sulphide concentrate (Pezinok, Slovakia) was selected as input material for the testing acquirement of gold with the utilization of algae in mechanochemical processes. The chemical composition of this concentrate is presented in Table 1.

| Components [g/t] | Components [%] |
|-----------------|----------------|
| Au 112          | Ag 154         |

Table 1. Chemical composition of the sulphide concentrate (Pezinok, Slovakia).

The mechanochemical activated of the complex concentrate in the mill Attritor is characterized by an increase in specific surface area. The effect of milling on the surface area of concentrate is summarized in Table 2. The original value of the surface area (0.49 m$^2$g$^{-1}$) increased to 3.4 m$^2$g$^{-1}$ without the use of algae. In the case of use algae, the Dinobryon/Surirella were measured the significantly higher values of the surface area 10.2 m$^2$g$^{-1}$ and 14.9 m$^2$g$^{-1}$.

Table 2. Specific surface area, $S_A$ for samples of concentrate (Pezinok, Slovakia): non-activated, mechanochemical activated (MA) and mechanochemical activated (MA)/type of algae.

| Samples            | $S_A$ [m$^2$g$^{-1}$] |
|--------------------|-----------------------|
| non-activated       | 0.49                  |
| MA concentrate      | 3.4                   |
| MA concentrate/Dinobryon | 10.2                  |
| MA concentrate/Surirella | 14.9                 |

The milling in stirred ball mill was led to amorphization of the gold-bearing minerals present in the concentrate, which ones decompose following of mechanochemical process with the utilization of algae to set nano gold free in the leach. The significant change after due to intensive milling was increased of the input value of the amorphization of the non-activated concentrate to 61% without the
use of algae (Table 3). In the case of use algae, Dinobryon/Surirella in the mechanochemical process were measured the considerably higher values of amorphization 84 to 92 %.

**Table 3.** Amorphization, A for samples of concentrate (Pezinok, Slovakia): non-activated, mechanochemical activated (MA) and mechanochemical activated (MA)/type of algae.

| Samples                      | A [%]  |
|------------------------------|--------|
| non-activated concentrate    | 0      |
| MA concentrate               | 61     |
| MA concentrate/Dinobryon     | 84     |
| MA concentrate/Surirella     | 92     |

Mechanochemical activation of sulphide concentrate (Pezinok, Slovakia) and siliceous shells of specified limnetic algae of genera (Dinobryon, Surirella) in the thiourea solution caused changes in the physico-chemical properties of gold minerals as well as algae mineral constituents. These structural changes had a decisive influence on the formation of gold nanoparticles (100 nm) into thiourea solution under the specific reaction conditions mentioned above, from which they were subsequently fixed in the cellular matrix of mechanochemically activated algal shells. The cause of the formation of gold nanoparticles was the action of biomolecules that algal cells secrete while they defend against the chemical effect of metal ions present in the solution. In the case of thiourea leaching of activated sulphide concentrate in the presence of non-activated algae, no nanoparticles of gold were obtained even after 6 hours (Figures 1A, 2C). Nanoparticles of gold were obtained after 120 minutes by described the mechanochemico-biological process after activating the concentrate and algae at the same time (Figures 1B, 2D).

**Figure 1.** SEM micrograph of the: A - non-activated sample algae Dinobryon and activated sample sulphide concentrate, B - mechanochemical activated sample (sulphide concentrate and algae Dinobryon), gold nanoparticles attached in algal cells.
Figure 2. SEM micrograph of the: C - non-activated sample algae Surirella and activated sample sulphide concentrate, D - mechanochemical activated sample (sulphide concentrate and algae Surirella), gold nanoparticles attached in algal cells.

4. Conclusions
The nanoparticles of gold obtained by the described way may have different uses in practice, such as accelerating the decomposition of hazardous substances or eliminating pollutants in contaminated water, soil, and air. Acquisition nanoparticles of gold through this process would also lead to the elimination of algae from the aquatic environment where they are dangerous not only for aquatic plants and animals but also for humans. For example, such an aqueous environment with algae Dinobryon and Surirella from the site (Třeboň, Czech Republic) are shown in Figures 3 and 4. It is generally known that defined algae absorb carbon dioxide and emit oxygen, thus playing an important role in preserving life on Earth.

Figure 3. The aquatic environment with algae Dinobryon (Třeboň, Czech Republic).

Figure 4. The aquatic environment with algae Surirella (Třeboň, Czech Republic).

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