

Leaching of gold from flotation waste by thiourea

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Abstract

Throughout human history, gold has been the most sought-after and well-known precious metal in the world. It is synonymous with wealth in the financial market and jewellery. However, its use has a wide range of applicability in biomedicine, electronic engineering and other industries. Primary gold resources are limited and have been significantly depleted in recent decades. To cover the current demand, it is necessary to process secondary sources containing gold such as heaps, tailings, lean ores or electrical waste. New and especially more efficient technological procedures are needed for the processing of these secondary sources. From an environmental point of view, a hydrometallurgical process is considered to be more appropriate than a pyrometallurgical process, in which very toxic fumes enter the air. This work investigates the leaching of gold from flotation wastes using thiourea. It is flotation waste that is the target group of materials that are a source of precious metals. An interesting gold content is present in our waste sample (Hodruša Hámre tailings pond), but its evaluation depends on the setting of suitable technological conditions. In this work, thiourea is used as an alternative leaching agent to toxic cyanide, which is banned in Slovakia and many countries around the world due to its high environmental risk. The results of the study are described with respect to the gold recovery under optimized thiourea leaching conditions.

Keywords

thiourea, gold leaching, non-cyanide leaching, flotation waste



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Introduction

The consumption of metals is increasing with the development and the massification of new technologies, which concerns a growing number of metals from the periodic table. These evolutions are increasing the pressure on the global supply chains, which in turn contributes to risks of scarcity for various metals. The extraction of metals from primary geological sources as well as recycling end-of-use consumer goods have to adapt to meet this soaring demand (Guillaume and Boltoeva, 2020)

Current technologies for processing primary and secondary sources of precious metals offer a wide range of ecologically and economically profitable work processes. The goal of today's consumer society, which places high demands on living standards, especially in the electronics industry, is to reduce production costs, albeit at the expense of environmental quality, product quality and, ultimately, human health. That is why in recent years, laws and legislative measures have been adopted at the national and international level, which tighten emission quotas and limit the factors of soil, water and air pollution. In Slovakia, too, there is a gradual tendency to balance the profit of precious metals not only in terms of input costs to the selling price of the product but also to take into account the management costs of processing waste and subsequent remediation or revitalization of the environment burdened by the production process. We are the only country in Central Europe that has an active mining activity of gold-bearing ore. The ban on the processing of this ore with dangerous sodium cyanide in our territory has both positive and negative responses. Although a foreign mining company exports gold-bearing concentrate outside Slovakia, it processes it by cyanide leaching. But it is only a matter of time before the ban on the use of cyanides is gradually extended to all developed countries around the world. For the time being, we still have to solve the issue of processing secondary material such as flotation waste, electrical waste and less balance stocks, in which precious metals are found in lower concentrations. However, safer technological processes for obtaining gold and silver are financially and sometimes more time-consuming. Therefore, we offer a summary of basic and well-studied methods in this area.

The hydrometallurgical process is currently a key technological process for the selective extraction of precious metals or unwanted heavy metals in the processing of lean ores with a possible recovery of almost all elements. (Boyden, 2016; Qi, 2017; Norgate, 2007).

Gold is a precious metal and is present in the earth's crust at an average concentration of 0.004 ppm (Li and Miller, 2006). It is a high-density metal that is characterized by high thermal and electrical conductivity. It is not subject to corrosion and is highly resistant to most acids, bases and salts. Thanks to its unique properties, it is used in electronics, biomedicine, the space industry, also for the production of jewellery, decorating porcelain and glass, or minting coins for the purpose of currency or as an investment commodity. In nature, gold represents the country's ore wealth; its largest primary resources are mined mainly in South Africa (South Deep gold mine), Russia (Olimpiada gold mine), South America (Chile Norte Abierto gold mine) and North America (Carlin Trend gold mine), Indonesia (Grasberg gold mine) and Australia (Boddington gold mine) (Li and Miller, 2006). The concentration of gold in these rich mineralizations is around 18-47 g / t and usually occurs in mineral systems containing mainly sulphides of other metals. The demand for gold is constantly growing, and its price on the world market has been at its highest level since World War II (i.e. \$ 1,886,400 per ounce). Consumption of gold is growing globally by about 7% per year (Kamar, 2007).

Gold, as one of the few metals, occurs in nature even in an unmerged state; otherwise, it is part of quartz veins and sulfide minerals such as marcasite (FeS_2), chalcopyrite (CuFeS_2) and pyrite (FeS_2), jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$), boulangerite ($\text{Pb}_5\text{Sb}_4\text{S}_{11}$), which were also mined and processed in Slovakia (Jesenák, 2011). The extracted ore is then converted to a concentrate by various technologies. It then enters the pyrometallurgical or hydrometallurgical process. Pyrometallurgical processing is not suitable due to volatile sulfur oxides and other heavy metals.

In hydrometallurgy, the leaching process is influenced by the surface heterogeneity of mineral structures and also by their solid phase properties (Baláž, 2000). Many sulphide minerals are characterized by heat resistance and considerable resistance to various chemical influences (Havlik, 1995). When extracting precious metals by the leaching system, difficulties arise due to significant variability in the composition of the elements. Therefore, it is not possible to unambiguously determine the most effective leaching system for all types of minerals. Many studies describe the successful leaching of gold by alternative methods in the absence of cyanide: leaching with thiosulfate (Zhu, 1994; Molleman and Dreisinger, 2002), leaching with thiourea (Deng and Liao, 2002; Murthy, 2003), leaching with halogens (Havlik, 1995; Li, 1992) and in thiocyanates (Fleming, 1986; Munoz and Miller, 2000). Of all these studies of non-cyanide reagents, thiourea was of the greatest importance in the chemical and metallurgical industries.

Materials and methods

The original mineral raw material represents polymetallic mineralization containing precious metals (Au, Ag, Cu, Pb, Zn) in quartz from the Slovak gold mine Rozália in the locality Hodruša - Hámre. Gold is bound to sulphides, quartz, pyrite and carbonates in the form of grains and thin wires in places as small as 2 mm. The waste was formed after foam flotation of ore composed of 90% andesite in a mixture with fine-grained pyrite and quartz (veins from 1-15 cm) (ŠGÚDŠ, 2011). The size of gold grains ranges from 10-40 μm as part of quartz or carbonates or as part of grains of polymetallic sulfides (galena, sphalerite, chalcopyrite) (Jesenák, 2011; Sulek, 2006).

Flotation waste, which was processed during gold extraction, was used from a sludge pond, which is situated near the village of Hodruša. As an unused product after the flotation process, it consists of a mixture of sands of a predominantly light grey colour.

Tab. 1. Results of monitoring the chemical composition of sediments in the Hodruša tailings pond in ŠHRO for the years 2007-2012

Fe	Al	Mn	Ni	Co	Pb	Zn	Cu	Cd	Cr	As	Sb	Hg
(%)	(%)	(%)	(g/t)	(g/t)	(g/t)	(g/t)	(g/t)	(g/t)	(g/t)	(g/t)	(g/t)	(g/t)
4.5	6.2	1.0	14.3	12.7	495.0	1082.2	360.0	5.5	27.7	13.0	7.2	0.1

Source: (ŠTÁTNY GEOLOGICKÝ ÚSTAV DIONÝZA ŠTÚRA (ŠGÚDŠ), 2013, Vplyv ťažby nerastov na životné prostredie, Správa za rok 2012, Spišská Nová Ves)

Results of analyzes in Tab. 1 confirmed a significant content of several heavy metals in the sediments of the tailings pond. A sampling of our sample was performed from a depth of 0 to 40 cm; then, it was homogenized and quartered.

XPS analysis

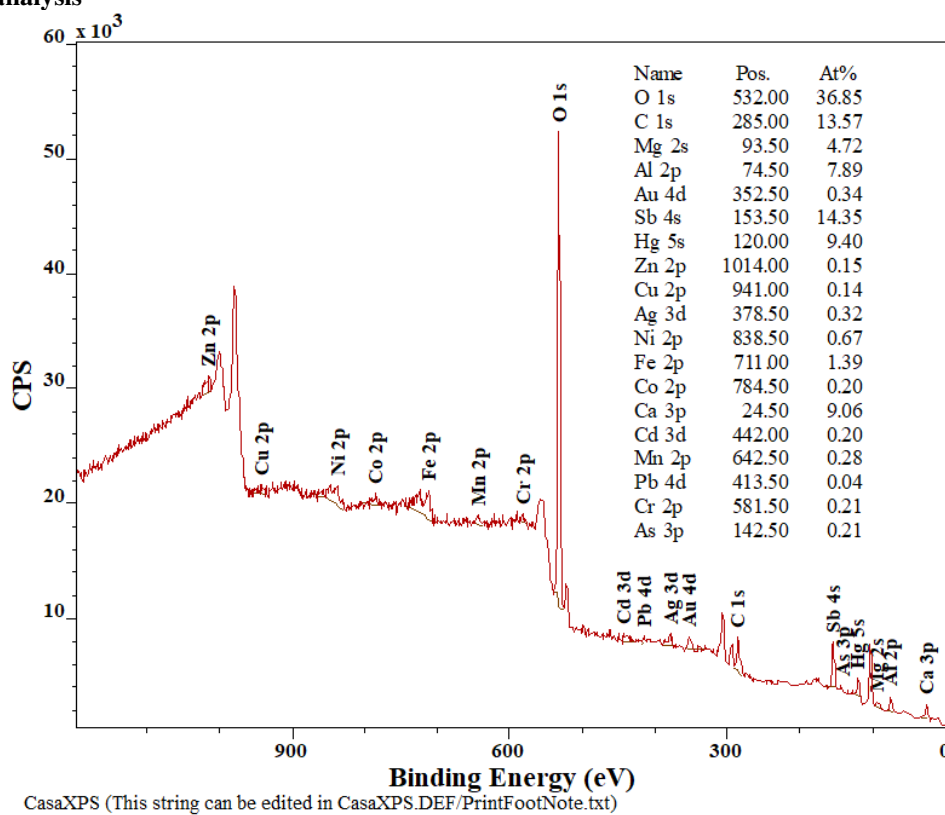


Fig 1. XPS analysis of the gold sample in flotation waste before thiourea leaching

Source: Author's analysis

The sample surface was characterized by X-ray photoelectron spectroscopy (XPS) spectral analysis on a SPECS instrument with a PHOIBOS 100 SCD electron analyzer at a non - monochromatic X-ray source. This analysis is a non-invasive method for the qualitative determination of the material surface to a depth of 10 nm. The measurement was performed at room temperature under an ultrahigh vacuum of 1.02×10^{-8} mbar, while the transition energy of the electrons was 70 eV using an AlK α anode. The measured data were processed by the CASA XPS software and modified by the Shirley and Tougaard method.

The analysis showed (Fig. 1) in the flotation waste, the proportion of gold 0.35% of the sample. The assumption of high content of other heavy metals such as antimony (Sb - 14.35%) and mercury (Hg - 9.40 %) was confirmed, which is an undesirable factor during processing.

Tab. 2: Chemical composition of the sample

	O	C	Mg	Al	Au	Sb	Hg	Zn	Cu	Ag	Ni	Fe	Co	Cd	Ca
%	36.75	13.53	4.71	7.87	0.34	15.28	9.38	0.15	0.14	0.32	0.66	1.38	0.20	0.25	9.03

Source: Author's analysis

High-resolution spectra of gold in flotation waste before thiourea leaching confirmed a presence of gold in an unbound form in oxidation state 0. The amount of gold in oxidation state 0 is 77.55%. The rest of the gold is in oxidation state +I. These results are in good agreement with Turner N.H., Single A.M., 1990.

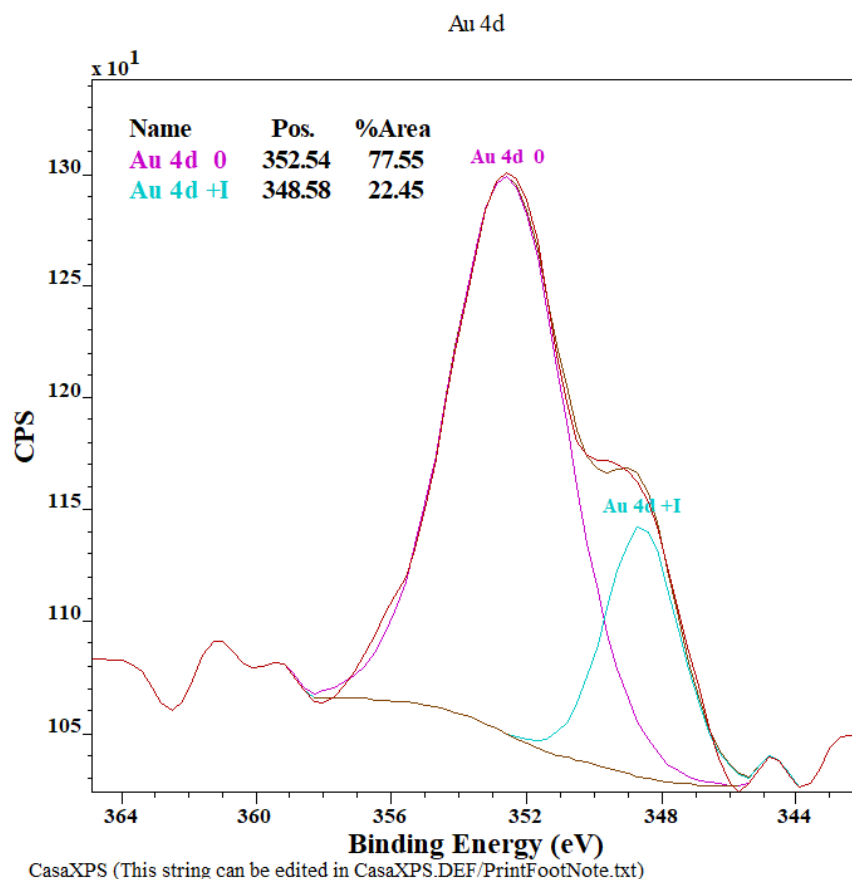


Fig. 2. XPS high-resolution spectra of gold

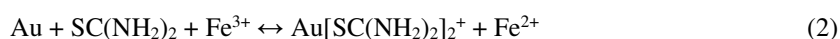
Source: Authors' analysis

Leaching process

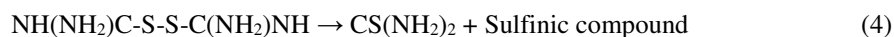
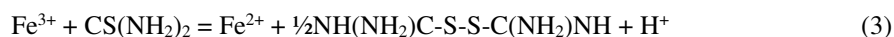
Cyanidation is the most widespread gold mining process in hydrometallurgy. A more environmentally friendly and safer alternative is the leaching of gold in a thiourea reagent. Leaching in sodium cyanide is not only very toxic but also requires a highly alkaline environment, and the leaching time is more than 24 hours. In addition, cyanidation has been found to be inefficient for some complex and highly resistant mineral complexes such as sulfides and carbonates. The result is high consumption and low gold recovery. Leaching in thiourea is less toxic; it takes place in an acidic environment and at the optimal time of 2-4 hours. Of course, much depends on the type of mineral and the preparation of the sample itself. Many works define ideal conditions for thiourea leaching at a redox potential of 200 mV, pH 1.5, and with 0.4% thiourea, 90% of gold has been leached after 2 hours. The rate of consumption of thiourea was higher - 25 kg / t. The reactions proceed according to the following Eq. 1 and 2 (Li and Miller, 2006):



The thiourea solution forms with Au^+ a stable cation complex $\text{Au}[\text{SC}(\text{NH}_2)_2]_2^+$ (as shown in Eq. 2). However, the gold ion Au^{3+} oxidizes the thiourea during the leaching and reduces itself to the gold ion Au^+ and only then passes into a stable complex with the thiourea as in Equation 1. This is why an acidic environment in leaching with $\text{pH} < 3$ is suitable. It had the best effects of ferric sulfate (Li and Miller, 2006).



The preferred oxidant is ferric sulfate for its mild oxidation potential and rapid gold dissolution kinetics. An important fact is that the standard potential of the iron / iron ion pair is 771 mV and the potential of thiourea / formamidine disulfide is 420 mV. Therefore, we can say with certainty that an excessive amount of ferrous iron causes the decomposition of thiourea. The first oxidation product of thiourea using ferrous iron is formamidine disulfide, and its presence has been demonstrated by HPLC and UV / visible spectroscopy (Bukka et al., 1992). Formamidine disulfide can be further decomposed according to the following reaction equations (3), (4), (5) (Li and Miller, 2006):



Formamidine disulfide may decompose or oxidize irreversibly during leaching in solution, and this causes high consumption of thiourea (Li and Miller, 2006). Therefore, we can state that the reaction between thiourea and ferrous iron is the main cause of thiourea decomposition.

However, it is difficult to draw a general conclusion for optimal conditions for gold leaching in thiourea from the fact that all studies have worked with different mineral systems and under different conditions. In this context, experiments were started, and a detailed study was performed on the dissolution kinetics of gold in flotation waste. All experiments with the dissolution of gold in acidic thiourea solutions and using ferric sulphate as an oxidizing agent were designed to investigate the effect of leaching under different conditions. It was important to determine the parameters that control and positively affect the kinetics. The results are presented in this article. As a reference point, the experiments were performed at an initial concentration of thiourea of 10 g/l and ferric sulfate 5 g/l with a constant ratio of 2:1. The conditions were determined with emphasis on the efficient, economical and environmental aspects of the leaching system.

Results and discussion

The leaching experiments were performed in a glass reactor at a constant ambient temperature of 20°C. The solution was freshly prepared for each experiment. The initial volume of the solution was 500 ml, and the $\text{pH} < 3$ was continuously adjusted by the addition of hydrochloric acid. Ferrous sulphate (5 g/l) was used as an oxidizing agent, and the concentration of thiourea in both cases was 10 g/l.

Tab. 3. Input material analysis and flotation waste analysis.

Conditions	Input raw material	Flotation waste
Analysis – Au content (g/t)	22	1.2
Recovery (g/t)	13.7	1.0
Recovery (%)	62	83

After 4 hours of leaching the flotation waste, the gold recovery was an optimal 83%. The recovery of gold from the input raw material was 62%, which is significantly lower than the sample from the sludge (Fig. 2). The difference in gold recovery was due to the different grain size of the material. The larger reaction surface of the sludge material sample exposed the free surfaces of the gold particles, which subsequently reacted with the thiourea to form a stable complex.

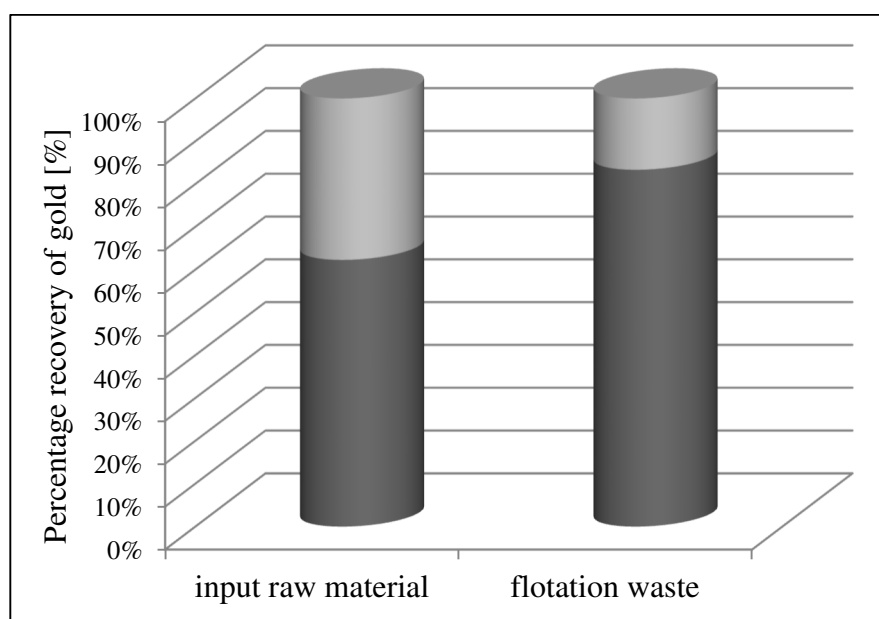


Fig. 3. The percentage recovery of gold from feedstock and flotation waste after leaching in thiourea.

Source: Authors' analysis

An experiment to determine the kinetics of gold leaching from flotation waste in thiourea was performed at room temperature 20 °C. The concentration of thiourea and ferric sulphate was constant in all cases. The leaching times were set at 120, 240, 360 and 480 minutes at a constant mash density and constant stirring (570 min⁻¹).

Tab. 4: Kinetics of gold leaching from flotation waste in thiourea.

	Flotation waste			
	120	240	360	480
Weight of sample (g)	113.8	113.8	113.8	113.8
Weight of CS(NH ₂) ₂ (g)	5	5	5	5
Weight of Fe ₂ (SO ₄) ₃ · 9 H ₂ O (g)	2.5	2.5	2.5	2.5
Leaching time (min)	120	240	360	480
Stirring (min ⁻¹)	570	570	570	570
Analysis – Au content (g/t)	1.2	1.2	1.2	1.2
Recovery (g/t)	1.0	0.9	1.0	0.9
Recovery (%)	83.3	75.0	83.3	75.0

The results show that a sufficient time for leaching gold from flotation waste is an initial value of 120 minutes. The subsequent extension of the experiment is insignificant due to the linear course of the curve, which represents the upper limit of the leaching process.

Tab. 5. Influence of thiourea concentration on gold leachability.

Flotation waste				
Weight of sample (g)	113.8	113.8	113.8	113.8
Weight of CS(NH ₂) ₂ (g)	5	7.5	10.0	12.5
Weight of Fe ₂ (SO ₄) ₃ · 9 H ₂ O (g)	2.5	3.8	5.0	7.5
Leaching time (min)	240	240	240	240
Stirring (min ⁻¹)	570	570	570	570
Analysis – Au content (g/t)	1.2	1.2	1.2	1.2
Recovery (g/t)	0.9	1.0	1.0	1.0

Increasing the concentration of thiourea above 10 g/l does not affect the leachability of gold. Therefore, from an economic and environmental point of view, it is appropriate to use this lowest concentration of thiourea.

Tab 6. Effect of mixing on the leachability of gold from flotation waste

Flotation waste		
Weight of sample (g)	113.8	113.8
Weight of CS(NH ₂) ₂ (g)	5	5
Weight of Fe ₂ (SO ₄) ₃ · 9 H ₂ O (g)	2.5	2.5
Leaching time (min)	240	240
Stirring (min ⁻¹)	570	-
Analysis – Au content (g/t)	1.2	1.2
Recovery (g/t)	0.9	0.6

Summary and conclusion

The global trend of using secondary raw materials and mining of less balance deposits of precious metals is also current in Slovakia. We have important mining areas for copper and iron ores. The relatively high proportion of precious metals, gold and silver in polymetallic ores attracts investors from abroad. Gold-bearing ore has been successfully mined in Banská Hodruš for decades, which is currently the last active mining area in gold mining in Slovakia. At present, mining is ensured by quality technology, and complications occur only with the efficient extraction of precious metals from mineral complexes.

Leaching processes as part of hydrometallurgy have more advantages in recovering precious metals from secondary materials and lean ores than their pyrometallurgical processing. With tightening emission quotas, it is better to invest in a greener leaching agent than to pay fines for exceeding them. The most suitable chemical way to recover gold is to leach the material with thiourea in a strictly acidic environment and experimental study of noble metal extraction by this method under different conditions. Our goal was to design the ideal conditions for the chemical leaching of gold from flotation waste in terms of economically viable, environmentally acceptable and technologically manageable. Experimental results showed that at room temperature 20°C and a leaching agent concentration of 10 g / l, 83% of the gold had already been leached out of solution after 2 hours. However, the consumption of thiourea was a significant 44.25 kg / t to flotation waste (2 € / 1 kg). This value of the reagent concentration is maximal; further increasing it under the same reaction conditions does not lead to more efficient extraction. It is convenient to significantly reduce the consumption of the leaching agent and to adjust the reaction conditions (temperature, appropriate choice of oxidizing agents, possible chemical pretreatment and reuse of the leaching agent). From an economic point of view, this leaching mechanism is not acceptable, as the method of recovering Au from the solution after leaching has not been solved experimentally. The complexity of these technological nodes requires a more detailed and long-term analysis of chemical factors.

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