



## **NEW POSSIBILITIES IN LEACHING OF GOLD ORES**

Lappeenranta–Lahti University of Technology LUT

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### **ABSTRACT**

The thesis is oriented to alternative methods for cyanide leaching in gold processing. This thesis aims to show the methodology of new leaching processes, point out possible alternatives in the market for processing raw materials and approach the research process of new reagents on samples from waste after flotation processing of gold ores. The thesis is bringing a closer look at the functioning of methods that have the potential to substitute banned cyanide leaching. In the experimental part, the thesis focuses on three different leaching methods, emphasising factors influencing the processes.

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## SYMBOLS AND ABBREVIATIONS

### Symbols

°C	degree Celsius
$\text{g.cm}^{-3}$	gram per cubic centimeter
$\text{g.kg}^{-1}$	gram per kilogram
g/l	gram per liter
g/t	gram per ton
kg/t	kilogram per ton
$\text{mg.l}^{-1}$	mass concentration, milligram of the given substance per unit volume (liter)
ml	milliliter
mm	millimeter
Ppm	parts per million
Q	quantity
t	time
$\mu\text{m}$	micrometer
wt. %	mass percentages

### Chemical formulas

CaO	Calcium oxide
Cu	copper
$\text{Fe}_2\text{O}_3$	Iron oxide
$\text{H}_2\text{O}$	water
$\text{H}_2\text{SO}_4$	Sulfuric acid

HCN	Hydrogen cyanide gas
CH <sub>4</sub> N <sub>2</sub> S	thiourea
I <sub>2</sub>	iodine
N	nitrogen
Na <sub>2</sub> O	Sodium oxide
NaCN	Sodium cyanide
NaOH	Sodium hydroxide
NH <sub>4</sub> <sup>+</sup>	ammonia
O <sub>2</sub>	oxygen
PbO	Lead oxide
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	thiosulfate
Sb	antimony
Zn	zinc

#### Abbreviations

AES	Atomic emission spectrometry
CIL	Carbon in leach
CIP	Carbon in pulp (coal in a container for adsorption)
DES	Deep eutectic solvents
ICP	Mass spectrometry with inductively coupled plasma
IL	Ionic liquids
RPM	Revolutions per minute
RRSB	Rosin, Ramler, Sperling and Bennet distribution

## Table of contents

Abstract

Acknowledgements

Symbols and abbreviations

1	Introduction .....	5
2	Gold and its extraction.....	6
2.1	Precipitation .....	7
2.1.1	Electrolysis.....	7
2.1.2	Cementation .....	8
2.1.3	Crystallization.....	9
2.2	Flotation .....	9
2.2.1	Surface properties of particles .....	11
2.2.2	Surface character of gold .....	12
2.2.3	Reagents used in flotation.....	13
3	Leaching of gold.....	14
3.1	Cyanidation .....	16
3.2	Thiosulfate leaching .....	18
3.2.1	Advantages.....	19
3.2.2	Disadvantages .....	19
3.3	Thiourea leaching.....	20
3.4	Leaching in ionic liquids and deep eutectic solvents .....	22
3.5	Leaching with reagent CNLite .....	26
3.5.1	Usage .....	26
3.6	Fire assay - gold content analysis.....	27
3.6.1	Preparation .....	28
3.6.2	Collection.....	29
3.6.3	Separation .....	30
4	Experimental part .....	32
4.1	Description of the sample.....	32

5	Leaching of gold-bearing ore waste after flotation treatment in thiourea solution .....	36
5.1	Thiourea leaching results for gold.....	38
5.1.1	Gold leaching kinetics .....	40
5.2	Thiourea leaching results for antimony.....	40
5.2.1	Antimony leaching kinetics .....	42
6	Leaching of gold-bearing ore waste after flotation treatment in deep eutectic solvents	43
6.1	Leaching results in deep eutectic solvents for gold .....	45
6.1.1	Gold leaching kinetics .....	46
6.2	Leaching results in deep eutectic solvents for antimony .....	46
6.2.1	Antimony leaching kinetics .....	48
7	Leaching of gold-bearing ore waste after flotation treatment with CNLite reagent ....	49
7.1	Results of leaching with CNLite reagent .....	51
7.1.1	Financial aspect of the experiment .....	53
8	Conclusion.....	54
	References.....	57



## FIGURES

Figure 1. Macroscopic gold (Krupka, 2021).....	6
Figure 2. Flotation cells (Made-in-China, 2022).....	10
Figure 3. Flotation process (VSB-TUO, 2021).....	10
Figure 4. Flotation foam.....	11
Figure 5. Hydrophilic and hydrophobic particles (Tahir&Rafique M.&Rafique M.S., 2020, 130).	12
Figure 6. Impact of collectors on contact angle (Michaud, 2015) .....	12
Figure 7. Adsorption of gold on active coal surface (Michaud, 2013) .....	14
Figure 8. Influence of the gold presence in the ore on leaching kinetics (Špaldon, 1986, 11–15) ..	15
Figure 9. Carbon in leach process scheme (Michaud, 2013) .....	17
Figure 10. Thiourea (ChemCraft Ltd., 2022).....	21
Figure 11. Choline chloride (NIH, 2022).....	23
Figure 12. Deep eutectic solvents (Soltanmohammadi&Jouyban&Shayanfar, 2021, 439).....	24
Figure 13 Separation scheme of 2 compounds using iodine as electrocatalytic oxidation agent (Jenkin et al., 2016) .....	25
Figure 14. Reagent CNLite .....	27
Figure 15. Ceramic crucible with melted sample (Jenkin et al., 2016, 18–24) .....	29
Figure 16. Collection of metals (IMPI, 2015).....	30
Figure 17. Pb ball (IPMI, 2015).....	31
Figure 18. Nature of the sample used for leaching experiments .....	32
Figure 19. Particle size distribution curve.....	35
Figure 20. Preparation of chemicals for experiments .....	36
Figure 21. A trio of leaching experiments with different temperatures .....	37
Figure 22. Filtration of the leached material .....	38
Figure 23. Kinetics of gold leaching in thiourea solution .....	40
Figure 24. Leaching kinetics of antimony in thiourea solution.....	42
Figure 25. Chemicals .....	43
Figure 26. Kinetics of gold leaching in deep eutectic solvents .....	46
Figure 27. Leaching kinetics of antimony in deep eutectic solvents.....	48
Figure 28. Constant mixing of the material.....	49
Figure 29. Leaching process with CNLite with automatic NaOH control .....	50

## TABLES

Table 1. Chemical composition of the sample .....	33
Table 2. Au content in grain size fractions .....	33
Table 3. Results of gold leaching - thiourea.....	39
Table 4. Results of leaching antimony - thiourea.....	41
Table 5. Leaching results for gold - DES.....	45
Table 6. Leaching results for antimony - DES.....	47
Table 7. Results of the leaching of the Hodruša-Hámre control sample.....	51
Table 8. Results of the leaching of the Čučma sample .....	52

# 1 Introduction

This thesis's assigned topic is "New possibilities in leaching of gold ores".

Gold is a very desirable raw material, and the demand for it increases in proportion to the development of new technologies. This demand calls for research in the field of financially efficient mining and treatment of gold-bearing ores. This work focuses precisely on the recovery of gold from tailings after treatment, thus tracking the recovery of gold from less enriched ores, where there is still a useful residual component. Due to the law restrictions concerning cyanide gold leaching, there is a need for alternative leaching reagents that would bring similar leaching results with required effectivity. Alternatives must show promising gold leaching results, be financially reasonable and meet health and environmental standards. In this master thesis three leaching agents were examined, to study their leaching effect on chosen sample. Market currently offers several other conventional gold leaching technologies. However, their effectiveness does not allow them to be used for ores with lower gold content. Due to this boundary a lot of usable flotation waste is not furtherly processed, which is also the case of sample examined during experiments in this master thesis. Unused material usually occupies an area that could be reclaimed and used for other purposes. Leaching with appropriate reagent could not only bring economically favorable reprocessing option for material stored in mentioned localities, but also be used on directly processed gold ores, which would on one hand result in a lower amount of waste and at the same time increase the profit for gold processing companies.

## 2 Gold and its extraction

Gold has many important properties, which are reflected in its price. It is also rare from the point of view of representation in the earth's crust. It is not only its appearance, but mainly its high thermal and electrical conductivity, malleability, resistance to many factors and corrosion. It is widely used in electrical engineering and electronics, but it is also used in industries such as construction and various branches of medicine, all because of the above-mentioned properties. (Franzen&Mesarčík, 2006, 24–25)

For the reasons mentioned above, scientists are still trying to come up with methods that would be able to extract gold as efficiently as possible and process it appropriately. There are multiple gold mining techniques in the world. The choice of a suitable method also depends on the nature of the occurring gold - whether it is gold in macroscopic (Figure 1) or microscopic form. In the case of macroscopic gold, it is possible to obtain it by gravity methods. Other methods such as flotation are used for microscopic Gold below 75  $\mu\text{m}$ . If none of the methods can effectively release the gold, the leaching method or a combination of the mentioned methods comes into play. Give a brief introduction to what each chapter is about. Write at least two sentences under the chapter heading. (Franzen&Mesarčík, 2006, 24–25)



Figure 1. Macroscopic gold (Krupka, 2021)

Gold is the most inert metal. It fuses with only a small number of metals. It is most often found with silver. Atomic gold is distributed in the crystalline lattice of sulphide minerals. It is usually concentrated in arsenopyrite, the highest known concentration being 17 700 ppm. In larger arsenopyrite crystals, it is mostly arranged inhomogeneously. Therefore, the gold that occurs in sulfides below 20  $\mu\text{m}$  is more significant. Colloidal gold is more commonly present in pyrite than arsenopyrite. Its size varies between 5-500  $\mu\text{m}$ . It is more reactive than coarser gold, thanks to a larger surface area – it is soluble even in lower concentrations of the cyanide solution. (Chryssoulis&McMullen, 2005, 21–71)

## 2.1 Precipitation

Precipitation is a crucial operation after the leaching process, thanks to which it is possible to obtain the final product - a beneficial component. There are several methods of metal precipitation and choosing the proper one depends on several factors. (Špaldon, 1986, 84)

The most important factors in precipitation include:

- Nature of the raw material
- Composition of the solution
- Product purity
- Other (the price of electricity, price of reagents, safety)

The most famous methods of metal precipitation:

- Electrolysis - precipitation with direct current
- Cementation based on substitution reactions
- Crystallization

### 2.1.1 Electrolysis

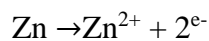
It is most often used to obtain metals from solutions after leaching. This method has two variants:

- Electrolytic precipitation
- Electrolytic refining

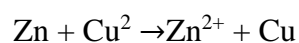
The difference between precipitation and refining is that refining occurs with soluble anodes (they dissolve under current action). Cathodes are used to transfer current in the electrolyte and discharge cations. They are insoluble. Electrolytic refining does not consume electricity, which means that energy consumption is much lower. (Špaldon, 1986, 84)

### 2.1.2 Cementation

If metal is immersed in a solution of its own salt, the result will be a transition into the solution in the form of ions. This creates a potential difference between the electrode and the solution. An example is zinc, a less noble metal, which easily loses ions and quickly goes into solution. (Špaldon, 1986, 84)



This phenomenon can be demonstrated in a copper sulfate solution in which a zinc plate is immersed. (Špaldon, 1986, 84)



Similar examples are displacement from solution in the case of copper by iron, cadmium and gold by zinc. The rule is that a more noble metal will displace a less noble one. (Špaldon, 1986, 84)

### 2.1.3 Crystallization

It is used in hydrometallurgical processes to obtain products or purify the solution from impurities. This process includes two steps:

- Germ formation
- Crystal growth

Germs can be formed either naturally or by adding solid substances to the solution. These create a surface on which crystals can grow. An example is  $\text{Al}(\text{OH})_3$  particles. The supporting factors for crystal growth are rapid cooling, mixing, purity of the solution, high concentration, and the presence of sharp points. (Špaldon, 1986, 84)

## 2.2 Flotation

Flotation is one of the essential processes in the treatment of gold-bearing ores. By mechanisms of flotation process the gold content in processed mass can be increased by the way of separating particles with gold content and particles without gold content or low gold content. Particles with gold content are influenced in the way they change the character to hydrophobic and are rising above the liquid phase in bubbles. Hydrophilic particles do not have tendency to connect with bubbles and are forced by gravitational power to sediment in liquid phase. Whole process is explained in more detail later in this chapter.

This step plays a vital role in the gold leaching itself because it changes the character of the grains contained in the material - the flotation concentrate contains higher values of gold contents than the waste after flotation. The samples included in this diploma thesis, on which the leaching experiments were performed, were also treated by flotation. (Kmet', 1992)

Treatment of raw materials through flotation is based on the physical and chemical properties of the grains intended for separation. Its principle uses the different abilities of minerals to stick to the surface of the phase interface. Flotation occurs in specially adapted devices called flotation cells that can be seen on a scheme on Figure 2. (Kmet', 1992)

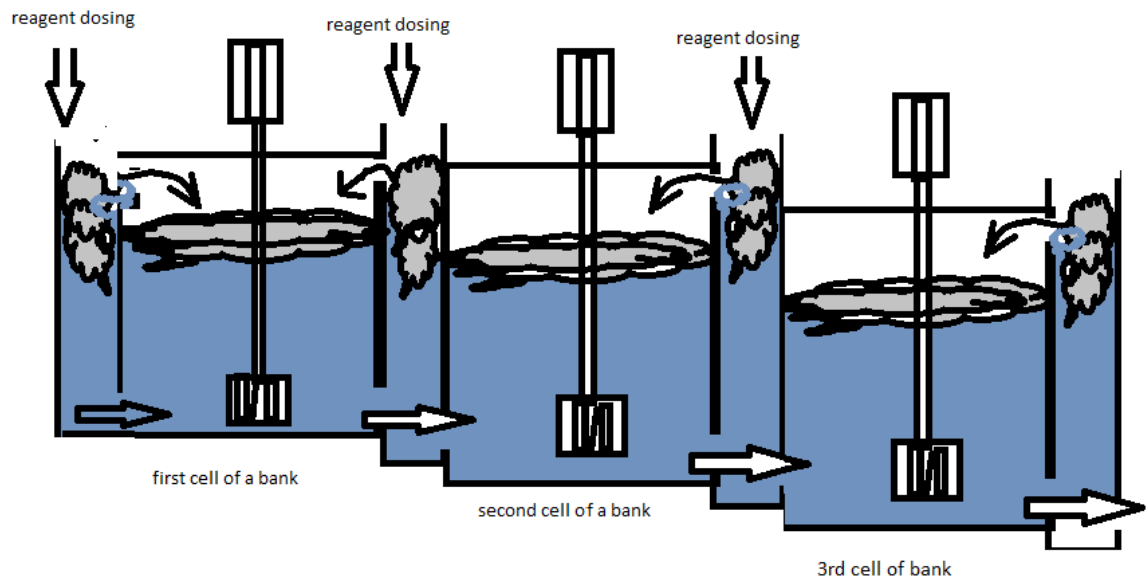


Figure 2. Flotation cells (Made-in-China, 2022)

Adsorption of reagents at the interface of the solution and mineral surfaces changes the free surface energy, thereby affecting the possibility of mineral flotation (Figure 3). (Kmet', 1992)

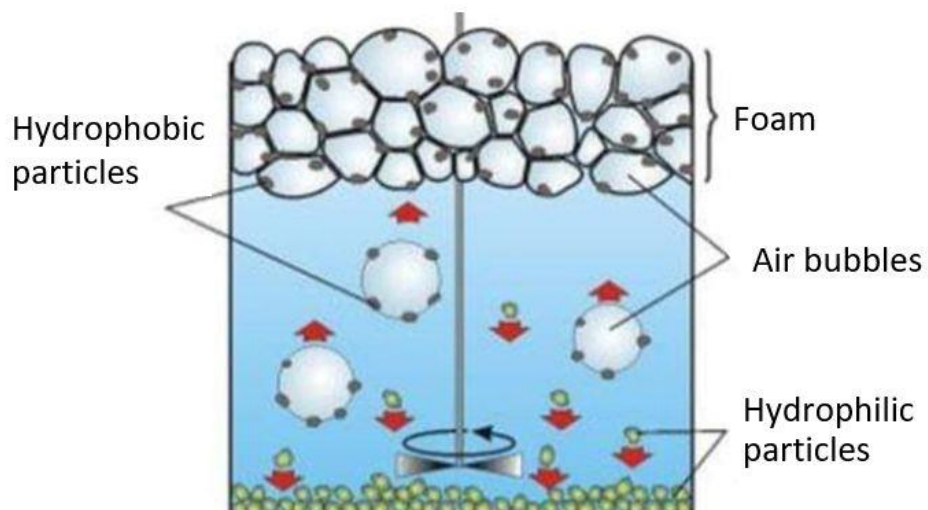


Figure 3. Flotation process (VSB-TUO, 2021)



Thanks to the surfactant, the gold grains become hydrophobic. These grains try to escape the aquatic environment, which is facilitated by rising air bubbles. Air bubbles settle in the foam product on the surface. The foam (Figure 4) is skimmed off to form a concentrate. (Manhattan Gold&Silver, 2014)



Figure 4. Flotation foam

### 2.2.1 Surface properties of particles

Hydrophobicity was derived from two words of Greek origin: hydro, meaning water, and phobos, meaning fear. A hydrophobic surface is a surface that has the ability to repel water. The hydrophobicity of the surface can be measured by the size of the contact angle between the water droplets and the surface of the solid phase. Water droplets in contact with a hydrophobic surface will flow easily and maintain a spherical shape. The contact angle to the surface of the solid phase will have a value greater than 90 degrees, while materials with a significant contact angle greater than 150 degrees are considered superhydrophobic. The opposite are hydrophilic surfaces on which water drops touch a larger part of their surface, and their contact angle is very small and does not exceed the value of 90 degrees. A graphical display of angles is shown in Figure 5. (Tahir&Rafique M.&Rafique M.S., 2020, 119–138)

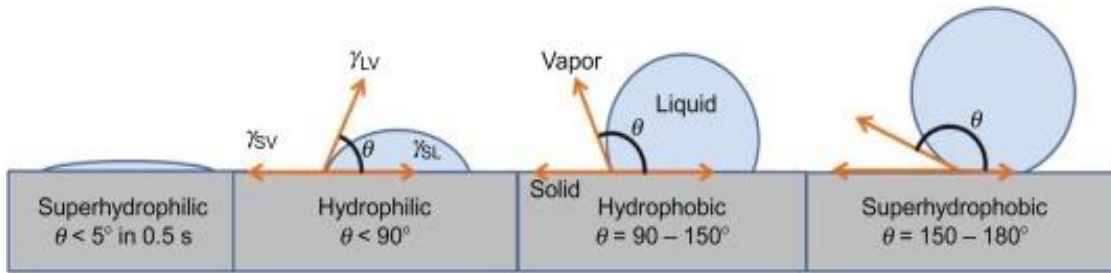


Figure 5. Hydrophilic and hydrophobic particles (Tahir&Rafique M.&Rafique M.S., 2020, 130)

### 2.2.2 Surface character of gold

Several research works have dealt with the hydrophilic or hydrophobic nature of pure gold and the related measurement of the contact angle of gold. After various investigations of the surface of gold and reassessment of whether or not there is a contact angle on gold, scientists concluded that the surface of pure gold is hydrophilic; therefore, the contact angle represents a zero value and cannot be measured. In cases where contact angles were measured on the surface, it became clear over time that this was not due to the properties of gold, but the cause was the remains of organic contaminants on the surface of the particles. (Dunne, 2016, 315–338)

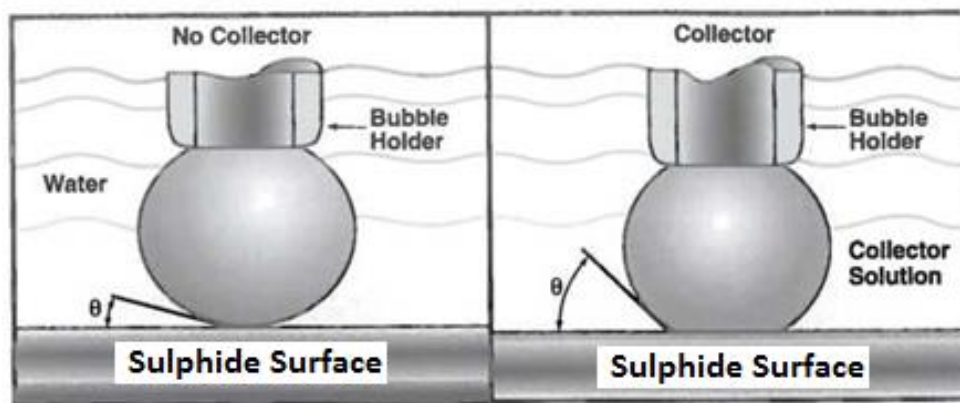


Illustration of contact angle,  $\theta$ , with and without the presence of a collector.

Figure 6. Impact of collectors on contact angle (Michaud, 2015)

The hydrophobicity of gold is obtained by adding collectors (Figure 6), and no flotation device relies solely on the natural flotation of grains to recover gold. Naturally occurring or liberalized gold is optimally regenerated in a flotation circuit at pH values close to a neutral environment together with a suitable collector. (Dunne, 2016, 315–338)

### 2.2.3 Reagents used in flotation

Each used reagent performs a different function in the mineral flotation process.

The first group of reagents are collectors. These are organic substances whose task is to adsorb onto the surface of mineral grains. By adsorbing to the surface of the grain, its hydrophobicity increases, which firmly connects the surface of the mineral with the air bubble. This is the principle of the whole flotation. Controlling flotation reagents can be organic or inorganic substances and are added to flotation to support or prevent the adsorption of collectors on the surface of particles. Due to their influence, the hydrophobicity and hydrophilicity of minerals can be distinguished. Control reagents are divided into suppressing, reviving and modifying. Reviving reagents support the adsorption of collectors and thereby increase the hydrophobicity of selected mineral grains, for which was the revitalizing reagent chosen. Reagents designed to prevent the adsorption of scavengers are referred to as suppressing reagents. Due to their effect and hydrophilicity, the grains do not connect with the bubbles. Modifying flotation reagents are reagents for adjusting the pH of the liquid environment. (Kmet', 1992)

### 3 Leaching of gold

The principle of steeping can be explained most efficiently using the example of tea preparation. When tea is added to hot water, the aroma dissolves in the water, not in the tea leaves. The tea leaves remain in the solid phase, while the aromas are already part of the liquid phase. Subsequently, after a simple separation of these phases, for example on filter paper, the scent is also separated from the tea leaves. The same is true with gold leaching, where the gold is in liquid form with a leaching agent (Michaud, 2013). Leaching with mixing is used for fine-grained material in the form of a suspension. There are two methods of leaching with mixing: the case where the material is mixed constantly and intermittently. In this thesis, the first of the mentioned methods is used. The advantage of continuous mixing is the possibility of automating the leaching process and the mixture's homogeneity during the entire experiment. The next step is the adsorption of gold on the surface of activated carbon (Figure 7). Thanks to the phenomenon of attraction of the negative charge to the positive, the gold is captured on the surface of the coal present. (Špaldon, 1986, 11–15, Michaud, 2013)

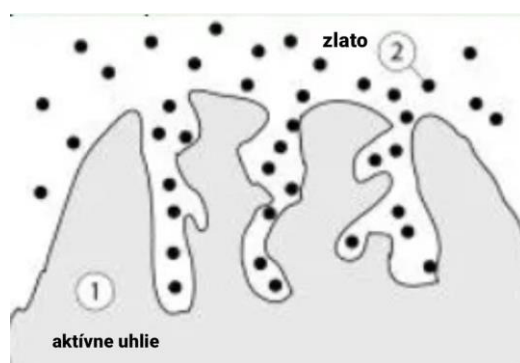


Figure 7. Adsorption of gold on active coal surface (Michaud, 2013)

An important fact in leaching is the economic factor. Several leaching agents can leach gold from gold-bearing ores with varying effectiveness. However, the problem is that not all of them can balance the costs related to their activity with their effectiveness. It is necessary to consider their price, the cost of chemicals required for the desired course of leaching, the

consumption of electricity, or the leaching time itself. Of course, the effectiveness of leaching does not depend purely on the chosen method but primarily on the composition of the starting ore.

The overgrowth of grains in the leached material is essential in leaching kinetics. Figure 8 graphically shows the impact of overgrowing the utility component in five different models. (Špaldon, 1986, 11–15)

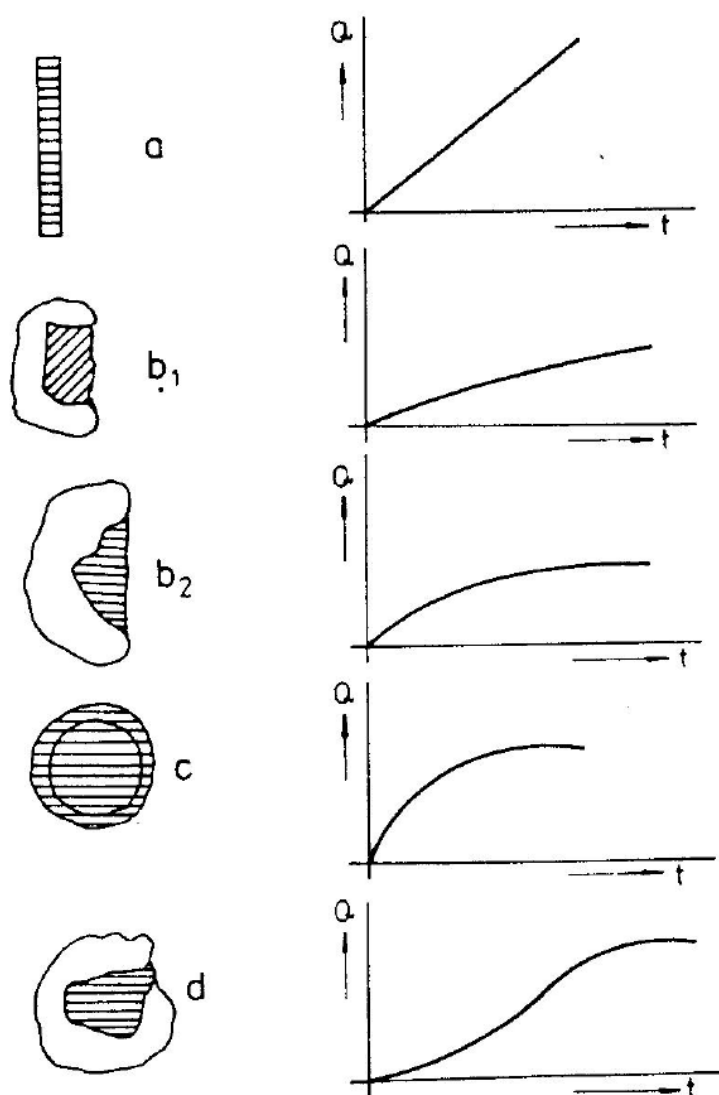


Figure 8. Influence of the gold presence in the ore on leaching kinetics (Špaldon, 1986, 11–15)

If the grain has a simple flat shape, as shown in case a, the dependence of the amount of material  $Q$  passing into solution in time  $t$  will be represented by a straight line, provided that the thickness of the grain is much smaller than its length and width. In cases b1 and b2, when the grain is located in the mineral cavity, dissolution occurs from only one side, and the dissolution rate is almost constant. A more significant deviation from the curve in the case of b2 is caused by the uneven circumference of the dissolving grain. If the grain has a spherical shape (case c), its circumference decreases during leaching, which causes the curve to curve proportionally with time. In the case of d, the grain is embedded in the rock for most of its surface. Because of this, the curve also changes its shape proportionally. (Špaldon, 1986, 11–15)

### 3.1 Cyanidation

Among the most famous methods of gold leaching (Figure 9) are those that use cyanide, royal jelly or thiosulfate. Cyanide leaching is the oldest and still the most frequently used method. However, cyanide is toxic, and its long-term effects lead to soil and ecosystem poisoning. Royal jelly is produced by worker honeybees. It consists of carvins, amino acids, vitamins, minerals, and proteins. Leaching with royal jelly is less toxic and still financially acceptable, but it is also not an ideal option. The costs of thiosulfate leaching are tolerable, and at the same time, this method is slightly more environmentally friendly, which makes thiosulfate leaching attractive from an economic point of view. (Kappes, 2005, 456–478; Špaldon, 1986, 57–59; Morávek, 1992; Deschênes, 2005, 479–500)

Cyanidation takes place in an alkaline environment. In the cyanidation process, gold is dissolved in a solution of cyanide salts. It takes place faster at elevated temperatures. The process is more intensive with constant mixing. (Špaldon, 1986, 11–15)

The technological procedures of the most widespread method of obtaining gold from ores in the world - cyanide leaching - consist in the physical contact of the gold present in the ore with the leaching solution. The concentration of the leaching agent is very low, typically 0.1%. Isolation of dissolved gold is carried out either by precipitation with powdered zinc from the liquid phase, or by adsorption on activated carbon directly from the suspension after leaching with subsequent desorption and electrolytic exclusion of gold from the leachate at the cathode. The last step, usually performed in a gold ore processing plant, is

remelting the zinc precipitate. (Kappes, 2005, 456–478; Morávek, 1992; Deschênes, 2005, 479–500)

The formed gold cyanide complex is extracted by adsorption onto activated carbon. Two methods are distinguished. In the CIL (carbon in leach) method, coal is added directly to the reaction vessels, meaning that both leaching and adsorption take place simultaneously in the same place. Another method is CIP (carbon in pulp). In this case, leaching is first carried out in tanks separately, followed by adsorption to carbon in tanks specially made for adsorption. (Dananaj, 2010)

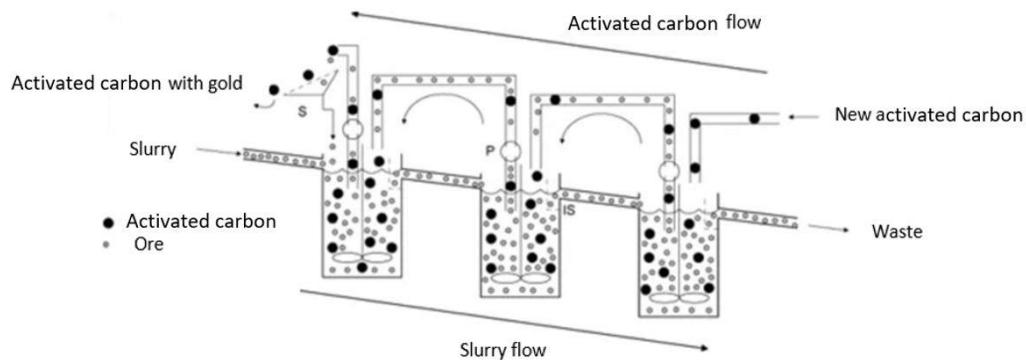


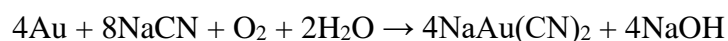
Figure 9. Carbon in leach process scheme (Michaud, 2013)

Referring to the available documents of the Ministry of the Environment of the Slovak Republic, it is currently prohibited to use cyanide-based technologies to process gold-bearing ores in Slovakia. Cyanide leaching is considered dangerous in terms of environmental impacts. Mining companies, not only in Slovakia, but also in other countries where cyanidation is prohibited, are looking for suitable alternatives to replace this method. Cyanide leaching is very effective if its impact and other negatives are not considered. So far, it has not been possible to find an approach that could fully compete with cyanidation regarding the results achieved versus the costs incurred. (MZPSR, 2012)

For cyanidation to be effective, the ore must have a porous nature or be sufficiently comminuted to allow direct contact of the gold with the cyanide. Sulfide minerals (pyrrhotite) may also be present, which cause the formation of acids by their oxidation, thereby consuming the oxygen present. If oxygen is not present in the solution, the cyanide and gold reaction will not occur, so it must be supplied to the system by aeration. At the same time, the acid formed must be neutralized (most often with lime); otherwise, hydrogen cyanide gas (HCN) will start to form. It is fatally poisonous and is associated with other risks, such as the possibility of absorbing cyanide salts through the skin or its form in wastewater if handled poorly. The consequences of cyanide contact with the human body can be fatal for a person, as it prevents the body from using oxygen. (Deschênes&Hall&Fulton, 2003, 353–361; Core, 2022)

Residual values of cyanide after leaching are effectively detoxified into non-toxic products, for example, by oxidation with air in the presence of sulfur dioxide or oxidation with hydrogen peroxide. Most of them degrade in the final result to carbonates and ammonium ions, and to a lesser extent, they turn into complexly bound non-toxic complexes. There are several different procedures for leaching gold and extracting it from the solution. (Kappes, 2005, 456–478; Morávek, 1992; Deschênes, 2005, 479–500)

An example of a possible cyanide leaching procedure is the following equation:



### 3.2 Thiosulfate leaching

Thiosulfate is less aggressive leaching agent compared to cyanide. From technological point of view it brings more advantages, such as higher efficiency for gold associated with ores that have a shorter leaching time, meaning they are leached sooner. For some gold bearing ores, this method is more feasible alternative to cyanide method from technological and financial point of view. (SGS, 2008)

Complication in the chemistry of the ammonia–thiosulfate–copper process are complexing ligands, namely ammonia and thiosulfate, the redox group  $\text{Cu}^{+2}$ ,  $\text{Cu}^{+}$ , and also the stability of thiosulfate in solution. Key part of the leaching is to maintain the concentration of



thiosulfate, ammonia, copper, and oxygen in the leaching solution (Xu et al., 2017, 222). The following equation describes the leaching of gold in an alkaline thiosulfate solution:



### 3.2.1 Advantages

The advantage of thiosulfate leaching is that, like cyanide, it is an alkaline process (pH 8 to 10 is usually used), which prevents corrosion. Thiosulfate leaching can bring an advantage over cyanide in these cases:

When leaching pre-precipitated ores, thiosulfate can yield significantly better recovery than cyanide. Pre-precipitated ores are carbonaceous material which absorbs the gold cyanide complex and does not absorb the gold thiosulfate complex. (SGS, 2008; Xie et al., 2021, 3508)

Thiosulfate leaching of gold-bearing ores is a step forward when concerning the environmental impact of cyanide. Unlike cyanide, the chemicals in thiosulphate leaching are harmless and non-toxic. In places where cyanide is prohibited or subject to intense negative environmental responses, thiosulfate leaching has a potential to be used. Key chemicals used in the leaching process are ammonium thiosulfate and ammonium sulfate, commonly used as fertilizers. (SGS, 2008)

### 3.2.2 Disadvantages

Thiosulfate leaching is not as widespread as cyanide leaching, so less information is available about it. This makes optimizing operations a bit more difficult. The process is based on the reaction between gold and thiosulfate anion. To achieve the best possible result using the smallest possible amount of reagent, it is important to pay attention to physical parameters such as temperature and density of the mash. Thiosulfate leaching is complicated and requires the presence of ammonia for its operation. It requires high consumption of reagents, which causes higher costs. Another disadvantage is efficiency - the thiosulfate complex is 10 times weaker than the cyanide complex. At the moment, no operation would be able to extract gold with the help of thiosulphate leaching economically. Thiosulfate

leaching still does not match the effectiveness of cyanide. For comparison, thiosulfate leaching requires a much higher reagent concentration to achieve comparable extent of leaching values. A typical thiosulfate solution is mixed at a reagent concentration from 5 to 20 g/l, while in cyanide leaching, the concentration is much lower, between 0,25 and 1 g/l. This difference results in higher reagent consumption. At the same time, the cost of thiosulfate is approximately one-fifth lower as compensation. In thiosulfate leaching, recycling the reagent back into the leaching process or its reuse as a fertilizer remains an important point, which minimizes its losses. Another shortcoming is poor absorbability with activated carbon. For this reason, applying the CIP (carbon in pulp) and CIL (carbon in leach) methods is not an option, and it is necessary to use alternative technologies. (SGS, 2008)

### 3.3 Thiourea leaching

Thiourea (Figure 10) is a white crystalline solid occurring naturally and in synthetic form. It is a non-cyanide-based type of solvent. Today it is used to melt silver and gold, but it once had other uses. It was added as an ingredient to hair and cleaning products. When heated, thiourea emits harmful oxides of sulfur and nitrogen. The chemical formula  $\text{CH}_4\text{N}_2\text{S}$  denotes it. (National Center for Biotechnology Information, 2022; Michaud, 2017)



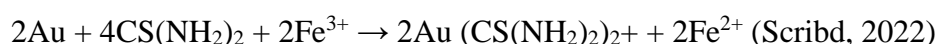
Figure 10. Thiourea (ChemCraft Ltd., 2022)

It is prevalent as a leaching agent for gold extraction worldwide. However, due to its toxicity, an adequate replacement is being sought. One of the possible alternatives is thiourea. The complexes it forms with gold are significantly weaker than cyanide complexes (15 times weaker). When leaching, thiourea also requires special conditions, especially an ultra-acidic environment, which is associated with higher financial costs for leaching. (National Center for Biotechnology Information, 2022; Michaud, 2017)

Thiourea, as a leaching agent, also poses a possible health risk. Long-term exposure to this agent can cause bone marrow damage in humans, decreasing red and white blood cell levels and platelets. It, therefore, represents a potential human carcinogen. Regarding the toxicity of thiourea,  $10 \text{ g.kg}^{-1}$  is a lethal dose for humans, and values for mammals are also determined. It has been found to be carcinogenic to trout and rats. In terms of human exposure, it is not carcinogenic to a certain extent and is even used in medicine for thyroid diseases (National Center for Biotechnology Information, 2022). The first interest in thiourea as a gold leaching agent date back to around 1941. The kinetics of thiourea dissolution also began to be studied. It was found that it must be performed in an acidic solution. It was essential to set conditions required for the experiment. As an acidic medium, acids such as

nitric, sulfuric or hydrochloric were used. Under conditions where both the oxidant and the acid were appropriately chosen, it was found that thiourea, as an extractant, dissolves gold up to 12 times faster than sodium cyanide. The oxidants used in the experiment were, for example, sodium peroxide, hydrogen peroxide,  $\text{Fe}^{3+}$  ion, ozone, dissolved oxygen and potassium permanganate (Smith&Abbott&Ryder, 2014, 11060–11082). In terms of kinetics, the concentration of thiourea and the applied oxidizing agents are very important. In acidic solutions, thiourea dissolves the given material easily (Dune, 2016, 315–338).

The following equation describes the formation of a stable complex when gold is dissolved in a thiourea solution (in an acidic environment):



### 3.4 Leaching in ionic liquids and deep eutectic solvents

The term ionic liquids refer to molten salts in the liquid phase even at temperatures below 100 °C. They contain anionic and cationic components and are strong solvents. Unlike molten salts operating at high temperatures, they use not organic but inorganic cations. DES uses two fundamental facts to prevent solidification and the formation of crystalline structures in substances. One is the size of the cations, which must be large and at the same time meet the required asymmetry, and the second condition is the delocalized charge of the anions. (Jenkin et al., 2016, 18–24)

Most common and first developed Type III DESs (amines, alcohols, carboxylic acids) that consist of hydrogen bond donor (HBD) and choline chloride have simple preparation, inexpensive reagents, are versatile and do not react with water. DES type I are composed of non-hydrated metal halides and quaternary ammonium salts, that have high melting points. Type II DES involves the use of hydrated metal halides that can be used in moisture environment, since they are insensitive to it. The last ones are type IV DES formed by metal halides with amides or alcohols. Deep eutectic solvents (DES) and ionic liquids have often been used interchangeably, despite the names referring to two different types of solvents. DES can also be distinguished from ionic liquids based on the different number and type of components. DES are mixed of two or more uncharged components with lower melting point than the melting point of individual components. Ionic liquids are molten salts composed of

charged components (one kind of anion and cation) with point of melting below 100 °C. The process of creating DES consists of mixing the corresponding components at moderate temperatures (up to 100 °C). Unlike ionic liquids, additional DES purification is not necessary, and DES purity is based on the purity of the each component. DES can form hydrogen bonds, are hydrophilic and due to that can be dissolved in liquids. There are two types of DES, which include natural DES (NADES) and therapeutic DES (THEDES). NADES can be formed from natural products. These products are organic acids, amino acids, sugars, choline halides or urea. They are chemically diverse, renewable, biodegradable and with low toxicity level. THEDES have pharmaceutical and therapeutic properties, active pharmaceutical ingredient acts as a DES component. (Smith&Abbott&Ryder, 2014, 11060–11082, (Khandelwal&Tailor&Kumar, 2016, 345–386, Pena-Pereira&De la Calle, 2019, 184–190).

Ionic liquids are perceived as an ecological method resulting from low vapour formation. Likewise, some of the ionic liquids are intentionally made from low-toxic ions, such as amino acids, imidazoles, and especially choline, which is used in gold leaching and the form of choline chloride (Figure 11) was also used for experiments in this thesis. (Hartley, 2013)



Figure 11. Choline chloride (NIH, 2022)

Choline is not an unknown substance in the world of science. It is very substantial as a nutrient, found naturally in food, but also as a supplement for diets. Choline is origin for methyl groups necessary for metabolic processes. The human body uses choline phosphatidylcholine and sphingomyelin synthesis, which are essential for cell membranes.

For that reason animal and plant cells are dependent choline, without which they would be unable to have memory, moods, control muscles or other nervous system functions. (NIH, 2022)

DES are type of ionic liquids (ILs). The reason why they are classified as ionic liquids is that they have many similar properties. The terms deep eutectic solvents and ionic liquids are often confused in the literature, but it should be noted that they are not identical agents. Deep eutectic liquids are formed from Lewis and Brønsted acids and bases. Although DES and IL share the same physical properties, their chemical properties are more radically different. Research on ionic liquids has expanded, especially in the last 20 years. DES (Figure 12) contain large asymmetric ions with low melting points. Delocalization of the charge occurring through hydrogen bonds, for example, between halide ions and a hydrogen donor residue, is responsible for lowering the mixture's melting point relative to the individual components' melting points. (Tahir&Rafique M.&Rafique M.S., 2020, 119–138)

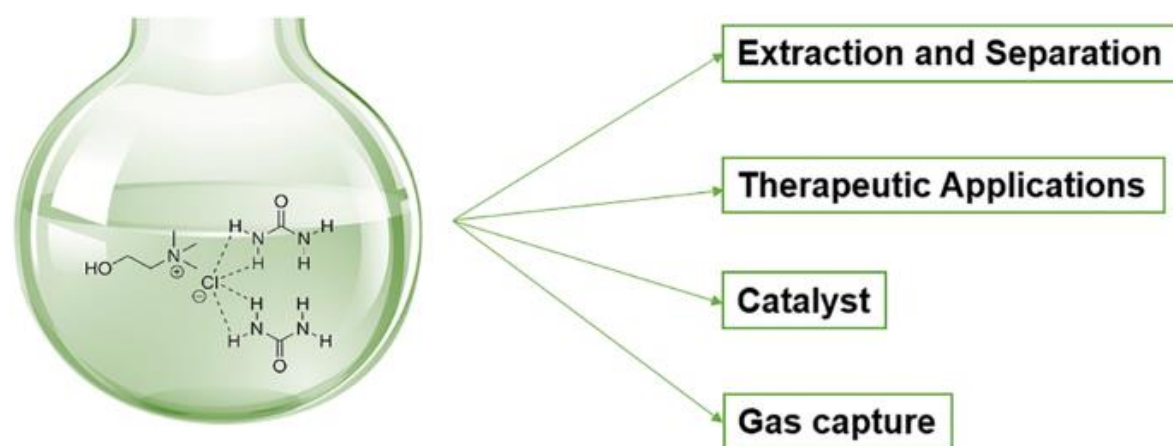


Figure 12. Deep eutectic solvents (Soltanmohammadi&Jouyban&Shayanfar, 2021, 439)

The advantages of DES are mainly their non-flammability and non-volatile properties - thanks to which no vapours are produced. Their preparation is not difficult and needs partial heating, which is an advantage in terms of production costs (Pena-Pereira&De la Calle, 2019, 184–190). Iodine in DES is used as an oxidizing agent. This allows minerals to dissolve. Iodide ( $\text{I}^-$ ) is a waste product during the dissolution of gold according to the following equation:



Iodine has the potential to be used as an electrocatalyst, being continuously obtained from reduced iodide by electrochemical oxidation at the positive anode. Dissolved metals are selectively captured at the negative cathode due to the possible adjustment of the electrode potential. The assumption of quantitative separation of gold and silver should be feasible given their difference in redox potentials. (Abbott et al., 2011, 471–481, Jenkin et al., 2016)

Figure 13 shows metal that is concentrated on cathode while the rest of the material remains in liquid phase.

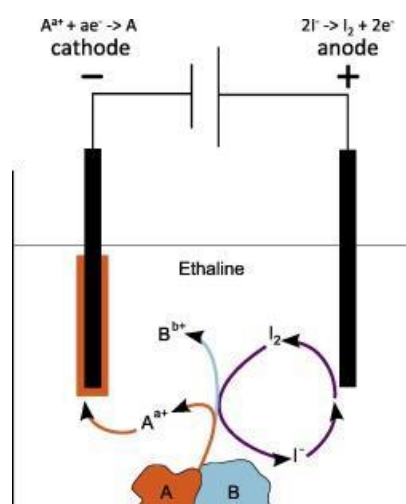


Figure 13 Separation scheme of 2 compounds using iodine as electrocatalytic oxidation agent (Jenkin et al., 2016)

DES most often occur with a density of 1,0–1,35 g.cm<sup>-3</sup>. However, possible deviations caused by different methods for determining densities, the solvents' quality, or preparation must be considered. The differences in the densities of individual DES are driven by their content, for example, the presence of water, the type of hydrogen bond donors, or the ratio of the components present (Moradi&Farzi, 2021, 1). DES are polar solvents because of the extensive network of hydrogen bonds. Their ion conductivity is weak due to higher viscosity. However, viscosity may change with temperature. (Khandelwal&Tailor&Kumar, 2016, 345–386)

### 3.5 Leaching with reagent CNLite

CNLite leaching agent is intended for gold recovery. The manufacturer is the Chinese company Yantai CNLite Mineral Processing Reagents co., LTD, which is located in Yantai, Shandong Province. The manufacturer has not disclosed this leaching mixture's detailed composition or principle of operation. However, available sources assume a structure based on sodium oxide ( $\text{Na}_2\text{O}$ ), nitrogen (N), ammonia ( $\text{NH}_4^+$ ), calcium oxide (CaO) and iron oxide ( $\text{Fe}_2\text{O}_3$ ).

#### 3.5.1 Usage

Oxidized gold and silver ores, sulfide ores, electrical waste, tailings after cyanide leaching, waste after processing gold-bearing ores, leaching in pools, and CIP leaching. CIL – this process is characterized by the parallel leaching of gold and its adsorption on coal. Usually, 6 to 10 leaching vessels are used, with 85-90% of the material reaching a grain size of 74 micrometres. This reagent is mixed at a concentration of 40-45% and a pH of 10-11. CIP – similar to conventional cyanide leaching, the concentration and oxygen content must be controlled. The added CNLite reagent should cover from 0,05% to 0,08% of the total volume (Yantai Xinhai Materials Technology co., Ltd., 2022). It is a mixture of a solid phase in the form of a powder soluble in water. The mixture is inhomogeneous in nature and tends to clump. The CNLite reagent (Figure 14) has a character close to other reagents available on the market, such as Eco-Goldex, CNFree and the like. For this reason, it is possible to expect a similar principle of operation. The Eco-Goldex mixture contains several substances, which are individually weaker than cyanide, but their combination has a significantly stronger effect, which could even compete with cyanide. In the past, samples of the Eco-Goldex mixture were analyzed in accredited laboratories to review the cyanide content. The cyanide content above the detection limit was not detected in the samples, so this method should not fall under the legally prohibited cyanide leaching. In the same way, the samples of the CNLite mixture did not show a cyanide content higher than the detection limit during the analyses. (Brezáni, 2021)





Figure 14. Reagent CNLite

A possible controversial substance in the CNLite reagent is sodium ferricyanide. Even though it has cyanide in its name, its level of toxicity is low, and, above all, it is not released during leaching. The release could occur in a highly acidic environment, but the pH values during leaching with this reagent are in the neutral range. Based on information from the manufacturer, this leaching agent can be a full-fledged replacement in operations where cyanide was used even without needing to change the operation's original leaching process or equipment. At the same time, it brings a benefit in the form of a more negligible environmental impact. (Brezáni, 2021)

### 3.6 Fire assay - gold content analysis

More than 200 analytical techniques are used to analyse the concentration of precious metals in materials. The fire assay method is a standard, classic, analytical approach used to determine the content of precious metals in silver and gold-bearing ores. Although this method requires more time and is more complicated than instrumental analyses, it is more reliable and accurate. It is a common technology that was recorded thousands of years ago.

The term fire assay dates to ancient times when the fire was used to achieve high temperatures for the pyro metallurgical reactions that also occur in this method (IPMI, 2015). Fire-powered furnaces were used, but over time they were replaced by gas furnaces and later replaced by high-temperature electric laboratory furnaces that are still used today. The origin of the fire assay technique dates back to ancient Asia Minor, where traces of lead processing from lead ore were discovered. Very pure silver was produced from these lead ores as early as 2000 BC. The first detailed written references to the art of processing minerals and metals by the fire assay method were found in *De Re Metallica*, published in 1556 by the German scholar Georg Agricola (Battaini&Bemporad&De Felicis, 2014, 9–20). The fire assay method is still used to analyse gold and silver ore samples. It is also used to analyse secondary or waste materials and to separate platinum group metals. It is a group of six chemical elements placed together in the periodic table of elements - namely Platinum, Palladium, Rhodium and Indium. The only two elements from this group not used for this analysis are Osmium and Ruthenium. (Sen Gupta&Beamish, 1962, 1761–1764)

The fire assay process consists of three main steps:

1. Preparation
2. Collection
3. Separation

### 3.6.1 Preparation

The first step in sample preparation is processing, which is performed by grinding the sample into a fine powder. This phase is necessary to mix the sample well with the chemicals of the same powder form. To obtain an approximate composition, samples can be evaluated by another method, such as the XRF method, to determine better the number of reactants that need to be added to the process. A thoroughly weighed sample and reactants are then mixed. (IPMI, 2015)

### 3.6.2 Collection

The collection phase involves melting in a ceramic crucible designed explicitly for melting samples at high temperatures (Figure 15). The contents of the crucible are heated until they form a glass-like slag, where a series of reactions occur that fuse the precious metals present into an alloy. (IPMI, 2015)



Figure 15. Ceramic crucible with melted sample (Jenkin et al., 2016, 18–24)

A classic example is lead smelting, where lead oxide reacts with the molten slag and reduces it to fine globules of lead. Precious metals are absorbed into them during the slag fall and collect at the bottom of the crucible as a deposit of the alloy of precious metals and lead.

All chemicals used in the harvesting process have a specific function. Activity and viscosity are important chemical and physical properties of slag. The ratio of chemicals demonstrated in the example of quartz ore is as follows: 15g of the sample itself, 20g of  $\text{Na}_2\text{CO}_3$ , 40g of  $\text{PbO}$ , 3g of  $\text{Na}_2\text{B}_4\text{O}_7$  and 3g of flour. Once the reaction is complete, the contents of the crucible are poured into another already breakable crucible, where it is left to cool, and the metal alloy is separated from the slag. Lead is used to collect precious metals (Figure 16). (IPMI, 2015)

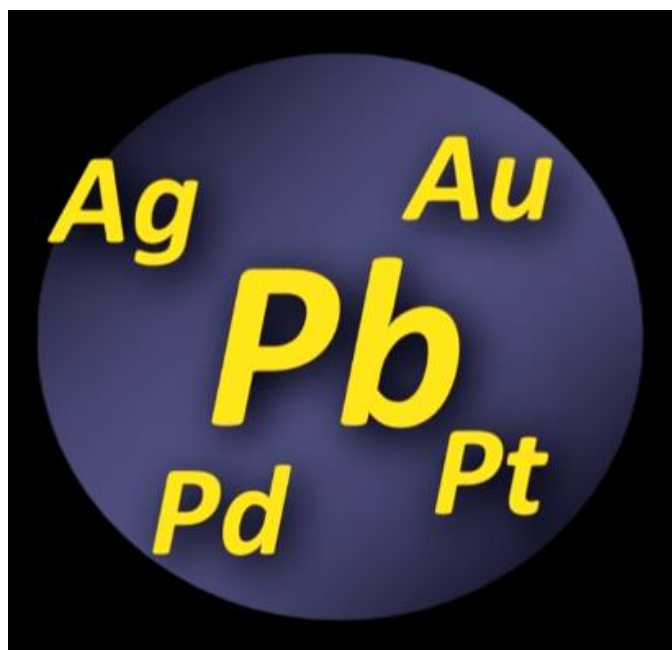


Figure 16. Collection of metals (IMPI, 2015)

Metal samples can be processed by the fire assay method using lead. Silver is also sometimes added to help completely dissolve the sample into a lead alloy for cupping. Platinum group alloys are analysed much more complexly by the fire assay method. Other metals or metal compounds, such as nickel sulfides, are sometimes added as collectors if platinum group metals are present. (IPMI, 2015)

### 3.6.3 Separation

The third step in the fire assay method is the separation of precious metals from the collector - lead. This process is called cupellation, as the precious metals are separated in a band. It is a porous ceramic container that usually resembles a shallow cup and is made of porous bone ash or calcium phosphate. A ball of the lead alloy is inserted into the band and heated in a furnace to 850°C. As the alloy melts, the lead oxidises on the surface of the liquid molten metal. The lead oxide is then absorbed into the band. This process continues until all the lead is absorbed. Only a small ball (Figure 17) remains in the band containing precious metals. This ball is then weighed and analysed to determine the content of precious metals using instrumental analytical methods such as ICP and AES. (IPMI, 2015)



Figure 17. Pb ball (IPMI, 2015)

If silver is also present in the gold sample, the bead can be further analysed by dissolving the silver present in a nitric acid solution, leaving us with pure gold. Mass raasdf can then calculate concentrations. Low concentration samples will produce tiny beads, so silver is sometimes added to the fire assay process to achieve a larger precious metal bead, which improves the accuracy of the results. Fire assay is the most important of the series of precise analyses of the presence of precious metals. It is a highly accurate analytical method used for both primary and secondary sources of precious metals. (IPMI, 2015)

## 4 Experimental part

In this thesis, the experimental part deals with the comparison of three leaching agents. Each reagent was subjected to a series of experiments, where the factors influencing the leaching efficiency were monitored. These reagents are deep eutectic solvents, thiourea and the experimentally less tested modern reagent CNLite. All of the methods represent a possible alternative to cyanide leaching. The dependence on time, concentration, and the temperature was monitored in terms of influencing factors. Each experiment was subject to its own methodology, and their procedures differed. Their detailed description is characterized in the subsections of individual experiments.

### 4.1 Description of the sample



Figure 18. Nature of the sample used for leaching experiments

The place of origin of the sample used in the experiments is a tailings pond after mining activity in the Čučma area in Slovakia. Preliminary information about the sample mainly indicates increased Antimony, Aluminum and Gold content. The sample (Figure 18) is

harmless to health and contains no substances posing a health risk. It comes from the flotation treatment of antimony ore containing precious metals. No further processing of the ore was carried out during the experiments.

The density of the sample was determined to be  $2,68 \text{ g.cm}^{-3}$ . This value was determined pycnometrically. The sample tended to form clumps, but these could be effectively shattered by applying not much mechanical force. The pH value of the examined sample was 7,03.

The initial analysis of the sample for leaching determined the following composition (Table 1):

Table 1. Chemical composition of the sample

Fe	S	Au
2,20%	1,10%	1,8 g/t

The gold content was also determined separately for the  $<45 \mu\text{m}$  and  $>45 \mu\text{m}$  fractions. For the finer fraction, the gold content was 1,1 g/t, and for the coarser fraction 0,7 g/t (Table 2).

Table 2. Au content in grain size fractions

Au	Below $45 \mu\text{m}$	1,1 g/t
Au	Above $45 \mu\text{m}$	0,7 g/t

Even though the sample was not further processed during the leaching experiments in this thesis, since a higher gold content was found in the finer fraction, there is a possibility of enriching the ore by further processing - hydraulic sorting. After this, the sample would be composed of finer-grained material, and thus a higher content of precious metals in the sample can be assumed.

## Laser diffraction – grain size analysis of the sample

Because the sample had a fine-grained, sandy character that was already visible (if we do not consider clumps of material), the grain size analysis was not carried out by classical sieve analysis but by laser diffraction. This step aims to sort into grain size classes and based on their representation, determine the nature of the grains contained in the material. Using wavelength measurement, laser diffraction can define the size of even very small grains. This method is a measurement technology for determining the size distribution of the particles contained in a sample. It is performed in either an air stream or a liquid, where the laser beam is focused on the particles, and the deviation of the scattering angle is monitored. Each such angle is characteristic of the corresponding particle size. (Microtrac MRB, 2022)

An accredited laboratory performed laser diffraction of the material at a pressure of 3,0 bar. The particle shape factor was set to 1, corresponding to a spherical particle shape. The results of the analysis are shown in figure 19.

Representing values of the sample are listed below:

- Median  $x_{50} = 32,01 \mu\text{m}$
- $x_{10} = 3,63 \mu\text{m}$
- $x_{90} = 118,73 \mu\text{m}$
- $x_{16} = 5,72 \mu\text{m}$
- $x_{84} = 100,14 \mu\text{m}$
- $x_{97} = 149,57 \mu\text{m}$



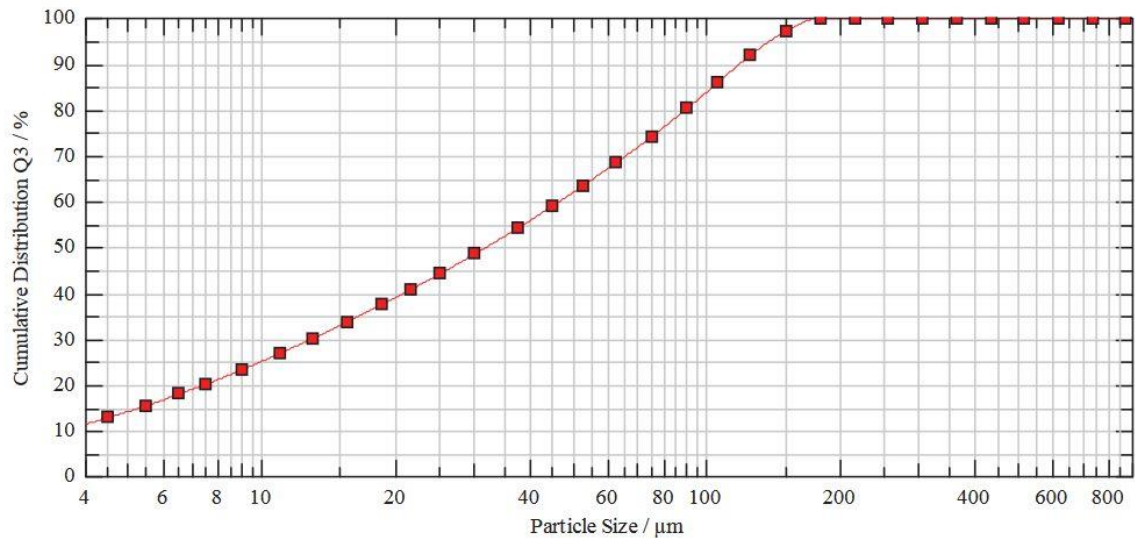


Figure 19. Particle size distribution curve

The graphical display in Figure 19 is a particle size distribution curve showing the percentage representation of the cumulative weight yield of the subsieve product as a function of the particle size. This graph shows the percentage representation of individual particle sizes in the measured volume.

## 5 Leaching of gold-bearing ore waste after flotation treatment in thiourea solution

The first of the leaching tests was an experiment investigating the extent of leaching of waste after flotation in the Čučma sample. A solution of thiourea  $\text{CS}(\text{NH}_2)_2$  and ferric sulfate  $\text{Fe}_2(\text{SO}_4)_3$  was used for leaching. The experiment focused on the leaching of gold, but the content of leached antimony was also monitored to compare the leaching curves of individual components. In this experiment, several trials were performed, which differed in duration and were tested at three different temperatures. During leaching, the homogeneity of the mixture was ensured by constant mixing during the entire length of leaching.

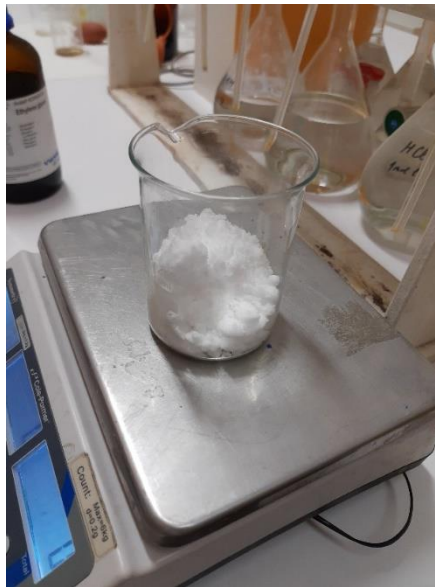


Figure 20. Preparation of chemicals for experiments

Chemicals used in the experiment (Figure 20):

- $\text{CS}(\text{NH}_2)_2$  – 5g
- $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  – 2.5g
- Distilled water – topped up to a volume of 500 ml
- $\text{H}_2\text{SO}_4$  (1:2)

The experiment procedure started by mixing thiourea  $\text{CS}(\text{NH}_2)_2$  and ferric sulfate  $\text{Fe}_2(\text{SO}_4)_3$ . Then distilled water was added to a volume of 500 ml. After heating to the required temperature, the sample was added. Only then was the measurement of the leaching time started, which corresponded to the given experiment.

Thiourea leaching takes place in a very acidic environment. The pH value was maintained in the range of 2 to 3 during the experiments. This value was continuously controlled and regulated by adding sulfuric acid  $\text{H}_2\text{SO}_4$  (1:2).



Figure 21. A trio of leaching experiments with different temperatures

Three experiments were conducted simultaneously for a given time interval, each with a different temperature. The temperatures used in the leaching experiments are shown in Figure 21:

- 60°C
- 80°C
- 100°C

In thiourea leaching, the experiments were in smaller volumes, so it was impossible to take samples after a certain time. For this reason, it was necessary to conduct all experiments separately. This resulted in a much larger number of individual experiments. A total of 21 experiments of thiourea leaching were executed. The examined time intervals were 15 min, 30 min, 1h, 2h, 3h, 4h and 5h.



Figure 22. Filtration of the leached material

The leached material was then filtered on filter paper, and its solid component was dried in a dryer to rid the material of residual water. After filtration (Figure 22), the material was subjected to Fire Assay analysis to determine the content of useful components.

### 5.1 Thiourea leaching results for gold

The part of the sample used for leaching in the thiourea solution contained 1,3 g/t Au before the leaching processes. In the experiments, a decrease in Au was observed, which perfectly

reflects the effectiveness of leaching because the share of gold is no longer in the solid phase of the product after leaching.

Table 3. Results of gold leaching - thiourea

Test number	Leaching time	Temperature (°C)	Au amount before leaching (g/t)	Au amount after leaching (g/t)	Au decrease (g/t)	Au decrease (%)
1	15 min	60	1,3	0,9	0,4	31
2		80	1,3	1,2	0,1	8
3		100	1,3	1,3	0,0	0
4	30 min	60	1,3	0,9	0,4	31
5		80	1,3	1,1	0,2	15
6		100	1,3	1,2	0,1	8
7	1 h	60	1,3	1,3	0,0	0
8		80	1,3	1,2	0,1	8
9		100	1,3	1,2	0,1	8
10	2 h	60	1,3	1,1	0,2	15
11		80	1,3	1,0	0,3	23
12		100	1,3	1,3	0,0	0
13	3 h	60	1,3	0,9	0,4	31
14		80	1,3	1,1	0,2	15
15		100	1,3	1,1	0,2	15
16	4 h	60	1,3	0,6	0,7	54
17		80	1,3	1,0	0,3	23
18		100	1,3	0,7	0,6	46
19	5 h	60	1,3	1,1	0,2	15
20		80	1,3	1,0	0,3	23
21		100	1,3	1,0	0,3	23

The highest drop in gold and, therefore, the highest extent of leaching can be observed during 4-hour leaching at a temperature of 60°C – 0,7 g/t Au. On the contrary, the case of the lowest decrease of Au is three zero values, indicating that in these experiments, it was impossible to leach gold into the solution. This was an experiment with a 30-minute soaking time. Zero values were found in two more cases at a temperature of 100°C, specifically at a leaching time of 15 minutes and also at 2 hours. The complete results of the experiments are shown in Table 3.

### 5.1.1 Gold leaching kinetics

Many experiments with different leaching times were carried out mainly to obtain information and an accurate picture of the activity of the leaching agent - in this case, thiourea. The experiment was pre-set for a 4-hour leaching time, where the best leaching results were expected. This hypothesis was confirmed at all three temperatures tested.

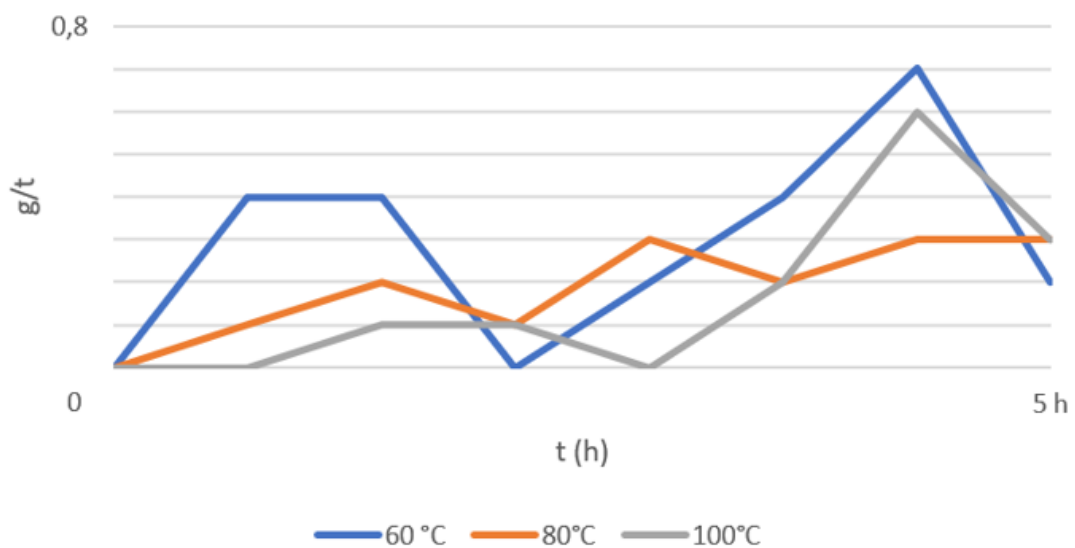


Figure 23. Kinetics of gold leaching in thiourea solution

The gold leaching kinetics graph in thiourea (Figure 23) does not reflect the analogue dependence of leaching on time. The results do not prove the implicit theory, where a gradual increase in extent of leaching with increasing leaching time was expected.

### 5.2 Thiourea leaching results for antimony

The sample used for leaching in the thiourea solution contained 6000 g/t Sb before the leaching processes. In the experiments, a decrease in Sb was observed, which reflects the effectiveness of leaching because it is the proportion of antimony that is no longer in the solid phase of the product after leaching.

Table 4. Results of leaching antimony - thiourea

Test number	Leaching time	Temperature (°C)	Sb amount before leaching (g/t)	Sb amount after leaching (g/t)	Sb decrease (g/t)	Sb decrease (%)
1	15 min	60	6000	2800,0	3200	53
2		80	6000	2500,0	3500	58
3		100	6000	2400,0	3600	60
4	30 min	60	6000	3200,0	2800	47
5		80	6000	3400,0	2600	43
6		100	6000	3100,0	2900	48
7	1 h	60	6000	2800,0	3200	53
8		80	6000	3300,0	2700	45
9		100	6000	3200,0	2800	47
10	2 h	60	6000	4000,0	2000	33
11		80	6000	3200,0	2800	47
12		100	6000	3700,0	2300	38
13	3 h	60	6000	4100,0	1900	32
14		80	6000	3800,0	2200	37
15		100	6000	3800,0	2200	37
16	4 h	60	6000	4400,0	1600	27
17		80	6000	4200,0	1800	30
18		100	6000	4200,0	1800	30
19	5 h	60	6000	3800,0	2200	37
20		80	6000	3900,0	2100	35
21		100	6000	4200,0	1800	30

Of the experiments performed, experiment number 3 showed the best values - with a leaching time of 15 minutes and a temperature of 100°C with a drop value of 3600 g/t. The 15-minute experiment showed the best values in all investigated temperatures.

The lowest value of Sb decrease was present in experiment number 17, with a leaching time of 4 hours and a temperature of 60°C. The measured value was 1600 g/t Sb. The results are shown in Table 4.

### 5.2.1 Antimony leaching kinetics

In the case of the kinetics of antimony leaching in thiourea (Figure 24), the effectiveness of the leaching agent on the sample should be directly proportional to the exposure time. 21 experiments were carried out to determine the course of action of the thiourea reagent over time. The assumed ideal leaching time of 4 hours was not confirmed, where the best leaching results were expected.

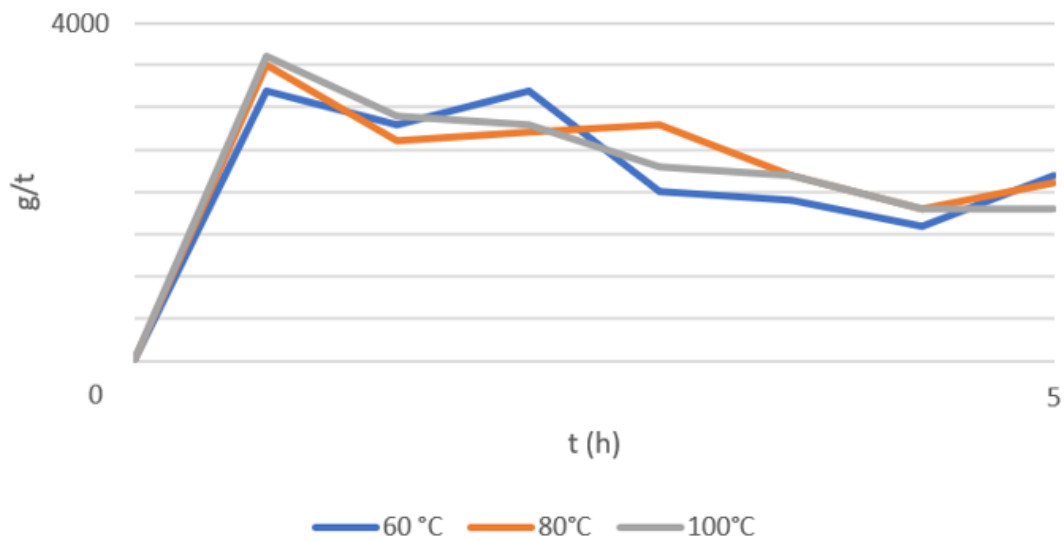


Figure 24. Leaching kinetics of antimony in thiourea solution

The graph of antimony leaching kinetics in the case of thiourea is not a reflection of the analogue dependence of leaching on time because the curve does not have an upward trend. The results do not prove the assumed theory, where a gradual increase in extent of leaching with increasing leaching time was expected.



## 6 Leaching of gold-bearing ore waste after flotation treatment in deep eutectic solvents

The extent of leaching test was also executed from the waste after flotation in the Čučma sample. DES – deep eutectic solvents – were used as the leaching agent. The experiment focused on the leaching of gold, but the content of leached antimony was also monitored to compare the leaching curves of individual components. In this experiment, several trials were performed, which differed in duration and were tested at three different temperatures. During leaching, we ensured the homogeneity of the mixture by constant mixing during the entire length of leaching.

Chemicals used in the experiment (Figure 25):

- $(\text{CH}_2\text{OH})_2$  – 77,4g
- $\text{C}_5\text{H}_{14}\text{ClNO}$  – 86,8g
- I – 1,9g



Figure 25. Chemicals

The experiment procedure started by mixing ethylene glycol (CH<sub>2</sub>OH)<sub>2</sub> and choline chloride C<sub>5</sub>H<sub>14</sub>ClNO. The mixture was heated to the required temperature with constant stirring to achieve homogeneity of the mixture. After heating to the necessary temperature, iodine and the sample were added. Subsequently, the measurement of the leaching time, which corresponded to the given experiment, was started.

The leaching took place at a pH value maintained in the range of 2 to 3 during the experiments.

Three experiments were conducted simultaneously for a given time interval, each with a different temperature. Temperatures used in leaching experiments:

- 60°C
- 80°C
- 100°C

The leached material was subsequently subjected to filtration, and its solid component was freed from the remaining water by drying it in a dryer. After filtration, the material was subjected to Fire Assay analysis to determine the content of valuable components.

Even in the case of leaching with deep eutectic solvents, these were experiments with smaller volumes, therefore the samples could not be taken after a specific time interval. For this reason, all experiments were performed separately, which resulted in a higher number of separate experiments. A total of 21 individual deep eutectic solvent leaching experiments were performed. The examined time intervals were 15 min, 30 min, 1h, 2h, 3h, 4h and 5h.

## 6.1 Leaching results in deep eutectic solvents for gold

The sample that was the subject of this experiment showed the already mentioned gold content in the initial analysis – 1.3 g/t. Here, too, the experiments observed a decrease in Au, which perfectly reflects the effectiveness of leaching because the share of gold is no longer in the solid phase of the product after leaching.

Table 5. Leaching results for gold - DES

Test number	Leaching time	Temperature (°C)	Au amount before leaching (g/t)	Au amount after leaching (g/t)	Au decrease (g/t)	Au decrease (%)
1	15 min	60	1,3	0,5	0,8	62
2		80	1,3	0,5	0,8	62
3		100	1,3	0,4	0,9	69
4	30 min	60	1,3	0,5	0,8	62
5		80	1,3	0,4	0,9	69
6		100	1,3	0,3	1,0	77
7	1 h	60	1,3	0,4	0,9	69
8		80	1,3	0,4	0,9	69
9		100	1,3	0,3	1,0	77
10	2 h	60	1,3	0,5	0,8	62
11		80	1,3	0,3	1,0	77
12		100	1,3	0,3	1,0	77
13	3 h	60	1,3	0,4	0,9	69
14		80	1,3	0,3	1,0	77
15		100	1,3	0,3	1,0	77
16	4 h	60	1,3	0,4	0,9	69
17		80	1,3	0,3	1,0	77
18		100	1,3	0,2	1,1	85
19	5 h	60	1,3	0,3	1,0	77
20		80	1,3	0,3	1,0	77
21		100	1,3	0,2	1,1	85

The highest drop in gold and thus the highest extent of leaching can be seen with 5-hour leaching at 100°C and 4-hour leaching at 100°C - which indicates a positive reagent reaction in the long-term presence of high temperature. The lowest extent of leaching value from the entire leaching was present more often - up to 4 times in the case of 60 and 80°C for 15 min,

once in the case of 60°C for 30 min, and once also in the case of 60°C for 2h, absolute values are shown in Table 5.

### 6.1.1 Gold leaching kinetics

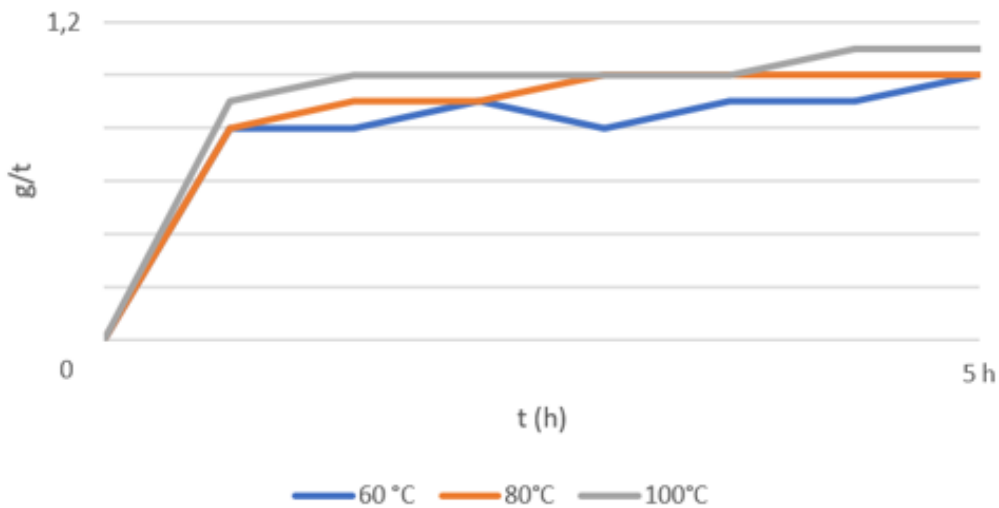


Figure 26. Kinetics of gold leaching in deep eutectic solvents

In the case of gold leaching kinetics in deep eutectic solvents (Figure 26), the effectiveness of the leaching agent on the sample was directly proportional to the exposure time. On the graph, it is possible to see the rising tendency of the curves at all temperatures used in the experiments. The highest of the three -100°C can be considered the most effective temperature. A value of 80°C followed it, and the least effective temperature was 60°C. Considering this temperature analogy, we can state that the leaching efficiency increases with increasing temperature.

### 6.2 Leaching results in deep eutectic solvents for antimony

The initial analysis of the sample showed an antimony content of 6000 g/t. As in each of the conducted experiments, the decrease in the content of Sb in the solid phase, or the extent of leaching into the solution, was monitored.

Table 6. Leaching results for antimony - DES

Test number	Leaching time	Temperature (°C)	Sb amount before leaching (g/t)	Sb amount after leaching (g/t)	Sb decrease (g/t)	Sb decrease (%)
1	15 min	60	6000	4940,9	1059	18
2		80	6000	4684,9	1315	22
3		100	6000	4623,5	1377	23
4	30 min	60	6000	5046,5	953	16
5		80	6000	4717,7	1282	21
6		100	6000	4428,9	1571	26
7	1 h	60	6000	4587,0	1413	24
8		80	6000	4243,5	1756	29
9		100	6000	4102,6	1897	32
10	2 h	60	6000	4772,3	1228	20
11		80	6000	4160,6	1839	31
12		100	6000	3980,5	2020	34
13	3 h	60	6000	4700,5	1300	22
14		80	6000	4114,8	1885	31
15		100	6000	4218,0	1782	30
16	4 h	60	6000	4229,3	1771	30
17		80	6000	4194,2	1806	30
18		100	6000	4448,1	1552	26
19	5 h	60	6000	4242,1	1758	29
20		80	6000	4060,8	1939	32
21		100	6000	4169,7	1830	31

The highest decrease in antimony and thus the highest extent of leaching can be observed during 2-hour leaching at a temperature of 100°C – 2020 g/t Sb. On the contrary, the case of the lowest decrease in Sb could be observed during 30-minute leaching with a temperature of 60°C – 953 g/t Sb. The complete results of the experiments are shown in Table 6.

### 6.2.1 Antimony leaching kinetics

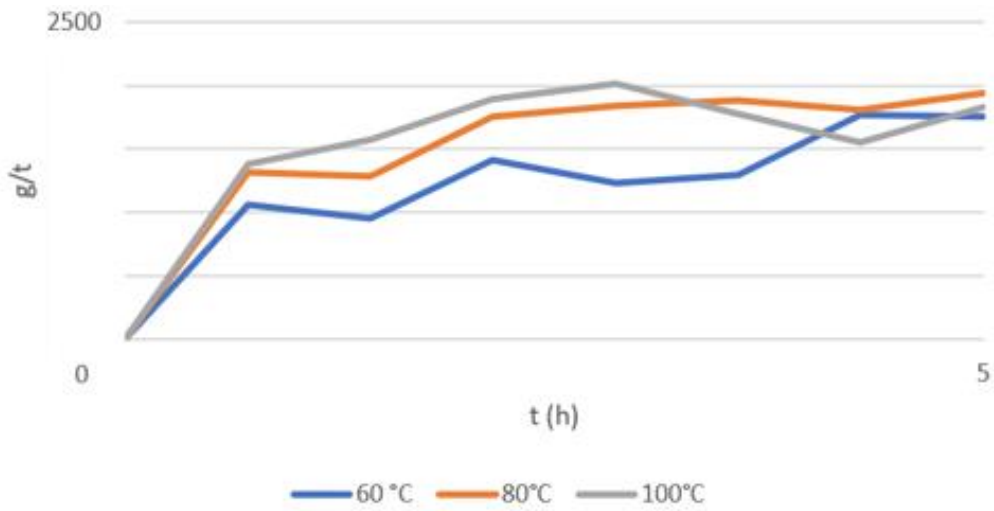


Figure 27. Leaching kinetics of antimony in deep eutectic solvents

In the case of antimony leaching kinetics in DES (Figure 27), the effectiveness of the leaching agent on the sample should be directly proportional to the exposure time. 21 experiments were performed to determine the course of action of DES over time. The obtained results confirmed the dependence on time and rising temperature. The assumed ideal leaching time of 4 hours, where the best leaching results were expected, was partially confirmed, as it showed promising results. Still, they fluctuated at a similar value from a leaching time of 1 h.

## 7 Leaching of gold-bearing ore waste after flotation treatment with CNLite reagent

Leaching with the CNLite reagent was carried out in containers containing 2000 ml of technical water. During the entire length of the experiment, constant mixing at 1000 RPM (Figure 28) was ensured to maintain the homogeneity of the material.



Figure 28. Constant mixing of the material

The same concentration was used in each experiment, which differed according to the experiment – variants with 40 wt.% and 50 wt.% were used. The total volume was 2500 ml. In the next step, the pH value was influenced by a 10% NaOH solution. CNLite reagent leaching takes place in an alkaline environment. The pH level was constantly monitored and maintained at a value of 11. Monitoring and automatic pH control were carried out using the automated device in Figure 29. After obtaining the desired pH, the CNLite reagent was added, and the leaching time started.



Figure 29. Leaching process with CNLite with automatic NaOH control

After 24 hours of leaching, samples representing the first investigated leaching interval were taken. Leaching continued smoothly for the duration of another 24 hours. After the end of the leaching process, additional samples were taken that represented the leachate after 48 hours. After the end of the leaching process, the samples were filtered, and the solid component was dried. The gold content was subsequently determined from the solid component, based on which we could evaluate the drop in gold content and calculate the gold contained in the liquid phase. In the conducted experiments, the factors affecting the process and the costs required for operation with this reagent were monitored. Namely: thickening, amount of reagent, leaching time and consumption of used chemicals.



## 7.1 Results of leaching with CNLite reagent

Sample Hodruša Hámre:

Two control tests were performed on a similar sample to confirm the accuracy of the predefined proportions of the necessary components for conducting experiments on the examined sample of Čučma. With these control tests, we established the methodology and procedure that would serve as a base for sample Čučma. The control sample represented the material from the tailings pond after the flotation treatment of gold-bearing ore from the Hodruša-Hámre deposit. The density of the sample was 2,6 g/cm<sup>3</sup>. Before leaching tests, this sample contained 1,1 g/t Au, and its detected pH was 7,36, subsequently adjusted to 11. In these two control tests, both variants of thickening were tested - 40 wt.% and 50 wt.%. 3 kg/t of reagent was used. The control tests' other conditions corresponded to those described in the leaching procedure.

Table 7. Results of the leaching of the Hodruša-Hámre control sample

Test number	Amount of reagent (kg/t)	Solids weight percentage (wt%)	Solid content (g)	Reagent content (g)	Leaching time (h)	Au amount before leaching (g/t)	Au amount after leaching (g/t)	Au decrease (g/t)	Au decrease (%)
1	3	50	1805,6	5,4	24	1,1	0,3	0,8	73
2	3	40	1326,5	4	24	1,1	0,2	0,9	82

Table 7 depicts the results of the leaching of the control sample. In leaching with a concentration of 50 wt.%, the gold content after 24 hours of leaching decreased to 0,3 g/t, and in leaching with a concentration of 40 wt.%, it declined to 0,2 g/t. This decrease between the value before and after leaching represents the gold content in the leachate - which reached 73% and 82% at the studied concentrations. We can conclude that the tests brought favourable results and fulfilled the calibration function before starting the tests on the primary Čučma sample.

### Sample Čučma:

The main monitored sample of Čučma contained a slightly smaller proportion of gold – 0.9 g/t. In the leaching tests, concentrations of 40 and 50 wt.% were used for each of the six experiments, which had a total duration of 48 hours. The tests differed in the amount of leaching agent. Values of 1,5 kg/t, 3 kg/t and 4,5 kg/t were used.

Table 8. Results of the leaching of the Čučma sample

Test number	Amount of reagent (kg/t)	Solids weight percentage (wt%)	Solid content (g)	Reagent content (g)	Leaching time (h)	NaOH consumption (kg/t)	Au amount before leaching (g/t)	Au amount after leaching (g/t)	Au decrease (g/t)	Au decrease (%)
1	3	40	1335,1	4	24	2,8	0,9	0,5	0,4	44
					48	3,6	0,9	0,3	0,6	67
2	3	50	1820,6	5,4	24	2,6	0,9	0,6	0,3	33
					48	3,7	0,9	0,5	0,4	44
3	1,5	40	1335,1	2	24	2,8	0,9	0,5	0,4	44
					48	4,0	0,9	0,5	0,4	44
4	1,5	50	1820,6	2,7	24	3,0	0,9	0,6	0,3	33
					48	3,6	0,9	0,6	0,3	33
5	4,5	40	1335,1	6	24	3,2	0,9	0,5	0,4	44
					48	3,8	0,9	0,3	0,6	67
6	4,5	50	1820,6	8,1	24	2,5	0,9	0,5	0,4	44
					48	3,5	0,9	0,5	0,4	44

The values in Table 8 demonstrate that it is more efficient to use lower thickening values. The obtained data also indicate the dependence of the amount of reagent used. It is visible that 1,5 kg/t of reagent is enough and brings a sufficiently low balance of gold in the solid phase after leaching. Higher values (3 kg/t) showed a similar result with 50 wt.% thickening. An experiment with 3 kg/t of reagent and a concentration of 40 wt.% yielded a slightly better result after 48 hours with a drop of Au of 67%. It is possible to say that a further increase in concentration (4,5 wt.%) does not bring better leaching results. During the experiments, the consumption of NaOH was also monitored, which ranged between 2.5 and 3,2 kg/t during a 24-hour leaching period and between 3,5 and 4,0 kg/t during a 48-hour leaching period.

### 7.1.1 Financial aspect of the experiment

According to the test results, it is possible to expect NaOH consumption at the level of approximately 2.8 kg/t of leached material in a 24-hour experiment and approximately 3.7 kg/t in case of a 48-hour experiment. It is a relatively low-cost item with a price of up to €0.7/kg without VAT. In total, it is therefore necessary to calculate the cost of pH adjustment at approximately €2/t for 24-hour leaching and €2.6 for 48-hour leaching. Alternatively, lime can be used to adjust the pH.

The price of the supplied reagent in 2021 (20 t container delivered from a manufacturer in China, including transport and customs clearance) was approximately €1.8/kg. With regard to the increase in transport prices in 2022, it is necessary to expect an increase and a price at the level of 2.0 to 2.2 €/kg. Considering the achieved results it is necessary to expect a price of approximately 6 to 6.6 €/t with a reagent dose of 3 kg/t and a price of 9 to 10 €/t with a reagent dose of 4.5 kg/t. The costs of the reagents (NaOH and CNLite) would therefore be approximately 8 to 9.5 €/t of processed material for a 48-hour leaching with a reagent dose of 3 kg/t. With a 48-hour leaching with a reagent dose of 4.5 kg/t, the cost of reagents would reach 12 to 12.5 €/t. In addition to the mentioned costs, it is necessary to consider the costs of unloading the material, manpower, electricity, as well as the costs of obtaining gold from the leaching solution (depending on the chosen technology and the volume of processed material).

At an Au price of approximately €50/g, the value of the gold in the delivered sample is approximately €45/t. Considering the achieved recovery into the solution of 67%, this is a value of approximately €35, which can be obtained from 1 t of such waste. When recovering Au from the solution after leaching, high recoveries are generally achieved, and it can be assumed that more than 95% of the Au that went into the solution would be able to get into the final products – precious metal ingots.

## 8 Conclusion

The title of this thesis is "New possibilities of leaching gold-bearing ores". The theoretical part of the thesis was firstly explaining gold and its extraction. Subparts were focused on techniques of extraction such as precipitation of the useful component from the liquid, that was defined by three options - electrolysis, cementation, and crystallization. Another subpart was aimed to flotation treatment, which dealt with the surface properties of particles, namely their hydrophobicity and hydrophilicity. Subsequently, the surface properties of the gold itself were also described. The chapter's content also included reagents used in flotation treatment. Chapter three described specific leaching methods such as cyanidation process, thiosulfate leaching, thiourea leaching, leaching in ionic liquids and deep eutectic solvents, last of the methods was less conventional way of leaching with the CNLite reagent, where its use and method of operation were described in detail. The last chapter of the theoretical part evaluated the gold content by the Fire Assay method, which was used in this thesis to analyse the metals present in the samples after leaching.

The experimental part of the thesis consisted of the description and nature of the samples and laser diffraction used to construct distribution curves. The main point of the experimental part was the actual leaching of gold-bearing ore after flotation treatment. Three different leaching agents were used in the experiments – thiourea solution, deep eutectic solvents and CNLite leaching reagent. The content of the experimental part was also an accurate description of the experiments with these reagents. A separate series of experiments was reserved for each leaching agent, in which the rate of extent of leaching into the ore solution was monitored. In the experiments, the kinetics of leaching was also observed based on the change of time in individual leaching experiments, from which it was possible to evaluate the rate of activity of the agents over time and to determine the ideal leaching time. There were 21 leaching tests in thiourea solution, 21 leaching tests in deep eutectic solvents and 14, but 24-hour, leaching tests using the CNLite reagent.

Leaching tests with thiourea solution and deep eutectic solvents took place at the same temperature conditions (60°C, 80°C and 100°C) and at the exact times (15min, 30min, 1h, 2h, 3h, 4h and 5h). Leaching tests with the CNLite reagent were carried out without temperature adjustment, and the leaching process was 24 and 48 hours long. The reason for

the differences in the conditions of the experiments was the different procedures for achieving the ideal activities of the leachers. From the executed leaching tests with thiourea solution, deep eutectic solvents and CNLite gold leaching reagent, we can conclude that the deep eutectic solvents gave the best results. In this case, the gold content of 1,1g Au was obtained in the leachate, representing 85% leaching into the solution. These were two leaching experiments with a duration of 4 and 5 hours. For both, the result was achieved at a temperature of 100°C. The highest value of gold leaching into the solution by thiourea was 0,7 g/t, and the percentage was only 54%. This value was obtained in an experiment with 4 hours and 60°C. The effect of time on leaching efficiency has not been clearly proven. Although the last-named CNLite reagent showed a gold content in the leachate of up to 0,9 g/t in the control sample, which represented 82%, in the target sample of Čučma, this value represented only 0,6 g/t or 67%. This phenomenon was caused by the chemical composition of the samples, which differed slightly. The Hodruša-Hámre sample obtained the best result during 24-hour leaching with a concentration of 40 wt.% and 3 kg/t of leaching agent. On the Čučma sample, the best value was obtained in two cases where the proportion of the leaching agent and the leaching time differed – 3 kg/t, 24h and 4,5 kg/t, 48 h. The thickening values were identical, namely 40 wt.%. The effect of time on leaching efficiency has not been clearly demonstrated. The Sb content was also determined in the experiments with deep eutectic solvents and thiourea. The aim was to compare the recovery of Sb and Au and their leaching kinetics. In tests conducted to determine the extent of leaching of antimony with thiourea and deep eutectic solvents, deep eutectic solvents showed lower values than thiourea. In the case of DES, a value of 2020 g/t Sb was achieved, representing 34%. The result was conducted in an experiment with 2 hours and 100°C. Meanwhile, the value was higher with thiourea, specifically 3600 g/t or 60%. The result was obtained during leaching at 15 minutes and 100°C. From these values, we can state the positive influence of higher temperature on the leaching process, where the maximums were obtained at the highest of the investigated temperatures – 100°C. The effect of time on leaching efficiency has not been clearly demonstrated.

From results we reached, there is visible slower kinetics in case of Sb compared to Au. Experiments were tailored and planned to analyse Au content. Sb kinetics was analysed only after the results from laboratory analyses, where higher amount was discovered. Therefore, kinetics of these two metals were compared. Presence and level of leaching effect of DES and Thiourea reagents to Sb were a side effect when determining Au levels.

After summarizing the results, we can state that each investigated method can effectively obtain a useful component from the ore intended for leaching. The influence of changing conditions in time for all investigated leaching agents, temperature for thiourea and deep eutectic solvents and concentration and amount of leaching agent in the case of CNLite reagent was not clearly demonstrated. The inconsistency in experiments can be subjected to minor human errors, that occur in such experiments, where every sample is packed, moved and weighted manually. Another possible reason for inaccurate results can be the analysed amount. In laboratory conditions only smaller amounts of samples are taken, with an emphasis to financial aspect of each experiment. More experiments, where average value can be created are multiplications of current costs. When smaller amount of sample is analysed, a phenomenon of significant amount of gold contain can be present. In this case it is difficult to avoid this issue. Even though the sample was not further processed during the leaching experiments in this thesis, since a higher gold content was detected in the finer fraction, there is a possibility of enriching the ore by further processing - hydraulic sorting. With this step, the sample would be composed of finer-grained material. Thus, a higher content of precious metals in the sample can be assumed, resulting in higher extent of leaching values.

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