Reprocessing of ore heap leach tailings at the Vasilkovsky GOK, Kazakhstan

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Abstract
Purpose. Representation in a generalized form of the conducted research on the development of technology for heap leaching of gold-bearing tailings at the Vasilkovsky GOK (Altyntau Kokshetau), which can be used to recover gold from technogenic deposits in Kazakhstan.

Methods. The research on the gold recovery from the ore beneficiation tailings at the Vasilkovsky deposit is conducted using direct cyanidation. Experiments are performed in open heat-resistant beakers equipped with a mechanical agitator. The preparation of the material for cyanidation consists of the following operations, such as grinding, water washing and alkaline treatment followed by cyanidation. The optimal cyanidation parameters are determined by performing a series of experiments with a change in one parameter at a constant value of others. After the optimal process duration is determined, a series of experiments are conducted with a change in the solids content in the pulp of 20, 25, 33, 50 and 100%. The concentration of cyanide in the solution is 0.1-1.0 g/dm³. The concentration of sodium thiosulphate in the cyanide solution is 0.5-5.0 g/dm³. The process temperature varies within 20, 30, and 40°C. The content of the nutrient medium is the sodium thiosulphate for use culture T10.

Findings. It has been determined that with an increase in the solids content in the pulp, the degree of gold recovery from tailings increases, reaching a maximum of 97.5%, with a ratio of (solid : liquid) S:L = 1:1. When the solids content in the pulp is below 50%, longer agitation leaching of the pulp is required to achieve a recovery of at least 85-90%, which, in turn, leads to high operating costs.

Originality. For the first time it has been found that the optimal solids content for maximum gold recovery in the pulp can be considered 50% (or S:L = 1:1).

Practical implications. Increasing the solids content in the pulp contributes to the duration of the solvent contact with the ore mass, which allows the use of less concentrated solutions of the leaching agent.

Keywords: heap leaching, gold, ore, beneficiation tailings, solution

1. Introduction

The development of the mining industry over the past century has been inextricably linked with scientific and technical progress. The emergence and introduction of new technologies for mining and processing of ores make it possible to develop deposits and their areas that were previously considered substandard [1]-[3].

The need to meet the increasing demand for mineral raw materials has led to the development of mineral deposits in the accessible areas of the Earth [4], [5]. Given that the content of most useful components does not exceed a few percent, more and more ore-bearing raw materials are extracted onto the earth’s surface [6], [7].

The problem of processing mineral masses recovered to the earth’s surface remains the least developed and therefore the most dangerous for the planet Earth [8]-[10]. Due to the lag of processing capabilities behind the capabilities of mining, as well as the unpredictable conjuncture of minerals, the urgency of this problem is increasing, making it global [11].

Percolation leaching lasts for several months, but due to colmatation processes, it cannot provide a complete metal recovery. Percolation leaching in combination with sorption and recovery of metals is becoming widespread [12]-[14].

A percolation leaching technology has been developed to recover precious metals from gold-bearing ores, placers and concentrates, followed by affinage and obtaining the final product with a purity of at least 99.95%. In contrast to the highly toxic methods known and used so far using cyanides or mercury, the new technology is based on a “soft” hydrochlorination reaction. The essence of the method is in the dissolution of gold and other precious metals (for example, platinoids) by exposing the raw material to “active” chlorine, which is formed directly in the reactor by mixing two reagents. Due to the metered supply of one of them, “active”
chlorine is formed in the amounts necessary for the dissolution of metals, and is practically not released into the atmosphere. This method of dissolution (leaching) of gold favorably differs from all other known methods [15]-[17].

Large in terms of reserves, the Vasilkovsky gold ore deposit is located in Kazakhstan, 17 km northwest of the city of Kokshetau. It was discovered in 1968 and has been developed by various methods since 1979. Gold is mined by the Swiss company Glencore (69.7%) and the Kazakhstan company Kazzinc LLP (21.3%). Proved gold reserves are 270 thousand tons with an average grade of 2 g/t in ores. The identified gold resources are 308 tons, with an average content of 1.9 g/t in ores. The deposit is composed of fine-grained gabbro and medium-grained quartz diorites intersected by quartz-arsenopyrite, quartz, tourmaline, and carbonate veins with inclusions of gold-bearing mineralization [18], [19].

Native virgin gold is confined to quartz-arsenopyrite veins and veinlets, as well as to areas of silification of host rocks with disseminated arsenopyrite. Single gold segregations or nest-like accumulations containing up to 15-20 characters are confined either to microfractures in quartz and arsenopyrite, to interstices of an arsenopyrite aggregate, or to fractures in dark-colored minerals of altered host rocks. Quite often, gold grains form close aggregates with bismuthine. Their shape is irregular, lamellar, hair-like, that is, xenomorphic. Sometimes crystals and drop-shaped gold formations are observed in bismuthine. Their sizes range from 0.0005 to 0.53 mm, with 79% of the measured grains ranging in size from ~0.0008 to ~0.008 mm [20]-[23].

Gold in ores is in association with copper and iron-bearing minerals. In order to leach gold, first of all, it is necessary to open these minerals. The gold dissolution velocity depends on the velocity of opening of the minerals with which it is associated [24], [25].

The ores in the oxidized zone are similar in mineral composition to sulphide ores, but they do not contain hornblende. The composition of ore minerals is dominated by hematite, chalcopyrite, chalcocite (CuS), bismuthine and native bismuth, which impregnate the silicate part of the rocks in the form of finely-dispersed formations.

Preliminary research on percolation leaching of oxidized gold-bearing ore is conducted using a sample of the composition, wt. %: SiO₂ – 64.2; Al₂O₃ – 8.1; Fe₂O₃ – 2.37; As – 0.22; Zn – 0.034, Cu – 0.045; Co – 0.023; S₃S – 0.35; Au – 1.58 g/t. Thus, preliminary research on the choice of a gold solvent has revealed the high efficiency of both cyanide and thiocarbanide leaching in the presence of an oxidizing agent such as sulphate Fe(III).

The ore of the Vasilkovsky gold ore deposit after flotation-gravitation beneficiation contains a certain amount of gold. The mastering of the heap leaching process of gold-bearing ores with cyanide solutions is carried out at Vasilkovsky Mining and Processing Plant, the largest heap leaching plant in the CIS countries [26], [27]. After dumping of individual heaps and their merging, an industrial heap has been formed with a total volume of gold-bearing ore of 1195 thousand tons. The full technology cycle includes heap irrigation operations with gold leaching, gold sorption from weak solutions using anion-exchange resins, its subsequent desorption with ion exchanger regeneration, as well as gold recovery from impregnated thiourea solutions by electrolysis.

In general, the obtained data on monitoring the industrial recovery of gold by heap leaching method at the Vasilkovsky GOK confirm the recommendations previously issued based on the results of previous research.

Neutralization of spent ore dumps is one of the largest environmental problems [28]-[32] that arise in the process of heap leaching of ores. After the recovery of gold, they contain a significant amount of cyanide residues and water-soluble arsenic compounds [33]. For the destruction of cyanides, it is proposed to use “active chlorine”. However, the relatively high cost of this technology and the additional environmental problems arising from its use have led to the search for a more rational solution to this problem [34].

2. Research methods

In order to recover gold from the ore beneficiation tailings at the Vasilkovsky deposit, research is performed on direct cyanidation [35], [36]. Experiments are carried out in open heat-resistant beakers equipped with a mechanical agitator. The preparation of the material for cyanidation consists of the following operations, such as grinding, water washing and alkaline treatment followed by cyanidation.

Water washing of the source material to remove water-soluble compounds from it is conducted in the mode of continuous agitation at a ratio of S:L = 1:5 for 120 seconds, and after settling, the liquid phase is decanted [37]. Alkaline treatment of heap leach tailings is performed in order to improve the performance of subsequent cyanidation. For this purpose, a novel achievement in pump manufacturing can be applied [38], [39].

The optimal cyanidation parameters are determined by performing a series of experiments with a change in one parameter at a constant value of others. First of all, the influence of the process duration on the gold recovery from ore into solution is determined. After the optimal duration of the process is determined, a series of experiments are conducted with a change in the solids content in the pulp of 20, 25, 33, 50 and 100%. The concentration of cyanide in the solution is 0.1-1.0 g/dm³. The concentration of sodium thiosulphate in the cyanide solution is 0.5-5.0 g/dm³. The process temperature varies within 20, 30, and 40°C. The content of the nutrient medium is the sodium thiosulphate for the used culture T10.

Cyanidation of heap leach tailings is performed at constant concentrations of cyanide and alkali. For this purpose, sodium hydroxide and cyanide are added to the pulp in the required amount to create a specified concentration of these reagents in the liquid phase. The solid phase and liquid phase residues are returned to the reactor. The loss of the liquid phase associated with the conducted chemical analysis and evaporation is replenished by adding a cyanide solution or water. When the concentration of cyanide and alkali is determined, the mass of reagents, necessary to achieve the initial concentrations, can be calculated. When cyaniding the heap leach tailings, replenishment is performed after 10, 20, 30, 60 minutes, and then every hour.

At the end of cyanidation, the gold-bearing solution is separated by filtration from the solid phase – tailings. The concentrations of cyanide, alkali, and gold are determined in the productive solution. The content of these components is calculated based on their concentration and the total volume of the solution in the pulp. After that, the degree of gold recovery and the specific consumption of cyanide for gold recovery are calculated. The agitation cyanidation tailings are poured with water, and while stirring, potassium permanganate is added to the solution until the color disappears, then
the permanganate solution is added again and stirred. These operations are repeated until the color ceases to disappear with stirring, which indicates the destruction of all cyanide. After that, the agitation leaching tailings are washed 3–4 times with water, regrinded, and analyzed for gold content. After each experiment, the consumption of reagents is calculated and the degree of gold recovery from the ore into the solution is determined by its amount in the filtrate and in the solid insoluble leaching residue.

After reaching 50% gold recovery during heap leaching of sulphide gold-bearing ore, in order to additionally recover the precious metal from this ore, samples are taken in which the gold content is 1.3–1.4 g/t. Then it is leached by agitation cyanidation method.

For agitation leaching, the tailings are regrinded to a grain size of 95% of the class 0.0075 mm, and then cyanidated. At the same time, the dependence is studied of gold recovery from tailings on the duration and temperature of the process, solids content in the pulp, concentration of sodium cyanide in an alkaline solution, content of sodium thiosulphate in an alkaline solution of sodium cyanide, as well as on the type of microorganisms used and the amount of nutrient for these biooxidants.

The influence of the process duration on the degree of gold recovery is studied at a temperature of 20°C with an alkaline solution of sodium cyanide containing 0.5 g/dm³ of cyanide and 1.0-sodium hydroxide. To ensure a more complete gold recovery from the tailings, the treated material and an alkaline solution of sodium cyanide are taken in the ratios of S:L = 1:3, which amounts to 25% of the solids in the pulp.

As noted above, the experiments are conducted in thermostatted beakers equipped with mechanical agitators, where sub-samples of the source raw material weighing 100 g and an alkaline solution of sodium cyanide at the above ratio are placed. The process is conducted in the mode of continuous agitation for 0.25 to 5 hours (or from 15 to 300 min) with periodic replenishment of the solutions at certain time intervals – 10, 20, 30, 60 minutes, and then every hour. After that, the finished pulp is separated into liquid and solid phases, after which the content of gold, alkali and free cyanide is determined in the filtrate and in the insoluble leaching residue.

### 3. Results and discussion

The obtained research data are presented in Figure 1. From the analysis of the degree of gold recovery dependence on the process duration, it follows that the maximum recovery of 92.3% with a minimum cyanide consumption of 0.5 g/dm³ is observed after 4 hours from the start of the experiment. A further increase in the process duration does not have a significant influence on the degree of gold recovery, and its value remains almost constant. It should be noted that gold from the ore up to 10% is recovered into solution already in the first 30 min of leaching, presumably, during this period, the most accessible forms of gold particles pass into solution.

The leaching of gold particles associated with sulphide minerals and gold particles covered with poorly soluble films is somewhat difficult, as evidenced by the formation of an inflection in the dependence curve of the recovery degree on the process duration (Fig. 1). The specific consumption of sodium cyanide with the optimal process duration of 240 min is about 0.290 t/kg of recovered gold (Table 1).

![Figure 1. Influence of the cyanidation process duration on the gold recovery from the Vasiliyevsky GOK ore tailings: Cyanide consumption: 1 – 0.1 g/dm³; 2 – 0.2 g/dm³; 3 – 0.5 g/dm³; 4 – 0.8 g/dm³; 5 – 1.0 g/dm³](image)

The study of the influence of solids content in the pulp on the process of gold recovery from tailings is conducted according to the methodology described above. It consists in using an alkaline solution of sodium cyanide containing 0.5 g/dm³ of cyanide and 1.0 sodium hydroxide for 4 hours at a temperature of 20°C, while the solids content in the pulp changes from 17.7 to 100% (or at S:L = 1:1, S:L = 1:2, S:L = 1:3, S:L = 1:4, S:L = 1:5).

### Table 1. Influence of the process duration on the specific consumption of sodium cyanide at a cyanide concentration of 0.5 g/dm³

| No. | Time (T), min | Residual concentration, g/dm³ | Q_{GNCN}, t/kg Au | Recovery of Au, % |
|-----|---------------|------------------------------|------------------|------------------|
| 1   | 60            | 0.5                          | 0.81             | 19.9             |
| 2   | 120           | 0.48                         | 0.85             | 257              |
| 3   | 180           | 0.45                         | 0.62             | 333              |
| 4   | 240           | 0.44                         | 0.48             | 290              |
| 5   | 300           | 0.40                         | 0.45             | 496              |

It has been determined that with an increase in the solids content in the pulp, the degree of gold recovery from tailings increases, reaching a maximum of 97.5%, with a ratio of S:L = 1:1. When the solids content in the pulp is below 50%, a longer agitation leaching of the pulp is required to achieve a recovery of at least 85–90%. This, in turn, leads to high operating costs and makes the use of this technological method of gold recovery from heap leach tailings inappropriate. Leaching at low solids content in the pulp and, consequently, at low concentrations of gold and impurities, reduces the diffusion resistance at the S-L interface, thereby increasing the dissolution of not only gold, but also gangue elements (Table 2).

### Table 2. Influence of the S:L ratio on the specific consumption of sodium cyanide at a cyanide concentration of 0.5 g/dm³

| No. | S:L | Residual concentration, g/dm³ | Q_{GNCN}, t/kg Au of Au, % | Content in the filtrate, mg/dm³ |
|-----|-----|------------------------------|---------------------------|--------------------------------|
|     | CN  | NaOH |                           | Fe | Cu | Co | Ni |
| 1   | 1:1 | 0.47 | 0.40                        | 0.043 | 97.5 | 3.2 | 5.8 | < 0.2 |
| 2   | 1:2 | 0.45 | 0.42                        | 0.164 | 85.2 | 2.4 | 6.3 | < 0.2 |
| 3   | 1:3 | 0.44 | 0.48                        | 0.298 | 84.8 | 1.8 | 7.2 | < 0.2 |
| 4   | 1:4 | 0.45 | 0.6                         | 0.418 | 69.4 | 0.9 | 4.2 | < 0.2 |
| 5   | 1:5 | 0.45 | 0.654                       | 53.4 | 0.9 | 3.7 | < 0.2 |

Increasing the solids content in the pulp increases the duration of solvent contact with the ore mass, which allows the use of less concentrated solutions of the leaching agent.
Thus, by reducing the solids content in the pulp, a high yield of gold per unit time can be achieved with a corresponding high gold recovery. However, due to the high consumption of sodium cyanide, water, significant energy consumption for mixing large volumes of pulp and the complexity of filtering the latter, this is not always expedient. Therefore, the optimal content of solids in the pulp can be considered 50% (or S:L = 1:1).

When choosing the optimal sodium cyanide concentration, it should be taken into account that its value is related to the oxygen content in the solution under given conditions. For example, at a temperature of 15°C and a pressure of $P = 0.021$ MPa, the oxygen solubility is 0.314·10$^{-4}$ mol/cm$^3$, so the optimal concentration of free (not bound into complex compounds) cyanide should exceed 0.1 g/dm$^3$ of NaCN. However, in practice, stronger cyanide solutions (0.2-0.5 g/dm$^3$ of NaCN) are usually used, since process cyanide solutions usually contain a significant amount of impurities that reduce the activity of cyanide solutions. Associated minerals, oxidized at a noticeable velocity, contribute to a decrease in the oxygen content consumed in side reactions. This leads to a decrease in the gold dissolution velocity, which is associated with the formation of dense films on its surface.

The study of the concentration influence of an alkaline solution of sodium cyanide on the degree of gold recovery from the tailings is conducted at an optimal process duration of 4 hours and an optimal content of S:L = 1:1 at a temperature of 20°C. The source raw material is leached using alkaline solutions of sodium cyanide, in which the content of the leaching agent is varied from 0.1 to 1.0 g/dm$^3$. In this case, the conditions of the experiment are kept the same, as in the studies on the influence of the process duration and the solids content in the pulp on the gold recovery given above. The decrease in the degree of gold recovery from the ore with an increase in the concentration of the used cyanide solution from 0.1 to 1.0 is associated with an insufficient presence of oxygen in the solution under these conditions.

At atmospheric air pressure above the solution and a temperature of 20°C, the solubility of oxygen in water is 0.27·10$^{-3}$ mol/cm$^3$. Therefore, it can be expected that an increase in the concentration of free CN$^-$ ions (not bound into a complex) above 1.62·10$^{-3}$ mol/cm$^3$ will not lead to an increase in the process velocity. At the same time, when free cyanide is deficient, improving the solution aeration also does not lead to an increase in the velocity. Therefore, it is necessary to control the composition of the solution so that the ratio of free CN$^-$ ions concentration to the concentration of O$_2$ is 5-6.

With a decrease in the sodium cyanide concentration in an alkaline solution, the degree of gold recovery from heap leach tailings increases and reaches a maximum value of 92.3% when the raw material is treated with a sodium cyanide solution containing 0.1 g/dm$^3$.

Figure 2 shows the dependence of the gold recovery velocity ($v$) on the cyanide solution concentration ($c$). The gradient angle tangent $lg v$ depending on $lg c$ [CN$^-$], which is found by the Van’t Hoff graphical method, has a fractional value of 0.96. This evidences the complexity of the ongoing processes and indicates the parallel flow of several reaction stages.

Thus, gold is most efficiently recovered from heap leach tailings at sodium cyanide concentrations of 0.1-0.2 g/dm$^3$. In this case, 91-92% of gold is recovered into the solution for 3-4 hours of agitation leaching at a low specific consumption of sodium cyanide 0.045-0.091 t/kg of gold.

With an increase in the concentration of the cyanide solution, the sodium cyanide specific consumption increases and reaches 1.05 t/kg of gold when using 1.0 g/dm$^3$, while the gold recovery practically does not increase. Therefore, cyanide concentration of 0.1-0.2 g/dm$^3$ is recommended as the optimal concentration for agitation leaching of gold from heap leach tailings.

With an increase in the process duration, the specific consumption of sodium cyanide increases. This is conditioned by its consumption not only for the recovery of gold, but also for the dissolution of gangue minerals, primarily for the dissolution of the minerals of iron, copper, cobalt, nickel and zinc, which are present in the tailings in sufficient quantity (Table 3).

Table 3. Influence of the concentration of sodium cyanide solution on the specific consumption of sodium cyanide

| No. | S:L   | Residual concentration, g/dm$^3$ | $Q_{NaCN}$, t/kg Au | Recovery of Au, % | Content in the filtrate, mg/dm$^3$ |
|-----|-------|----------------------------------|---------------------|-------------------|-----------------------------------|
|     |       | CN                     | NaOH     | Fe   | Cu   | Co   | Ni   |
| 1   | 1:1   | 0.09                  | 0.08     | 0.043 | 97.5 | 3.2  | 5.8  | < 0.2 |
| 2   | 1:2   | 0.18                  | 0.30     | 0.164 | 85.2 | 2.4  | 6.3  | < 0.2 |
| 3   | 1:3   | 0.26                  | 0.4      | 0.298 | 84.8 | 1.8  | 7.2  | < 0.2 |
| 4   | 1:4   | 0.44                  | 0.48     | 0.418 | 69.49| 0.9  | 4.2  | < 0.2 |
| 5   | 1:5   | 0.61                  | 0.88     | 0.654 | 53.47| 0.9  | 3.7  | < 0.2 |

It is known that the temperature is an important factor in the process of agitation leaching of gold-bearing ores. The study of the temperature influence on the gold recovery from tailings is carried out using an alkaline solution of sodium cyanide containing 0.5 g/dm$^3$ of cyanide and 1.0 sodium hydroxide, for 4 hours, at S:L = 1:1, in the range of 20-40°C.

The dependence of gold recovery degree on the process temperature is characterized by the presence of a clear maximum, indicating that with an increase in temperature from 20 to 40°C, the degree of gold recovery increases from 86 to 92.3% (Fig. 3). However, its further increase leads to a decrease in the product yield even at 40°C and the precious metal recovery reaches only 76%.

The dependence of the velocity constant on the reciprocal temperature of the process is described by the Arrhenius equation (Fig. 4), from which the calculated value of the process activation energy in the studied temperature range can be obtained. Based on the analysis of known gold solvents, it follows that alkali and alkali-earth metal thiosulphates are capable of dissolving gold with the formation of a double salt AuS$_2$O$_3$·3NaS$_2$O$_3$·H$_2$O.

To additionally recover gold from heap leach tailings with cyanide solution in the presence of sodium thiosulphate, experiments are conducted using solutions where the sodium thiosulphate content is varied within 0.05-0.5 g/dm$^3$.  

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4. Conclusions

Heap leaching is a promising method for involving gold from low-grade ores, dumps and small deposits into the field of gold recovery. This makes it possible to expand the ore base and improve the technical-and-economic performance of gold mining enterprises, which is essential for the mining industry in Kazakhstan. To increase the gold concentration, it is recommended to use a leaching solution in circulation or for sequential irrigation of several areas of the ore mass.

With an increase in the pause duration of irrigation, the velocity of recovery per unit time naturally decreases, although the gold recovery per irrigation can remain approximately the same. With a zero and one-day pause, Au recovery per a single irrigation is 1.37 and 1.43%, with a two-day pause – 1.23%, and with a three-day pause – 1.35%.

Based on the obtained data, for leaching of the oxidized gold-bearing ore of the Vasilkovsky deposit, it is recommended to use a pause in irrigation lasting from 0 to 2 days (until 20-25% of Au is recovered). After that, it can be increased up to 3 days, thereby creating conditions for the intensification of the natural oxidation processes of associated minerals due to the penetration of atmospheric oxygen into the pores and fractures of the ore. The optimal duration of a pause in irrigation with gold recovery of 20-40% is 1-3 days.

The conducted complex research on the sorption of gold and impurity metals makes it possible to recommend a change in the technological scheme of sorption in order to increase the efficiency of the process under the conditions of the Vasilkovsky GOK. In this case, the transition from a two-stage to a multi-stage counter-current process scheme is probably more efficient. The number of sorption stages should be chosen depending on the composition of the leaching productive solution in a given period and the temperature (seasonal) mode.

The results of research on the patterns for metal sorption make it possible to issue recommendations for improving the process efficiency under the conditions of the Vasilkovsky GOK. At the same time, it is recommended to change from two-stage to a multi-stage flexible sorption scheme, depending on the composition of the solutions and the seasonal temperature mode.

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тимальні параметри ціанування визначали виконанням серії дослідів зі зміною одного параметра за постійного значення інших. Визначивши оптимальну тривалість процесу, проводили серії дослідів зі зміною вмісту твердої речовини у пульпі 20, 25, 33, 50 та 100%. Концентрація ціану в розчинні становила 0.1-1.0 г/дм³. Концентрація тіосульфату натрію в ціаністому розчинні становила 0.5-5.0 г/дм³. Температура процесу змінювалася в межах 20, 30 і 40°C. Зміст живильного середовища – тіосульфат натрію для використовуваної культури T10.

Результати. Встановлено, що з підвищенням вмісту твердого в пульпі зростає ступінь отримання золота з хвостів, досягаючи максимуму 97.5%, при співвідношенні (тверді: рідке) Т:Р = 1:1. При вмісті твердого в пульпі нижче 50% для досягнення вилучення не менше 85-90% потрібно більш тривале агітаційне вилуговування пульпи, що, у свою чергу, призводить до великих експлуатаційних витрат.

Наукова новизна. Вперше встановлено, що оптимальним вмістом твердої речовини для максимального вилучення золота в пульпі можна вважати 50% (або Т:Р = 1:1).

Практична значимість. Підвищення вмісту твердого в пульпі сприяє збільшенню тривалості контакту розчинника з рудною масою, що дозволяє застосовувати менш концентровані розчини вилуговуючого реагента.

Ключові слова: кучне вилуговування, золото, руда, хвости збагачення, розчин

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