Prospects for use of chlorine-containing leaching solutions for extraction of associated useful components from spent ores of uranium deposits

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Abstract
Work aimed at diversification of production through the additional extraction of associated useful components at uranium mines. The peculiarity of the work carried out is the additional processing of spent uranium mines at the existing ones using the existing production infrastructure for the extraction of associated useful components. The technology of underground leaching is well developed for uranium deposits. The leaching of associated useful components differs from the leaching of uranium only in the reagents used, and they are fundamentally similar to the method of underground borehole leaching. Even if there are associated components in the uranium-bearing sands with a content of less than 1 g/t, up to 0.1 g/t production can be profitable. The use of ready-made infrastructure of uranium mines on spent blocks of deposits allows us to expect positive economic profitability in the future.

Keywords: uranium mines, associated valuable metals, associated useful components, underground well leaching, productive solution, chlorine-containing solutions.

Introduction

Today, sodium cyanide is the main reagent in the industrial hydrometallurgical process for extracting gold from ores.

Increasing requirements for environmental protection, especially in relation to the in situ leaching method, determine the relevance of the search for less toxic reagents - gold solvents. One of these reagents can be solutions containing active chlorine, both in the form of free halogen and in the form of hypochlorites. In this work, studies have been carried out on core samples obtained during the drilling of an exploration well at the Semizbay uranium deposit.

Literature review

Leaching of ores in situ, that is, by the PV method, excludes any ore preparation and imposes high environmental requirements, therefore, the use of cyanides in underground leaching is practically excluded. In the case of mining placer deposits containing large, hardly soluble in cyanides gold, the use of cyanides is also ineffective in the technological aspect.

In this regard, chlorine, iodine and bromine-containing reagents, which are environmentally safer than cyanide reagents, can be used as leaching agents. In the case of using the in situ leaching method, capital costs can be reduced by 2-4 times, therefore, the in situ leaching process can be cost effective with a higher chlorine consumption, with a duration of mining of ore deposits of several months, as well as when mining poor off-balance ores [1].

It is important to emphasize that in situ leaching of gold is carried out without cyanide, using hydrochloride technology, which makes it possible to ensure the environmental safety of the
work. Potassium and sodium hypochlorite obtained by electrolysis and gaseous chlorine are used as a solvent in the Ural deposits. [2].

In work [3], the results of studies on the leaching of gold from crushed ore to a size of -12 + 0 mm are given. The use of sodium acetate as a chemical additive in leaching gold on bottle dough from crushed ore to a particle size of -12 + 0 mm increases gold recovery by ~ 4% and improves the kinetics of gold dissolution.

According to the method [4], the efficiency of leaching both gold and silver is achieved by the fact that at the first stage of gold extraction, a weak chlorine solution (0.2-0.7%) is used, having a pH> 1.8, and at the second stage, a weak solution sodium thiosulfate (0.2-0.7%), having a pH of 7.5-8.5. Oxidation and dissolution of gold thus proceeds in a weakly acidic medium at a high oxidation potential (> 1200 mV). At the same time, sulfides, oxides, carbonate minerals, feldspars, organic compounds are exposed, which contributes to both the most complete gold recovery and an increase in the filtration permeability of the formation, in particular, due to the dissolution of carbonate cement. There is also no swelling of clays, which is characteristic of the alkaline medium, which is distinguished by the cyanide method.

Simultaneously with the leaching of gold, silver is oxidized and re-precipitated in the form of chloride, which facilitates its leaching with thiosulfate at the subsequent stage of mining.

The novelty of the proposed method consists in regulating the concentration of chlorine in the solution so that pH> 3 is maintained in the evacuated solution. This ensures the purity of the productive solution from the presence of iron, aluminum, zinc, copper due to their hydrolysis and reprecipitation in the formation. The oxidation potential in this mode remains high enough and ensures the retention of gold in solution.

When leaching ore from the Tas-Yuryakh deposit under normal conditions (T = 20 °C), with agitating the ore with chlorine water, a productive solution was obtained with pH = 6 and EMF = 1230 mV. At the same time, the degree of gold extraction was 98%. The productive solution was then treated with ammonia, as a result of which only traces of chlorine were found in it, while the pH increased and the redox potential decreased.

From productive gold-bearing solutions, gold was almost completely precipitated by cementation on zinc powder.

The method [5] includes preparing a leaching solution of hydrochloric acid and feeding it into the ore. The novelty is that immediately before feeding into the ore, the hydrochloric acid solution is neutralized by adding a solution of commercial alkaline sodium or potassium hypochlorite to it. Used sodium hypochlorite (TU-6-15-746-87) or obtained by electrolysis. A solution of sodium hypochlorite (TU-6-15-746-87) is served in an amount of 0.6 volumes with 1-4 volumes of hydrochloric acid solution.

The aim of the invention is to increase the efficiency of gold extraction, reduce the acidity of the process, ensure the selectivity of the process and eliminate the dangers associated with the preparation and use of chlorine water and the transition to arsenic solution.

This goal is achieved by the fact that gold leaching is carried out without preliminary acidification and washing of arsenic and iron with a neutral solution prepared immediately before feeding into the ore from commercial alkaline sodium hypochlorite (for example, sodium hypochlorite TU 6-15-746-87) and hydrochloric acid solution, with the following ratio of ingredients, g/l by volume.

A solution of sodium hypochlorite alkaline TU 6-15-746-87 (sodium hypochlorite 30-40) is served in an amount of 0.6 volumes with 1-4 volumes of hydrochloric acid solution.

As it was found experimentally, the decrease in the leaching efficiency with acidic chloride solutions (according to the prototype), when going into an iron solution, is due to the low redox potential of the medium: +700-800 mV, which does not ensure the stability of complex gold ions (AuCl₄⁻). The decrease in efficiency is also due to the sedimentation of gold by iron.

The efficiency of leaching according to the proposed method is ensured by the fact that the neutralization of the acid solution with an alkaline solution of hypochlorite is carried out immediately before feeding into the ore. Atomic chlorine, which is released when mixing solutions and did not have time to combine into a Cl₂ molecule, is very aggressive towards gold. Excess acid is neutralized with alkali from a commercial solution of alkaline hypochlorite.

In order to increase the recovery of gold in the method [6], leaching is carried out with a solution of hydrochloric or sulfuric acid with the addition of hypochlorite at the following ratio: 0.1 n HCl + (0.02–0.1) n NaClO, prepared immediately before its injection into the ore. Preliminary acidification of ores is carried out until the level of
iron concentration in the output solution decreases below 600 mg/l.

In order to increase gold recovery and eliminate the dangers associated with the preparation and use of chloride water, the following solutions are used for leaching:

\[ 0.1n \text{HCl} + (0.02-0.10) n \text{NaClO} \]

\[ \text{pH of the medium is 1.3-2.5, } \text{Eh} = \text{from +900 to +1300 mV} \]

In the claimed composition, HCl can be replaced by HSO_4 and other acids.

A method for extracting gold from ores, including preliminary acidification of ore with an acid solution, preparation of a leach solution and leaching with an acid solution containing active chlorine in the form of Cl_2 differs in that, in order to increase gold recovery, reduce the consumption of chemical reagents and eliminate and using chlorine water, the preparation of the leaching solution is carried out immediately before its injection into the ore, while hypochlorite is added to the acid solution at a pH of 1.3-2.5, Eh from +900 to +1300 mV.

The use of aqueous solutions of chlorine for the opening and leaching of gold (hydrochlorination) is becoming more widespread in the practice of enrichment of refractory ores and concentrates [7–13].

In [14], the leaching of the concentrate was carried out for 10 hours at a ratio of S: L = 1:10 and a current density on the electrodes of 50 A / m². As a result of the experiments, it was found that the rational concentration of NaCl salt in the solution is 250 g / dm³, since a subsequent increase in its concentration to 300 g / dm³ leads to a slight (by 1.1%) increase in gold recovery from 34.6% to 35.7%. A flotation gold-bearing concentrate with a size class of 74 µm, containing 60–65% arsenopyrite and 52.5 g / t gold, was used as the test product.

In [15], an alternative non-cyanide method of gold leaching from oxidized ores of the Malmyzh deposit (Khabarovsk Territory) was investigated. The initial gold content in the ore is 0.8-0.95 g / t. The initial gold content in the ore is 0.8-0.95 g / t. The solution was prepared by electrolysis of a sodium chloride (NaCl) solution with a concentration of 20 g / l with the addition of 0.1 N hydrochloric acid (HCl). The optimal conditions for obtaining a solution with the maximum concentration of active chlorine required for gold leaching have been determined. A study of gold extraction by agitation with preliminary action on the pulp by preoxidation and cavitation (ultrasound) was carried out. Analysis of samples of the liquid phase of the pulp for gold was carried out using atomic absorption spectroscopy. Direct hypochlorite leaching resulted in 23.0% gold recovery in 4 hours and 72.7% in 24 hours. After preoxidation followed by leaching with hypochlorite, gold recovery was 80.2% and 98.8% in 4 and 24 hours, respectively. After ultrasonic treatment, the yield of gold in the liquid phase of the pulp was 36.7-66.5% for 4 hours of agitation. The process of re-precipitation of the extracted gold into the solid phase and a decrease in its yield during prolonged agitation after preliminary ultrasonic treatment of both the initial hypochlorite and the pulp were revealed. Re-precipitation occurs due to the transition of the pH of the medium to the neutral region. Consequently, the process of extracting gold with a chloride-hypochlorite solution must take place in an acidic environment.

**Experimental part**

Based on the analysis of scientific sources, a chlorine-containing solution of the following composition was selected for experimental work on the leaching of associated useful components:

\[ \text{Ca (ClO)}_2 + \text{HCl} \text{(hydrochloric acid with calcium hypochlorite), pH = 3.00.} \]

Laboratory experimental work on agitational leaching was carried out on samples of core material from ores of the "Semizbay" deposit from the supra-ore, ore and sub-ore intervals.

After agitational leaching of ores, the productive solutions were analyzed to determine the concentration of associated elements by the atomic absorption method and are presented in Table 1.

According to the data obtained, the highest yield of components into solution was achieved in the ore interval. Iron concentration - 514.80 mg/dm³, aluminum - 148.81 mg/dm³, scandium - 0.068 mg/dm³, lanthanum - 0.23 mg/dm³.

**Recovery of gold (Au) in pooled technological samples.**

Studies to determine the content of gold in technological samples were carried out in the laboratory "Technologies for the hydrocarbon and mining and metallurgical sectors and related service industries" of JSC "IMiO" in Almaty. Analyzes in solutions were performed according to the method (MVI reg. No. KZ 07.00.01996-2014) on a Varian AA240 atomic absorption spectrometer and the assay method was used to determine gold in core samples. The results of analyses of
Table 1 - Concentration of accompanying elements of technological solutions

| No. | No. samples | Fe$_{total}$ mg/dm$^3$ | Al, mg/dm$^3$ | La, mg/dm$^3$ | Sc, mg/dm$^3$ | Leaching solution concentration, g/l | Rock interval |
|-----|-------------|------------------------|--------------|--------------|--------------|-----------------------------------|---------------|
| 1   | AP-4-1(C)   | 27,79                  | 20,74        | 0,063        | 0,00095      | 12                                 | Supra-sternum interval |
| 2   | AP-5-1(C)   | 71,84                  | 71,98        | 0,10         | 0,047        | 24                                 | Ore interval    |
| 3   | AP-6-1(C)   | 514,80                 | 50,34        | 0,14         | 0,031        | 48                                 | Breast interval |
| 4   | AP-4-2(C)   | 243,98                 | 72,82        | 0,13         | 0,046        |                                   |               |
| 5   | AP-5-2(C)   | 446,79                 | 148,81       | 0,23         | 0,068        |                                   |               |
| 6   | AP-6-2(C)   | 133,79                 | 38,48        | 0,077        | 0,021        |                                   |               |
| 7   | AP-4-3(C)   | 1,19                   | 0,64         | 0,0081       | 0,00088      |                                   |               |
| 8   | AP-5-3(C)   | 0,02                   | 14,26        | 0,035        | 0,0013       |                                   |               |
| 9   | AP-6-3(C)   | 0,020                  | 2,26         | 0,023        | 0,0014       |                                   |               |

Table 2 - The result of the chemical analysis of prefabricated core samples by the assay method for gold

| No. | No. samples | Au g/t | Interval          |
|-----|-------------|--------|-------------------|
| 1   | A-6-1(C)    | 0,34   | Supra-sternum     |
| 2   | A-6-2(C)    | 0,34   | Ore               |
| 3   | A-6-3(C)    | 0,34   | Breast            |

Table 3 - Comparison of gold recovery from ore samples at different concentrations

| No. | No. samples | Au mg / dm$^3$ | Leaching solution concentration, g / l |
|-----|-------------|----------------|----------------------------------------|
| 1   | A-6-1(C)    | 0,006          | 12 (Supra-sternum)                      |
| 2   | A-6-2(C)    | 0,0167         | 24 (Ore interval)                       |
| 3   | A-6-3(C)    | 0,046          | 48 (Breast spacing)                     |

technological samples for gold are presented in Tables 2 and 3.

The results of X-ray phase analysis are shown in Figure 1. In the range from 800 to 2050 nm, the decomposition spectrum exhibits pronounced fluctuations of the main peaks of uranium - U, iron-Fe, copper-Cu, manganese-Mn, zinc-Zn. Also in the decomposition spectrum there are vibrations of rare earth elements such as osmium-Os, rhenium-Re, neodymium-Nd, actinium-Ac, scandium-Sc, cesium-Ce, bismuth-Bi, etc. It is worth noting that the decomposition spectra contain spectral lines of mercury-Hg and implicit vibrations of gold-Au.

With the formation of uranium ores in chemical composition, sulfide minerals arise along with which mercury is formed, since they are genetically related in chemical nature. Mercury, in turn, forms compounds with gold in the amalgamation reaction. Therefore, the presence of implicit reflections of gold and pronounced spectra of mercury indicates the probable finding of gold.

Figure 1 - Results of X-ray phase analysis of a core sample
The Au recovery is shown in Figure 2. The result obtained characterizes a solution of the composition HCl + CaClO + H2O with a concentration of 48 g/l as more effective for Au than a solution with a concentration of 24 g/l and 12 g/l. The recovery of Au at a concentration of 48 g/l reached 67%.

Conclusions

The laboratory and experimental work on agitational leaching on samples of core material from ores of the Semizbay deposit of the supra-ore, ore and sub-ore intervals showed that a chlorine-containing solution of the composition Ca (ClO)2 + HCl (hydrochloric acid with calcium hypochlorite) at pH = 3.00.

The highest gold yield into solution was achieved in the under-ore interval. The gold recovery rate is 67%. The highest yield of accompanying components is observed in the ore interval. The concentration of iron - 514.80 mg/dm3, aluminum - 148.81 mg/dm3, scandium - 0.068 mg/dm3, lanthanum - 0.23 mg/dm3, which is possibly a consequence of the effect of acid treatment in the extraction of uranium.

To date, the use of the method of leaching with calcium hypochlorite in combination with hydrochloric acid has not found application in industry for the extraction of gold on an industrial scale. In this work, the experiments were carried out directly on the ore material and the result was achieved allowing the application of this method on an industrial scale.

Thus, in-situ leaching of spent uranium deposits for the extraction of associated useful components is a promising area of research.

Conflict of interests. On behalf of all authors, the correspondent author declares that there is no conflict of interests.

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Figure 2 - The degree of extraction of Au during agitational leaching with a CaClO solution with the introduction of oxidants at various concentrations

![Figure 2](image-url)
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Псевдоспособ подземного выщелачивания благородных металлов, преимущественно золота и серебра, из руд на месторождениях урановых месторождений.

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АННОТАЦИЯ

Работа нацелена на диверсификацию производства за счет дополнительного извлечения попутных полезных компонентов из отработанных руд. Особенность проводимой работы состоит в использовании существующей производственной инфраструктуры для добычи попутных полезных компонентов. Технология подземного выщелачивания хорошо отработана для урановых месторождений. Выщелачивание попутных полезных компонентов отличается от выщелачивания урана только по используемым реагентам, и они принципиально схожи методом подземно – скважинного выщелачивания. Даже при наличии в ураноносных песках попутных компонентов с содержанием ≤ 1 г/т, вплоть до 0,1 г/т производство может быть рентабельным. Использование готовой инфраструктуры урановых рудников на отработанных блоках месторождений позволяет ожидать положительную экономическую рентабельность в перспективе.

Ключевые слова: урановые рудники, попутные ценные металлы, попутные полезные компоненты, подземное скважинное выщелачивание, хлорсодержащие растворы.

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