Investigation of the solid oxidizer effect on the metal geotechnology efficiency

Khalidilla Yussupov\textsuperscript{1,2}, Erbolat Aben\textsuperscript{1,2,3}, Dalekhan Akhmetkanov\textsuperscript{1,2,3}, Khairulla Aben\textsuperscript{2,3}, Saltanat Yussupova\textsuperscript{1,2,3}

\textsuperscript{1} Satbayev University, Almaty, Kazakhstan
\textsuperscript{2} CSA Global, West Perth, Australia
\textsuperscript{3} Non-Profit JSC “Almaty University of Power Engineering and Telecommunications named after Gumarbek Daukeyev”, Almaty, Kazakhstan

\textsuperscript{*}Corresponding author: e-mail y.aben@satbayev.university

Abstract

\textbf{Purpose.} The research is aimed at increasing the useful component content in a pregnant solution during in-situ leaching (ISL) using a solid oxidizer and increasing the ferric iron concentration in the leaching solution based on laboratory research.

\textbf{Methods.} Laboratory research is performed on a specially developed model electrolyzer for obtaining comparative data on divalent iron oxidation to trivalent iron and the change in the useful component content in a pregnant solution. Firstly, tests are conducted with a basic leaching solution, then on the oxidation of the leaching solution with a solid oxidizer in the form of a lead dioxide plate. Tests are conducted by changing sulphuric acid concentration within 5-50 g/l, amount of divalent iron ions in the solution from 0.5 up to 4.0 g, lead dioxide plate surface area from 19 to 76 cm\textsuperscript{2}. The leaching time is up to 10 hours.

\textbf{Findings.} The results of laboratory research on determining the oxidation degree of divalent iron ions and change in the oxidation-reduction potential (ORP) depending on the sulphuric acid concentration and on the initial concentration of divalent iron ions in the initial solution are presented. With a change in the sulphuric acid concentration from 5 to 50 g/l, the oxidation value of divalent iron ions increases from 26.5 to 96.5\%, and with an increase in the initial solution concentration of divalent iron, the oxidation degree of divalent iron naturally decreases from 95.2 to 58.8\%. In the initial leaching solution, the divalent solution concentration is 312 mg/l, and that of the trivalent solution is 288 mg/l. After oxidation with a solid oxidizer, the divalent and trivalent iron concentrations are 56 and 392 mg/l, respectively. In the course of further laboratory research using core materials from a uranium deposit, it has been revealed that when leaching with a basic solution, the uranium content in the pregnant solution is 19.36 mg/l, and when leaching with a solution after oxidation with a solid oxidizer, it is 27.9 mg/l, which is by 8.54 mg/l more.

\textbf{Originality.} New dependences have been determined of the oxidation degree of divalent iron ions to trivalent one on the sulphuric acid concentration and on the initial concentration of divalent iron ions, as well as the useful component content in the pregnant solution on the leaching time when using a solid oxidizer.

\textbf{Practical implications.} Using of a solid oxidizer, it is possible to increase the trivalent iron concentration in the leaching solution and the useful component content in the pregnant solution compared with the basic technology, thereby reducing the time of mining uranium reserves. Proposed technology is environmentally friendly, with low capital costs.

\textbf{Keywords:} geotechnology, in-situ leaching (ISL), oxidation, pregnant solution, trivalent iron, sulphuric acid

1. Introduction

Today, the mining-metallurgical complex (MMC) is one of the most important strategic sectors of the economy of the Republic of Kazakhstan. The MMC now accounts for over 7\% of GDP, 19\% of industrial output, and over 35\% of manufacturing output. More than 300 thousand people are employed at the enterprises of the industry, which is approximately 3.6\% of the total employed population in the republic. Kazakhstan is the 13\textsuperscript{th} largest country in the world in terms of total solid mineral production. The available resource base at the current level of production in the country, according to estimates, will last only 30-40 years, whereas today only about 10-15\% of the reserves and predicted resources of explored deposits are involved in mining. At the same time, Kazakhstan, while occupying a leading position in the world in terms of the volumes of certain mineral reserves, is among the last in terms of their quality [1].

At the same time, about 30 billion tons of industrial waste has accumulated in the republic at present. About a third of it is technogenic waste from non-ferrous metallurgy enterprises, and at least 10\% of the waste is toxic. Some slag dumps have been found to have higher metal content than the mined ore. Currently, no more than 2\% of waste is recycled and disposed of [2]. Based on this, considering the prospects for the development of the mining-metallurgical complex of Kazakhstan, it seems necessary to emphasize the need to strengthen the resource- and energy-saving policies.
It is obvious that in order to preserve solid minerals for future generations, as well as reduce waste from the mining-metallurgical complex, it is necessary today to use the latest technologies for the fullest recovery of useful raw materials at the lowest cost [3].

New, so-called geotechnological methods of mining mineral raw materials, which have been developing in recent years, fully meet this objective of mining and further increase in the efficiency of mining the fields. They are based on the transformation of minerals in their place of occurrence through thermal, mass transfer, chemical and hydrodynamic processes into a liquid or gaseous state suitable for transportation and further processing. Geotechnological methods of mining are implemented, as a rule, through wells drilled from the surface to the deposit [4], [5].

The successful development of such technologies will result in an artificial increase in reserves of mineral resources, as losses and technogenic waste will be reduced to zero. Dissolved metals will eventually be recovered into concentrates directly in underground workings, since there will be no need for ore transportation, crushing, grinding, flotation processes, dumping and transportation of tailings, etc. Mineral production and end-product quality will increase significantly [6], [7]. Such technologies will be created because they are the production part of a new direction in the Earth science – geo-engineering, which is currently declared one of the most important directions of the Fourth Industrial Revolution by the World Economic Forum in Davos.

However, despite all the advantages of geotechnological mining methods, they have a number of disadvantages, one of which is the dependence of their efficiency on oxidation-reduction potential (ORP) of the process solution. For example, when leaching with sulphuric acid solutions, the ORP value of leaching solutions is determined by the trivalent iron concentration. It is known that the trivalent iron concentration can be increased by using various oxidizers [8].

Currently, in the geotechnology of metals by in-situ leaching method, various oxidizers are used, such as atmospheric oxygen, hydrogen peroxide, sodium nitrite (NaNO2) and potassium bichromate (K2Cr2O7) and others [9], [10].

One of the oxidizers is hydrogen peroxide (hydrogen dioxide), since H2O2 is the simplest representative of peroxides. The hydrogen peroxide advantage is that it is one of the most powerful oxidizers, more powerful than chlorine or potassium permanganate. Hydrogen peroxide is also formed when water is exposed to sunlight, which is a natural way to clean the environment. Therefore, hydrogen peroxide does not have problems with its decomposition products, which are present in other oxidizers. Hydrogen peroxide is miscible with water in any concentration and therefore the problem of its safe handling is easily solved by its dilution [11]. Depending on ore composition, as well as the leaching conditions, the use of hydrogen peroxide at the Semizbay field resulted in savings in leaching solution and sulphuric acid. Depending on the leaching conditions and solid phase concentration, the addition of hydrogen peroxide has increased the total oxygen concentration in the system, and also contributed to deeper leaching by direct oxidation [12].

To reduce excess acid consumption, the ore-bearing seam colmatation caused by iron ion deposition and low leaching rate in conventional acid leaching of a uranium sandstone-type deposit, the authors of [13] propose a low-acid leaching technology with the addition of liquid oxygen to the solution. The leaching mechanism for the sandstone-type uranium ore with a low content of acid and oxygen, the oxidation of iron ions under acidic conditions, and the factors influencing the oxidation process of iron ions have been studied. Kinetic modeling of the oxidation of uranium minerals with oxygen shows the interaction of uranium and iron deposition in acidic solution. The research results have revealed that under low acidity conditions, the kinetics of iron oxidation with oxygen is between the first and second order reaction, which can reduce the deposition of iron ions, and then reduce the influence of iron ion deposition on uranium leaching, so as to improve the uranium leaching rate. This research confirms the possibility of oxygen oxidation of uranium and uranium leaching under low-acidity conditions, which is an important guiding factor for efficient leaching of uranium deposits with high acid consumption.

In alkaline in-situ uranium leaching, oxygen is the most common oxidizer, and bicarbonate is the complex-forming agent. For uranium deposits in sandstones with high reduction capacity or difficult hydrogeological conditions, oxidation with oxygen is ineffective. Therefore, these uranium deposits require an effective leaching method. In the paper [14], a typical sandstone uranium deposit, characterized by a high content of sulphates, chlorides in groundwater and hard-to-recover uranium leaching, was chosen to study the effects of synergistic oxidation with oxygen. Based on pressure leaching studies and field trials, oxidizers such as hydrogen peroxide, potassium permanganate and sodium dichloroisocyanurate were tested. Leaching tests have shown that the minor oxidizer sodium dichloroisocyanurate exhibits good synergistic oxidation with oxygen and leaching effects on uranium minerals. The results also show that hydrogen peroxide does not exhibit oxidative effects when used as a single oxidizer. Although potassium permanganate is good at oxidizing uranium when used as a single oxidizer, it has an inhibitory effect on the oxidation of uranium minerals with oxygen.

The study [15] proposes a technology for intensifying uranium recovery by introducing sodium nitrite into the leaching solution with additional supply of compressed air or oxygen into the leaching solution for providing catalytic oxidation of divalent iron ions with dissolved oxygen. The results of laboratory and experimental-industrial work proved a positive effect with simultaneous supply of sodium nitrite and pure oxygen to the solution, which leads to the achievement of trivalent iron concentrations up to 1.0-1.2 g/l.

Analysis of various leaching intensification methods shows that they all accelerate the process and increase the degree of the useful component extraction. However, these oxidizers are not universal, they are expensive and difficult to use in industrial conditions [16], [17]. Therefore, the choice of an effective oxidizer has a significant impact on increasing the proportion of trivalent iron and the useful component content in the pregnant solution.

The purpose of this research is to increase the useful component content in a pregnant solution and reduce the time for mining uranium reserves during in-situ uranium leaching by using a solid oxidizer and oxidation of divalent iron to trivalent iron in the leaching solution based on laboratory research on core materials from a uranium deposit.

The research objectives are:

- to conduct laboratory research on a model sulphuric acid solution to determine the influence of the concentration of sulphuric acid, divalent iron ions in the initial solution on
the divalent iron oxidation to trivalent iron when using a solid oxidizer;
− to conduct laboratory research on core material from uranium deposit to determine the change in the uranium content, ORP value and trivalent iron concentration depending on the time of leaching with a basic solution without an oxidizer and using a solid oxidizer to compare the leaching results.

2. Materials and research methods

Core materials were sampled from the eastern and western flanks of the Central site of the Central Mynkuduk field. Field determination of core material is gray sand. The core material was sampled at different well depths at intervals of every 20 cm. A total of 6 m of core has been sampled from each flank. To determine the average uranium content in core material, all cores were crushed, and the uranium content ranges from 0.035% and 0.04%. The Central Mynkuduk field is located in the Turkistan Region of the Republic of Kazakhstan. The core material is wrapped in paraffin paper to eliminate oxidation.

A method using a solid oxidizer in the form of lead dioxide is proposed for oxidizing divalent iron to the trivalent iron state and increasing ORP value of the solution.

Источник ссылки не найден! Ошибка!

Источник ссылки не найден. When divalent iron is oxidized, the metal oxide is reduced to form a compound of this metal in the lowest oxidation degree in the solid state. The resulting compound is oxidized anodically and the original oxide is formed again, that is, the reagent required for oxidation is regenerated. The processes are repeated cyclically and the oxidizer is almost not consumed.

Lead dioxide is known to be a strong oxidizer and can therefore be used for iron oxidation. Oxidation is performed in a sulphuric acid solution containing divalent iron ions. The proposed method schematic diagram is shown in Figure 1.

![Figure 1. Schematic diagram of electrolyzer for the oxidation of divalent iron ions: 1 – electrolyzer with separated electrode spaces; 2 – lead dioxide electrode; 3 – graphite electrode; 4 – anionite membrane (AM); 5 – solution containing divalent iron ions; 6 – sulphuric acid solution](image)

In the proposed method, a lead dioxide oxidizer is used as a plate-shaped electrode. The galvanic couple is formed in the form of a “lead dioxide – graphite” system. They are placed in an electrolyzer with separated electrode spaces 1 and an anionite membrane 4. A lead dioxide electrode 2 is installed in the first space, and a graphite electrode 3 is installed in the second space. The second space is filled with a sulphuric acid solution containing divalent iron ions. The lead dioxide electrode and the graphite electrode are interconnected by copper wires in series in an electrical circuit with an ammeter, which makes it possible to determine the electrochemical oxidation rate of divalent iron ions.

In this case, the course of the oxidation reaction of divalent iron ions to the trivalent iron state is explained as follows: when lead dioxide electrode is connected to a graphite electrode, an electromotive force is established between them. As a result of this, the graphite electrode produces an oxidation reaction of the divalent iron ions to the trivalent iron state: Fe(II) → e → Fe(III).

On the second electrode, the lead dioxide reduction reaction occurs: PbO₂ + SO₄²⁻ + 4H⁺ + e → PbSO₄ + 2H₂O.

Lead dioxide anodes are manufactured in a similar way to the lead sulphate battery anode used in all cars. A lead plate with lattice holes is covered with a paste consisting of a mixture of lead dioxide and a sulphuric acid solution. When solidifying, the paste seizes well and becomes hard.

At the first stage, laboratory research is conducted with a model sulphuric acid solution to determine the influence of the concentration of sulphuric acid, divalent iron ions in the initial solution on the divalent iron oxidation to trivalent iron when using a solid oxidizer. At the second stage, in order to compare the leaching results, laboratory research is first conducted with a basic solution without an oxidizer, then with the use of a solid oxidizer on core material from the uranium deposit. In this case, the change in the uranium content, ORP value and divalent-trivalent iron concentrations are determined. The leaching time is up to 10 hours. During laboratory research, the sulphuric acid concentration varies in the range of 5-50 g/l by simple dilution with water and appropriate acid doses. The amount of divalent iron ions in solution is from 0.5 up to 4.0 g, the surface area of the lead dioxide plate is from 19 to 76 cm².

For laboratory research, the core material is placed in a transparent vessel (Fig. 2).

![Figure 2. Core material: 1 – core; 2 – transparent vessel for core placement; 3 – inlet for leaching solution; 4 – pregnant solution tap](image)

When performing laboratory research on core material, the leaching time is 9-10 hours, the amount of leaching solution is 12 liters. The pregnant solution is sampled every hour, with a total of 21 samples taken, 9 with the basic technology (without oxidizer) and 10 with the proposed technology (using solid oxidizer). The pregnant solution samples are
poured into 100 ml containers. The ORP value is determined using the IT-1101 device, and the uranium content, the divalent-trivalent iron concentrations – in the mine laboratory using bichromate titration method and complexometric titration method, respectively. The degree of divalent iron oxidation to trivalent iron is determined by the difference in their concentrations in the initial and oxidized solutions.

3. Results and discussion

Laboratory research is conducted to study the influence of sulphuric acid concentration in the initial solution on the divalent iron oxidation to trivalent iron.

Research has revealed that increased sulphuric acid concentration leads to increased oxidation degree of divalent iron ions and ORP value of the solution. With a divalent iron ion content of 1.0 g/l and a sulphuric acid concentration of 50 g/l, the oxidation degree of divalent iron ion reaches 96.5%. If ORP value in the absence of sulphuric acid is 0.574 V, then with a sulphuric acid concentration of 50 g/l – 0.821 V.

By processing the research data, dependency graphs of the oxidation degree of divalent iron and ORP value have been obtained with a change in the sulphuric acid concentration in the solution (Fig. 3).

![Figure 3. Oxidation degree of divalent iron ions and change in ORP value depending on the sulphuric acid concentration](image)

Further research is conducted to reveal the dependence of the oxidation degree of divalent iron ions on their initial concentration in solution.

Research has determined that with an increase in the initial divalent iron concentration in the solution within the range of 0.5 to 5 g/l, the oxidation degree of divalent iron naturally decreases from 95.2 to 58.8%, the same pattern is observed with ORP value. Figure 4 shows the dependencies of the oxidation degree of divalent iron ions and ORP value on the initial divalent iron ion concentration.

Thus, the laboratory research results have shown that when using a solid oxidizer, an increase in the oxidation degree of divalent iron to trivalent iron is observed.

To determine the influence of a solid oxidizer on the leaching process intensification, further laboratory research is conducted on core material from a uranium deposit. As already mentioned, the research was first conducted with a basic solution, then with the use of a solid oxidizer.

The research results with a basic solution have revealed that with an increase in leaching time, ORP value changes insignificantly, from 334 to 342 mV. In this case, the trivalent iron concentration decreases from 288 to 260 mg/l, and the divalent iron concentration increases from 312 to 325 mg/l.

![Figure 4. Degree of divalent iron oxidation and change in ORP value depending on the initial iron concentration](image)

During the leaching period, the uranium content in the pregnant solution changes insignificantly and varies within 18.0-21.2 mg/l. In general, the average uranium content in the pregnant solution is 19.36 mg/l, the divalent iron concentration increases by 4%, and the trivalent iron concentration decreases by 10%. By processing the research data, dependency graphs of divalent-trivalent iron concentrations, ORP and uranium content values on the leaching time with the basic solution without oxidation have been obtained (Fig. 5).

![Figure 5. Dependences of divalent-trivalent iron concentrations, ORP and uranium content values on the leaching time with the basic solution without oxidation](image)

When conducting the next series of laboratory research, a solution with the same divalent-trivalent iron content is oxidized using a solid oxidizer. After that, the divalent-trivalent iron content is 56 and 392 mg/l, respectively. When using a solid oxidizer, there is also a gradual increase in the divalent iron concentration from 56 to 224 mg/l, while the trivalent iron concentration decreases from 392 to 358 mg/l. The ORP value ranges within 365-379 mV, and the uranium content at the beginning rises to 40.1 mg/l, then decreases to 19.2 mg/l. In general, the average uranium content in pregnant solution is 27.9 mg/l.

By processing the research data, dependency graphs of divalent-trivalent iron concentrations, ORP and uranium content values on the leaching time using a solid oxidizer have been obtained (Fig. 6). The decrease in the trivalent iron concentration, ORP value and the increase in the divalent iron concentration are explained by the fact that during laboratory research, the leaching solution is oxidized using a solid oxidizer only at the beginning of the experiment.
After processing the laboratory research data, dependency graphs of the uranium content in the pregnant solution and the trivalent iron concentration on the leaching time have been obtained with the basic technology, using a solid oxidizer (Figs. 7 and 8). From the graphs obtained, it can be seen that the best parameters are achieved with the use of a solid oxidizer.

![Graph of uranium content vs. leaching time](image1.png)

**Figure 7. Dependences of the uranium content in the pregnant solution on the leaching time with the basic technology, using a solid oxidizer**

The research results show that when using a solid oxidizer, the sulphuric acid concentration in the leaching solution has a significant influence on the divalent iron oxidation to trivalent iron. Given that at the Kazakhstan uranium mines, the sulphuric acid concentration during leaching ranges from 5 to 15 g/l, then the use of a solid oxidizer will lead to the divalent iron oxidation to trivalent iron from 26 to 48%, and ORP from 0.65 to 0.74 V.

When the divalent iron concentration in the solution changes from 1 to 5 g/l, there is a decrease in the oxidation degree of divalent iron from 95.2 to 58.8% and ORP value. At the studied field, the divalent iron concentration ranges from 1.11 to 2.23 g/l, while, according to the laboratory research results, the degree of its oxidation can reach 90-97%, which correspondingly leads to an increase in the trivalent iron concentration.

The results of core material leaching with the basic technology and using a solid oxidizer show that the average uranium content in the pregnant solution is 19.36 and 28.4 mg/l, respectively, that is, by 9.04 mg/l more compared to the basic technology. The decrease in the uranium content in the pregnant solution after a certain leaching time is explained by a gradual decrease in the amount of uranium in the studied core material.

When comparing the results of laboratory research with a solid oxidizer with previous research on the solution saturation with oxygen and hydrogen peroxide, it has been revealed that the average uranium content in the solution increases by 37% when oxidized with a solid oxidizer, by 23% when the solution is saturated with oxygen, and by 25% when using hydrogen peroxide compared to the basic solution. At the same time, it is necessary to take into account the high cost of hydrogen peroxide and the complexity of saturating the leaching solution with oxygen. Moreover, the use of various chemical oxidizers leads to groundwater pollution and requires special transportation and storage methods.

The proposed technology is characterized by a simple design, is easily integrated into the leaching solution line, is environmentally friendly, and its use will reduce the time for mining uranium reserves in technological blocks and, accordingly, reduce the end-product cost. Therefore, in the future, for practical application of the proposed technology, it is necessary to conduct experimental-industrial tests at an operating uranium mine.

### 4. Conclusions

For the first time, it has been proven that lead dioxide can be used for divalent iron oxidation, resulting in an increase in ORP value, trivalent iron concentration and useful component content in the pregnant solution during in-situ uranium leaching.

The dependences of the oxidation degree of divalent iron ions and the change in ORP value on the initial concentrations of iron ions and sulphuric acid have been obtained when using a solid oxidizer. It has been determined that an increase in the sulphuric acid concentration in the solution when using a solid oxidizer leads to a significant increase in ORP and the oxidation degree of divalent iron to trivalent iron. With an increase in the divalent iron concentration in the initial leaching solution, there is a decrease in the degree of its oxidation to trivalent iron in percentage. For example, with a change in the sulphuric acid concentration from 5 to 50 g/l, the oxidation degree of divalent iron ions increases from 26.5 to 96.5% and ORP value increases from 0.65 to 0.82 V.

The use of a solid oxidizer during leaching increases the uranium content in the pregnant solution and reduces the time of mining uranium reserves. Laboratory research has determined that the average uranium content in the pregnant solution increases by 9.04 mg/l when using a solid oxidizer compared to the basic technology. After 9 hours of core
material leaching. 174.24 mg have been recovered using the basic technology and 255.6 mg using a solid oxidizer, which reduces both the uranium mining period by 46.6% and the end-product cost. The research performed with the basic and proposed technologies on core materials, as well as comparison with the results of previously conducted research show a significant increase in the oxidation degree of divalent iron to trivalent iron, ORP value and the uranium content in solution, which proves good perspectives of this technology.

The conducted research results can be used at enterprises mining uranium by the method of in-situ leaching.

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