

## Applying The Fe<sup>3+</sup> Oxidizer As An Improvement In The Efficiency Of Uranium Extraction

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**Abstract :** Almost all industrial uranium deposits in the Republic of Uzbekistan are located in the Kyzylkum region. For the development of these deposits, the Navoi Mining and Metallurgical Combine (NMMC) was created, which is one of the world elite of uranium producers. The products manufactured by the plant provide a significant inflow of foreign currency to the Republic and therefore have significant national economic importance.

**Keywords:**

The developed uranium ores are characterized by extremely difficult mining and hydrogeological conditions of occurrence, which completely exclude their development by traditional mining methods. Today, all uranium production is carried out by in-situ leaching of PV through a system of geotechnical wells drilled from the surface.

Currently, in the Kyzylkum province, underground leaching is being successfully developed at the uranium deposits of the Navoi Mining and Metallurgical Combine. For many years, uranium (oxides, rarely coffinite) has been considered as the main useful component in the deposits of Central Kyzyl Kum.

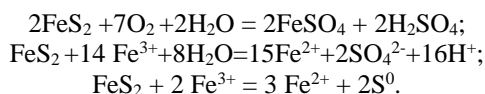
In recent decades, geotechnological methods of mining have become widespread in world practice, which have a number of advantages over the traditional and expensive mining method. Among them, a special place is occupied by geotechnology (underground leaching) of metals (uranium, copper, nickel, iron, zinc, molybdenum, aluminum, gold, etc.) from poor-balance and off-balance ores in the place of their occurrence in the subsoil using chemical reagents with subsequent processing into the surface of the obtained productive solutions.

Leaching is the process of selectively extracting one or more valuable components from an ore, ore concentrate or semi-finished product into an aqueous solution.

Fe<sup>3+</sup> ions are a very effective, affordable and cheap uranium dioxide oxidizer. With the participation of the process, the redox potential of this system will depend on the ratio of ferric and ferrous iron, almost complete oxidation of uranium dioxide is achieved at a ratio of  $2\text{Fe}^{2+} \setminus \text{Fe}^{3+} \setminus \setminus = 1$ . Iron minerals in the ore are often the source of ferric ions.

The iron content in circulating solutions of in-situ leaching (ISL) during the development of the deposit is about 1 g / dm<sup>3</sup> due to the ore iron that has passed into the solution. However, under natural conditions, the leaching of its own amount of ore ferric iron is insufficient, since iron (III) is consumed in side reactions involving pyrite and organic matter.

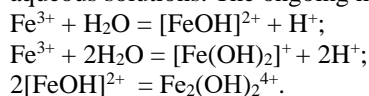
It was found in the work that pyrite present in ores actively interacts with iron (III) salts in solution according to the reactions:



The mechanism of interaction of organic matter with iron (III) salts in solution is revealed. Organic matter is also an active reductant of ferric iron. As a result of the interaction, an almost complete reduction of iron (III) to iron (II) occurs, which significantly reduces the driving force of process (1) and leads to low rates of uranium extraction into solution.

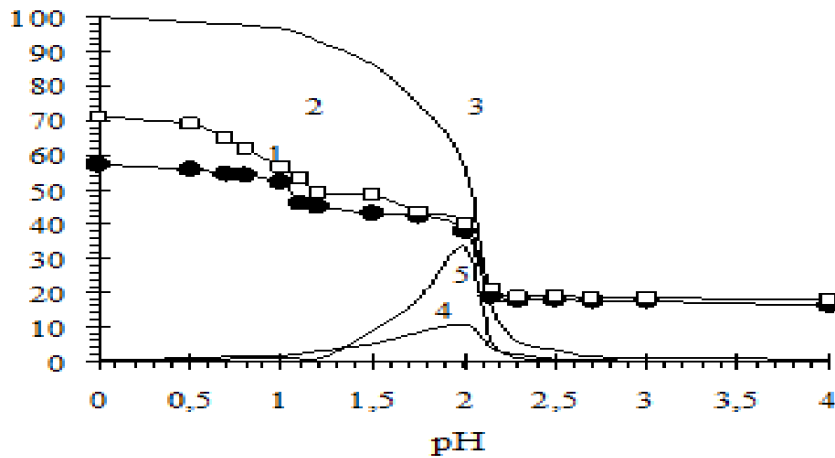
From this it follows that for an effective UW of uranium it is necessary to develop a continuous process of regeneration of iron (II) salts accumulating in a solution in an iron (III) salt. Regeneration must be carried out with an additional artificially introduced oxidant.

The leaching performance in the presence of an oxidizing agent is influenced by the hydrolysis of iron (III) in aqueous solutions. The ongoing hydrolysis processes are described by the reactions:



The calculation of the distribution of ionic forms of iron (III) depending on pH was carried out using the corresponding constants of hydrolysis and the equation of the material balance of the components. The results of calculating ionic forms for a solution with an iron (III) content of 1 g / dm<sup>3</sup> are shown in the figure.

- (1) in the course of the curves of the dependence of the extraction of uranium and the dependence of the content of unhydrolyzed forms of iron (III) on pH, there is a significant similarity. Consequently, non-hydrolyzed forms of iron are kinetically the most reactive ionic forms of Fe (III).



**uranium extraction and distribution of ionic forms of iron (III)%**

Graph 1. - Uranium extraction from ore and distribution of ionic forms of iron (III) during leaching with solutions with iron (III) content 1 g / dm<sup>3</sup>:

- 1 - ε (%), day;      3 – the proportion of iron in the form Fe<sup>3+</sup>, %;  
 2 - ε (%), 30 day;      4 – the proportion of iron in the form FeOH<sup>2+</sup>, %;  
 5 - the proportion of iron in the form of Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, %

Therefore, the maximization of the acid concentration, which ensures the maintenance of the maximum concentration of non-hydrolyzed forms of iron, is an important condition for an effective UW of uranium. Test experiments on ore leaching using pyrolusite, sodium nitrate, potassium dichromate and hydrogen peroxide revealed that sodium nitrite is the most promising oxidant due to the complexity and staging of the interaction mechanism, which allows achieving a higher oxidation effect of iron (II) and, accordingly, higher recovery rates uranium.

Use of sodium nitrate (NaNO<sub>2</sub>) as an oxidizing agent

The table shows the results of determining the activation energy of leaching for Fe and NO<sub>2</sub>.

In the presence of these oxidants, at the first stage of leaching, the reaction takes on the order of iron (III) and sodium nitrite, equal to 0.52 and 0.82, respectively. The obtained experimental data make it possible to derive the kinetic equations of the leaching processes. (3)

For the first stage leach without the use of an oxidizing agent, the following equation applies to describe the reaction rate V:

$$V = K_1 \cdot e^{-\frac{21000}{RT}} \cdot C_{\text{Fe(III)}}^{0,52},$$

where K<sub>1</sub> is a constant value;

C<sub>Fe(III)</sub> - concentration of iron (III) in solution.

For the regime using iron (III) salts as an oxidizing agent at the initial stage of leaching, the following equation is applicable to describe the reaction rate:

$$V = K_2 \cdot e^{-\frac{15000}{RT}} \cdot C_{\text{Fe(III)}}^{0,52}$$

where K<sub>2</sub> is a constant.

When using sodium nitrate as an oxidizing agent at the initial stage of leaching, the kinetic equation is as follows:

$$V = K_3 \cdot e^{-\frac{12000}{RT}} \cdot C_{\text{Fe(III)}}^{0,52} \cdot C_{\text{NaNO}_2}^{0,82},$$

where K<sub>3</sub> is a constant;

C<sub>NaNO<sub>2</sub></sub> - concentration of sodium nitrate in solution.

At the stage of additional leaching, both without the use of oxidants and with their presence in the solution, the kinetic regularities are described by the general equation:

$$V = K \cdot e^{-\frac{900}{RT}}$$

where K is a constant.

The second stage of leaching is characterized by the absence of the influence of the concentration of oxidizing reagents on the leaching process. At the first stage of leaching, intensive leaching of coffinite and pitchblende occurs, while at the second stage, there is practically no increase in recovery over time. No coffinite or pitchblende was found in the leaching cakes, while X-ray phase analysis showed that uranium in the phase of organic matter, brannerite and leucoxene practically did not undergo dissolution. Therefore, the second stage was identified with the leaching of sparingly soluble leucoxene and brannerite.

It follows from the analysis that at the initial stage, in the absence of an oxidizing agent, the process proceeds in a transient diffusion-kinetic regime. As follows from the calculated data, salts of nitrous acid and salts of iron (III) are catalysts for the leaching process, which make it possible to lower the activation energy of the leaching process. The introduction of catalysts provides a decrease in the value of the activation energy from 21 to 12-15 kJ / mol, that is, to values typical for diffusion leaching modes. As a result, kinetic hindrances are completely eliminated, and the process goes into the intradiffusion regime.

Consequently, the leaching of uranium ores in the presence of oxidants and also without the addition of oxidants Fe and NO<sub>2</sub> proceeds in two stages: the stage of intensive leaching of uranium, characterized by the process proceeding in a mixed diffusion-kinetic mode, is replaced by a slow stage of additional leaching of residual uranium, which occurs in the intra-diffusion mode.

Based on this, the possibility of extracting up to 54-55% of uranium from off-balance ores, about 54-57% from ordinary ores, and up to 73% from rich ores, that is, a part of uranium confined to coffinite and pitchblende, was substantiated. The additional leaching of coke and brannerite is significantly hampered under the conditions of underground leaching. When determining the activation energy corresponding to an area with a high degree of leaching, low values were obtained, at the level of 0.9-1 kJ / mol, indicating the limitation of the process by internal diffusion through the hard shell of the mineral.

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