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The study of change in extraction degree under the influence of oxidizers while leaching Uranium ore with sulfuric acid

Sulfuric acid is extensively used in uranium production with In-Situ Leaching method. The influence of various components on the extraction degree has to be studied in order to optimize the solution spending and extraction degree of uranium. In the context of this article, the extraction degree and overall dynamics of the leaching process is studied by numerically calculating concentrations of dissolved uranium mineral. The calculation is implemented along the path of leaching solution from injection well to production well. Properties that is being studied is the change in extraction degree. The change in extraction degree over time at production well is calculated first without and then with addition of oxidizers, which in case of this work were Iron and Pyrolusite. On the basis of chemical processes a mathematical model was created to simulate uranium extraction process. The results show that adding Iron and Pyrolusite to leaching reaction can increase overall extraction degree of uranium minerals.

Key words: extraction degree, sulfuric acid, oxidizer, in-situ leaching, uranium, numerical modeling.

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Күкірт қышқылымен уранды шаймалау кезінде өндіру дәрежесіне тотықтандырғыштың әсерін зерттеу

Жер асты шаймалау әдісінде уранды қышқыл арқылы өндіру кең таралған әдіс болып табылады. Әр-түрлі химиялық компоненттердің өндіру дәрежесіне әсерін зерттеу аталған процестің тиімділігін арттыруға мүмкіндік береді. Берілген мақалада өндіру дәрежесі мен процестің жалпы динамикасы айдайтын ұңғы мен өндіру ұңғысы арасында таралатын еріген уран концентрациясын сандық модельдеу арқылы зерттеледі. Өндіру ұңғысындағы өндіру дәрежесінің өзгерісі тотықтырғышты, яғни қарастырылып отырған жағдайда темір мен пиролюзитті қосқан және қоспаған жағдайы есептелінді. Уранды жер асты шаймалау әдісін симуляциялау үшін берілген химиялық процесстің негізінде математикалық модел құрылды. Алынған нәтижелер шаймалау процесі кезінде темір мен пиролюзитті қосу пайдалы компоненттің өндіру дәрежесін өсіруіне алып келетінін көрсетті.

Түйін сөздер: өндіру дәреже, күкірт қышқылы, тотықтырғыш, жер асты шаймалау, уран, сандық модельдеу.

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Изучение влияния окислителей на степень извлечения при выщелачивании урана растворами серной кислоты

Кислотное выщелачивание наиболее популярный метод производства урана методом подземного скважинного выщелачивания. Исследование влияние различных химических компонентов на степень извлечения может значительно оптимизировать данный процесс. В контексте текущей статьи, исследуется степень извлечения и общая динамика процесса путем численного моделирования концентрации растворенного урана.

Моделирование производится вдоль пути следования выщелачивающего расствора от закачной скважины до откачной скважины. Изменение степени извлечения на откачной скважине вычисляется с и без добавления окислителей, которыми в нашем случае являются железо и пиролюзит. С учетом закона действующих масс; на основе химической процессов была построена математическая модель для симуляции процесса выщелачивания урана. Результаты показывают, что добавление железа и пиролюзита в процессе выщелачивания могут повысить степень извлечения полезного компонента.

Ключевые слова: степень извлечения, серная кислота, окислитель, подземное выщелачивание, уран, численное моделирование.

1 Introduction

In 2015 Kazakhstan was number one country by uranium production accounting for as much as 39% of all produced uranium in the World [2]. About 80% of all known Kazakhstan's uranium resources can be recovered using in-situ leaching (ISL) method. In fact, 45% of share of uranium production can be attributed to ISL method [1].

There are two main techniques for leaching of uranium ore: acid and carbonate. the main factor for determining which technique to use is the type of the ore [3]. The solution that is used at ISL mines in Kazakhstan is sulphuric acid (H_2SO_4) [1], while the most common of uranium ores that are: Uraninite (UO_2, U_3O_8) and Coeffinite($U[SiO_4,(OH)_4]$) [4]. Uranium ore mainly exists in four- and six-valent compounds. Unlike six-valent, four-valent uranium ore dissolves with complications. In fact, evidence show that most of it stays underground after leaching was conducted. Therefore, adding oxidizers to leach remaining four-valent uranium, becomes a necessity. By adding oxidizers the speed of four-valent uranium leaching can be increased, thus rising overall extraction degree. One of the most common oxidizers used in uranium industry is Iron (Fe) along with Manganese Dioxide (MnO_2) also known as Pyrolusite [3].

In the context of this article, computational methods are used to study the effects of Iron and Pyrolusite on uranium leaching process. The results of kinetics for the reactions with and without Iron along with Pyrolusite were achieved and compared to identify the effects of said oxidizers on uranium leaching.

2 Chemistry of acid leaching

Uranium trioxide leaching proceeds by the following chemical formula:

$$UO_{3(solid)} + 2H^{+}_{(liquid)} \longrightarrow UO^{2+}_{2(liquid)} + H_2O_{(liquid)}, \tag{1}$$

$$UO_3 + H_2SO_4 \longrightarrow UO_2SO_4 + H_2O, \tag{2}$$

This reaction happen relatively fast and without complications [3].

Experimental evidence show that Iron is the oxidizing agent which accelerates uranium dioxide leaching by the following scheme [3]:

$$UO_{2(solid)} + 2Fe^{3+}_{(liquid)} \longrightarrow UO^{2+}_{2(liquid)} + 2Fe^{2+}_{(liquid)}, \tag{3}$$

Iron which plays the role of oxidizing agent decreases its valence which is a major issue, since it is no longer available for succeeding reactions. To return it to its original valence, Pyrolusite is added by the following principle:

$$2Fe^{2+}_{(liquid)} + MnO_{2(solid)} + 4H^{+}_{(liquid)} \longrightarrow 2Fe^{3+}_{(liquid)} + Mn^{2+}_{(liquid)} + 2H_2O_{(liquid)} \tag{4}$$

Hence, overall life cycle should look as follows:

$$Fe^{2+} + \text{oxidizer} \longrightarrow Fe^{3+} + U^{4+} \longrightarrow Fe^{2+} + \text{oxidizer} \longrightarrow Fe^{3+} + U^{4+} \longrightarrow \text{and etc.} \tag{5}$$

The resulting chemical model is described by the system in the formula number (6).

$$\begin{cases} H_2SO_{4(liquid)} \longrightarrow 2H^{+}_{liquid} + SO^{2-}_{4(liquid)} \\ Fe(OH)_{3(solid)} + 3H^{+}_{liquid} \longrightarrow Fe^{3+}_{(liquid)} + H_2O_{(liquid)} \\ UO_{2(solud)} + 2Fe^{3+}_{(liquid)} \longrightarrow UO^{2+}_{2(liquid)} + 2Fe^{2+}_{(liquid)} \\ 2Fe^{2+}_{(liquid)} + MnO_{2(solid)} + 4H^{+}_{(liquid)} \longrightarrow \\ 2Fe^{3+}_{(liquid)} + Mn^{2+}_{(liquid)} + 2H_2O_{(liquid)} \\ UO_{3(solid)} + 2H^{+}_{(liquid)} \longrightarrow UO^{2+}_{2(liquid)} + H_2O_{(liquid)} \\ UO^{2+}_{2(liquid)} + 3SO^{2-}_{4(liquid)} \longrightarrow [UO_2(SO_4)_3]^{4-}_{(liquid)} \end{cases} \tag{6}$$

3 Mathematical model

The domain under consideration is one dimensional from injection well to production well, where the distance between them is equal to L.

To model uranium acid leaching numerically, let us introduce the following conventions:

C_1	H^+	hydrogen concentration
C_2	SO_4^{2-}	sulfuric oxide concentration
C_3	Fe^{3+}	iron(III) concentration
C_4	Fe^{2+}	iron(II) concentration
C_5	UO_2^{2+}	oxidized uranium dioxide concentration
C_6	$[UO_2(SO_4)_3]^{4-}$	uranyl sulfate concentration
C_{s1}	$Fe(OH)_3$	iron hydroxide concentration
C_{s2}	MnO_2	pyrolusite concentration
C_{s3}	UO_3	uranium(VI) trioxide concentration
C_{s4}	UO_2	uranium(IV) dioxide concentration
$\vec{U}$		velocity field
ϕ		porosity
K		filtration coefficient
h		hydraulic pressure
$k_i, i = \overline{1,6}$		rate of reaction, where i is respective number of chemical equation from formula (6)
$D_i, i = \overline{1,6}$		diffusion coefficient

Due to the fact that leaching process take place in porous subterrain environment, Mass Conservation Law and Darcy's Law equations are used for modeling purposes.

$$div(\vec{U}\phi) = 0 \tag{7}$$

$$\vec{U}\phi = -Kgrad(h) \tag{8}$$

By substituting the Darcy's Law in to Mass Conservation Law we will obtain the following hydraulic head equation.

$$div(Kgrad(h)) = 0 \tag{9}$$

By using Law of Mass Action we can derive the following differential equations that are used for a numerical research:

$$\begin{cases} \frac{\partial C_{s1}}{\partial t} = -\frac{k_2}{(1-\phi)\rho_s} C_{s1} C_1^3 \\ \frac{\partial C_{s2}}{\partial t} = -\frac{1}{(1-\phi)\rho_s} (-k_4 C_{s2} C_4^2 C_1^4 + k_7 C_7 C_8^2) \\ \frac{\partial C_{s3}}{\partial t} = -\frac{k_5}{(1-\phi)\rho_s} C_{s3} C_1^2 \\ \frac{\partial C_{s4}}{\partial t} = -\frac{k_3}{(1-\phi)\rho_s} C_{s4} C_3^2 \\ \frac{\partial C_1}{\partial t} + \vec{U} gradC_1 = div(D_1 gradC_1) + \frac{1}{\phi\rho_l}(-3k_2 C_{s1} C_1^3 - 4k_4 C_{s2} C_4^2 C_1^4 - 2k_5 C_{s3} C_1^2) \\ \frac{\partial C_2}{\partial t} + \vec{U} gradC_2 = div(D_2 gradC_2) + \frac{1}{\phi\rho_l}(-3k_6 C_5 C_2^3) \\ \frac{\partial C_3}{\partial t} + \vec{U} gradC_3 = div(D_3 gradC_3) + \frac{1}{\phi\rho_l}(-2k_3 C_{s4} C_3^2 + 2k_4 C_{s2} C_4^2 C_1^4 + k_2 C_{s1} C_1^3) \\ \frac{\partial C_4}{\partial t} + \vec{U} gradC_4 = div(D_4 gradC_4) + \frac{1}{\phi\rho_l}(2k_3 C_{s4} C_3^2 - 2k_4 C_{s2} C_4^2 C_1^4) \\ \frac{\partial C_5}{\partial t} + \vec{U} gradC_5 = div(D_5 gradC_5) + \frac{1}{\phi\rho_l}(k_3 C_{s4} C_3^2 + k_5 C_{s3} C_1^2 - k_6 C_5 C_2^3 \\ \frac{\partial C_6}{\partial t} + \vec{U} gradC_6 = div(D_6 gradC_6) + \frac{k_6}{\phi\rho_l} C_5 C_2^3 \end{cases} \tag{10}$$

Initial and boundary conditions for mentioned differential equations are as follows:

$$\begin{array}{llll} h|_{x,t=0} = 0 & C_1|_{x,t=0} = 0 & C_2|_{x,t=0} = 0 & C_3|_{x,t=0} = 0.004 \\ C_4|_{x,t=0} = 0.001 & C_5|_{x,t=0} = 0 & C_6|_{x,t=0} = 0 & C_{s1}|_{x,t=0} = 0.04 \\ C_{s2}|_{x,t=0} = 0.09 & C_{s3}|_{x,t=0} = 0.002 & C_{s4}|_{x,t=0} = 0.001 & \end{array}$$

$$\begin{array}{llll} h|_{x=0,t} = h_0 & \frac{\partial h}{\partial x}|_{x=L,t} = 0 & C_1|_{x=0,t} = 0.2 & C_2|_{x=0,t} = 0.1 \\ C_3|_{x=0,t} = 0 & C_4|_{x=0,t} = 0 & C_5|_{x=0,t} = 0 & C_6|_{x=0,t} = 0 \\ C_{s1}|_{x=0,t} = 0 & C_{s2}|_{x=0,t} = 0.02 & C_{s3}|_{x=0,t} = 0 & C_{s4}|_{x=0,t} = 0 \end{array}$$

$$\frac{\partial C_1}{\partial x}|_{x=L,t} = \frac{\partial C_2}{\partial x}|_{x=L,t} = \frac{\partial C_3}{\partial x}|_{x=L,t} = \frac{\partial C_4}{\partial x}|_{x=L,t} = \frac{\partial C_5}{\partial x}|_{x=L,t} = \frac{\partial C_6}{\partial x}|_{x=L,t} = 0$$

$$\frac{\partial C_{s1}}{\partial x}|_{x=L,t} = \frac{\partial C_{s2}}{\partial x}|_{x=L,t} = \frac{\partial C_{s3}}{\partial x}|_{x=L,t} = \frac{\partial C_{s4}}{\partial x}|_{x=L,t} = 0$$

where $k_i, i = \overline{1,6}$ are usually determined experimentally, while in our case they are constant and equal to one, since all reactions are occurring at the same time.

4 Results

The idea is to study the kinetics of leaching process from injection well (where leaching solution is injected) to production well (where leaching solution containing dissolved uranium mineral is obtained). Therefore, one dimensional problem was considered, and results were achieved by using implicit method for pressure calculation and explicit method for concentration calculation [5].

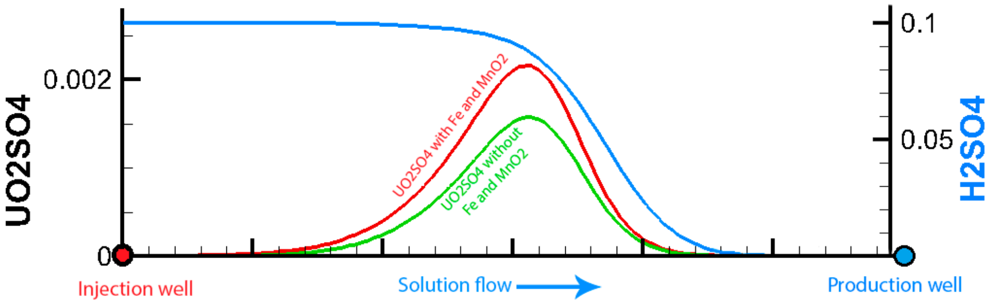

Figure 1–Kinetics of leaching process from injection well to production well

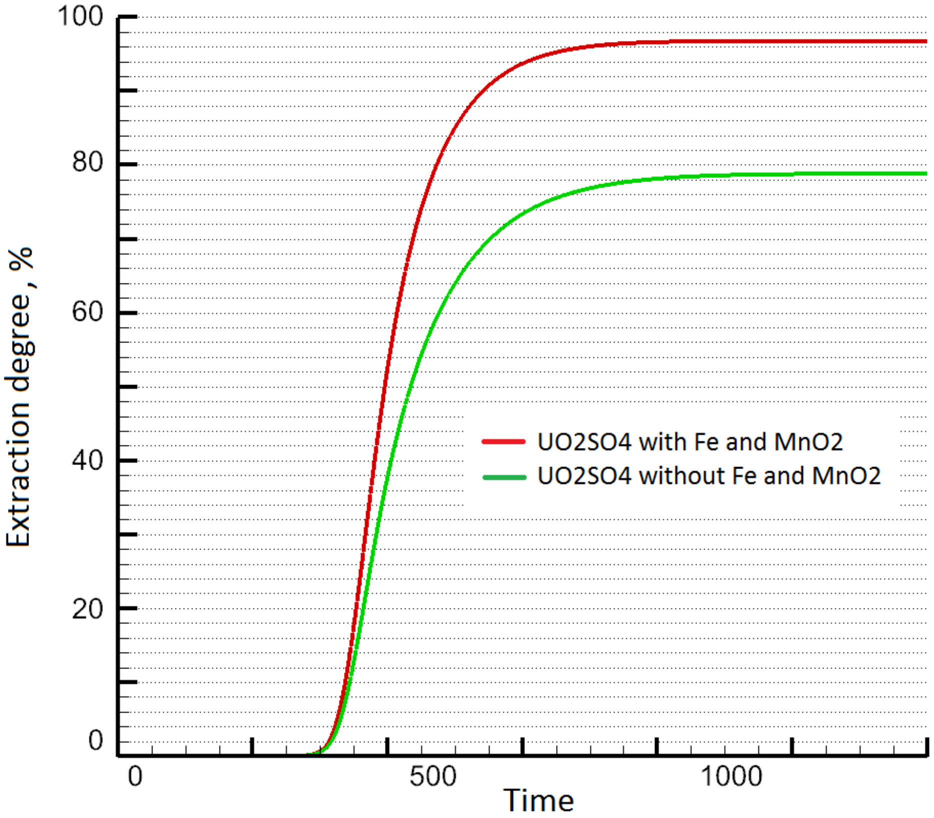

Figure 2–Extraction degree of Uranyl Sulfate by numerical time

In Figure 4, after some time when leaching front has reached middle point between injection and production wells, the concentration of Uranyl Sulfate is indicated by red and green lines, for leaching with and without oxidizers respectively. The blue line shows the decreasing concentration of sulfuric acid. It can be clearly seen that Uranyl Sulfate concentration is higher when Iron and Pyrolusite participate in reaction.

Extraction degree of Uranyl Sulfate by numerical time at production well for both cases (with and without Fe and MnO_2) can be examined on Figure 4. Evidently, Iron and Pyrolusite positively affect extraction degree of uranium components when added.

5 Conclusion

A work has been done to numerically demonstrate that presence of Iron and Pyrolusite in Uranium leaching reactions can increase the extraction degree of Uranium as well as increase overall reaction speed. The results show that extraction degree can be increased depending on concentrations of oxidizers, whereas without addition of oxidizers sulfuric acid would only leach six valent uranium (UO_3), leaving most of four valent uranium (UO_2) underground. The addition of oxidizers increase the speed of dissolution of four valent uranium, thereby increasing overall extraction degree.

In future, the influence of other components on leaching process can be studied in a similar fashion without expensive laboratory experiments. This work was accomplished within the GF4/3290 project under financial support from Ministry of Education of Kazakhstan.

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