Analyzing a denitration process in the context of underground well uranium leaching

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Abstract

Purpose is to increase a sorbent denitration degree in the context of underground uranium leaching while optimizing reagent concentration as well as a degree of the solution activation on the basis of laboratory research.

Methods. Analysis has been applied as well as scientific generalization of scientific-and-engineering information, laboratory research, statistic processing, and analysis of the research results. The laboratory experiments involved specific mixture to obtain comparative data of sulfuric solution activity and identify optimum degree of the solution activation for denitration. After processing, the solution from activator was analyzed as for its activity; the bulk was poured into a tank for repetitive experiments. First, the research did not involve the solution activation; then, activation with 4-15 minutes was added. Sulfuric acid concentration was 20 and 25 g/dm\textsuperscript{3}; L-S ratio was 1/8; and washing time was 40, 60, and 120 minutes.

Findings. Laboratory research results have been demonstrated concerning sorbent denitration in terms of varying degrees of activation, sulfuric acid concentration, and response time. It has been demonstrated that it is sufficient for washing solution activation to activate reagent only before extra intensification of a mother solution resulting in the reduced volume of the solution being processed and costs. It has been determined that five- to nine-minute activation period is the efficient interval factoring into the decreased nitrate content in the sorbent after washing to compare with 9-18% in terms of a basic technique depending upon a reagent concentration.

Originality. New dependences of a sorbent denitration degree as well as nitrate content within a solution upon sulfuric acid concentration and the solution activation degree have been defined.

Practical implications. Washing solution activation results in the increased denitration degree of a sorbent to compare with the basic technique. The proposed method is more preferable owing to low capital costs. Moreover, it is integrated easily in the available system being also absolutely sustainable.

Keywords: denitration, sorbent, sorption, desorption, activation, sulfuric acid, uranium

1. Introduction

The current progress of science and technology is determined by the unprecedented extent of technological development differing in a very rapid growth of specific power of production facilities. Global consumption of basic energy has become huge [1], [2]. The accelerate progress of nuclear energetics, becoming more important component in power generation, is the feature of the technological revolution [3]-[6]. Such an enormous scale of nuclear power industry needs its adequate natural uranium supply. Hence, uranium demand will increase [7], [8]. It can be satisfied at the expense of traditional methods of industrial ore extraction (i.e. underground mining or open-pit mining); and operation of deposits being of hydrogenic origin mainly being represented by poor ores or lean ones as well as deposits occurring under complex mining and geological, and hydrogeological conditions [9]-[12]. Until recently, deposits of group two (i.e. uranium-bearing occurrences of poor and lean ores) have not been involved in the traditional mining methods from the viewpoint of their feasibility. The problem, being very important in terms of the national economic significance, has been almost solved. The last decade is principal as for the development and industrial implementation of geotechnological uranium production called as underground leaching (UL) [13], [14]. For some enterprises, the UL method has become the key one in the process of uranium mining. There is no doubt that the number of such enterprises will increase in future.

Currently, poor deposits of hydrogenic genesis, occurring within the permeable argillo-arenaceous formations of depression zones of the earth’s crust, are the raw materials base
Current, residual nitrate ion content in sorbent is 6-11%; in this context, sulfuric acid concentration varies from 25 up to 36%. Hence, denitrification degree is not sufficient. The abovementioned results in the resin deteriorating as for the uranium, loss of nitrate ions, and the increased consumption of ammonia nitrate as well as sulfuric acid consequently.

1.1. Current state of denitrification process at the research subject

Uranium deposit Mynkunduk is the research subject. The occurrence is within Betpak-Dala plateau being a large plain upland limited northerly and westerly by the dissected erosion scarp with up to 80-100 m height; in the south, it is inclined gently to the Shu River valley of the Republic of Kazakhstan. Uranium mineralization at Mynkunduk deposit occurs within the permeable sand levels; it is controlled by epy boundaries of layer oxidation being parts of one regional oxidizing front. Generally, two chalk beds are the ore-bearing ones at the deposit. They are Mynkunduk bed (Lower Touronian stage) and Inkuduk bed (Upper Touronian-Coniacian-Santonian stage). Within Tsentralny site, uranium mineralization is connected with Mynkunduk level. The Tsentralny site is characterized by the availability of rather thick gray clay lentils observed in the lower share of the level as well as along its section on the whole. The abovementioned stipulates significant lithofacial heterogeneity of Mynkunduk level. Integrally, section of the level corresponds to the determined regularity: lower sublevel is represented by channel and mainstream facies; bar and channel sand deposits prevail in its upper sublevel. In this context, role of clay levels becomes more important from east to west; thickness of the layers as well as their extension is observed. The major uranium share is in the dispersed easily extracted form, disseminated within loose permeable porous sand aggregate. Together with finely crystalline pyrite, uranium minerals form the thinnest powdering on fragmentary grains and thicker powdering (i.e. incrustations) on aggregate pyrite grains. In some cases, they can even act as cement.

Denitrification purpose is to regenerate sorbent into initial (i.e. sulfate) form being applicable for a sorption process as well as decrease specific consumption of desorbing agent at the expense of recycle and later use of nitrate ions NO₃⁻ [19].

Anionite conversion from a nitrate form into sulfate one is described with the help of following chemical equation:

$$2 \text{R}_2\text{N}^+ - (\text{NO}_3^-)^2 + \text{SO}_4^{2-} = (\text{R}_2\text{N})_2^+ - (\text{SO}_4)^2^- + 2 \text{NO}_3^-$$

Denitrification of PS processing has been organized in DNK 2000 columns being mass-exchange sorption-type devices with vertical drainage system of reusable solutions (Fig. 1).

To process the available amount of the desorbed anionite, the operation procedure involves modular use of DNK columns functioning as follows:
- supply of initial denitrating solution to the column base;
- delivery of a denitration barren solution from the column to a unit where desorbing solutions are prepared;
- discharge of the denitrated solution from the column for further processing step.

Denitrating solution is prepared on the basis of washing barren solutions, washing unit of the regenerated sorbent, and filtration barren solutions intensified additionally up to 25-35 g/dm³ strength with the help of the concentrated sulfuric acid solution supplied from a warehouse of liquid reagents. Horizontal mixture is applied to intensify agitation of the solutions.
Sulfuric acid concentration is the most important influential factor for denitrification process. The increased its content forces denitrification degree significantly.

On the other hand, increase in sulfuric acid concentration in the denitrification solution results in its increased content within denitrification barren solution as well as in the desorbing solution.

Sorbent denitrification is a sorption-desorption process influenced by numerous factors. First, it concerns a type of desorbing agent and its concentration. In this context, sulfuric acid is meant; sulfate particularly; and hydrosulfate ions especially which content increases along with the increase in sulfuric acid concentration.

Moreover, following factors also influence a denitrification process:
- operating space-column diameter ratio forming denitrification front;
- amount of the propelled resin and the process frequency.

The factors are interdependent. Among other things, decrease in the propelled resin amount results in the increased frequency of the resin contact with a live solution portion approaching continuous process of the denitrification (ideal conditions are meant):
  - linear velocity of denitrifying solution supply. Increase in a linear velocity heightens concentration difference of the transferred ions;
  - specific consumption of the denitrating solution per resin amount;
  - temperature.

These are the basic factors influencing anionite denitrification under the production conditions.

If sorption modes (i.e. amount of the propelled anionite; frequency; capacity etc.) influence operational characteristics of processing area, then running characteristics of denitrification as well as desorption are identified in accordance with the sorption process stage. First of all, optimization of the active scheme of a pregnant solution processing, using apparatus retooling of regeneration unit of ion-exchange material, involves more qualitative and efficient implementation of the main equipment. Currently, the process stage operation applies modular mode, i.e. independent use of denitrification columns.

Advantages of the operation of regeneration devices are as follows: no agitation of anionite from different production modules; minimization of shutdown of processes as well as idle equipment periods in repair cases or if part substitution is required; and possibility to organize operation of process stages in terms of various parameters and conditions. However, low degree of a sorbent conversion (i.e. no more than 60%) is the disadvantage of individual use of denitrification columns.

It is possible to note than insufficient completeness of anionite denitrification first depends upon low chemical activity of the process itself being stipulated by higher sorbent affinity for nitrate ions. Hence, the authors have proposed a technique of mechanical activation of a washing solution which helped increase a degree of the sorbent denitrification.

1.2. Purpose of the research and its tasks

Purpose of the research is to increase a degree of sorbent denitrification in the context of underground uranium leaching owing to the optimization of reagent concentration as well as activation degree of the solution based upon the laboratory studies.

The research tasks are as follows:
- to develop a procedure and manufacture a device for laboratory works;
- to identify dependences of nitrate content in resin upon the activation and washdown periods in terms of different concentrations of sulfuric acid;
- to determine changes in nitrate concentration in resin depending upon the activation period as well as washing if different amounts of washing solution are activated;
- to elaborate and analyze the laboratory research results.

2. The laboratory research procedure

The two methods were applied to carry out the laboratory studies using: a model denitrification device and a mixer. The laboratory facility, shown in Figure 2, consists of a pump and a column to denitrify a tank for solution. The laboratory mixture, shown in Figure 3, consists of a motor, propeller agitator, and tank for solution. The paper represents the results of laboratory studies with the use of a mixer. The key problem, being solved in the process of the laboratory research, is to obtain comparative data of sulfuric solution activity and identify the required degree of the solution activation for denitrification.

Resin for the denitrification was divided into thirty-nine 50-gram test portions and six 35-gram test portions. Since the paper represents laboratory studies involving a mixture, twenty-eight 50-gram test portions were applied. The laboratory research was carried out with 25 g/dm³ sulfuric acid concentration, and 20 g/dm³; 1/8 l-s ratio; and 40-, 60-, and 120-minute washing time.
First, the laboratory studies did not involve the solution activation; then, activation was performed during 4, 5, 6, 8, 10, 12, and 15 minutes. After the resin washing, it was delivered to a laboratory to determine residual nitrate concentration.

The solution was activated with the help of a laboratory device consisting of a pump, a current activator, a tank for solution, and a drawoff tap [20]. The procedure to process solution by means of activator is as follows. A working sulfuric solution is tanked, and electric motor of a pump is started. The pressurized solution passes through the activator, and comes back to the tank.

Every time after next in turn amount of sulfuric solution is processes, it is tanked separately; the device is washed with water to avoid corrosion of the pump parts.

To process following amount, 2.0 liters of a solution with the initial concentration are tanked. Then, the pump is started for 8-10 seconds to make a mixture with residual washing water during motion.

The solution is the initial one relative to which comparison is made with activity of a solution processed finally by means of activator.

When the processing is completed, the solution from activator is analyzed as for its activity; the bulk is tanked for repetitive experiments after definite time. It should be noted that industrial activation of the whole washing solution needs significant material cost; hence, stage one of the laboratory research involves reagent activation only.

3. Results and discussion

Laboratory analysis of resin from the mine has shown that nitrate concentration is 186.03 g/l. The resin was sampled at a Tsentralny Mynkunduk mine. Strong-base anionite of Ambersept 920 USO4 type has been applied as well as macropore cross-linked polystrene with 735 g/l specific gravity; 750-950 μmol average particle size; and concentration of less than 0.710 mm fine crystals. Large crystals (i.e. those being larger than 1.180 mm) amounted to 5%; moisture content was 4%; H2SO4 content was no less than 92.5%; and ammonia nitrate content was 60%. Sulfuric acid has also been selected for the desorption process; expressed in terms of nitrogen on a dry basis, total concentration of nitric nitrogen and ammonium nitrogen was no less than 34.0%.

Table 1 demonstrates results of the laboratory studies carried out using a mixer.

Processing of the data, represented in Table 1, has helped obtain changes in the nitrate content in resin depending upon activation period as well as washdown period, if sulfuric acid concentration is 20 g/l (Fig. 4).

<table>
<thead>
<tr>
<th>Activation period, minutes</th>
<th>H2SO4 concentration, g/l</th>
<th>Washing period, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>No activation</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>No activation</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>40</td>
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<td>6</td>
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<td>8</td>
<td>20</td>
<td>60</td>
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<tr>
<td>10</td>
<td>20</td>
<td>60</td>
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<tr>
<td>12</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>No activation</td>
<td>25</td>
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<td>No activation</td>
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<td>12</td>
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<td>60</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
<td>60</td>
</tr>
</tbody>
</table>

Data analysis of the laboratory research has shown that if washdown lasts 40 minutes and sulfuric acid concentration is 20 g/l, then the solution activation results in the maximum decrease of nitrate content being only 13% to compare with the traditional method; average decrease was 7%. In terms of 60-minute washdown and up to 8-minute solution activation, maximum nitrate content decrease turned out to be 10% to compare with the traditional technique; average decrease was 8.5%. Increase in sulfuric acid concentration up to 25 g/l along with the 40-minute washdown period has resulted in 18% maximum decrease in nitrate content to compare with the traditional method; average decrease was 9%. Maximum nitrate decrease is achieved if the solution is activated 5 to 9 minutes; further 10-15-minute increase in activation period factors into the decreased nitrate content being 5% on average.

Concurrently, the Table 1 explains that 20 g/l sulfuric acid concentration results in the increased washdown degree. In turn, 25 g/l concentration decreases the washdown degree, i.e. not always increase in sulfuric acid concentration delivers a positive result. The decreased degree of resin denitration, depended upon time increment of a solution activation, is explained by the reagent heating and evaporating during its activation.
Processing of the data, represented by the Table 1, demonstrates changes in nitrate content in resin depending upon the activation and washdown periods if sulfuric acid concentration is 25 g/l (Fig. 5).

Stage two of the research involved 30, 50, 80 and 100% activation of a washing solution. In this context, sulfuric acid concentration was 25 g/l; and washing period amounted to 60 minutes. Table 2 demonstrates results of the laboratory studies carried out using a mixer.

Table 2. Results of laboratory studies carried out with the use of a mixer

<table>
<thead>
<tr>
<th>Activation period (minutes)/solution, %</th>
<th>H\textsubscript{2}SO\textsubscript{4} concentration, g/l</th>
<th>Washing period, minutes</th>
<th>Nitrate content, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>six-minute activation of 30% solution</td>
<td>25</td>
<td>60</td>
<td>124.0</td>
</tr>
<tr>
<td>six-minute activation of 50% solution</td>
<td>25</td>
<td>60</td>
<td>117.1</td>
</tr>
<tr>
<td>six-minute activation of 80% solution</td>
<td>25</td>
<td>60</td>
<td>115.9</td>
</tr>
<tr>
<td>six-minute activation of 100% solution</td>
<td>25</td>
<td>60</td>
<td>117.4</td>
</tr>
<tr>
<td>eight-minute activation of 30% solution</td>
<td>25</td>
<td>40</td>
<td>127.3</td>
</tr>
<tr>
<td>eight-minute activation of 50% solution</td>
<td>25</td>
<td>40</td>
<td>124.0</td>
</tr>
<tr>
<td>eight-minute activation of 80% solution</td>
<td>25</td>
<td>40</td>
<td>119.5</td>
</tr>
<tr>
<td>eight-minute activation of 100% solution</td>
<td>25</td>
<td>40</td>
<td>117.2</td>
</tr>
</tbody>
</table>

According to Table 2, 30% activation of washing solution factors into more than 7% decrease in nitrate content to compare with the traditional method. 50% and 100% solution activation results in the 12% decrease of nitrate content in resin to compare with the traditional technique. Decrease in washdown period down to 40 minutes as well as activation time increment up to 80 minutes leads to similar results.

Processing of the Table 2 data has made it possible to obtain changes in nitrate content in resin depending upon the activation and washdown periods if sulfuric acid concentration is 25 g/l and different amounts of a washing solution are activated (Fig. 6). As it is understood from Figure 6, nitrate content in resin depends upon different solution amounts. Up to 60% activation of the whole supplied solution demonstrates significant decrease of nitrates in sorbent.

Further activation of the supplied solution (i.e. more than 60%) results in minor nitrate decrease; sometimes, nitrate increase in the sorbent is observed. Comparison of denitration degree, involving washing solution with a reagent activation only and activation of different shares of the whole washing solution (Tables 1 and 2), shows average 7-8% difference. The abovementioned can be considered as similar results.

4. Conclusions

The operating procedure of mechanical activation of a washing solution increases denitration degree of a sorbent. Moreover, it excludes the necessity to activate the whole amount of a washing solution. Minimization of nitrate concentration in sorbent is observed if up to 60% of the whole washing solution is activated.

It has been proved that reagent activation before PS intensification is quite sufficient to activate a washing solution. Hence, decrease in the processed solution amount is observed as well as expenditures connected with sorbent denitrination.

Increment of the time, required to activate a washing solution, results in the decreased degree of a sorbent denitrination which can be explained by a reagent heating and evaporating during its activation. In this context, denitration degree does not experience its decrease owing to the increased activity of the washing solution. 5-9-minute reagent activation is considered as the efficient time resulting in the decreased nitrate content in the sorbent after washdown to compare with 9-18% demonstrated by the basic process depending upon a reagent concentration.

In the process of the washing solution activation, increase in sulfuric acid concentration up to 20 g/l factors into a higher washdown degree. Its further increase results in the decreased degree of a sorbent washdown, i.e. not always increase in sulfuric acid concentration delivers a positive result.

Acknowledgements

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Економіка, стабільність і вплив на регіони, зокрема на Україну: наслідки, альтернативи, інновації

Doslіdження процесу денітрації при підземному свердловинному вилукуванні урану

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Мета. Підвищення ступеня денітрації сорбенту при підземному вилукуванні урану за рахунок оптимізації концентрації реагента та ступеня активації розчину на основі лабораторних досліджень.

Методика. Використано аналіз і науково-технічну інформацію, лабораторні дослідження, статистична обробка та аналіз результатів досліджень. Лабораторні дослідження проводились на спеціально розроблений мішалці для отримання порівняльних даних активності сірнокислотного розчину і визначення оптимального ступеня активації розчину для денітрації. Після обробки розчин з активатора брали на дослідження активності, а основний об’єм зливали в ємність для проведення повторних досліджень. Дослідження проводилися в різних концентраціях розчину, з постійною активацією від 4 до 15 хвилин. Концентрація сірної кислоти – 20 та 25 г/л, співвідношення Р/ГТ – 1/8, час промивання – 40, 60 і 120 хвилин.

Результати. Наведено результати лабораторних досліджень з денітрації сорбенту при різному ступені активації, концентрації сірної кислоти та часу реакції. Встановлено, що для активації розчину для промивання досить активувати лише реагент перед дозикуванням маточного розчину, в результаті чого зменшується об’єм обробленого розчину і витрати. Зазначено, що ефективним часом активації реагенту є час від 5 до 9 хвилин, що призводить до зниження вмісту нітрату в зоні реагенту в сорбенті після промивання у порівнянні з базовою технологією від 9 до 18% залежно від концентрації реагенту.

Наукова новизна. Встановлено нові залежності ступеня денітрації сорбенту від часу промивання в різних концентраціях сірної кислоти та ступеня активації розчину.

Практична значимість. Активация промивного розчину призводить до підвищення ступеня денітрації сорбенту у порівнянні з базовою технологією. Запропонована технологія відрізняється низькими капітальними витратами, легко інтегрується в існуючу систему та екологічно абсолютно безпечна.

Ключові слова: денітрація, сорбент, сорбція, десорбція, активація, сірча кислота, уран

Исследование процесса денитрации при подземном свердловинном выщелачивании урана

X. Исусов, Е. Абен, А. Омиргали, А. Рахманбердиеv

Цель. Повышение степени денитрации сорбента при подземном выщелачивании урана за счет оптимизации концентрации реагента и степени активации раствора на основе лабораторных исследований.

Методика. Использованы анализ и научное обобщение научно-технической информации, лабораторные исследования, статистическая обработка и анализ результатов исследований. Лабораторные исследования проводились на специально разработанной мешалке для получения сравнительных данных активности сернокислотного раствора и определения оптимальной степени активации раствора для денитрации. После обработки раствор из активатора брали на исследование активности, и основной объем сливали в емкость для проведения повторных экспериментов. Исследования проводились без активации раствора, затем с активацией от 4 до 15 минут. Концентрация серной кислоты – 20 и 25 г/л, соотношение JT – 1/8, время промывки – 40, 60 и 120 минут.
Результаты. Приведены результаты лабораторных исследований по денитрации сорбента при различной степени активации, концентрации серной кислоты и времени реакции. Установлено, что для активации промывочного раствора достаточно активировать только реакент перед доукреплением маточного раствора, в результате чего уменьшается объем обрабатываемого раствора и затраты. Определено, что эффективным временем активации реагента является время от 5 до 9 минут, что приводит к снижению содержания нитрата в сорбенте после промывки по сравнению с базовой технологией от 9 до 18% в зависимости от концентрации реагента.

Научная новизна. Установлены новые зависимости степени денитрации сорбента и содержания нитрата в растворе от концентрации серной кислоты и степени активации раствора.

Практическая значимость. Активация промывочного раствора приводит к повышению степени денитрации сорбента по сравнению с базовой технологией. Предлагаемая технология отличается низкими капитальными затратами, легко интегрируется в существующую систему и экологически абсолютно безопасна.

Ключевые слова: денитрация, сорбент, сорбция, десорбция, активация, серная кислота, уран