

## Increase of uranium extraction from hardly soluble uranium ores

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### Abstract

Researches on sulphuric-acid leaching of uranium in the filtrational and agitation modes are conducted. Traditional oxidizers such as: iron (III) solution, ammonium persulfate, sodium oxo-perborate, – and developed by us catalyst, which contains manganese, cobalt, nickel and iron were used as intensifiers of process. Total concentration of metals in the catalyst made 0.3 g/dm<sup>3</sup>.

Influence of oxidizers and the catalyst on extraction of uranium depending on concentration of sulfuric acid, ratio of T:Fe and time of leaching is investigated. Optimum concentration of sulfuric acid was 25 g/dm<sup>3</sup>.

When using traditional oxidizers there observed increase of extraction of uranium at increase of T:Fe ratio: up to 41.5 mg/dm<sup>3</sup> for solution of ferric iron, to 39.9 mg/dm<sup>3</sup> for ammonium persulfate and up to 39.4 mg/dm<sup>3</sup> for sodium peroxoborate. When using the catalyst as an intensifier uranium concentration in solution grows at increase of T:Fe ratio up to 1:4, where its further increase promotes the content of uranium in solution to remain constant and equal 43 mg/dm<sup>3</sup>.

When using the catalyst as an uranium leaching process intensifier, rather than traditional oxidizers, the tendency to the further growth of extraction of uranium at increase in time of leaching process is observed.

When the catalyst is present, there is reduction of consumption of sulfuric acid to 9.71 g/g of uranium, and also selectivity of process increases.

Efficiency of intensifiers of leaching process of uranium increases in the following row: SP < AP < Fe(III) < catalyst.

The X-ray fluorescent analysis of solutions after processing of a center mark by sulfuric acid without catalyst and sulfuric acid with the catalyst is carried out. It is established that addition of the catalyst promotes increase of selectivity of process of uranium leaching.

Keywords: URANIUM, SULPHURIC-ACID LEACHING, HARDLY SOLUBLE URANIUM ORE, CATALYST

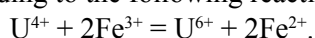
### 1. Introduction

From year to year the difficulties connected with extraction extent of uranium from ores, and also mudding of wells with formation of calcium sulfates, and low extraction of uranium (VI) during sulphuric-acid leaching vitriolic leaching increase. Now at underground leaching of uranium into processing there

included more complex and persistent uranium ores that is shown in the decrease of uranium content in productive solutions. Besides, in general underground leaching of uranium is characterized by rather big duration of leaching which takes 10 years and more. The consumption of reagent makes over 90 kg per 1 kg of uranium. The main problem of increase in production

of uranium is transfer of uranium (IV) to a soluble state at underground leaching according to the existing technologies [1].

At the present time, when uranium leaching, as a rule sulphuric-acid leaching at atmospheric or elevated pressure in autoclaves is applied. It is known that additives of oxidizers are especially necessary when in ore there is a high content of tetravalent uranium and leaching by solutions of sulfuric acid without additives of oxidizers is complicated. For increase of extraction extent of uranium there used sulfuric acid in a mixture with oxidizers – salts of ferric iron, ammonium persulfate and other oxidizers [2]. Concurrent to uranium iron in tervalent state acts as an oxidizer, and in the course of leaching recovered in iron (II) according to the following reaction:



Today the investigations of influence of traditional oxidizers on leaching process of hardly opened uranium-bearing ores, and search of new intensifiers for increase of extraction of uranium from persistent raw materials are of great interest.

## 2. Materials and Methods

Leaching of uranium was carried out in the filtration and agitation modes.

Uranium extraction from core material was carried out in the filtration mode in tubes without additives (control solution) and with addition of traditional oxidizers: ammonium persulfate (AP), sodium peroxoborate (SP) and iron (III).

Samples of core material were crashed to the fineness less than 2 mm and averaged. Uranium content in core material was 0.04%. Core material was loaded into filtration tube with a diameter of 3.5 cm and 0.5 m long. Previously ore was washed out by water. The solution was fed in a column by means of the peristaltic pump, at a filtration speed through the ore of 10 m/days. The mass of ore in a column was 0.6 kg.

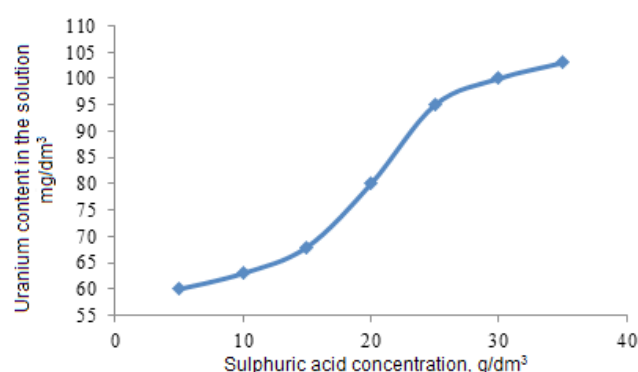
For experiments on agitation leaching the part of core material was crushed up to fineness of 0.074 mm. Agitation leaching was carried out in a glass with mechanical mixing of a pulp at the room temperature

(25° C). The hinge of core material was 250g. Extraction of uranium in agitation mode was carried out with addition of ammonium persulfate, sodium peroxoborate, iron (III) and new, developed by us, catalyst containing manganese, cobalt, nickel and iron. Total concentration of metals in the catalyst was 0.3 g/dm<sup>3</sup>. Preliminary researches of catalytic activity of this catalyst in oxidation of uranium were conducted by us in works [3-5].

## 3. Results and discussions

### 3.1. Leaching in seepage conditions

There was previously defined the dependence of uranium extraction on the concentration of sulfuric acid without addition of oxidizers was defined. Data of experiments are given in figure 1.



**Figure 1.** Influence of concentration of sulfuric acid on uranium extraction

For this ore optimum concentration of sulfuric acid is 25-30 g/dm<sup>3</sup>.

Further a series of experiments on leaching of uranium ores in tubes depending on Fe:T ratio were set.

Leaching was carried out according to the scheme accepted on uranium mines:

- acidulation of Fe:T = 0.2; 25 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>
- active leaching of Fe:T = 0.4; 12.5 g/dm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub>
- leaching of Fe:T = 0.6; 6.25 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>
- preleaching of Fe:T = 0.8; 1.0 g/dm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub>

Results of experiments on extraction of uranium are given in tables 1 - 4 and in the figure 2.

**Table 1.** Leaching in the standard mode (without addition of oxidizer)

Fe/T	U <sub>me</sub> <sup>2</sup> mg/dm <sup>3</sup>	ORP, W	Inorganic acidity, g/dm <sup>3</sup>	pH	Fe <sup>+2</sup> , g/dm <sup>3</sup>	Fe <sup>+3</sup> , g/dm <sup>3</sup>
0,2	30	0,28	-	7,93	-	-
0,4	210	0,394	7,12	1,14	0,3	0,12
0,6	160	0,402	20,8	0,67	1,58	0,18
0,8	90	0,409	16,3	0,78	1,57	0,12
1,0	50	0,406	16,17	0,78	0,93	0,12
1,2	30	0,402	16,00	0,78	0,6	0,12

1,4	20	0,370	10,7	0,96	0,4	0,1
1,6	5	0,370	6,3	1,2	0,43	-
1,8	4	0,350	3,8	1,41	0,23	-
2,0	3	0,340	2,5	1,6	0,2	-

**Table 2.** Leaching in the presence of ammonium persulfate in quantity of 1g/dm<sup>3</sup>

Fe/T	U <sub>me</sub> , mg/dm <sup>3</sup>	ORP, W	Inorganic acidity , g/dm <sup>3</sup>	pH	Fe <sup>+2</sup> , g/dm <sup>3</sup>	Fe <sup>+3</sup> , g/dm <sup>3</sup>
0,2	20	0,243	-	6,79	-	-
0,4	570	0,252	5,2	1,28	-	-
0,6	450	0,546	14,3	0,84	-	1,47
0,8	290	0,696	19,6	0,7	-	1,66
1,0	190	0,706	24,01	0,61	-	1,62
1,2	100	0,676	17,24	0,75	-	0,62
1,4	20	0,748	12,1	0,91	-	0,6
1,6	10	0,761	9,7	1,0	-	0,2
1,8	9	0,73	8,9	1,05	-	0,1
2,0	8	0,753	3,2	1,5	-	0,2

**Table 3.** Leaching in the presence of sodium peroxoborate in quantity of 1g/dm<sup>3</sup>

Fe/T	U <sub>me</sub> , mg/dm <sup>3</sup>	ORP, W	Inorganic acidity, g/dm <sup>3</sup>	pH	Fe <sup>+2</sup> , g/dm <sup>3</sup>	Fe <sup>+3</sup> , g/dm <sup>3</sup>
0,2	50	0,4	-	7,01	-	-
0,4	520	0,45	3,2	1,49	-	0,2
0,6	400	0,5	7,8	1,1	-	1,1
0,8	290	0,6	15,9	0,79	-	1,5
1,0	200	0,6	14,3	0,84	-	1,5
1,2	115	0,6	11,4	0,94	-	0,7
1,4	55	0,59	9,6	1,0	-	0,6
1,6	10	0,59	9,2	1,0	-	0,2
1,8	9	0,6	9,8	1,0	-	0,2
2,0	8	0,59	3,8	1,41	-	0,1

**Table 4.** Leaching in the presence of trivalent iron in quantity of 1g/dm<sup>3</sup>

Fe/T	U <sub>me</sub> , mg/dm <sup>3</sup>	ORP, W	Inorganic acidity , g/dm <sup>3</sup>	pH	Fe <sup>+2</sup> , g/dm <sup>3</sup>	Fe <sup>+3</sup> , g/dm <sup>3</sup>
0,2	30	0,3	-	6,8	-	-
0,4	300	0,35	6,4	1,18	-	0,5
0,6	520	0,55	16,8	0,77	-	1,6
0,8	380	0,68	19,9	0,69	-	1,8
1,0	260	0,67	21,1	0,67	-	2,1
1,2	170	0,67	18,5	0,75	-	1,7
1,4	90	0,65	12,0	0,91	-	1,4
1,6	40	0,61	10,6	0,97	-	1,4
1,8	15	0,66	7,4	1,12	-	1,3
2,0	10	0,65	4,7	1,32	-	1,1

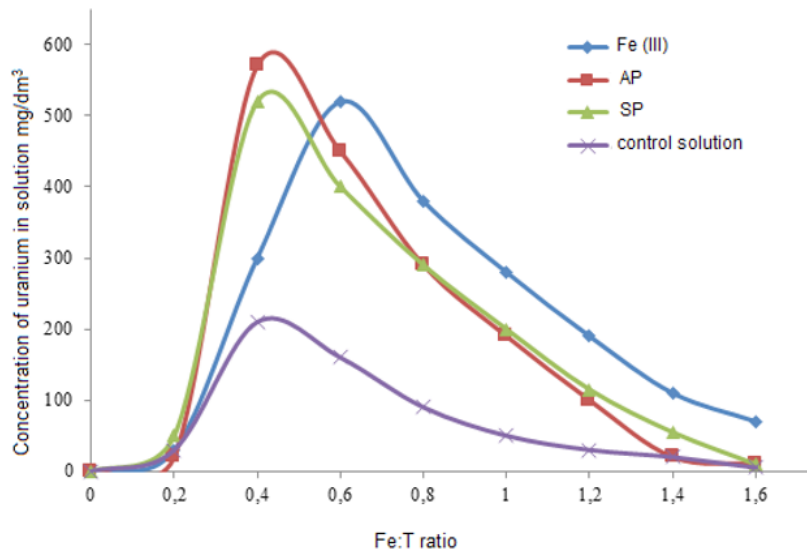


Figure 2. Dependence of uranium concentration on Fe:T ratio

In table 5 data of the conducted researches on extraction of uranium from uranium ore in the presence of various oxidizers and consumption of sulfuric acid are generalized.

Data of experiments show that introduction of an oxidizer when leaching of uranium leads to increase of grade of uranium extraction. Influence of ammonium persulfate and sodium peroxoborate on uranium extraction process is almost identical and leads to increase of grade of target metal extraction by 1.3 times in comparison with control solution (without addition of oxidizer). However the acid consumption in case of use of ammonium persulfate is twice less (15.95 g/g of uranium) in comparison with that in case of sodium peroxoborate (33.70 g/g of uranium).

Table 5. Influence of oxidizers on extraction of uranium and consumption of sulfuric acid

Oxidizer	Uranium extraction, %	Acid consumption, g/g of uranium
Control solution	30.10	39.11
Ferric iron solution	90.75	12.20
Ammonium persulfate	83.35	15.95
Sodium peroxoborate	82.85	33.70

The maximum effect was observed during application as an oxidizer of ferric iron solution, reached grade of uranium extraction made 90.755%, an acid consumption is minimum as compared with other oxidizers (12.20 g/g of uranium).

In the course of work there were measured oxidation-reduction potentials of the leaching solutions. Data are provided in table 6.

As is seen from the table 6 solution of sulfuric acid with concentration of 25 g/l possesses high oxidation-reduction potentials (630 mW), nevertheless leaching only by sulfuric acid occurs unsatisfactorily.

Table 6. Oxidation-reduction potential of leaching solutions

Oxidizer	pH	ORP, mW
25 g/dm <sup>3</sup> H <sub>2</sub> SO <sub>4</sub>	0.59	630
25 g/dm <sup>3</sup> H <sub>2</sub> SO <sub>4</sub> +1g of sodium peroxoborate	0.61	650
25 g/dm <sup>3</sup> H <sub>2</sub> SO <sub>4</sub> + 1g of ammonium persulfate	0.59	700
25 g/dm <sup>3</sup> H <sub>2</sub> SO <sub>4</sub> + Fe <sup>3+</sup> 1,0 g/dm <sup>3</sup>	0.73	685

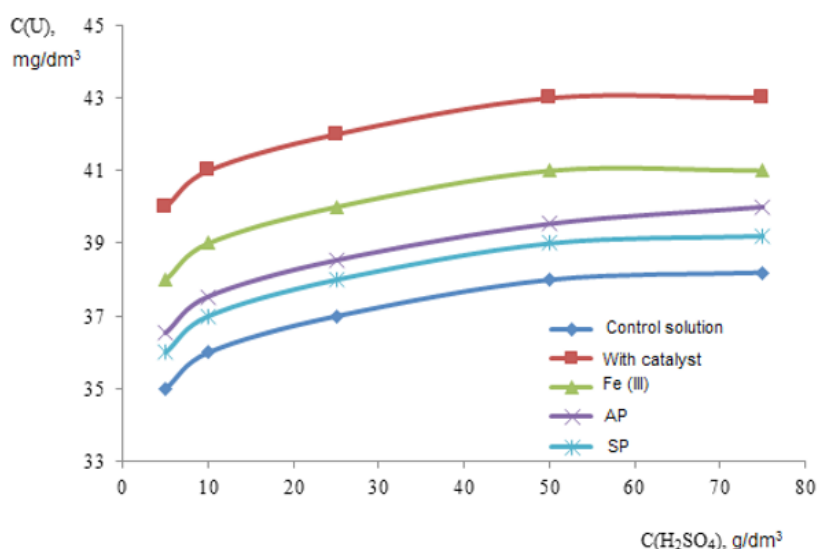
The relation of ions of ferric to ferrous iron in solution also influences the speed and grade of dissolution of uranium; extraction decreases with increase in quantity of ions of ferrous iron even if concentration of trivalent ions remains constant. The big ratio of ions bivalent/trivalent iron is especially important when leaching more refractory uranium ores.

### 3.2. Leaching in agitation mode

Researches of influence of concentration of sulfuric acid on extraction of uranium in stationary conditions in the presence of the catalyst, iron (III), ammonium persulfate and sodium peroxoborate are conducted. Results of probes are presented in table 6 and in figure 3.

**Table 6.** Research results of influence of concentration of sulfuric acid on uranium extraction in the presence of the catalyst, iron (III), ammonium persulfate and sodium peroxoborate.

Sulphuric acid concentration, g/dm <sup>3</sup>		5	10	25	50	75
U, mg/dm <sup>3</sup>	Without catalyst	35	36	37	38	39
	With catalyst	40	41	42	43	43
	Fe (III)	38	39	40	41	41
	AP	36,54	37,54	38,54	39,54	40
	SP	36	37	38	39	39,2



**Figure 3.** Dependence of extraction of uranium on concentration of sulfuric acid

As one may see in the figure 3, the increase in concentration of sulfuric acid from 5 mg/dm<sup>3</sup> to 75 mg/dm<sup>3</sup> promotes increase of uranium extraction in all studied cases. By efficiency process of uranium leaching can be located in the following row (there provided corresponding content of uranium in solution in brackets):

catalyst (43 mg/dm<sup>3</sup>) > Fe (III) (41 mg/dm<sup>3</sup>) > AP (40 mg/dm<sup>3</sup>) > SP (39,2 mg/dm<sup>3</sup>).

Researches of influence of T:Fe ratio on extraction of uranium in stationary conditions in the presence of catalyst, iron (III), ammonium persulfate and sodium peroxoborate are conducted. Results of probes are presented in table 7 and in figure 4.

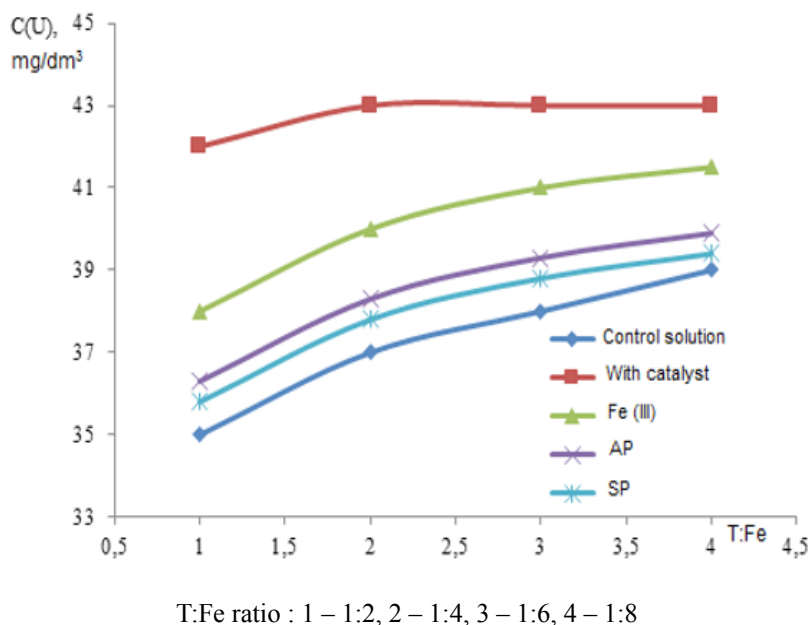
**Table 7.** Research results of influence of T:Fe ratio on uranium extraction in the presence of the catalyst, iron (III), ammonium persulfate and sodium peroxoborate.

T:Fe ratio		1:2	1:4	1:6	1:8	Acid consumption, g/g of uranium
U, mg/dm <sup>3</sup>	Without catalyst	35	37	38	39	39,11
	With catalyst	42	43	43	43	9,72
	Fe (III)	38	40	41	41,5	12,20
	AP	36,3	38,3	39,3	39,9	15,96
	SP	35,8	37,8	38,8	39,4	33,70

As it is seen from figure 4, change of T:Fe ratio significantly influences the leaching of uranium from solution without use of the catalyst, the content of uranium increases from 35 mg/dm<sup>3</sup> to 39 mg/dm<sup>3</sup> at increase of T:Fe from 1:2 to 1:8. In case of use of traditional oxidizers there also observed increase of extraction of uranium at increase in a ratio of T:Fe: to 41.5 mg/dm<sup>3</sup> for solution of trivalent iron, to 39.9 mg/dm<sup>3</sup> for ammonium persulfate and to 39.4 mg/dm<sup>3</sup> for sodium peroxoborate. When using the catalyst as an

intensifier, dependence of uranium leaching on this indicator is less expressed: concentration of uranium grows in solution at increase of T:Fe ratio to 1:4, where its further increase promotes the content of uranium in solution to remain constant and equal 43 mg/dm<sup>3</sup>.

When using the catalyst as an intensifier of process of uranium leaching there is a reduction of consumption of sulfuric acid to 9.71 g/g of uranium (table 7).



**Figure 4.** Dependence of extraction of uranium on T:Fe ratio

Researches of influence of leaching time on uranium extraction in stationary conditions in the presence of the catalyst, iron (III), ammonium persulfate

and sodium peroxoborate are conducted. Research results are presented in table 8 and in figure 5.

**Table 8.** Research results of influence of time on uranium extraction in the presence of the catalyst, iron (III), ammonium persulfate and sodium peroxoborate

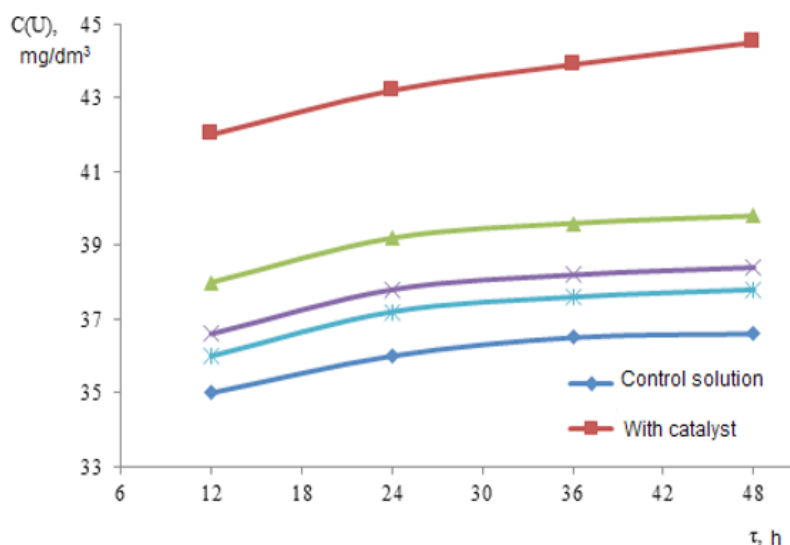
Time, h		12	24	36	48	Acid consumption, g/g of uranium
U, mg/dm <sup>3</sup>	Without catalyst	35	36	37	39,11	39,11
	With catalyst	42	43,2	43,9	9,72	9,72
	Fe (III)	38	39,2	39,6	12,20	12,20
	AP	36,6	37,8	38,2	15,96	15,96
	SP	36	37,2	37,6	33,70	33,70

The content of uranium in leaching solution without use of the catalyst was 35 mg/dm<sup>3</sup> after 12 hours of experiment and increased up to 38 mg/dm<sup>3</sup> after 48 hours after the beginning of leaching. In case of application of traditional oxidizers increase of extraction of uranium was also observed at increase in time of leaching. When using the “Mukhamedzhan-1” ca-

talyst after 12 hours of experiment extraction of uranium of 42 mg/dm<sup>3</sup> was reached, at increase in time of leaching this size changes insignificantly – to 44.5 mg/dm<sup>3</sup>. In this case, as opposed to traditional oxidizers, the tendency to the further growth of extraction of uranium at increase in time of process of leaching is observed (figure 5). It testifies to uranium extrac-

tion increase by sulphuric-acid leaching from almost insoluble uranium-bearing ores in the presence of the

catalyst and to the possibility of its almost full extraction at increase in time of process.



**Figure 5.** Dependence of uranium extraction on time

The X-ray fluorescent analysis of solutions after processing of a center mark by sulfuric acid without catalyst and sulfuric acid with the catalyst was carried out. Results of the analysis are presented in table 9.

As it is seen from table 9, addition of the catalyst leads to double increase in the content of uranium in solution. Concentration of calcium, iron, sulfur and zinc in solution with the catalyst decreases. Concentration of other elements changes insignificantly. It testifies to increase of selectivity of process of uranium leaching in the presence of the catalyst.

**Table 9.** Results of the X-ray fluorescent analysis of solutions after processing of a core by sulfuric acid without catalyst and sulfuric acid with the catalyst

Element	Concentration, %	
	Without catalyst	With catalyst
Si	0,163	0,168
P	2,810	2,814
S	64,516	59,716
Cl	0,962	0,962
K	1,251	1,256
Ca	10,478	6,022
Fe	6,374	4,616
Ni	0,013	0,014
Zn	0,241	0,182
U	12,192	24,265

#### 4. Conclusion

Researches on sulphuric-acid leaching of uranium in the filtration and agitation modes are conducted. As intensifiers of the process traditional oxidizers were used: iron (III) solution, ammonium persulfate, sodium peroxoborate – and the catalyst developed by us.

Influence of oxidizers and the catalyst on extraction of uranium depending on concentration of sulfuric acid, a ratio of T:Fe and time of leaching is investigated. Optimum concentration of sulfuric acid for the studied hardly soluble uranium ore was 25-30 g/dm<sup>3</sup>.

It is shown that change of T:Fe ratio significantly influences the leaching of uranium in case of use of traditional oxidizers: increase of extraction of uranium at increase in a ratio of T:Fe is observed: up to 41.5 mg/dm<sup>3</sup> for solution of trivalent iron, up to 39.9 mg/dm<sup>3</sup> for ammonium persulfate and up to 39.4 mg/dm<sup>3</sup> for sodium peroxoborate. When using the catalyst, concentration of uranium grows in solution at increase of T:Fe ratio up to 1:4, where its further increase promotes the content of uranium in solution to remain constant and equal 43 mg/dm<sup>3</sup>.

Use of the catalyst at extraction of uranium leads to reduction of a consumption of sulfuric acid up to 9.71 g/g of uranium

When using the catalyst as leaching process intensifier, as opposed to traditional oxidizers, the tendency to the further growth of extraction of uranium at increase in time of process of leaching is observed. It speaks for uranium extraction increase by sulphuric-acid leaching from hardly soluble uranium-bearing ore in the presence of the catalyst and to possibi-

lity of its almost full extraction at further increase in time of process.

Efficiency of intensifiers of process of leaching of uranium increases in the following row: SP < AP < Fe (III) < catalyst.

The X-ray fluorescent analysis of solutions after processing of a core by sulfuric acid without catalyst and sulfuric acid with the catalyst is carried out. It is established that addition of the catalyst promotes increase of selectivity of uranium leaching process.

### Acknowledgement

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