



RESEARCH ARTICLE

THE IMPACT OF AMMONIUM BIFLUORIDE COMPLEX ON COLMATAGING FORMATIONS DURING THE PROCESS OF IN SITU URANIUM LEACHING.

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Abstract

The causes of performance degradation geotechnical wells during ISL of uranium and detail researched the chemical sedimentations from uranium deposits. Identified effective complex of chemical reagents, which can remove sedimentations during sulfuric acid leaching of uranium. Performed laboratory research on samples of sediments and proved the concentration of the composition complex chemicals reagents. Demonstrated effective impact on permeability of the host rock during ISL of uranium.

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Introduction:-

In situ leaching (ISL) of ores with natural permeability involves replacing the pore fluid in the rock layer with the solvent, which interacts with the solid and liquid phases of rocks. As a result, various physical and chemical processes occur in the bowels of the earth [1]. The long-observed operation of geotechnical wells that were used for exploitation of uranium deposits by ISL method exhibits the decrease in their productivity over time. One of the main productivity loss causes can be attributed to the increase in hydraulic resistance and reduced filtration in rock layers due to colmatation formation stemming from precipitation of dissolved substances in the process solutions, or mechanical movement of particles of the ore-bearing horizon, and gas excretions.

Mechanical colmatation is the result of clogging of water filter orifices by sand, clay, gravel and blockage of the pore channels by mechanical suspension. Sand and clay precipitate only partially, sometimes completely overlapping the filter. Clogging of filter and formation zones created by drilling fluids containing clay particles can also be attributed to a mechanical colmatation [2]. Thus, the swelling of clay mineral in an aqueous medium and alteration of the pore space of the formation structure can be observed.

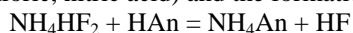
Chemical, ion exchange and gas colmatation types are caused by changes in the chemical composition of ground layer waters during ISL as a result of impact from application of chemical materials. The presence in water of dissolved calcium, magnesium and iron cations and the violation of the balance of carbon dioxide lead to the formation of sparingly soluble precipitation [3]. The allocation of carbonate sediments in the filter zone occurs intensively, however when remove the intensity of the precipitation decreases. During the reaction of leaching solutions with the host rock in the liquid phase, the accumulation of a number of the major rock-forming minerals (besides ore) occurs. The amount and kinetics of the transition of these elements into productive solutions depends on the type of lixiviant, end concentration, redox potential, temperature, solubility of the rock-forming

minerals and the size of the active surface of the mineral particles which in turn largely determines the intensity of mass transfer in the solution –solid system.

The purpose of the laboratory work has been reduced to the selection of chemical reagent, capable of changing the balance of the system and transferring of insoluble in a sulfuric acid treatment compounds into a liquid phase, or convert solid colmatants into easily soluble compounds. The technology that is heavily used in the oil and gas industry was taken as the basis for this work. Specific acid treatment ore-bearing rocks with a special solution are used for cleaning the pore spaces, creating new solutions movements channels and improvement of the available sizes, as well as the dissolution of clays in the near wellbore area [4].

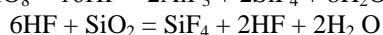
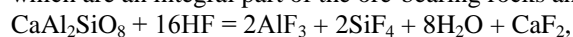
The analytical work for the selection of the formulation of the most effective solution was conducted on the samples of colmatant and ore-bearing rocks. Ammonium bifluoride (NH_4HF_2) and surfactants for loosening colmatant were used as additives to the sulfuric acid solution.

The ammonium bifluoride was selected due to its ability to exchange reaction with mineral acids (sulfuric, hydrochloric, nitric acid) and the formation of hydrofluoric acid.



where— HAn (H_2SO_4 ; HCl ; HNO_3).

Hydrofluoric acid, resulting from the reaction, easily reacts with siliceous and aluminosilicate compounds, which are an integral part of the ore-bearing rocks and of precipitation of bridging:



As a result, the dissolution of colmatant and parts of clastic sand takes place, generally increasing the effective porosity of the array block. This hydrofluoric acid is fully utilized due to the large amount of silica contained in the sands. Results of laboratory investigations indicate the possibility of using ammonium bifluoride as an additive in a sulfuric acid solution for effective chemical treatment technology wells [5,6].

Reagents included in ammonium bifluoride complex.

500 ml of 2% ammonium bifluoride solution is combined with 50 ml of a 2% solution sulfoaminovoy acids (CAA) and sodium tripolyphosphate (STPP) and mixed with 100 ml of 10% hydrochloric acid HCl . This mixture of chemicals is conventionally denoted by the CBF. The reagents that are used for the preparation of a fluoride complex for processing colmatant are described below:

Common inhibited hydrochloric acid (HCl) 31, 27, 24% concentration. Comes in tanks. Shipping and handling is carried out by means of special acid equipment. The storage is performed in rubberized containers within bund areas.

Hydrochloric acid (HCl) - a solution of hydrogen chloride in water, emits smoke on air, forming a mist. Hydrochloric acid vapors strongly irritate the respiratory tract and mucous membranes. Prolonged exposure to hydrochloric acid vapor may cause respiratory tract catarrh, as well as the opacification of eye cornea. Skin contact causes irritation and burns.

Ammonium bifluoride ($\text{NH}_4\text{F} \cdot \text{HF} + \text{NH}_4\text{F}$). Its acidity in terms of hydrofluoric acid is 25%, reagent density 1.27 g / cm^3 . Despite the fact that the use of ammonium bifluoride requires an increased consumption of hydrochloric acid to prepare a working solution (same part HCl participates in the conversion reaction of ammonium bifluoride in HF), reagent is especially useful in remote areas, because it can be stored and transported by conventional methods. Ammonium bifluoride is supplied in polyethylene bags nested in four-five-layer paper bags, weighing not more than 25 kg. Ammonium bifluoride is stored in covered warehouses, protecting it from moisture penetration. Material is a toxic agent. At higher concentrations in the air accepted limit by (0.2 mg / m^3) may cause a violation of the central nervous system, disease bone tissue, eye, skin.

Surface active agents (surfactants) such as disolvan, sulphonol, prevotsell, progol. Sulphonol comes in double kraft bags, and the other surfactants are transported and stored in steel drums. Liquid surfactants (disolvan, prevotsell) are dissolved in ethyl alcohol, thus are toxic and easily flammable.

Sulfuric acid H_2SO_4 is a strong dibasic acid, exhibiting the highest degree of sulfur oxidation. Under normal conditions, the concentrated sulfuric acid is a heavy, oily, colorless and odorless liquid with sour, "copper" taste. Sulfuric acid can also be represented as a mixture with water, or with sulfur trioxide SO_3 . Sulphuric acid and oleum are highly corrosive substances. By inhalation of these substances, they cause shortness of breath, cough.

Hydrofluoric acid (HF) 40% has concentration density of 1,15g / cm³. Transportation and storage of hydrofluoric acid must be carried out in plastic containers. Hydrofluoric acid - hydrogen fluoride solution in water, emits smoke in the air, forming mist. Hydrofluoric acid vapors strongly irritate the respiratory tract and mucous membranes, prolonged exposure to hydrofluoric acid vapor may cause srespiratory tract catarrh, blurred cornea of the eye. Skin contact can causes severe burns[7].

Laboratory experiments have shown that the most effective colmatating mixture composition is a solution of 10% sulfuric acid or hydrochloric acid with the addition of ammonium bifluoride 2-2.5% by weight.

Colmatant phase composition was monitored by X-ray diffraction analysis, which was carried out on the X-ray diffractometer X'Pert MPD PRO (PANalytical). Shooting conditions: CuK_{α} - radiation, Ni - filter, $U=30$ kV, $I=10$ mA, the rotational speed of 1000 pulses/s, the time constant $\tau = 5$ s, $2\theta = 10^{\circ} - 90^{\circ}$. Intensities of diffraction maxima were evaluated on a 100 point scale as a percentage of the highest line. The processing of experimental data and the interplanar spacings were performed according to the Wulff- Bragg formula. Phase analysis of the chemical composition of bridging materials were determined according to X-ray crystallographic data of the international community.

JEOL 6510EX electron microscope was used to acquire images of the surface sediments with high (up to 0.4 nm) spatial resolution, as well as for information about the composition, structure and other properties of the near-surface layers of the micro-diffractions. The method is based on the principle of interaction of the electron beam with the object under study.

The physico-chemical analysis results discussion.

The goal of the study was to evaluate the dissolving ability of different chemicals of varying sediment concentrations in controlled laboratory settings. Then, select the optimal chemical composition based on the analysis results.

For the pilot study the sedimentation from the interior surface of the submersible pumps from four fields located in the Syrdarya uranium ore province. Dried precipitates №1 is a dust-like mixture with the presence of large homogeneous formations and sand particles. Dried precipitates №2 is a white powder with beige spots.

For physical and chemical analysis purposes the samples of colmatant were ground in an agate mortar to a powder. The powder was examined by x-ray analysis. Stable reflection X-ray radiograph colmatant №1 (Fig. 1) shows a high crystallization sediment-chemical compounds. Analysis of the values of interplanar distances confirms the existence of feldspar particles, silica-alumina complex ferrous and plaster. Amorphous state is noticeable due to weak reflection of X-rays.

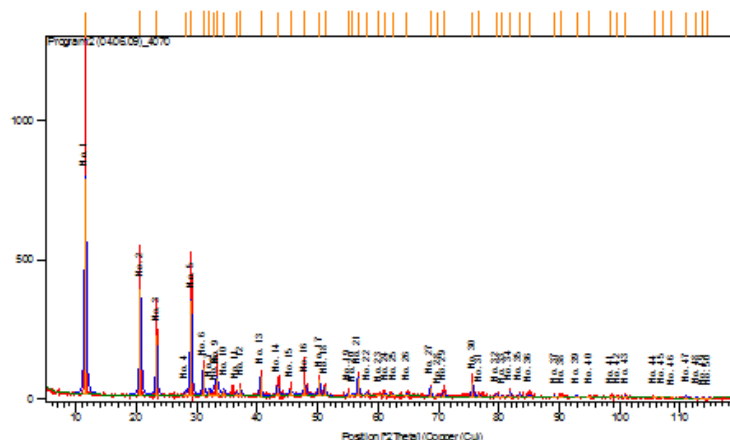


Figure 1:- The XRD pattern colmatant to chemical treatment.

The X-ray diffraction of colmatant in Table 1 shows the quantitative chemical and mineralogical composition of colmatant objects. The data in Table 1 show that colmatant is majorly based (about 70%) on a chemical compound ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), mineral - gypsum. The remainder of the colmatant comprises from gibshite rock-forming minerals, anorthite and amphibole (3%, 20%, 7%, respectively).

Table 1:- Chemical composition colmatant №1

	Reference code	The name of composition	Chemical formula	Content [%]
	00-036-0432	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	70
	01-075-1690	Gibshite	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1.53}(\text{OH})_{5.88}$	3
	01-087-1616	Anorthite	$\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$	20
	01-081-1135	Amphibole	$(\text{Ca}_{5.76}\text{Mg}_{0.24})(\text{Al}_{4.44}\text{Fe}_{0.48}\text{Si}_{2.08}\text{O}_{16})\text{Cl}_{2.76}$	7

These results prove satisfactory matching to published data of interplanar spacings with the experimental values_{experimental} and line radiographs (Appendix A1 и A2).

Drip method was used to determine dissolving properties of ammonium bifluoride and mineral acids in processing precipitations. The №1 sample was treated with the composition complex of ammonium bifluoride, №2 sample was processed by solvent composition of 12% hydrochloric acid, №3 sample was subjected to the treatment of 12% sulfuric acid. During processing a marked penetration of fluids precipitate to varying degrees with a slight change in the amount and color of colmatant object. The drying of processed materials is held at room temperature under a fume hood at atmospheric conditions. After drying, precipitates were triturated in an agate mortar to study phase composition of treated samples. The results of X-ray analysis of the sample №1 (Figure 2) showed the polycrystalline nature of the crystallization of the samples, as well as changes in the crystal chemical and mineralogical composition compared to the original colmatant.

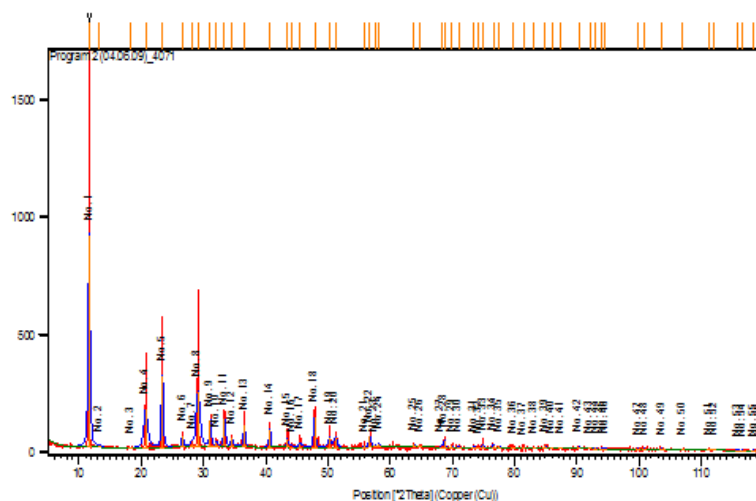


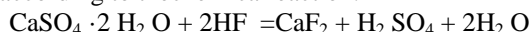
Figure 2:-colmatant №1 diffractogram after chemical treatment.

Characteristics of spectral reflections of the X-ray radiograph (Figure 2) remainsimilar in their colmatant diffraction patterns to those before the processing (Fig. 1).This is explained by the fact that all the minerals in the composition of colmatant is of isistructuralcrysallizationtype. Table 2 shows the quantitative phase and mineral composition data of colmatants after chemical processing with ammonium bifluoride.

Table 2:- Chemical composition colmatant after chemical treatment.

	Reference code	The name of composition	Chemical formula	Content [%]
	01-085-1569	Granite	$\text{Ca}_{2.83}(\text{Al}_{5.66}\text{Si}_{10.34}\text{O}_{32})(\text{H}_2\text{O})_{7.1}$	13
	01-073-2041	Gelit	$\text{Ca}_2(\text{Al}(\text{AlSi})\text{O}_7)$	4
	01-074-1559	Andradite	$(\text{Ca}_{2.97}\text{Mg}_{.02}\text{Mn}_{.01})(\text{Fe}_{1.99}\text{Al}_{.01})(\text{Si}_4)_3$	2
	01-072-0467	Orthosilicate	$\text{CaAl}_2\text{Si}_2\text{O}_8(\text{H}_2\text{O})_4$	38
	01-089-8754	Grossular	$\text{Ca}(\text{Al}_4\text{Si}_2\text{O}_{11})$	1
	01-072-2375	Epidote	$\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$	5
	01-089-7304	Pirop	$(\text{Mg}_{0.92}\text{Fe}_{0.05}\text{Ca}_{0.03})_3\text{Al}_2(\text{SiO}_4)_3$	5
	00-041-1479	Clinozoisite	$\text{Ca}_2\text{Al}_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$	32

TheresultsofX-rayanalysisofthesample №1 showedthe dissolution ofcolmatagingschemicalcompoundof gypsumaccording to thechemicalreaction:



The reaction products are strong electrolytes (CaF_2 , H_2SO_4) which dissociate into ionsin aqueous solution. Calcium cationsareinvolved in the formation the minerals of different composition (Table 2), showing that increase in the amounts of calcium containing minerals.Solutions of the fluoride ions react with siliceous and aluminosilicate compounds. Sulfuric acid acts as a leaching agent.

Study of the surface colmatantusing scanning electron microscope (Figure 3) shows the frame structure of the mechanism, with a complex association of groups of atoms and molecules, as well as the lack of gaps between the lateral planes, proving close-packed nature of the crystallization colmatagings chemical compounds.

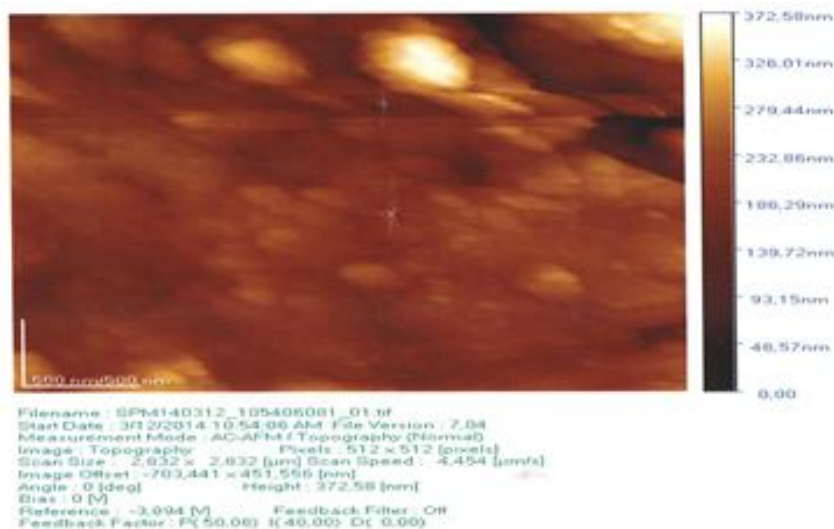


Figure 3:- Image colmatant surface before processing.

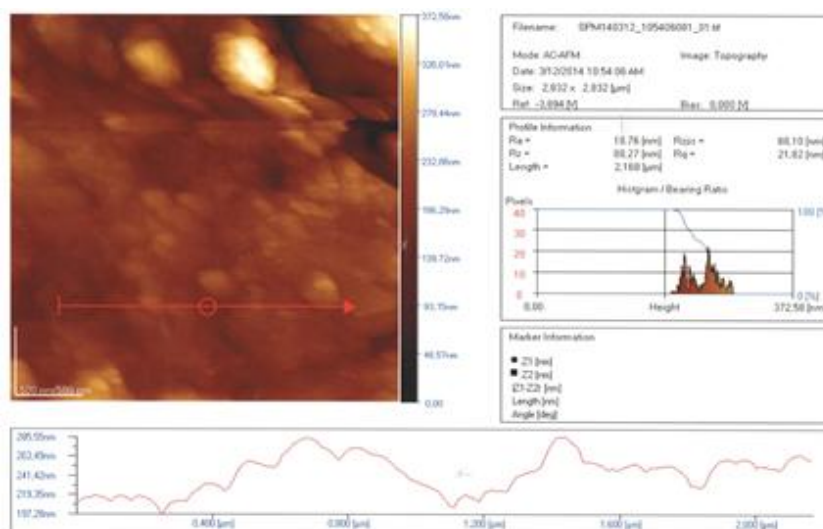


Figure 4:- Topography of the colmatant surface prior to treatment.

Figure 4 shows a picture of the surface microdiffraction colmatating objects. The profile of the histogram shows that the surface is formed by polymerization of silicate to the skeletal structure, which represents an infinite body-tallies framework of SiO_4 tetrahedrons and AlO_4 , in the cavities of which there are other ions, as a result of the drying process, they can turn into a clay and various kinds of silica. Structure without rupture, solid, formation of voids and cracks were not observed.

Post chemical processing (complex of ammonium bifluoride, 12% hydrochloric acid and sulfuric acid) drying and preparation of colmatant samples was performed at room temperature for 24 hours. The results of electron diffraction studies (Figure 5) showed a change in the morphology of the surface of the colmatant. As the result, new chemical formations are being composed within colmatating substance. Chemical formations can be described as smears, with discontinuous streaks and cracks.

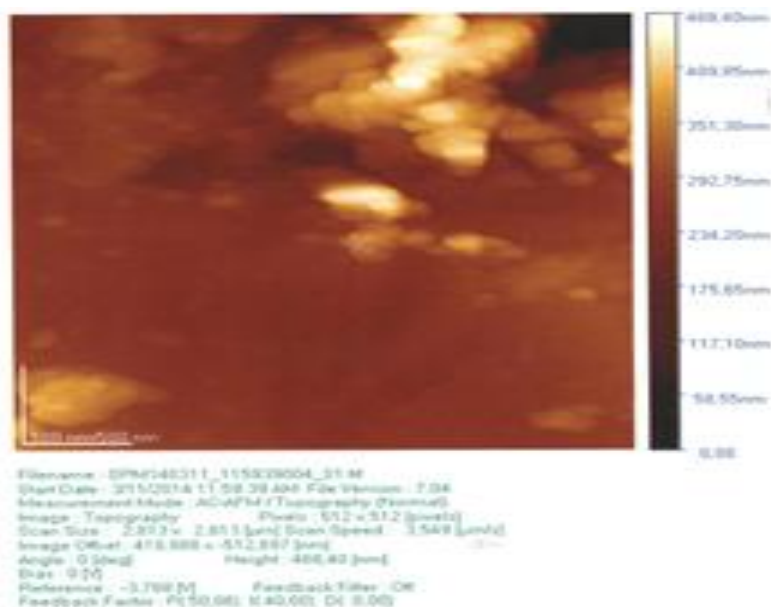


Figure 5:- Image of the colmatant surface after chemical treatment.

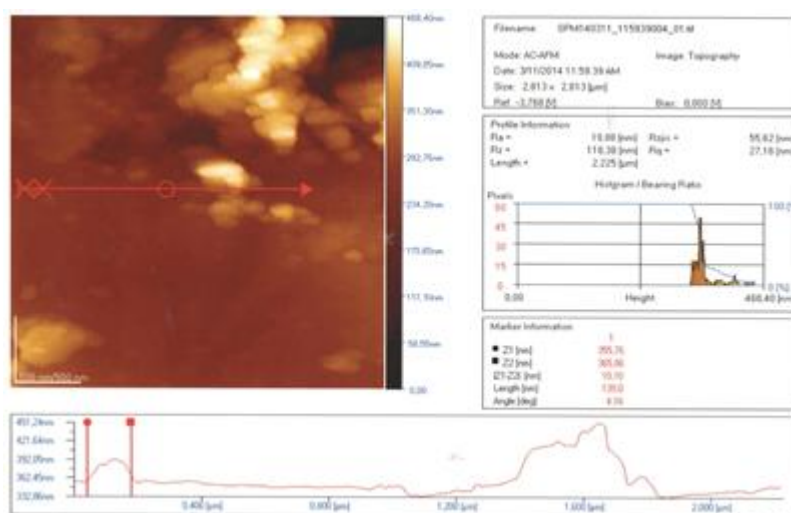


Figure 6:- Colmatant surface topography after chemical treatment.

Microdiffraction of colmatant surface after chemical treatment is shown on Figure 6. The surface histogram profile shows a surface discontinuity in a region varying from 200 nm to 300 nm, which proves the structural transformation of colmatant, as well as changes in the chemical composition of the sediment-systems.

Investigation and analysis of laboratory experiments shows that chemicals differently affect the colmatant sediments, depending on the composition and concentration. However, the ammonium bifluoride's effect is strong. According to the electron diffraction, the complex of ammonium bifluoride is the most workable, effectively dissolving the gypsum and producing the maximum depth of a deepening in the sample by destroying the crystal structure colmatant. Thus, the ammonium bifluoride shows better characteristics compared to the solution of 12% hydrochloric or sulfuric acid.

The dissolving capabilities of the tested solutions are directly depended on the chemical composition of colmatant formations and quantitative characteristics of sediment-rock. Its main component, gypsum, is a product of the chemical process of sulfuric acid leaching, its content is 70% by weight of the colmatant. Laboratory studies have shown the effectiveness of ammonium bifluoride usage as an additive in sulfuric acid solutions that are effective for carrying out chemical treatments of colmatant. The complex of ammonium bifluoride - 10% solution of sulfuric acid or hydrochloric acid with the addition ammonium bifluoride 2-2.5% by weight was developed. X-ray

diffraction and electron analysis revealed the complete dissolution of the main colmatant element – gypsum. As the result of chemical processes new formations were observed. Changes were found in the surface morphology and in the formation of voids and cracks of colmatant. To sum up, the ammonium bifluoride complex can be successfully used as a chemical reagent for treating geotechnological wells during their regeneration.

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