



In Situ Biogeochemical Barriers for Contaminated Groundwater Treatment near Uranium Sludge Storages [†]

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Abstract: The contamination of groundwater by uranium, nitrate, ammonium, and sulfate near uranium sludge storage sites due to the degradation of engineering safety barriers is an urgent problem during their long-term operation. The purification of such multicomponent contaminants is a complex task and one of the promising methods for this purpose is in situ bioremediation using the metabolic potential of aborigenic microflora. The work focused on the geochemical, geological, and microbiological parameters of groundwater with multi-component contamination near the uranium sludge storage sites of four chemical plants. In conditions of extreme nitrate contamination (up to 15 g/L), denitrifying bacteria were found to be the dominant group of microorganisms. In conditions of nitrate–ammonium contamination, bacteria responsible for the Anammox process were found. In laboratory, optimal conditions were selected to stimulate microflora to promote nitrate removal. For this purpose, sources of carbon (acetate, whey) were added to the water samples in concentrations necessary for the complete removal of nitrate by microbial denitrification. The experiment was carried out at ambient temperature in hermetically sealed vials. Uranyl nitrate was added to the samples at a concentration of 5 mg/L for uranium. It was found that nitrate removal contributes to the cycle of anaerobic processes of authigenic sedimentation because of sulfate and iron reduction processes, which provide the formation of a mineral geochemical barrier for uranium immobilization. As a result of the experiment, after 3–6 months, depending on the concentration of nitrate in the groundwater sample, the uranium content in the liquid phase decreased by 92–98%.

Keywords: sludge storage; uranium; nitrate ion; sulfate ion; bioremediation



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1. Introduction

At nuclear fuel cycle enterprises, the storage of large volumes of solid radioactive waste after ore processing and uranium enrichment in open sludge storage facilities lead to contamination of the environment with anions of mineral acids (mainly nitrate and sulfate ions) and uranium, primarily of upper aquifers [1]. One of the methods for restoring the quality of water in underground aquifers is in situ bioremediation, since it allows efficient and low-cost immobilization of a pollutant by using the metabolic capabilities of underground microflora by stimulating it by injecting soluble organic compounds into the reservoirs.

The aim of this work was to analyze the behavior of uranium in biogeochemical processes during bioremediation of groundwater in the area of the sludge storage sites of four plants under laboratory conditions and to apply the method in real conditions.

2. Materials and Methods

2.1. Study Objects

The objects of the study were the sludge storage sites of four large nuclear fuel cycle plants in Russia: AECC Angarsk, ECP Zelenogorsk, NCCP Novosibirsk, and CHMZ Glazov. These plants compose different units of the nuclear fuel cycle. However, they all operate on natural uranium, the residual concentrations of which in the solutions are neutralized and discharged into near-surface sludge collectors. Regardless of the stage of the nuclear fuel cycle, at which the liquid uranium-containing wastes are produced, the approved technological approaches to their neutralization cause similar characteristics of phase and mineral composition. Acid uranium-containing solutions are neutralized with Ca(OH)₂ lime slurry. During neutralization, the solution is quickly supersaturated with the respect to calcite, gypsum, dolomite, barite, and bassanite. If the original solutions contain high concentrations of fluoride ion, then during neutralization there is an active formation of fluorite, which in some cases can comprise the bulk of the wastes.

Despite the general similarity, the plants have individual differences related both to the operational characteristics of sludge collectors (mineralization and salt composition of discharged slurries, the volume of solutions, and the presence and condition of seals) and the natural conditions of the sludge storage sites (geomorphological position, thickness and protection of aquifers, composition of background groundwater, etc.). For most sites, natural groundwater is hydrocarbonate calcium–magnesium with a mineralization of less than 1 g/L. Because of the interaction of water with the sludge, it becomes nitrate and sulfate–nitrate, and the proportion of sodium and potassium increases and prevails over other cations. The maximum mineralization can reach 15–20 g/L (Table 1).

Table 1. Chemical composition of groundwater in the territory of sludge storage facilities.

		AECC			ECP			NZHK			CHMZ		
		Natural	Middle	Polluted	Natural	Middle	Polluted	Natural	Middle	Polluted	Natural	Middle	Polluted
Eh	mV	115	136	34	166	90	94	−4	−29	57	−70	162	195
pH		7.39	7.10	9.78	7.35	6.70	7.50	7.01	6.51	7.40	7.20	7.80	6.50
CO ₃ [−]		96	89	412	267	215	204	393	151	195	54	212	319
+ HCO ₃ [−]		27	1620	3720	0.55	143	800	24.4	1920	590	21.4	1585	780
SO ₄ ^{2−}		6.45	49	350	1.61	65	17	21	750	2984	10.9	1131	2260
Cl [−]		0.28	0.20	103	9.1	16.5	68	1.0	1.1	120	7.8	88	292
NH ₄ ⁺		0.98	45.4	2440	0.80	2330	11,500	5.9	900	4740	11.5	3460	7100
NO ₃ [−]		33.9	299.1	114.6	77.8	602	5340	103	556	804	132	1113	2940
Ca ²⁺	ppm	5.25	94.22	1519	11.74	70.73	127	12.40	563	2013	100	1058	1549
Na		18	120	5.0	25	60	120	35	160	72	31	29	76
Mg		0.72	3.09	139	1.99	5.00	11.0	1.83	8.92	91	16.5	234	47
K		7.54	7.11	1.27	5.73	5.47	7.00	6.74	1.19	4.87	3.20	12.4	19.7
Si		0.04	0.08	0.13	0.07	0.09	0.09	0.11	0.08	0.13	0.14	2.4	3.1
Al		13.9	1.66	3.33	1.59	2.03	15.4	5.26	3.46	2.65	1.40	5.10	67
Fe		0.41	0.07	0.81	1.1	0.73	2.2	1.3	2.1	2.5	0.83	1.0	2.4
Mn		0.20	0.31	1.16	0.40	1.29	10.0	0.53	0.47	0.07	0.01	0.01	0.39
P		0.09	0.24	0.26	0.23	3.0	5.6	2.0	0.86	3422	0.01	1.90	4930
U	ppb												

2.2. Analysis Methods

The values of Eh, pH, and electric conductivity were determined using a Hanna pH/Ion Meter (HI 9025 C, Hanna Instruments, Ronchi di Villafranca, Italy) equipped with various combination electrodes.

The trace element composition of water was measured by high-resolution inductively coupled plasma mass spectrometry (ICP-MS) (ELEMENT FINNIGAN MAT) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Advantage); anion concentrations were determined with a KAPEL[®]-105M (LUMEX, Saint Petersburg, Russia) capillary electrophoresis system at the analytical center of the Sobolev Institute of Geology and Mineralogy, SB RAS.

The laboratory modeling of biological processes was conducted by adding electron donors and carbon sources (whey and acetate) to groundwater samples and cultivating at ambient temperature. Groundwater (100 mL) was sealed in hermetic vials with an initial air gas phase. Uranyl nitrate was added to the samples at a concentration of 5 mg/L for uranium. Aliquots were taken for analysis every 5–7 days.

3. Results and Discussion

3.1. Biological Purification of Polluted Water

Aerobic organotrophic, denitrifying, and sulfate- and iron-reducing bacteria were identified based on the results of formation fluid sample inoculations on selective culture media. The maximum number of organotrophic bacteria was in samples taken from points with medium pollution; in the highly polluted site of the AECC and CHMZ, their number was lower than in the uncontaminated areas of the aquifer (Figure 1). Therefore, by example of four plants, it was found that in the nitrate, sulfate, and ammonium pollution zones, microbial community activation processes occurred, followed by an increase in the total number of cells compared with background samples.

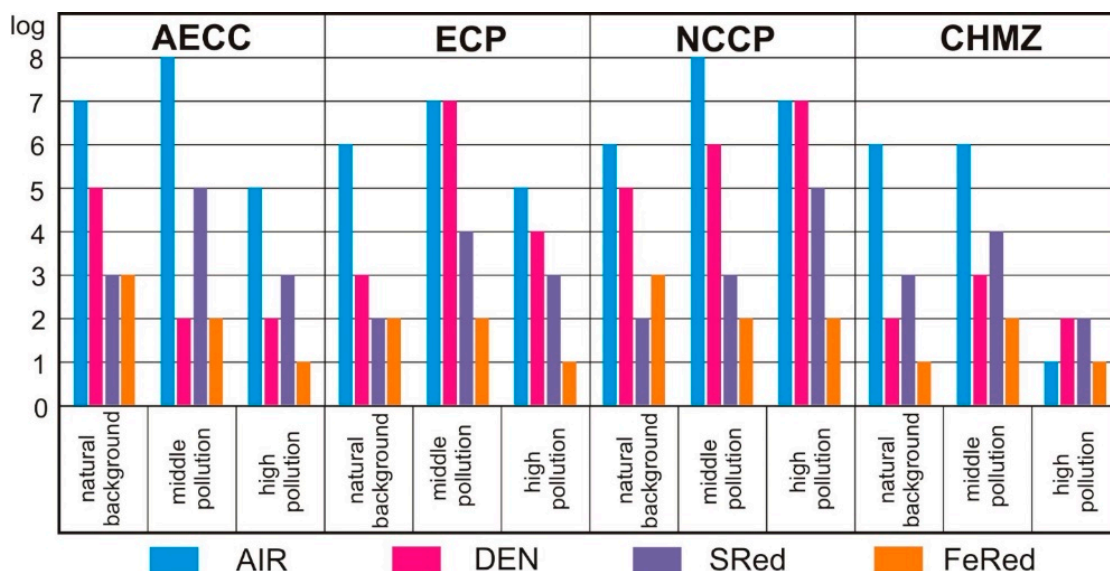


Figure 1. Microbial populations (log cell number/mL) of the main physiological groups in groundwater samples determined by inoculation to selective media.

Table 2 shows data on the rates of removal of nitrate and sulfate by the microbial community of isolated samples found after stimulation with stoichiometric sugar concentrations in laboratory conditions. It was found that in unpolluted samples, the removal of sulfate occurred in 7–14 days; in contaminated samples, the time for removal of sulfate depended on the concentration of nitrate ions. At the point of maximum contamination, the removal time of nitrate reached 180 days and sulfate 210 days. In a zone with a high nitrate ion content, biological in situ stimulation for the nitrate removal may be therefore inefficient.

Thus, the microbial community of groundwater after the stimulation by water-soluble electron donors can lead to the removal of nitrate and the reduction of sulfate with the formation of sulfide mineral phases in reducing conditions. The shift of Eh in the samples to the reduction region led to the intensification of anaerobic processes of denitrification and sulfate reduction and, as a consequence, to the reduction of uranyl ions. Thus, by stimulating the development of the microbial community, the immobilization of uranium significantly increased and the spread of nitrate, sulfate, and uranium contamination decreased.

Table 2. Table of rate of nitrate and sulfate removal in isolated groundwater samples after stimulation of the microbial community with sugar.

The Media		Duration of NO ₃ ⁻ Decomposition, Days	Rapidity of NO ₃ ⁻ Decomposition, ppb/Day	Duration of SO ₄ ²⁻ Decomposition, Days	Rapidity of SO ₄ ²⁻ Decomposition, ppb/Day
AECC	natural	0	0.08	12	27 *
	middle	5	1.5	30	324
	polluted	20	32.5	75	186
ECP	natural	0	0.8 *	0	0.55 *
	middle	25	58.2	40	5.7
	polluted	180	54.8	210	4.4
NZHK	natural	0	0.8	7	25 *
	middle	7	20	45	274
	polluted	75	36.4	130	7.9
CHMZ	natural	0	0.8	14	21 *
	middle	45	38.4	90	1585
	polluted	90	54.6	130	780

* Complete dissolution occurred in the first day, the rate is underestimated.

3.2. Future Work on the Formation of Barriers in Situ

The next stage of our research work will include the application of the bioremediation method in situ. For the formation of biogeochemical barriers at the local sites, a number of conditions will be taken into account:

1. Groundwater velocity. In all cases described, this is the water of the first surficial aquifer, which is drained by nearby logs. It is important that the time before the release of this water to the surface is sufficient for the dissolution of nitrate and sulfate (at least 2–3 months), otherwise the water comes to the surface and falls into oxidative conditions in which denitrification and sulfate reduction processes do not occur;
2. The presence of available electron donors and carbon sources (organic matter, hydrocarbonates, and hydrogen);
3. The pH values must be in the range of 6–9. In the case of ammonium contamination, an increase in pH values above 8.5 leads to the formation of ammonia;
4. Biological processes require biogenic elements (P, K, N, and S). If the content of sulfur and nitrogen compounds in contaminated areas is usually high, then in our case the limiting factor will be the content of phosphorus, which must be added when stimulating microbial processes. In addition, the addition of phosphates can lead to the formation of poorly soluble phosphate–uranium phases that contribute to the immobilization of uranium;
5. The concentration of nitrate ions should not be below 5 g/L; in the case of a higher concentration, the rate of removal of nitrate ions and reduction of sulfates may be lower than the rate of water exchange;
6. The composition of the host rocks should be optimal for biofouling (the presence of clay phase and ferriferous minerals apart from quartz). The formation of biofilms on rocks provides the formation of microbial communities resistant to toxic loads. Biofouling of pure quartz is generally not very high [2];
7. The presence of bacteria of a reducing branch of the nitrogen cycle in the microbial community capable of both dissimilative and assimilative reduction of nitrate. Only dissimilative reduction of nitrate at its high concentrations can lead to the accumulation of nitrite, which is more toxic than nitrate and reduces or stops microbial processes [3];
8. To form a stable biogeochemical barrier with reduced redox potential optimal for sulfate reduction and the formation of sulfide-ferriferous mineral phases, conditions of limited oxygen access to the aquifer are required [4].

4. Conclusions

Our studies showed that using the proposed approach results in a partial or full reduction of uranium, ammonium nitrate, and other compounds; distribution can be reached at all sites. While the production facilities are being operated, the injection of reagents for the sustainable development of the biogeochemical barrier should be carried out with a frequency sufficient to change the compounds into solid (U, S) as well as gaseous (N) phases. After decommissioning and preserving the facilities, it is necessary to provide for a margin of stability of barriers, thereby preventing degradation by background water, which will gradually replace contaminated technogenic solutions.

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