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SHORT COMMUNICATION

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REMEDICATION OF THE SERBIAN SOILS CONTAMINATED BY RADIONUCLIDES IN THE FUNCTION OF THE SUSTAINABLE DEVELOPMENT

Phosphate-induced metal stabilization (PIMS) using apatite stabilizes uranium in situ, by chemically binding it into the new low-solubility ($K_{sp}=10^{-49}$) phase. Uranium-phosphate-autunite is stable across a wide range of geological conditions for millions of years. A large area of contaminated soil is suitable for in-situ remediation that involves minimizing the mobility of the uranium. Laboratory study was conducted to quantify different forms of apatite sequestration of uranium contaminant. The experiment was done with natural phosphate from Lisina deposit (14.43 % P_2O_5), with non-treated samples, phosphate concentrate samples with 34.95 % P_2O_5 and mechanochemically activated of natural apatite. Different concentration of P_2O_5 in apatite, pH, reaction time, solid/liquid ratio was investigated. The concentrate at pH 5.5 for 7 days sorbed around 93,64 % and nature apatite, with 14,43 % P_2O_5 , for 30 days sorbed 94.54 % of the uranium from the water solution, concentration 100 $\mu\text{g U/ml}$. The results show that mineral apatite "Lisina" is very effective for the treatment of contaminated soils - in situ immobilization of U. Mechanochemical activation of natural apatite in vibration mill immobilized 85.37 % of uranium in the 7-day period of acting. This research on natural apatite from the deposit "Lisina" for immobilization of uranium was the first one of this type in our country.

Key words: uranium; remediation; apatite; phosphate concentrate.

se of reactive media for remediation of metals and radionuclides is presently being considered for a multitude of field applications. A reactive medium can be mixed into the soil or waste, or emplaced as a permeable reactive barrier to treat a shallow groundwater or the surface seeps. A reactive medium is any material that has specific chemical reactivity towards one or more chemical constituents *via* mechanisms such as adsorption, exchange, oxidation-reduction, or precipitation. Materials used for remediation in the field must be effective, inexpensive and readily available in multiple-ton quantities to be able to treat large volumes of water or soil. The apatite mineral group has been shown to be effective both in sequestering dissolved metals and in transforming soil-bound metals to less soluble phases. Utilizing apatite minerals as a remediation method puts to use

long-recognized geochemical principles. Apatite minerals form naturally and are stable across a wide range of geologic conditions for hundreds of millions of years [1-4]. Over 300 apatite minerals exist, with elements from the entire periodic table replacing calcium, phosphate, and hydroxide in the fundamental apatite crystal structure [5]. The bioavailability of ingested metal-apatite is also greatly reduced [6,7], making animal and human intrusion less dangerous if the metal-apatite phase should be ingested, and making bioremediation more effective in mixed waste environments. The reaction between the apatite and metals is rapid [4, 8-11], and so the treatment is effective immediately, requiring no time for the material to set up. The subject of many researches and published papers is hydroxy-apatite, *e.g.* Apatite II. As little as 1 % by weight of Apatite II can remediate most metal-contaminated soils [4] avoiding volume problems associated with many other methods.

Apatite as a reactive medium

The reactive media studied for applications to metal and radionuclide-contaminated sites consists of Apatite II, an inexpensive, primarily amorphous form

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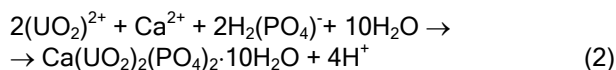
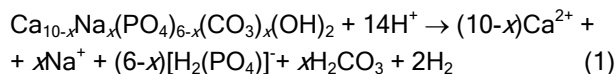
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of a carbonated hydroxy-apatite that has random nanocrystals of apatite embedded in it, resulting in efficient and rapid precipitation of various phosphate phases of metals and radionuclides, including uranium and plutonium. Apatite II is also an efficient non-specific surface adsorber and is available in multiple-ton quantities at low cost. This material stabilizes metals by chemically binding them into new stable phosphate phases (apatite and autunite minerals) and other relatively insoluble phases in the soil, sediment or in a permeable reactive groundwater barrier. Metals most effectively stabilized by this treatment are uranium, lead, plutonium, zinc, copper, cadmium, nickel, aluminum, barium, cesium, strontium, thorium, cerium, and other lanthanides and actinides. The relative contribution of adsorption and precipitation to metal removal depends upon the environmental conditions, the mineral phases present, and the metal concentration in a solution. Simple feasibility studies on the contaminated groundwater and soil under the site conditions determine which mechanism would dominate at any particular site. The nominal composition of Apatite II is $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ where $x < 1$. For U removal *via* precipitation, the overall reaction is actually a dissolution reaction of the Apatite II followed by precipitation of autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$, on existing Apatite II surfaces, simplified as:



The degree of protonation of the phosphate and carbonate, and the exact actinide species involved, depend upon the pH and aqueous chemistry. Reaction (1) does not usually lead to reaction (2), but provides a constant supply of phosphate to the solution to induce the reaction (2) whenever $(\text{UO}_2)^{2+}$ is in solutions contacting the apatite.

Our investigations, done in order to determine the effects of using domestic natural apatite "Lisina" for uranium immobilization, are the first one of this type in our country. Phosphatic ore deposit is in southeast Serbia, near the city of Bosilegrad. The estimated data for phosphate quantities in Bosilegrad are 68×10^6 t, with the average content P_2O_5 9.6 %. Mechanochemical activation, in order to obtain better material reactivity, was performed with fine and ultra-fine milling in high energy vibration mills. By the process of mechanochemical activation certain quantity of energy was transmitted to material crystals and it led to degeneration of crystal lattice. The effect of performed mechanochemical activation of apatite was fractional amorphization and increase of apatite solubility.

EXPERIMENTAL

The laboratory study was realized with 4 different types of apatite samples:

a) natural apatite (samples were taken from domestic "Lisina" phosphate deposit, with the average content of P_2O_5 9.26 %. Samples were prepared by the process of washing and wet milling. Technical characteristics of apatite used for the adsorption were as follows: average content of P_2O_5 : 14.3 %, particle size: 0.074 mm.

b) apatite concentrate (natural apatite was prepared with the procedure of flotation and concentration, and then treated by the process of magnetic separation in order to obtain high quality apatite concentrate. Technical characteristics of concentrate apatite used for the adsorption were as follows: average content of P_2O_5 : 34.95 %, particle size: 0.074 mm.

c) mechanochemically activated apatite; activation period: 15 min (particle size: $<40 \mu\text{m}$; $d_{av} = 9.5 \mu\text{m}$).

d) mechanochemically activated apatite, activation period: 30 min (particle size: $<32 \mu\text{m}$; $d_{av} = 7.0 \mu\text{m}$).

Natural apatite samples were mechanochemically activated by milling in a highly reactive vibration mill "Kad Humboldt Wedog" during the time of 15 and 30 min.

A different apatite forms effect on uranyl ion immobilization was investigated with the change of experimental conditions: pH value (pH 5.5, 0.001 M CaCl_2 and pH 7.0, 1 M CH_3COONa), reaction period (7, 30 and 60 days) and mass of adsorbents (5 and 10 g in 100 cm^3 of solution with concentration $100 \mu\text{g U/cm}^3$).

The uranium content was determined by fluorometric method by employing 26-000 Jarell Ash Division instrument (detection limit: 0.005 mg/kg, range: 0.05- 5 mg/kg, correlation coefficient: $R > 0.997$).

RESULTS AND DISCUSSION

Phosphate induced stabilization of uranium with natural apatite

In Table 1 we present the sorption effect of apatite forms depending on pH and solid/liquid ratio, in the reaction time of 7 days.

The obtained results for uranyl ion sorption on apatite in reaction period of 30 and 60 days, for different pH and mass of adsorbent are presented in Table 2.

The obtained results shows the adsorption index for uranyl ion >90 % in conditions pH 5.5 and in period of 30 days, and in period of 60 days the adsorption index increases on 98.09 %. The use of this ad-

sorbent is recommended for remediation of big low-level contaminated areas, as permeable reactive barrier or directly by addition of adsorbent in contaminated soil. The stabilization of uranyl ion with the addition of 5 g apatite is slower than one with 10 g, but with a trend for a continual increase.

Table 1. Sorption of uranyl ion for different pH and mass of adsorbent; the reaction period: 7 days

pH	Adsorbent mass* g/100 cm ³	Uranyl ion adsorption index, %			
		Natural apatite	Apatite concentrate	Mechanically activated apatite	
				15 min	30 min
7.0	5	10.80	36.88	12.80	14.73
	10	12.32	57.16	16.40	22.65
5.5	5	32.34	91.40	49.56	54.34
	10	48.27	93.62	77.04	85.37

*Solution with the concentration of 100 µg U/cm³

Table 2. Sorption of uranyl ion for different pH and reaction period of 30 and 60 days

pH	Adsorption, %			
	Reaction time, days			
	30		60	
	Natural apatite	Apatite concentrate	Natural apatite	Apatite concentrate
7.0	18.07	48.53	37.19	91.92
	24.61	81.01	72.38	95.19
5.5	44.74	97.17	64.04	≈100
	94.54	97.96	98.09	≈100

The highest adsorption index is obtained with pH value 5.5, minimal initial adsorbent mass and in the 7-day period the adsorption index > 90 % was obtained. The adsorption index of apatite on pH 7.0 was much lower but with a tendency to increase with the increase in the apatite acting period. On the basis of these results we assumed that a new complex compound, autunite, with very high stability level was formed, what was confirmed with the fact that an autunite phase was not dissolved in investigated cases even after 60 days and upon different experimental conditions. The apatite adsorbent, obtained by the process of mechanochemical activation, has a sorption capacity increased for ≈70 % compared to natural apatite. The apatite activated during only 30 min showed a great adsorption capacity of 85.4 % in 7 days.

Considering the obtained results, we can conclude that the apatite concentrate and two investigated mechanochemically activated apatites are very good for remediation of small soil areas with a higher level of radionuclide contamination - hot spots. The

natural mineral apatite, which showed the less adsorption capacity is recommended for large soil areas with low radionuclide contamination and can be very useful, especially considering both environmental and economical effects.

CONCLUSION

Natural phosphate Lisina, with the average P₂O₅ content of 14.43 % is a very reactive, convenient material that assures chemical components for *in situ* uranium by chemically binding it into a new low-solubility ($K_{sp} = 10^{-49}$) stable phase uranium-phosphate-autunite. The apatite concentrate with P₂O₅ content of 34.95 % shows much faster immobilization ability and is recommended if the economic moment allows it. By the process of mechanochemical activation, the adsorbent with around 70 % higher adsorption capacity than natural apatite is obtained. In this way, the obtained material achieved the adsorption level >90 % in 7 days of acting.

“Lisina” phosphate, natural concentrate or activated, can be used depending on characteristics and a specific demand for certain contaminated area, as: permeable reactive barrier, addition to contaminated soil in combination with convenient agrochemical measures, liner for contaminated ground.

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