

REMEDIATION OF URANIUM CONTAMINATED WATER AND SOIL USING PHOSPHATE- -INDUCED METAL STABILIZATION (PIMS)*

As a consequences of the past war activities a large area in Kosovo and some locations in South Serbia were contaminated by depleted uranium (DU) and toxic heavy metals. There is an urgent need for remediation of this contamination in order to prevent its possible long-term effects not only on the population in the contaminated regions but also on the neighboring countries. Therefore, it is necessary that together with permanent monitoring of environmental contamination, we proceed with research and development on selection of cost effective remediation technology appropriate for large areas such as contaminated water and soil.

Conventional remediation techniques: excavation, treatment (soil washing, chelating), conditioning and disposal as low-level radioactive waste are necessary for heavy contaminated sites. However, for a large area of contaminated soil and aquifer sediments in situ remediation is appealing since it is much less disruptive to the ecosystem and hydrology, reduces the risk of worker exposure during remediation and is typically less expensive than conventional technologies. In situ remediation involves minimizing the mobility of contaminants by transferring them to stable, nonlabile phases via chemically induced transformation.

Phosphate-Induced Metal Stabilization (PIMS) is a technology developed to treat the contamination in place, either by mixing the treatment amendment directly into the soil or by emplacing the amendments within a permeable reactive barrier passively treating groundwater. PIMS stabilizes a wide range of metals, especially uranium (U), plutonium (Pu) and lead (Pb) by chemically binding them into new stable phosphate phases and other low-solubility phases that are stable over geologic time. Metal sequestered in apatite minerals has great durability and leach resistance significantly exceeding other chemically stabilized forms. Although some form of apatite is necessary, most apatites do not have the suitable characteristics for optimal performance in the field.

A special form of apatite, Apatite II (UFA Ventures) has been found to be the most cost-effective apatite available, having optimal structural and chemical characteristics for metal and radionuclide remediation. This technology has been successfully demonstrated on contaminated soil and groundwater for U, Pb, Pu, Cd, Zn and Cu from mining sites and from DOE sites (USA). Certain apatite from Yugoslavia, which has demonstrated good sorption properties for Pb, will be tested in a laboratory feasibility study, simultaneously with Apatite II, for remediation of DU contaminated sites. Depending on site characteristics and requirements, it will be emplaced as a down-gradient permeable reactive barrier, mixed into contaminated soil or waste, used as a disposal liner or apatite can be combined with grout for improved stabilization performance.

The potential effects on human health and the environment arising from possible use of depleted uranium during the 1999 Kosovo conflict were discussed in detail in the preliminary report of UNEP/UNCHS Balkans Task Forces, published in October 1999 [1]. Even at that time it was not officially confirmed that DU had been used, further measurements were strongly recommended, with highest priority to finding DU pieces, heavily contaminated surfaces and other "hot spots". Some of these "hot spots" were identified [2] and according to Yugoslav authorities [3] a significant amount (estimated 10 tons) of DU was spread throughout the territory of Kosovo.

DU poses a serious threat to the environment. Metals readily leach from contaminated soils, sediments, rocks, waste piles, trenches, pits, and contained bodies of water. These leachates serve as sources of metal contamination to the environment, especially adjacent streams and underlying groundwater zones. Safe and cost efficient methods for treating and disposing of this pollution and waste has become increasingly important. Conventional treatment methods for DU and other radionuclides can be categorized into three groups: 1) separation, 2) structural containment, and 3) physical stabilization/solidification. These treatment methods are complex, costly, expand volumes, and some of them are only temporary solutions.

Efforts to mobilize and remove metals from the subsurface to below regulatory limits have not been successful because of the various intermediate solubilities and sorption properties that each metal and suite of metals exhibit under most environmental conditions. Alternately, metals can be stabilized in place to prevent them from migrating or leaching into groundwater. Many chemical additives have been studied to immobilize metals in these situations, e.g., lime, phosphate rock, carbonate rock, fly ash, clay minerals, zeolites, and sulfur and iron compounds. Among these materials hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), as well as some specific natural

PHOSPHATE-INDUCED METAL STABILIZATION (PIMS)

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apatites represent the most effective material used for immobilization of DU and other toxic heavy metals [4–19]. It was found that hydroxyapatite effectively immobilized uranium even from highly concentrated salt solutions and at temperatures up to 120°C [8]. The rate of immobilization is very fast for U with HAP being in excess by a factor of 10. From aqueous solutions, immobilization of U(VI) by calcium-deficient HAP gives uptake of 1.2 molU(VI)/molHAP [15]. Additions of HAP to sediments, having total U concentrations up to 2100 mg/kg lower aqueous U concentration to near proposed drinking water standards [16].

For these reasons, apatite remediation of heavy metals is an emerging technology that addresses the need to remediate metals in wastes, contaminated groundwater, sediments and soils, including agricultural soils. This technology stabilizes metals by chemically binding them into new stable phosphate phases (apatite 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 lead, zinc, copper, cadmium, nickel, uranium, barium, cesium, strontium, plutonium, thorium, and other lanthanides and actinides. The ultimate driving force for the robust performance of reactive phosphate with respect to metals is the extreme stability of these metal-phosphate phases [18]. The excellent stabilization efficiency comes from the extremely low solubility products of the resultant metal-apatites, e.g., for U-phosphate (autunite) $K_{sp} = 10^{-49}$, and for Pb-apatite (pyromorphite) $K_{sp} = 10^{-80}$. These metal phosphates are twenty to seventy orders of magnitude more insoluble than quartz. Combined with this stability, the rapid kinetics of the metal-phosphate precipitation ensures immobilization of the metals in the face of most possible transport mechanisms.

The most effective apatite technology was developed by the US company UFA Ventures [www.ufaventures.com] who successfully applied this approach in remediation of several sites in the US contaminated by DU and other heavy metals:

Uranium remediation at Oak Ridge and Los Alamos

Various reactive materials were tested for the removal of dissolved uranium (U) from DOE Y-12 facility NT-1 groundwater at Oak Ridge, Tennessee [19], including Apatite II, 3 different types of bone char, a mixed valent oxide iron filings, granular activated charcoal (GAC), phosphate rock, Nucon Nusorb, and Mersorb-3. The difficulty at this site is that the groundwater can have high total dissolved solids, especially nitrate ion, and contains elevated levels of many regulated metals including U, Cd, and Pb. Apatite II was shown to be almost ten times as effective as bone char for removing U, and many orders of magnitude more effective than the other materials including zeolite, activated charcoal, peat moss, zero valent iron and other forms of

reduced iron, even in the presence of high nitrate concentrations. Apatite II was also much more cost-effective. X-ray diffraction after batch tests showed meta-autunite crystallized on the surfaces of the Apatite II.

RESEARCH OF PIMS PERFORMED IN VINČA INSTITUTE

Investigation of physico-chemical, structural and sorption properties of HAP represents a part of the research program of the Radiation and Environmental Protection Laboratory of VINCA Institute of Nuclear Sciences for more than 15 years [20–25]. Primarily, we investigated phosphate precipitation as a method for removal of radioactive strontium by formation of insoluble phosphates. This research was performed in collaboration with Laboratory for Radiochemistry of the Moscow State University. It was established that co-precipitation of strontium with calcium phosphate lead to the substitution of Sr atoms by Ca atoms in the crystal lattice of HAP. Optimization of this process and structural and morphological changes of the solidified waste form were investigated in detail [20, 21].

Sorption properties of synthetic HAP for the removal of toxic heavy metals from aqueous solutions were further investigated. Hydroxyapatite was synthesized in the Radiation and Environmental Protection Laboratory, and properties of the solid phase were determined by chemical analysis, x-ray, BET and electron microscopy (SEM, EDS). The sorption capacity of synthetic HAP for cadmium was determined for different conditions (pH, temperature, ionic strength, zeta potential etc.). Optimal sorption conditions were established for the investigated type of apatite [22]. On synthetic HAP were also performed preliminary sorption experiments for lead removal.

Investigation of cohesive energy was initiated in 1996 in the Radiation and Environmental Protection Laboratory (INS Vinča), represented by the ion-ion interaction potential, as a stability factor of solid matrix-impurity systems. Based on the results of this research a theoretical criterion for prediction of the stability of the solid matrix – impurity system has been determined [pat. appl. P267/97]. This criterion was incorporated into specific software VINMATRIX that was developed for calculating the stability of complex polycomponent solid systems [23].

In order to fulfill the need to find an inexpensive, highly reactive phosphate material that is available in large quantities for the purpose of DU remediation and stabilization in soils, water and waste forms, we investigated properties of natural apatite (NA) from Lisina near Bosilegrad. In fact, there are over 300 apatite minerals alone with different compositions, different properties and different reactivities [24]. Only a few are applicable for metal immobilization and treatment [9, 18, 25]. For this reason, in near future, our investigation will

involve study of sorption properties of NA and stability of the NA/DU system.

Determination of stability of the NA/DU system

As a parameter representing the stability of the solid matrix – impurity (NA/DU) system we will use the ion–ion interaction potential $V(r_0)$, representing the main term of the cohesive energy of the solid matrix – impurity system. This basic physical parameter defines: (i) the capacity of the solid matrix for the incorporation of the impurity and (ii) the stability of the solid matrix – impurity system. For practical calculation of $V(r_0)$ for NA/DU system, the software VINMATRIX developed at the VINČA Institute of Nuclear Sciences will be used.

Sorption properties of NA

As a model system for investigation of the sorption properties of NA and HAP lead will be used. We will experimentally investigate (i) sorption kinetics at different conditions (concentrations, pH, temperature) and (ii) sorption capacity of NA for removal of lead. Results obtained in these experiments will be used as input data for calculations of different properties of NA/lead system, which will be performed by MINTEQA2 software.

PROJECTS SUBMITTED BY THE VINČA INSTITUTE

Based on the presented results the Institute of Nuclear Sciences VINČA has been defined several project proposals which concern practical application of PIMS for remediation of regions in South Serbia and Kosovo contaminated with DU and other heavy metals. These project proposals are made in collaboration with: Aristotle University of Thessaloniki (Greece) and UFA Ventures (USA), and were submitted for funding to different international organizations.

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IZVOD

PRIMENA FOSFATNO-INDUKOVANE STABILIZACIJE URANIJUMA
U REMEDIJACIJI KONTAMINIRANOG ZEMLJIŠTA I VODA

(Stručni rad)

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Kao posledica proteklih ratnih dejstava, velike oblasti na Kosovu kao i neke lokacije u južnoj Srbiji su zagađene osiromašenim uranijumom (DU) i toksičnim teškim metalima. Neophodno je da se što pre izvrši remedijacija zagađenih lokacija kako bi se sprečile dugoročne posledice, ne samo po stanovništvo u zagađenim oblastima već i u okolnim zemljama. Pored neprekidne kontrole zagađenih lokacija, potrebno je da se započnu istraživanja koja bi omogućila izbor najefikasnijih i ekonomski najprihvatljivijih tehnologija za remedijaciju velikih prirodnih površina kao što su kontaminirano zemljište i voda.

Standardne tehnike kao što su: iskopavanje, ispiranje, helatno kompleksiranje, kondicioniranje i odlaganje kao nisko-radioaktivni otpad su potrebne za jako zagađene lokacije. Međutim, za velike kontaminirane površine sa nižim stepenom zagađenja pogodnija je *in situ* remedijacija, koja podrazumeva smanjenje pokretljivosti metalnog zagađivača tako što ga hemijski transformiše u stabilnu čvrstu fazu. Ovaj postupak u znatno manjoj meri narušava ekosistem i hidrologiju, umanjuje rizik za radnike, značajno smanjuje troškove cele operacije čišćenja, a za neke lokacije predstavlja i jedino moguće rešenje.

Fosfatno-indukovana stabilizacija metala je tehnologija koja se zasniva na tretiranju zagađenja odgovarajućim hemijskim agensom direktno na terenu ili formiranju propusne reaktivne barijere kada je u pitanju tretman podzemnih voda. Ovaj metod, kojim je moguće stabilizovati veliki broj metala, posebno je pogodan za uranijum (U), plutonijum (Pu) i olovo (Pb). Stabilizacija se vrši hemijskim vezivanjem metalnih zagađivača u nove stabilne fosfatne faze ili druge nisko-rastvorljive faze za koje se pouzdano zna da su stabilne u geološkim vremenskim periodima. Tako je metal ugrađen u apatit značajno stabilniji, trajniji i otporniji na izlučivanje nego metal u drugim hemijski – stabilnim formama.

Jedan od problema u realizaciji ove tehnologije predstavlja izbor odgovarajućeg apatita za tretiranje zagađenja pošto većina raspoloživih apatita nema pogodne karakteristike potrebne za praktičnu primenu. Apatit II (UFA Ventures) je jedan od apatita čija optimalna struktura i hemijske karakteristike omogućavaju veoma efikasnu stabilizaciju zagađivača. Ova tehnologija je uspešno primenjena na lokacijama u okolini rudnika i na drugim DOE lokacijama (USA) za tretman zemljišta i podzemnih voda kontaminiranih U, Pb, Pu, Cd, Zn i Cu. Za remedijaciju DU kontaminiranih lokacija u našoj zemlji predložena je eksperimentalna preliminarne studija u kojoj bi se ispitala efikasnost Apatita II i određenog prirodnog apatita iz Jugoslavije, koji je pokazao dobre osobine za uklanjanje olova. U zavisnosti od karakteristika i specifičnih zahteva za pojedinu lokaciju apatit je moguće primeniti (i) u okviru propusne reaktivne barijere, (ii) direktno pomešan sa kontaminiranim zemljištem, (iii) dodat kao liner u okviru odlagališta ili (iv) kao dodatak cementu u cilju poboljšanja stabilnosti.

Ključne reči: Osiromašeni uranijum
• Fosfatno-indukovana stabilizacija metala • Remedijacija.
Key words: Depleted uranium • Phosphate-induced metal stabilization • Soil remediation.