

## REMEDIATION OF URANIUM CONTAMINATED WATER AND SOIL BY PIMS APPROACH

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### ABSTRACT

Contamination of soil by uranium (U) represents a permanent threat for food and water resources. For this reason, remediation is a very important measure for protection of the health of the population living in the vicinity of these contaminated sites. Phosphate-Induced Metal Stabilization (PIMS) represents one of the powerful methods for remediation of soil and water contaminated by U, including depleted uranium (DU). By this approach it is possible to stabilize metals in the form of phosphate phases and other low-soluble phases that are stable over geological time. PIMS is based on application of a special form of apatite of biological origin, Apatite II, to clean up metal and radionuclide contamination, in situ or ex situ. This biogenic apatite can be emplaced as a down-gradient permeable reactive barrier, mixed into contaminated soil or waste or used as a disposal liner. Here we will briefly describe the PIMS remediation protocol.

**Key words: depleted uranium, phosphate-induced metal stabilization, remediation**

### 1. Introduction

Uranium (U) most likely occurs as a contaminant in the environment as a result of mining operations, matching of depleted uranium (DU) munition or natural weathering of igneous rocks and ore bodies. In Serbia, DU contamination was detected on several locations as a consequence of past war activities [1 - 5]. Two main types of DU contamination were identified: (i) localized, characterized by significant contamination of soil near unexploded DU penetrators, and (ii) low level widespread surface contamination by micro-particles of DU dust generated by exploded DU munition.

For decontamination of sites in Serbia, as a first phase of complete soil remediation, simple bulk removal of unexploded DU penetrators and heavily contaminated surrounding soil was performed. The radioactive material, after removal from the contaminated sites, was stored at the interim storage for low- and intermediate-level radioactive waste at the Vinca Institute of Nuclear Sciences. This interim storage is under supervision of the International Atomic Energy Agency (IAEA).

However, the amount of unexploded DU penetrators found on the surface are small compared to the total amount of DU ordnance that had struck these locations so that the majority of penetrators are still buried in the ground, representing a risk of groundwater and food chain contamination [6]. According

to field and experimental data the chemical and physical properties of DU make it more liable for dispersion in soil than is the case of naturally occurring uranium [1]. Also, at present, the problem is that 5 years after the air strikes, due to corrosion and weathering, it would be more difficult to detect and removed DU penetrators from contaminated sites.

Therefore, complete remediation of DU contaminated soil and groundwater should involve a combination of: (i) physical removal of radioactive materials from “hot spots” and its disposal in combination with sieving, gravity separation and washing of soil, and (ii) *in situ* - chemical stabilization of DU followed by covering of site with clean, uncontaminated, vegetated soil.

In this paper we will briefly describe an approach based on Phosphate-Induced Metal Stabilization (PIMS) for in situ remediation of DU contaminated sites.

## 2. In situ remediation

In situ metal stabilization involves addition to the soil of additives (a reactive media) that have specific chemical reactivity towards one or more chemical constituents, via mechanisms such as:

- adsorption
- ion exchange
- oxidation-reduction
- precipitation

Many additives have been proposed for *in situ* metal stabilization: calcium phosphate materials, iron filings, zeolites, clay, or organics of different types. These materials can have varying ranges of specificity, e.g. adsorption of specific cationic species by a modified zeolite, precipitation of metals and radionuclides by apatite [7 – 9], or overall reduction of the system by zero valent iron, other iron phases, or microbial activity [10].

## 3. Apatite as reactive media

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. Investigation of physico-chemical, structural and sorption properties of apatite represents a part of the research program of our Laboratory for several years. We investigated phosphate precipitation as a method for removal of radionuclides by formation of insoluble phosphates [11], sorption properties of synthetic hydroxyapatite (HAP) for the removal of toxic heavy metals from aqueous solutions [12] and stability of the metal-phosphate phases [13]. All this research is the basis for selecting the most appropriate approach for chemical stabilization of metals in the environment.

## 4. Phosphate - Induced Metal Stabilization

Remediation technology based on apatite amendment is Phosphate-Induced Metal Stabilization. PIMS is a technology developed to treat the contamination in place, either by mixing the amendment directly into the soil or by emplacing the amendments within a permeable reactive barrier (PRB) passively treating groundwater [14]. Metal sequestered in apatite minerals has great durability and leach resistance significantly exceeding other chemically stabilized forms [15 – 16].

There are several natural forms of apatite, but most of them do not have the characteristics suitable for metal stabilization under field conditions. 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. Apatite II is a natural phosphate material of biological origin that incorporates metals into new stable phosphate phases that are non-leachable [14].

The ultimate driving force for the robust performance of Apatite II with respect to metals is the extreme stability of new metal-phosphate phases. 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 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.

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).

## 5. Uranium remediation at Oak Ridge and Los Alamos

As a proof-of-concept various reactive materials were tested for the removal of dissolved uranium (U) from DOE Y-12 facility NT-1 groundwater at Oak Ridge, Tennessee [16], including Apatite II, 3 different types of bone char, mixed valent oxide iron filings, granular activated charcoal (GAC), phosphate rock, Nucon Nusorb, and Mersorb-3. The difficulty at this site is that groundwater can have high totally 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 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.

Apatite II was also tested as a part of a Containerized Vat Leaching process for soil remediation at a depleted-uranium firing range at Los Alamos [17]. Ca-autunite was identified as newly-precipitated U-bearing phases on the surface of Apatite II after treatment, from HR-TEM images.

## 6. Field application

The use of apatite or other reactive media for remediation of metals and radionuclides is presently being considered for a multitude of field applications. A reactive media can be:

- mixed in with soils or waste as amendment
- emplaced as a liner or barrier surrounding the contaminated site, disposal site or waste form
- emplaced as a Permeable Reactive Barrier (PRB) in a trench or excavation to treat shallow groundwater or surface seeps
- mixed into waste
- placed into a tank or any container so that contaminated water can flow-through it

Soil mixing is easy and can be carried out immediately, using existing construction equipment and can be performed on location. Also, it requires a small amount of reactive media and is economical.

## 7. Conclusions

Presented data point out that the protocol representing a combination of excavation and PIMS technology is suitable for application in remediation of DU contaminated sites in south Serbia.

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## References

- [1] UNEP, "Depleted Uranium in Serbia and Montenegro, Post-Conflict Environmental Assessment", United Nations Environment Programme, Geneva, Switzerland, 2002.
- [2] S. Pavlovic, R. Pavlovic, S. Markovic, I. Plecas, XX Symp. Yugoslav Soc. Radiation Protection, Tara, Yugoslavia, November 3-5, 1999, p. 45.
- [3] M. Radenkovic, D. Djordjevic, J. Joksic, S. Djogo, P. Pfindt, J. Raicevic, 5-th Regional Conference on Environment and Food Quality, Novi Sad, Serbia and Montenegro, September 4-5, 2003, p. 47.
- [4] S. Djogo, M. Radenkovic, D. Djordjevic, J. Joksic, J. Raicevic, Sixth Intl. Symp. Exhibition on Environmental Contamination in Central and Eastern Europe, Prague, Czech Republic, September 1-4, 2003, p. 205.
- [5] M. Radenkovic, J. Joksic, D. Todorovic, M. Kovacevic, J. Raicevic, First Intl. Meeting (APHY2003), Badajoz, Spain, October 14-18, 2003, p. 153.
- [6] UNEP, "Depleted Uranium in Bosnia and Herzegovina, Post-Conflict Environmental Assessment", United Nations Environment Programme, Geneva, Switzerland, 2003.
- [7] J. L. Conca, E. Strietelmeier, N. Lu, S. D. Ware, T. P. Taylor, J. Kaszuba, J. V. Wright, Chapter 8, in "Groundwater Remediation of Metals, Radionuclides, and Nutrients, with Permeable Reactive Barriers", Elsevier Sciences, USA, 2002, p. 221.
- [8] C. C. Fuller, J. R. Bargar, J. A. Davis, M. J. Piana, Environ. Sci. Technol., **36** (2002) 158.
- [9] A. Krestou, A. Xenidis, D. Panias, Mineral Engineering, **17** (2004) 373.
- [10] R. W. Puls, D. W. Blowes, R. W. Gillham, J. Hazard. Mater., **68** (1999) 109.
- [11] S. Raicevic, Z. Vukovic, T. L. Lizunova, V. F. Komarov, J. Radioanal. Nucl. Chem., **204** (1996) 363.
- [12] I. D. Smiciklas, S. K. Milonjic, P. Pfindt, S. Raicevic, Sep. Purif. Technol., **18** (2000) 185.
- [13] S. Raicevic, J. V. Wright, J. Vujic, J. L. Conca, in *Scientific Basis for Nuclear Waste Management XXVIII*, edited by Hanchar J., (Mater. Res. Soc. Proc. **824**, San Francisco, CA, USA, 2004) p. CC8.34.1.
- [14] J. L. Conca, "Phosphate-Induced Metal Stabilization (PIMS)", Final Report to the U. S. Environmental Protection Agency #68D60023, Research Triangle Park, NC, 1997.
- [15] S. Raicevic, I. Plecas, M. Mandic, Proc. 4rd Intl. Yugoslav Nuclear Soc. Conf. (YUNSC-2002), Belgrade, Serbia&Montenegro, September 30 - October 4, 2002, p. 263.
- [16] W. D. Bostick, R. J. Stevenson, R. J. Jarabek, J. L. Conca, Advances in Environmental Research, **3** (2000) 488.
- [17] N. Lu, H. Xu, J. Wright and J.L. Conca, in *Applied Mineralogy in Research, Economy, Technology, Ecology and Culture*, edited by Rammlmair, J. Mederer, Th. Oberthür, R.B. Heimann and H. Pentinghaus (A.A.Balkema Publishers, Rotterdam, Vol. 2, 2001) pp. 603.