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NEW URANIUM REMEDIATION APPROACH BASED ON MINERAL ROW MATERIALS AND PHYTOACUMULATORS

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ABSTRACT: Environmental uranium contamination based on human activity is a serious problem worldwide. Widespread use of nuclear energy, application of weapons with depleted uranium, nuclear testing, coal combustion, oil and gas production, production and application of phosphoric fertilizer, mineral processing and formation radioactive waste landfill, improper waste storage practices and uranium tailings are the main anthropogenic sources of uranium entering the environment. State of the environment and the concept of sustainable development require the development of new technological solutions that would reduce impact of human activities on the environment. The subject of this paper is a development new concept hybrid, combined, remediation technology for cleanup uranium contaminated soils which includes: i) proper selection of hyperaccumulating plants, with the ability to accumulate an exceptionally high uranium content in the shoots, ii) application of amendments: synthetic and nature organic agents with aim of improving the mobilization of uranium and increasing the efficiency of phytoextraction and iii) application reactive materials (adsorbents) based on aluminosilicate minerals for immobilization and transformation of excess uranium, that plant didn't accept. Subject of this research was determination the effectiveness of mobilization of uranium, with natural and modified zeolite, apatite, diatomite and bentonite, individually and in mixtures. The use of adsorbents with faster and stable action, together with the materials with slower acting, provide synergistic effect of reactive materials mixtures for in situ stabilization of uranium ions. Such a treatment would provide a prevention of inclusion of uranium in the food chain and protection of the population from ionizing radiation.
KEYWORDS: uranium remediation, mineral row materials, phytormediation

INTRODUCTION

Widespread use of nuclear energy, application of weapons with depleted uranium, nuclear testing, coal combustion, oil and gas production, production and application of phosphoric fertilizer, mineral processing and formation radioactive waste landfill, improper waste storage practices and uranium tailings are the main anthropogenic sources of uranium entering the environment. All these human activities resulted in soil contamination with uranium, ie. "Technologically-Enhanced Naturally Occurring Radioactive Material." – TENORM.

Important sources of uranium in serbian area are certain technological processes of production, such as production and combustion of coal in vicinity of power plants, the production of phosphoric acid, phosphate fertilizers, phosphogypsum and other.

So,near the thermal power plant "Kolubara" and "Nikola Tesla", strength of the equivalent dose is in the range from 1.42 to 4.87 nSv / h. These values are 3 to 4% above the natural level of radiation, but are 3-4 times more than the highest level of nuclear power in normal operation and in the immediate vicinity [1].

Production and use of phosphate fertilizers is another important source of uranium in our environment.

The concentration of uranium in phosphate ore is 12 to 180 Bq/kg. In Serbia are imported annually about 1,000,000 tons of phosphorite for production of mineral fertilizers. The average concentration of uranium in phosphorite imported was 150 Bq / kg. This mean that annually imported about 150 tons of uranium or 50 TBq of radioactivity, which ere applied to Serbian agricultural solis [2].

Waste rock dumps and uranium mines only in southeast of Serbia in Gabrovnica- Kalna, who stopped mining ore and uranium flotation process forty years ago, is one of the sources of uranium mines in the surrounding area. Barren soil contained uranium in range from 15,33 mg/kg to 17 mg/kg, which today cover an area of about 0.1 km2. (Stojanović and Milojković, 2011) [1].

These data indicate that the sources of uranium in Serbia result of natural geological and geochemical origin of sediments, rocks and soils (NORM) and present "background of natural ionizing level".

Technological processes in power plants and production of phosphate fertilizers and their use has contributed to the increased the concentration of uranium in certain areas and present the main form of TENORM. According to some estimates the "natural level of ionizing radiation", in Serbia, has increased about 30 times in the last 40 years [2].

Finally, during the NATO aggressions in Yugoslavia were bombing 112 sites in Kosovo and Metohija and 12 locations in southern Serbia with depleted uranium (DU) ammunition. On this occasion around 10 tonnes of DU was introduced into environment.

The degree of contamination ranges from the bottom limit of 200 Bq/kg to 235,000 Bq/kg in sample of soil, mainly agricultural land, or 1 000 times above the naturals level. In wars of the past 20 year (1991 Gulf War, the Bosnia and Serbia war, the 2003 invasion of Iraq) approximately 1.4 million DU missiles were used. During Gulf War I (1990–1991), approximately 320 tonnes (equivalent to over 1 million 30-mm rounds) of DU munitions were used by the US forces, and approximately 1 ton of DU was fired from UK tanks.

During the Bosnia–Herzegovina conflict (1994–1995), approximately 3 tonnes of DU was fired in NATO airstrikes, and about 10 tonnes of DU was fired during the 1999 Kosovo conflict. During the 2003 Iraq War, approximately 2 tonnes of DU was fired by the UK MOD, the amount of DU fired by USA forces has not yet been disclosed, but speculative figures range between 170 and 1700 tonnes [3,4].

Today, unfortunately, in Serbia encounter with "invisible threat" use of depleted uranium ammunition, with highly radioactive and chemotoxic effect on human health.

Hybrid, combined, remediation technology for cleanup uranium contaminated media, with synergistic effects are increasingly being used for environmental and economic efficiency. Integrated management of soils contaminated with uranium, based on results obtained in Institute for nuclear and other mineral raw materials in Belgrade. Conceptual approach is a synergy of physical, chemical and biological remediation processes and techniques. In situ treatment includes a combination phytoextraction and phytostabilisation with uranium hyperaccumulator plants with application of uranium immobilization materials, based on Serbian (domestic) aluminosilicate minerals. Such a treatment would provide a prevention of inclusion of uranium in the food chain and protection of the population from ionizing radiation.

The objective of any remedial action is to reduce the risks to human health and the environment to acceptable levels by removing or reducing the source of contamination or by preventing exposure to it. Various strategies have been proposed for the remediation of contaminated environments in order to reduce the detrimental chemical and biological technologies. Environmental uranium contamination based on human activity is a serious problem worldwide [5].

Uranium is one of the radionuclide whose mobility in soils strongly varies depending on soil type and physico-chemical properties. Distribution of uranium in the lithosphere and hydrosphere is performed in conditions of complex chemical and physical-chemical natural processes, including mechanisms of degradation of minerals that contain uranium. Solubility of uranium in the soil primarily depends on the environmental pH, redox potential, soil structure and mineral composition of the solid phase, concentration of inorganic compounds, the quantity and type of organic compounds in soil and soil solution, soil temperature, pressure, moisture content and microbial activities [6,7,8]. Sorption of U(VI) onto soil particles is higher at lower pH values in soils and decreases strongly with increasing pH. The reduction of U(VI) to U(IV) by abiotic and biotic processes, as well as its re-oxidation has received considerable attention because the oxidation state of uranium has a significant effect on its mobility in the natural environment [9].

The cycle of mobilization of uranium in nature begins with U(IV) oxidation but the process of contamination of uranium in nature stops, when U(VI) is reduced or immobilized. However, with changing conditions in nature, U(IV) uranium can oxidize to U(VI), and so the cycle will start again.

Immobilization of uranium as precipitation from solution is the only way for nature to protect from the spread of uranium and its radioactive products. Fixation of uranium can be described by two main mechanisms:

- *precipitation (oxido-reduction), and*
- *adsorption.*

Precipitation process may begin in the form of uranium, uraninite, autunite, and uranium phosphite [$U(PO_3)_4$] low solubility, to $Kp=10^{-49}$ as a basis of their stability in the long geological period under very different conditions, important from the point of view of environmental protection and production of healthy and safe food [2].

METHODS AND TECHNIQUES FOR URANIUM REMOVAL

Remediation technologies for treatment of uranium contaminated soils and groundwater could be applied as either ex situ or in situ techniques. According to Gavrilescu et al, [7] can be classified methods and techniques for uranium removal as: Natural attenuation, Physical processes, Chemical methods, Biological methods and Electrokinetic methods. These techniques can be applied individually or in combination (hybridization) and they are presented on Figure 2.

Each one of the above fundamental technical choices will direct decision makers to substantially different paths with regard to their subsequent choices, actions and potential results, making available significantly different technological options for application, within a remediation program, which involves multidisciplinary environmental research on characterization, monitoring, modeling and technologies for remediation.

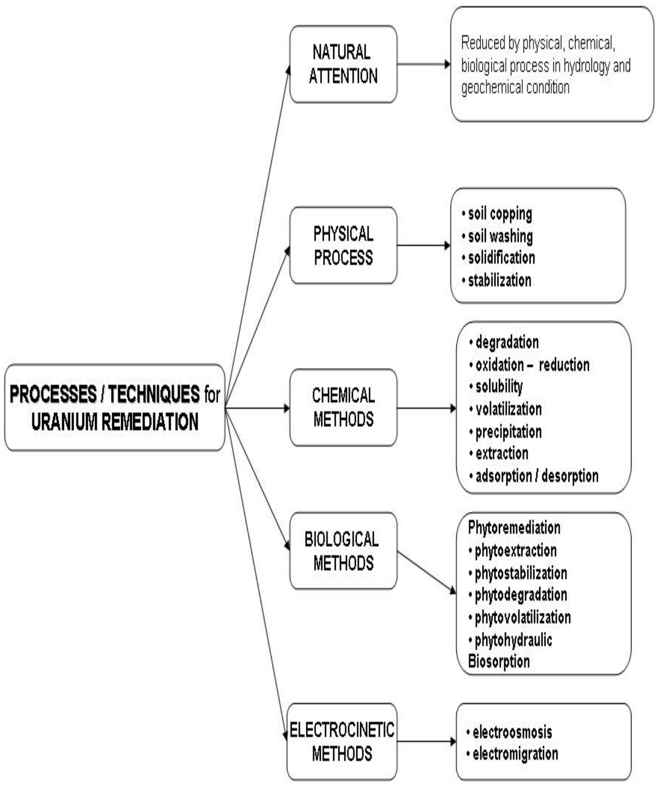

Figure 2. Processes and techniques for uranium removal

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Biological method

In situ remediation techniques are more suitable for radioactive contamination due to reduced exposure of workers during the construction or transportation. Among the remediation techniques currently used, soil excavation is the most common treatment for radioactively contaminated soils as well as encapsulation size separation, soil washing, electrokinetics and ion exchange [6].

However, these in situ techniques are expensive compare to phytoremediation techniques.

Phytoremediationinvolves the use of plants to extract, sequester and/or detoxify the pollutants present in soil, water and air. This technique may be particularly useful for remediation of a wide variety of contaminated surfaces (usually 15-30 cm deep), including soil, water or wetland systems.

Plant-assisted remediation of soil can generally occur through one or more of the following mechanisms:

phytostabilization, phytodegradation / phytotransformation, phytovolatilization, rhisodegradation, phytohydraulics, phytoextraction.

Phytoremediation offers advetntages such as: cheap and simple option, better metal recycling, better public acceptance and less destruction to remediation sites. Phytoextraction efficiency is determined by the metal availability, which is influenced by pH, redox potential and metal complexation.

The major disadvantage of the technique is the time of requirement - from 18 to 60 months or even decades Phytoextraction, a type of phytoremediation, use of metal-accumulating plants (hyperaccumulators) that can transport metals from the soil to the roots and and concentrate them in above-ground plant tissue - shoots [9, 10,11]. Hyperaccumulators plants are those plants that adopt the pollutants from the soil at a much higher rate than other plants (100 to 1000 times). According to the PHYTOREM data base sunflower is recognized as hyperaccumulator of uranium. PHYTOREM was developed by Environment of Canada and this database consist of 775 plants with capabilities to accumulate or hyperaccumulate one or several of 19 key metallic elements. Species were considered as hyperaccumulators if they took up greater than 1000 mg/kg dry weight of most metals. Plants hyperaccumulators like sunflower had content of uranium more than 15000 mg kg^{-1} dry weight [12].

There are two general approaches to phytoextraction:

- *continuous, and*
- *chemically enhanced phytoextraction.*

The first approach uses naturally hyperaccumulating plants with the ability to accumulate an exceptionally high metal content in the shoots. Another method is the application of synthetic and nature organic agents in order to improve the mobilization of uranium and increase efficiency of phytoextraction. A key to the success of U phytoextraction is to increase soil U availability to plants [13].

In literature there have been numerous reports about amendments in phytoremediation compaunds that increase the uptake of uranium by varius plants. Addition of chelates increases the mobility of metals in the soil and form complexes with metals reducing the positive charges and thus affects the availability of metal to plants. Amendments could be organic compounds: synthetic chelating agents (ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl-ethylenediamine-N,N',N'-triacetic acid (HEDTA), diethylenetrinitrilopentacetic acid (DTPA)), natural fulvic acid, humic acid and more natural low molecular weight organic acids (citric, malic, oxalic, and acetic acid). The most frequently used is EDTA, which has been reported as more effective than other synthetic chelators for several heavy metals [13].

Phisical and chemical method

During the selection of remediation technologies one of the key factors is the optimal choice of immobilization materials, based on efficiency and the price. Therefore, there is a need for application of alumosilicate minerals as sequestering agents (apatite, zeolite, clay, diatomite,bentonite,etc.), that will enable hydrological control and in situ, long term, immobilization (solidification/stabilisation) of uranium.

Mechanisms of action these materials are different and depend on their type and characteristics as well as and chemical and physical-chemical properties of contaminated soils. The most common mechanisms are adsorption, exchange, oxidation-reduction, or precipitation.

Addition of chelating agents in order to enhance phytoextraction may promote leaching of the pollutants (uranium) into groundwater. Therefore, there is a need for application of properly selected sequestering agents that will enable hydrological control and immobilization (solidification/ stabilisation) and transformation of excess uranium, which plant didn't accept. Furthermore, sequestering agents can be used as ground cover in perennial phytoremediation, for adsorption of uranium, which can leach from fallen leaves in autumn (Figure 2).

Stojanović et al., [2,14], conclude that setting time for uranium ions follows the rule:

organomodif. zeolites (modified with quaternary ammonium ions)> phosphate concentrate (34.95 P_2O_5%) > organomodif. bentonite > diatomite > mechanochemically activated apatite > natural bentonite > natural zeolite > natural phosphate (14.43% P_2O_5).

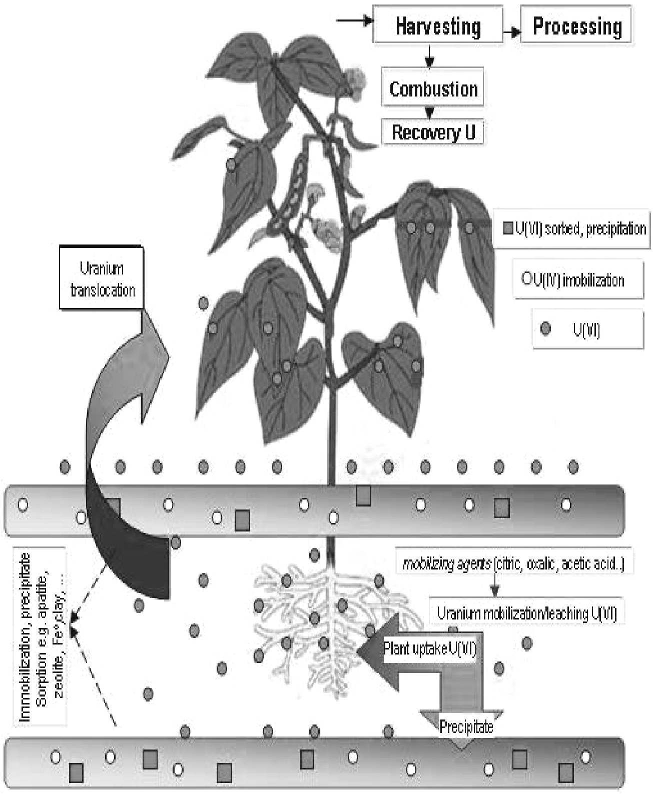

Figure 2. Hybrid technology for remediation of uranium polluted soils

Application of fast - acting sequestering agents (diatomite, organomodif. zeolite and bentonite) with slow - acting adsorbent (natural phosphate), achieves a synergistic effect of mixtures of reactive materials like a permanent solution for the "in situ" stabilization of uranium ions in the remediation of soil contaminated by uranium.

Mixture of apatite and organomodified zeolite confirmed the synergism of action of these materials which is reflected in the rapid binding of uranium with organomodified zeolite and the formation of stable phase uranium-phosphate-autunite. Application of this mixture eliminates the risk of desorption of organomodified zeolite due to changes in soil conditions. For the remediation of large areas of contaminated soil with a lower level of radionuclides application of natural apatite is justified. If the economic effect is not important, natural apatite reactivity can be increased mechanochemically with vibratory mill or applying the concentrate with high content of P_2O_5 - 34.95% [15].

Modified zeolite with NH_4^+ ions, increases the solubility of phosphate rock (PR) through the exchange of cations Ca^{2+}, can be described by the following equation(1):

$$PR + NH_4^+\text{- zeolite} \leftrightarrows Ca^{2+}\text{- zeolite} + NH_4^+ + PO_4^{3-} \quad (1)$$

To extend the possibility of their use on different soil types, it is necessary to design a functional material which should contribute to greater phospho immobilization in wide range of soil pH [16].

Preliminary results showed that the addition of modified zeolite (with 2M ammonium sulphate solution) increase PR dissolution due to removal of Ca^{2+} by zeolite through cation exchange. In time period of 24 h it increased the PR phosphate rock dissolution from 0.406 mg P/dm^3 to 3.621 mg P/dm^3 which was confirmed by an increase in pH value and decrease in concentration of Ca^{2+} ions. Such hybrid materials can be applied for stabilization of uranium contaminated soils and as natural phosphate fertilizers.

CONCLUSIONS

Remediation of soil contaminated with uranium requires a holistic approach including the use of secure "environmental friendly" materials that are cheap, easily applicable and available locally. The results confirm the applicability of the studied natural and modified aluminosilicate materials (zeolite, apatite, bentonite and diatomite) individually and in mixture.

The use of adsorbents with faster and stable action, together with the materials with slower acting, provide synergistic effect of reactive materials mixtures for in situ stabilization of uranium ions. Hybrid technology represents a permanent solution and means integrated management strategy for contaminated site which includes:

- *proper selection of plants (hyperaccumulators uranium),*
- *improving mobility of uranium with amendments (organic agents), and*
- *application sequestering agents for immobilization and transformation of excess uranium, which plant didn't accept.*

These technologies combine: chemical, physical, and/or other biological processes.

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