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URANIUM SOILS DECONTAMINATION BY WASHING METHOD

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A remediation method is presented in order to limit the pollution degree due to mining activities of soils with radioactive uranium. The washing method of polluted soils was investigated. For remediation of radioactive soils the following systems were used: a) water, b) 0.1 M sulfuric acid, and c) sodium chloride solution (100 g / L sodium chloride + 10 g / L sodium carbonate). The washing conditions in a system with mechanical agitation were: mass ratio solid/liquid 1:2, contact time 2 hours, temperature 20° ± 2°C. Experimental investigations were performed on four types of soils, which have been characterized in terms of particle size distribution, texture and chemical composition. It was established the remediation degree for each type of soil and reagent.

Keywords: chemical remediation, uranium, soils composition, particle size distribution

1. Introduction

The existent mining areas and processing uranium ores have already represented a risk factor for the environment - moreover in the case of natural disasters. The cessation of mining activities involving uranium ore extraction is a huge threat to soil and surface water caused by the increase of radioactive contaminated groundwater levels. In the mining area there are different amounts of minerals deposited (dumps) that can generate pollution trough the action of rainwater and environmental factors. Global concern for environmental protection and reintroduction of radioactive contaminated soils in rehabilitated land circuit is an important and perpetual task. Consequently, an environmental protection goal is to develop a process for uranium rescuing of the soils.

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Remediation of accidentally polluted soils with heavy metals is one of the biggest challenges for environmental protection [1]. The techniques which are most frequently used are expensive (a medium cost for these technologies is 600 \$/t) and, in recent years, there is an increased interest in finding new and innovative solutions for efficient removal of contaminants, in order to save groundwater and soil.

The existing methods for soil remediation may be divided in: *"in situ"* techniques, *"ex situ"* techniques (the confining/isolation of the contaminated area is a temporary solution). These methods can be further divided in biological and non-biological methods. The non-biological methods are subdivided in physical-chemical, thermal and others methods e.g. supercritical extraction and electro kinetics [2, 3].

Many conventional techniques for soil washing are based on the principle of adsorption of pollutants on soil fine particles such as mud, clay and humic material. These tend to adsorb sand and gravel particles on largely grain size particles [4].

The primary purpose of soil washing is to separate these fine components from the bulk mass of soil ground. If polluting materials can be detached from the majority of soil, a "concentrate" polluted soil is obtained. Any optimization of solvent penetration involves increasing the removal of soluble substances which are trapped inside solid particles. Several studies regarding removal of contaminants from polluted soils were elaborated [5,6].

A new method for soils remediation is based on extraction with citrate. Citrate is an extracting substance that does not alter the environment and is successfully used to decontaminate soils with lead, zinc, cadmium and copper [7].

The effect of soils microorganisms on the contaminants has been studied [8], and it was established that microorganisms catalyze redox processes which results in metal precipitation. For example, Fe^{2+} to Fe^{3+} oxidation leads to precipitation in $Fe(OH)_3$ solid form; the reduction of SO_4^{2-} ions in sulphides causes precipitation of Fe^{2+} or Hg^{2+} as sulphides; the reduction of uranium from its hexavalent state (U^{6+}), which is very soluble, to its tetravalent state (U^{4+}), insoluble and essentialy imobil, lead finally to a precipitate in the form of UO_2. Rate constants for the elementary processes involved (oxidation of UO_2 and dissolution of oxidized UO_2) are used to calculate the rates of oxidative UO_2 disoulution under various conditions, for which experimental data are available. The calculated rates are compared with the corresponding experimental values, with the assumption that the experimental data correspond to the steady-state system conditions [9].

Fungal leaching of heavy metals is an interesting biological treatment method of heavy metals (including uranium) from sediments dredged [10, 11]. It is based on the fungal production of weak organic acids that solubilise metals by forming water soluble complexes with them.

Several new remediation technologies have been developed in the last years for the decontamination of polluted sites and many of them have proved to be very promising to clean-up water and soils contaminated by a wide range of hazardous pollutants [12, 13]. In general, based on the process acting on the contaminant, remediation technologies are classified into four categories [13]: removal, separation, destruction, and containment. Removal, separation, and destruction are processes that reduce or remove the contaminant. Containment technologies, on the other hand, control the migration of a contaminant to sensitive receptors without reducing or removing the contaminant.

The technology presented in this article is based on *ex-situ* treatment, namely chemical remediation.

The aim of this paper consists in experimental investigation of soil washing method (chemical remediation) of uranium contaminated soils.

2. Experimental

Laboratory tests were performed on four soil types characterized in terms of particle size, texture and chemical composition. These characteristics of the four soil types are presented in the next paragraph. The soils have been previously artificially contaminated in the same conditions with uranium from mine water.

Soils particle size distributions were obtained by sieve analysis method, using Retsch Vibratory Sieve Shaker AS 200 with the following grain size: 0.056; 0.075; 0.1; 0.16; 0.2; 0.25; 0.5; 1; 2; 2.5 mm.

Measuring *soils texture* was made using a validated method (simplified Pipette method), thus obtaining the relative distribution of soil particles in three classes: sand (2.0 - 0.05 mm), silt (0.05 to 0.002 mm) and clay (<0.002 mm), (Panturu et al. 2008).

The method to establish the *soils composition* consists in the treatment of a soil sample dried at 105°C, with 150-200 ml water and 20 ml solution 5% sodium hexametaphosphate; the mixture has been homogenized for 2 hours. Then, the sample was sieved using a sieve of 0.053 mm, in order to collect sand fractions. The rest of the sample consisting of water, silt and clay was collected in a 600-800 ml glass beaker. After the settlement time has expired, the fraction containing clay settled and the silt particles within the sediment was dried at 105°C. Sand and silt fractions were directly calculated and expressed as the ratio between sand, respectively silt mass, and sample mass. Clay fraction was calculated as the difference between one and sand fraction and silt fraction.

Organic content of the soils is important, because uranium and a series of other pollutants have a certain affinity to bind the organic substances, either by adsorption to complex formation, or through redox processes. The main organic components are humic substances; their concentration was established by dry combustion method [14].

The soil samples were chemically characterized in terms of uranium content. Analytical methods for the determination of tetravalent uranium from samples containing uranium dioxide up to 2 g/L (liquid samples) or less than 0.5% (solid samples) were a spectrophotometric method (molecular absorption spectrometry) using a spectrophotometer type UV - VIS CECIL 1100. For solid samples, regardless of their content, gamma spectrometric method analysis with multichannel analyzer with pure Ge detector for γ radiation (0-3MeV)-ORTEC was used.

The four types of soils were treated during 24 hours with a synthetic solution which has the following chemical composition: 0,385 g U/L la pH=9 (this was the pH of the mine water), $CO^{2-}{}_3$= 10, 23 g/L; $HCO^{-}{}_3$= 3, 96 g/L; $SO^{2-}{}_4$= 7, 30 g/L; Cl^-= 0,450 g/L at pH=9.

Remediation was studied for each type of soil, using three reagents, namely: a) water; b) sulfuric acid H_2SO_4 0,1M solution; c) chloro - sodium solution consisting in: 100 g/L sodium chloride NaCl and 10 g/L sodium carbonate Na_2CO_3 in water. For remediation tests it was used a mechanical stirring system - pallets stirrer RW 16 IKA at the following conditions: the speed of 300 rot. /min.; the mass ratio solid: liquid of 1:2; the operating time 2 hours; the temperature 20^oC ($\pm 2^oC$).

3. Results and discussion

Particle size distribution of soils has a great importance to establish the applicability of the selected process. It has a direct effect on the ability of a soil washing system to separate contaminants from the bulk soil mass. Many soil contaminants tend to bind to the fine particle fraction of the soil (bind with the silt and the clay portion). These contaminants will be separated from the clean soil during the washing process, with the same extent as the fines are separated from the coarse sand and gravel fraction. If a tested soil has a relatively small percentage of silt and clay (<25%), the soil washing will be effective in contaminant reducing with a high probability. Therefore, the knowledge of the typical particle size distribution, which will be encountered throughout the contaminated soil area, can be particularly valuable as an early indicator of the potential effectiveness of soil washing in separating out the contaminants [15].

A suitable upper limit for soil washing corresponds to a proportion of 25-30% particles smaller than 20μm. A soil with a high content of large particles can be easily decontaminated.

Experimental results for particle size distribution analysis, as cumulative distributions are shown in Fig. 1 (where T is the percentage of passed solid against the vibratory sieve orifice size).

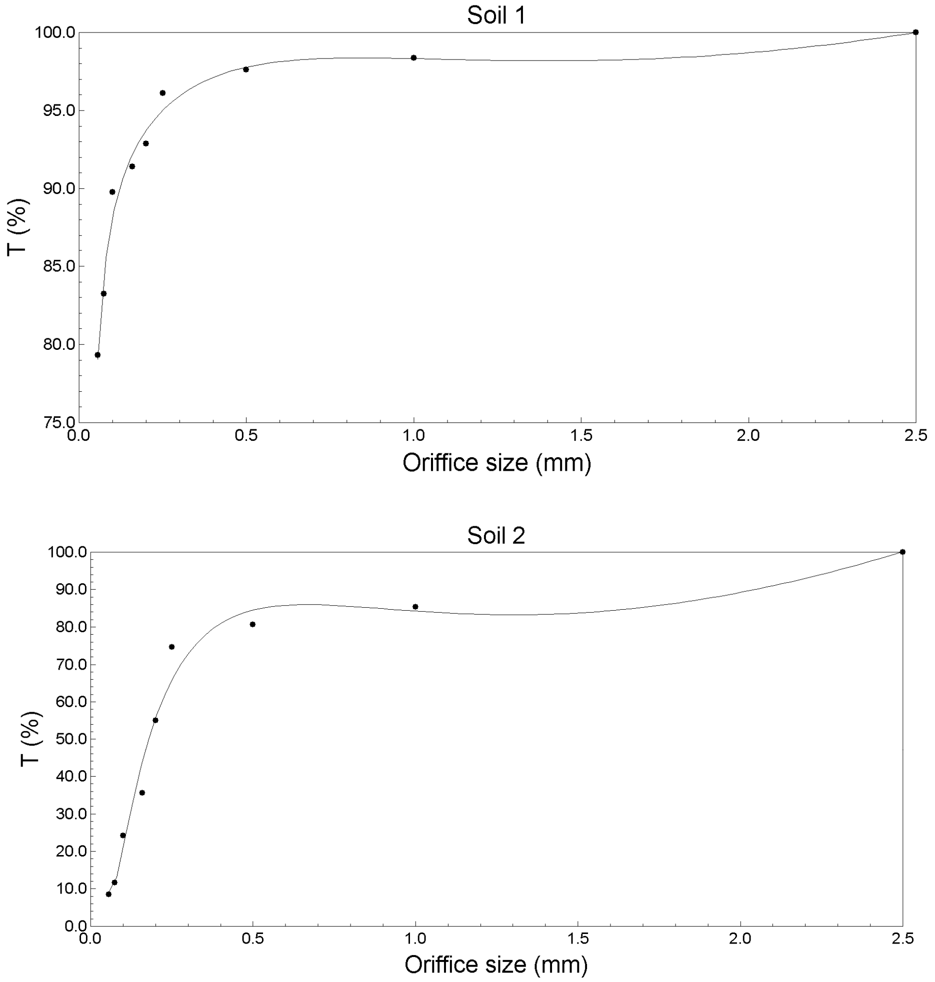

Fig. 1 (a).Particle size distribution analysis: cumulative distributions

Differential distributions are presented in Fig. 2 (where T is the percentage of passed solid and *l* is the vibratory sieve orifice size).

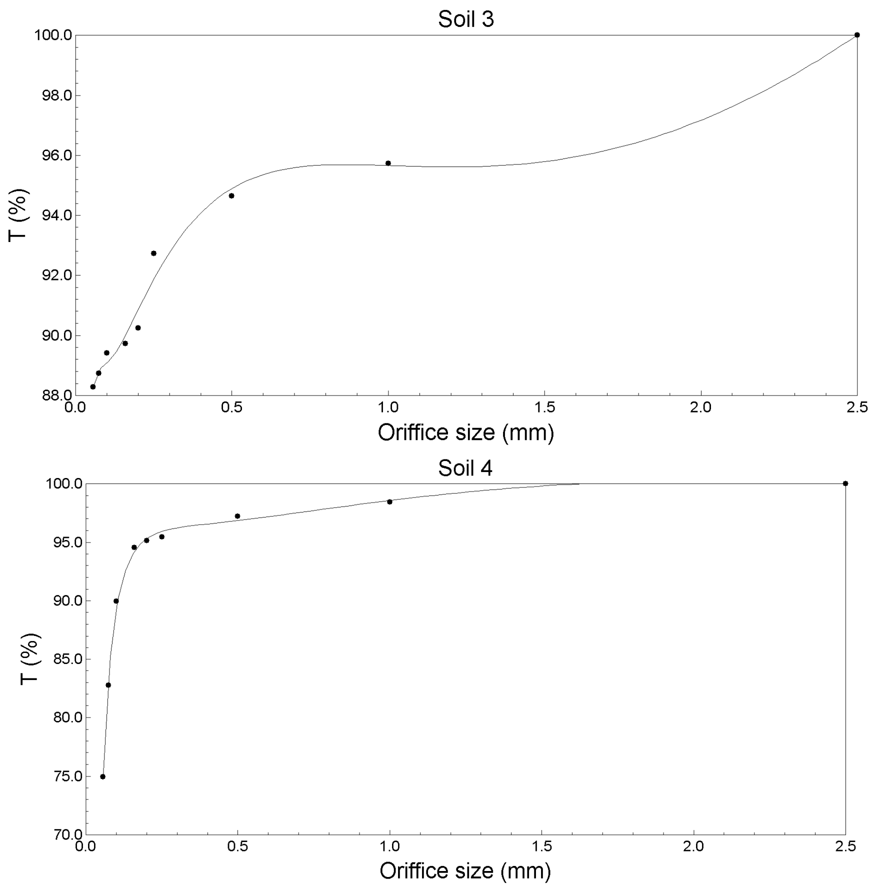

Fig. 1(b). Particle size distribution analysis: cumulative distributions

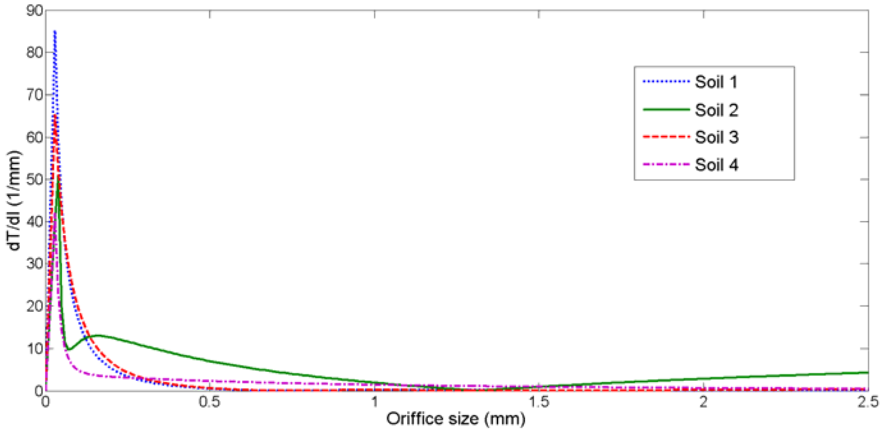

Fig. 2.Particle size distribution analysis: differential distributions (the percentage of the fraction between two consecutive sieves)

As seen, in the samples of soil 1, 3 and 4 dominate classes < 0.056 mm, and in sample of soil 2 dominate classes > 0.25 mm. These indicate that the sample of soil 2 will be decontaminated relatively easily, while the samples of soils 1, 3, and 4, with a large amount of fine fraction, will be decontaminated more difficult.

Experimental results on *the texture of the four soil types* are shown in Fig. 3.

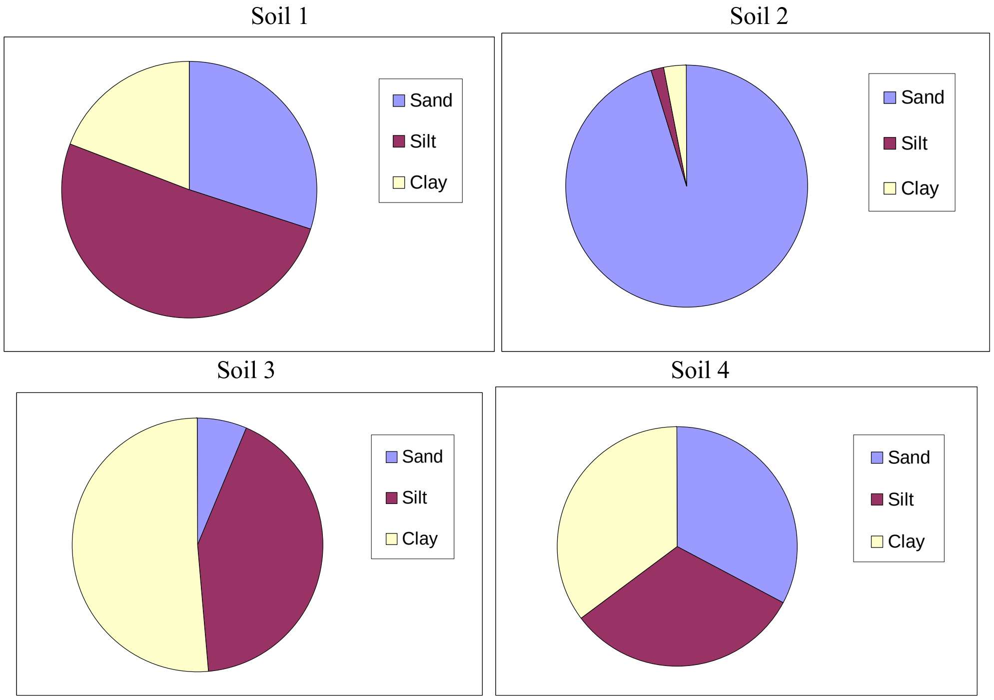

Fig. 3. Soils texture

It can be seen that the sample of soil 3 has the highest clay content, indicating a soil hard to be decontaminated. Soils 1 and 4 have the clay content at the upper limit (30%) - in the terms of the possibility of remediation by washing. Sample of soil 2 has low clay content, making it suitable for this remediation method.

The experimental results for *organic matter content* of soil samples, determined by dry combustion method are: for sample of soil 1: 0.03875, for sample of soil 2: 0.00293, for sample of soil 3: 0.05181, and for sample of soil 4: 0.02543, where concentrations are expressed in mass fractions.

Note that the sample of soil 3 has the highest content of organic matter, which is confirmed by the color of this soil sample.

The results concerning the initial *uranium content* are: for sample of soil 1: 3.98 ppm, for sample of soil 2: 2.15 ppm, for sample of soil 3: 5.74 ppm, and for sample of soil 4: 3.21 ppm.

Soil samples were placed in batch contact for 24 hours with the three reagents: water, sulfuric acid 0.1M solution and chloro-sodium solution. Remediation degrees of the four soils with these three agents, respectively the reducing of the uranium content in the soil, are presented in Fig. 4.

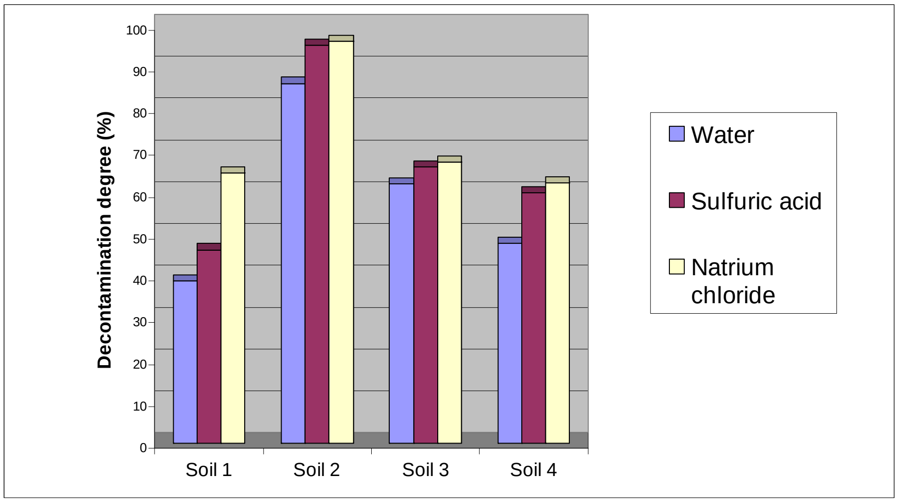

Fig. 4. Remediation degrees of the four types of soils with different three agents

As can be seen, the most efficient remediation agent for all types of soil was chloro-sodium solution. The degree of remediation is different, depending on soil type, namely the samples of soil 1, 3 and 4 present a low remediation degree (due to the large quantities of fine fraction of silt, clay and high organic matter content). Another explanation related to high remediation degree of chloro-sodium solution consists in fact that uranium was retained on soil samples through adsorption and complex formation processes.

Highest degree of remediation was achieved, as expected [16], for the sample of soil 2, which contains approximately 95.28% sand and 0.00293 organic matters. For this soil, all three remediation reagents are very effective.

4. Conclusions

Experimental investigations of uranium soils decontamination based on the washing method indicate that the respond to the action of extraction reagent is strongly dependent to the nature of the soil. The main factors in establishing of the performances of the remediation process are particle size distribution, texture and chemical composition of the soil, and organic matter content.

Remediation tests have revealed a degree of remediation of over 85% for all three remediation reagents used for sample of soil 2, characterized by large particles size and a very high sand concentration. The remediation levels of the samples of soils 1, 3, and 4, which are characterized by small particles size and high clay concentrations, does not reach a remediation degree of 70%, regardless of remediation reagent.

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