The Chemical Decontamination Process Intensification, using Ultrasounds

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This paper presents an intensive procedure used for the decontamination of the soils, which were radioactively contaminated by uranium, due to the occurrence of some antropic accidents, in order to limit the area’s pollution. The procedure used for the chemical decontamination of the polluted soils was the washing one and the decontamination degree is comparatively presented depending on the ultrasounds’ presence and absence. The lab tests were performed on five types of soils, which were characterized from the granulometric, structural and chemical composition viewpoint, all these aspects represent the main factors, which determine the applied decontamination procedure’s limits and performances correlated with its utilization costs. The decontamination procedure’s kinetics for each type of soils was analyzed, using successively three different types of reagents (water, 0.1 M sulphuric acid solution and chloro-sodic solution – 100 g/L sodium chloride + 10 g/L sodium carbonate in water) for a solid to liquid ratio of 1:2, during 2 h, at a temperature of 20°C in a mechanic stirring system respectively in ultrasounds field. It was observed that the decontamination degree increases with up to 15-20% in case of the ultrasound field utilization comparing to the first case.

Keywords: soil, decontamination, radionuclide, ultrasounds

The existence of the areas, where uranium ores are exploited and processed, represents already a risk factor for the environment and it becomes much more dangerous in case when natural catastrophes or some antropic accidents occurred. The uranium mining activities closure involves the vertical accession of the underground waters highly contaminated by the radioactive metals, which indeed represent a significant threat concerning the soils and surface waters pollution as well. It also must be mentioned that nearby the mining area different amounts of ore, which can generate pollution due to the pluvial waters and other environmental factors’ action, are stored.

The global public concern for the environment protection beside the necessity to reintroduce the soils, which were affected by the radioactive contamination caused by some natural catastrophes or antropic accidents, into the rehabilitated lands’ circuit determined the initiation of the present project, which aims to elaborate an intensive procedure in order to decontaminate them.

The decontamination of soils polluted by heavy metals represents one of the most important challenges for the environment technologies [1]. Most of the techniques currently used are expensive, therefore during the last years the public interest for getting some new and innovative solutions in order to make much more effective the contaminants’ removal aiming to save soils and table waters, increased.

Ultrasounds cause some mechanic, sonochemical and biological effects on soils. Intensification of the procedures, which are used to remove the contaminants from soils, by applying ultrasounds, is a new technology. Studies concerning the ultrasounds' application on earth science are very few and only in a conceptual stage [2].

The conventional chemical reactions are accelerated under ultrasounds action or even oriented towards getting some products completely different [3].

Many conventional techniques used to wash soil [4] grounds on the principle concerning the pollutants’ adsorption on soil very fine particles such as mud, clay and humic matter, which on their turn tend to be adsorbed by the raw sand and the coarse gravel. The main part of soil consists of coarse particles.

Soil washing primary aim is to displace and to separate the fine components out of its main body. If the pollutant materials could be detached from the main soil-body then a polluted soil “concentrate” volume would be obtained. The method that gave good results is the intensification with ultrasounds [5-6] of the contaminants extraction procedure. Under ultrasounds action the normal extraction of contaminants takes place and a number of factors contribute to its efficiency increasing. They are as follows:

- the asymmetrical collapse of the cavitation bubble nearby the solid surface causes a speed up microjet generation targeted toward the solid surface; the microjet can improve the transport velocity and to increase surface area by surface division;
- particles fragmentation caused by collision will increase the surface area;
- cavitation collapse will generate shock waves, which produce the particle break and the extraction agent can penetrate inside the particle through capillarity;
- the acoustic generation determines the diffusion layer perturbation on the surface;
- diffusion through the pores toward the reactive area will be intensified by the ultrasonic capillary effect.

Washing studies were performed on the soils polluted by substances, heavy metals (copper-Cu) or organic pollutants [7]. The possibility to use ultrasounds' power as a method for the processing techniques aiming to remediate the soils contaminated by heavy metals ball-shape, broken parts or alteration products was investigated. The ultrasounds power was used for soil
dispersion and for metals and metallic compounds removal from the particles surface instead of attrition technique. The soil diluted with water was treated using ultrasounds having a frequency of 22 kHz and a power of 100 up to 500 W. The ultrasounds increased the efficiency of soil remediation processes with 30% [8].

A new method for the extraction of heavy metals from the contaminated soils grounds on the extraction using sodium citrate under ultrasound's action [9]. Citrate is an extracting reagent, which does not affect the environment and it is used to remove the Pb, Zn, Cd and Cu out of soils contaminated by heavy metals. Ultrasound application intensifies the extraction of these metals after an exposure of 30 min in an ultrasound field of 19.5 KHz equivalent with a 24 h washing operation under normal conditions.

The technology for the decontamination of the soil contaminated by radionuclides, which will be described in the present paper, grounds on technologies applied ex-situ through the chemical treatment and the decontamination process intensification using the ultrasounds action.

The aim of the researches presented here was to determine the way in which the ultrasounds contribute to the improvement of the procedure used to the decontamination of soils radioactively polluted with uranium due to some antropic accidents or natural catastrophes occurrence, in order to limit the areas contamination. In order to remediate the polluted soils the chemical decontamination procedure through washing was applied and the decontamination degree is comparatively presented in the ultrasounds presence and absence.

Experimental part

Lab tests were performed on five types of soils characterized from granulometric, structural and chemical composition viewpoint, which represent the main factors that determine the applied decontamination process limits and performances correlated with the application costs.

The five types of soils were contaminated by 465 mg U/kg soil assuming that they were accidentally contaminated by the uranium-bearing solution resulted from the uranium ores alkaline processing activity; the synthetic uranium-bearing solution, which came in contact with soils for 24 h, had the following chemical composition: U=0.465 g/L; CO$_3$$^-$$^-$=11.60 g/L; HCO$_3$$^-$=5.80 g/L; SO$_4$$^2$-=6.70 g/L; Cl$^-$=0.354 g/L; pH=9.2.

The kinetics of the decontamination procedure for each type of soil, which was polluted with uranium, using three types of reagents namely water, 0.1M sulphuric acid (H$_2$SO$_4$); aqueous chloro-sodic solution 100 g/L sodium chloride+10 g/L sodium carbonate (Na$_2$CO$_3$) was analyzed.

Soils granulometric composition was determined by the sieve mesh analysis using a vibrating sieves set type Retsch REV . CHIM. (Bucureºti) having mesh sizes: 0.056; 0.075; 0.1; 0.16; 0.2; 0.25; 0.5; 1; 2; 2.5 mm.

In order to perform the decontamination tests in the ultrasounds' absence a mechanical stirring system consisting of a paddle agitator type RW 16 IKA, on a speed 300 turn/min, a mass ratio solid to liquid 1 to 2, operating for 2 hours at a temperature of 20°C was used.

In order to perform the decontamination tests under the ultrasounds field an ultrasounds bath type Retsch UR1at a frequency of 35 kHz and a power of 480 W was used and the other operating parameters were similar with the first case.

In order to keep on the ultrasound bath's temperature at about 20°C the water bath was thermostated using a ThermoHaake B12 thermostat.

In order to determine soil structure the simplified Pipette method [10] was used and the relative distribution of the soil particles on three main granulometric classes was obtained as follows: sand (2.0 – 0.05 mm), sludge (0.05 – 0.002 mm) and clay (< 0.002 mm).

The method consists in the treatment of a soil sample dried to 105°C (15 g, m$_{sand}$) with 150-200 ml water and 20 ml solution 5% sodium hexametaphosphate, which is homogenized for 2 h. Then the sample is sieved using a sieve of 0.053 mm in order to collect sand fraction (m$_{sand}$). The rest of the sample consisting of water, sludge and clay is collected in a 600-800 mL glass. After the settlement time expires the fraction containing clay settles and the sludge particles within the sediment is dried in a glass at 105°C (m$_{sludge}$). Sand and sludge fractions are calculated and clay fraction is determined through deduction as it follows:

$$\text{sand}\% = \frac{m_{sand}}{m_{sample}} \times 100$$  \hspace{1cm} (1)

$$\text{sludge}\% = \frac{m_{sludge}}{m_{sample}} \times 100$$  \hspace{1cm} (2)

$$\text{clay}\% = 100-(\text{sand}\% + \text{sludge}\%)$$  \hspace{1cm} (3)

Organic substances content is very important because uranium and a number of other pollutants own a high affinity to bind with the organic substances through adsorption, absorption, complexes compounds generation or through redox processes. The main organic components are the humic substances. They were determined using the dry combustion method [11]. This method consist in heating the soil at 400°C, when the organic fraction oxidises to carbon dioxide (CO$_2$) and water (H$_2$O), and the main minerals contained by the soil sample remain intact. Thus the organic substances are eliminated as gas, the mass loss can be used to assess the organic matter content.

Soil samples were chemically characterized as the uranium U, total iron oxide (Fe$_2$O$_3$total), iron (III) oxide and iron (II) oxide contents an moisture concerns before the contamination in case of an antropic accident. It is important to know the iron's content because the ions pair Fe(III) – Fe(II) influence the uranium's dissolution kinetics in acidic environment.

Analytical method used to determine the uranium content were as follows: spectrophotometric method for the samples containing up to 2 g U/L (the liquid sample) or less than 0.5% (the solid sample) using a spectrophotometer UV-VIS CECIL 1011 and the gamma spectrometry analysis method for the solid samples irrespective of content using a multi-channel analyser with a Ge detector for $\gamma$ radiations (0-3MeV) – ORTEC.

Results and discussions

The important criteria as soil wet processing concerns are the small sized particles content and the organic matter one as well. Therefore the characterization of the soil to be treated is top important.

Soils granulometric composition has a top significance when the applicability of the selected process is established. A content of 25-30% particles sized less than 20 μm is the upper limit for the application of soil washing. Instead a soil having a high content of large sized particles can be easily decontaminated. The experimental results for all five types of soils are presented on figures 1-5, which points out the granulometric composition.
As one can observe soil samples 1, 2, 3 and 4 are dominated by the class < 0.056 mm and 5 is dominated by classes > 0.25 mm therefore soil sample 5 will be relatively easy decontaminated while 1, 2, 3 and 4, having a higher amount of fine fraction will be much more difficult to decontaminate.

The experimental results concerning the structure of all five types of soil are presented on table 1. It can be observed the soil sample 2 has the highest content of clay, which indicates a soil very difficult to decontaminate. Soils 1 and 3 have the clay content at the upper limit (30%) as the possibility to decontaminate those using washing concerns. Soil 4 and 5 has a low content in clay which make them amenable to the selected decontamination method.

The organic matter content of soil samples, determined using the dried combustion method, is presented on table 2.

As one can observe soil sample 2 owns a higher content of organic matter, fact which is confirmed by sample’s colour.

The experimental results concerning the chemical analysis of soil samples are presented on table 3.

As one can observe the uranium content of soil samples are of ppms order (g/t). Decontamination process efficiency will be demonstrated by decreasing the uranium content in soil to the initial level.

The results showed on figures 6 and 7 outcomes from the performance of decontamination tests on soils in the absence of the ultrasounds.

As one can observe out of all the three decontamination reagents used (water, sulphuric acid 0.1 M and chloro-sodic solution) the most efficient one was the chloro-sodic solution for the all five soil samples.

The decontamination degree is different depending on the type of soil respectively for soil samples 1-4 the decontamination degree was low, due to the high amounts of fine fraction, sludge and clay beside the high content of

### Table 1
SOIL SAMPLES STRUCTURE

<table>
<thead>
<tr>
<th>Soil sample</th>
<th>Sand %</th>
<th>Sludge %</th>
<th>Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.33</td>
<td>32.67</td>
<td>34.00</td>
</tr>
<tr>
<td>2</td>
<td>6.66</td>
<td>42.66</td>
<td>50.76</td>
</tr>
<tr>
<td>3</td>
<td>12.00</td>
<td>52.66</td>
<td>35.33</td>
</tr>
<tr>
<td>4</td>
<td>30.00</td>
<td>51.33</td>
<td>18.67</td>
</tr>
<tr>
<td>5</td>
<td>96.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>

### Table 2
ORGANIC MATTER CONTENT OF SOIL SAMPLES

<table>
<thead>
<tr>
<th>Soil samples</th>
<th>Organic matter, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.854</td>
</tr>
<tr>
<td>2</td>
<td>5.287</td>
</tr>
<tr>
<td>3</td>
<td>2.885</td>
</tr>
<tr>
<td>4</td>
<td>4.075</td>
</tr>
<tr>
<td>5</td>
<td>0.19</td>
</tr>
</tbody>
</table>

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The decontamination degree is different depending on the type of soil respectively for soil samples 1-4 the decontamination degree was low, due to the high amounts of fine fraction, sludge and clay beside the high content of
organic matter. The uranium from the contaminating solution was accumulated on soils samples due to the adsorption and complexes generation processes, which explains the high efficiency of the chloro-sodic solution in decontamination process.

The highest decontamination degree was reached, as expected, in the case of soil sample 5, which contains 96% sand and has an organic substance content of 0.19%, when all three decontamination reagents were very effective. Soils decontamination in the ultrasounds presence pointed out the experimental results presented on figures 8 and 9.

As one can observe washing with clean water does not determine a satisfactory decontamination in the case of soil samples 1-4 the residual content being higher than 120 mg/kg, but in the case of soil sample 5 a very efficient decontamination was achieved. On the other hand the use sulphuric acid and especially chloro-sodic solutions for the samples 1-4 leads to a decontamination degree of 75-80% while in the case of sample 5 the decontamination is practically complete.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Uranium ppm</th>
<th>Fe$_2$O$_3$ total %</th>
<th>Fe$_2$O$_3$ %</th>
<th>FeO %</th>
<th>Moisture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>4.63</td>
<td>3.94</td>
<td>0.63</td>
<td>3.08</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>6.33</td>
<td>4.49</td>
<td>1.44</td>
<td>4.76</td>
</tr>
<tr>
<td>3</td>
<td>4.4</td>
<td>3.85</td>
<td>3.5</td>
<td>0.32</td>
<td>3.49</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>4.23</td>
<td>3.41</td>
<td>0.74</td>
<td>2.99</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>1.45</td>
<td>0.53</td>
<td>0.83</td>
<td>0.58</td>
</tr>
</tbody>
</table>

The highest decontamination degree was achieved, as expected, in the case of soil sample 5, which contains 96% sand and has an organic substance content of 0.19%, when all three decontamination reagents were very effective. One can observe that the decontamination degree significantly increases when the process is intensified.
under the action of the ultrasounds, when the results obtained following the tests performed under normal conditions (without ultrasounds) are compared with the ones obtained under the ultrasounds’ action (figs. 10-12).

Lab tests pointed out the behaviour of all five types of contaminated soil under the leaching reagent’s action in the presence and absence of the ultrasound field.

Conclusions

The behaviour of all five studied types of soil under the extraction reagents action in the absence and the presence of the ultrasounds was pointed out after the performance of the decontamination experiments using washing method.

The main factors that determine the limits and performances of the decontamination process used are: soils’ granulometric composition, structure, organic substances’ content and the chemical composition.

Granulometric composition shows that soils 1, 2, 3 and 4 are dominated by the class sizing less than 0.056 mm, and soil 5 is dominated by classes sizing more than 0.25 mm that makes sample 5 to be much more easier decontaminated than the other ones, which contain a high amount of fine fraction and are much more difficult to decontaminate.

Soil structure pointed out three main granulometric classes namely: sand (2.0-0.05 mm), sludge (0.05-0.002 mm) and clay (less than 0.002 mm). It was observed that the sample 2 has the highest content of clay which makes it difficult to decontaminate. Soils 1 and 3 have a content of clay at the upper limit (30%) from the possibility to decontaminate soils by washing viewpoint and the soils 4 and 5 have a low content of clay, which make them amenable to the selected decontamination method.

Content of organic substance (humic substances) is very important because uranium and a number of other pollutants present a high affinity to bind with it. Soil 2 has the highest content of organic substance (5.28 %) which makes it to be the most difficult to decontaminate.

Ions Fe(III) – Fe(II) interfere with the kinetics of the uranium’s extraction in acidic environment, therefore is important to know the initial contents of these components in soil.

The decontamination tests in the absence of ultrasounds field pointed out a decontamination degree higher than 85% in the case of soil 5 and for all of three used decontamination reagents compared to the decontamination degrees obtained for the other four samples 1-4, which independent of the used decontamination reagents, are not reaching values of 70%.

In the case when the ultrasound field is applied a significant increase of the decontamination degree is observed compared to the first case. For soils 1-4 the decontamination degree can reach values higher than 80% and in the case of soil 5 about 100%. This fact can be attributed to the cavitation, which provokes microjets both inside the particle’s pores and at the solid-liquid interface as well and improves the uranium diffusion speed.

The economic effects of ultrasounds’ utilization for the decontamination of soils radioactively polluted retrieves in the operation time decrease, decontamination degree increasing and the land reclaiming with a “green” soil.

Ultrasounds application to the polluted soils decontamination could be a very promising alternative to other used ones.

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