

# Uranium Extraction in Ultrasound Field from Contaminated Soils

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*A study of uranium anion complexes extraction, from radioactively contaminated soils, under the influence of ultrasonic field is presented. The dynamics of uranium extraction has been studied for four soil types characterized in terms of particle size, structure and chemical composition using three extraction reagent types: a) water, b) 0.1 M sulfuric acid solution, and c) chloro-sodium solution - 100 g / L sodium chloride + 10 g / L sodium carbonate, mass ratio solid/liquid 1:2, for 30 min, temperature 20° ± 2°C, in ultrasound field, frequency 24 kHz and power 400 W. If in case of decontamination in normal conditions the higher decontamination degree was approx. 80%; using ultrasound field led to a decontamination degree of almost 100%. Using ultrasound led to values of comparable or higher degree of soils decontamination with approx. 15-20% compared to classical decontamination by chemical cleaning. From economical point of view, decontamination using ultrasound of radioactive contaminated soils, compared to chemical cleaning in normal conditions, is an expensive method. This method can be used when is required a fast, and a more efficient decontamination,*

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Global concern for environmental protection and reintroduction of radioactive contaminated soils in rehabilitated land circuit is an important and perpetual task. The aim of this paper is to develop an intensification method for soil decontamination.

Remediation of accidentally polluted soils with heavy metals is one of the biggest challenges for environmental protection. The techniques which are most frequently used for soil remediation 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. [1]

Intensification of mass transfer processes in soil decontamination by applying ultrasound is a new technology, which produces a mechanical, biological and sonochemical effects. Studies of ultrasound applications in soil science are few and only at the conceptual level [2].

Conventional chemical reactions are accelerated under the action of ultrasound or are oriented towards achieving quite different products [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 goal is to dislodge soil wash and separate the fine components from large mass of soil. If polluting materials can be removed from the most soil, is obtaining a "concentrate" volume of polluted soil. Any optimizations of penetration of the reagent into the de-polluted material results in an increase in the removal of soluble substances which are trapped within the solid particles.

A method that has worked well is the intensification of extraction of contaminants with ultrasounds [5-6]. Using ultrasound as a mean of enhancing the process of mass and heat transfer is reported in the literature since the 1970s [7] applied to dissolution, adsorption, and desorption operations [8].

Under the influence of the ultrasound occurs an extraction of contaminants, and a number of factors contribute to increasing of the process efficiency. These factors are asymmetric collapse of the cavitations bubbles (in the vicinity of solid surface), which lead to a high-speed microjet, directed towards the solid surface; this microjet can improve the speed of transport and increase the surface area by dividing it; cavitation collapse will generate shock waves that cause particle breakage of extraction agent, which after that can penetrate inside the particle by capillary; particle fragmentation by collision will increase the surface area; generating sound to disturb the diffusion layer on the surface; diffusion through the pores until the reaction will be enhanced by ultrasonic capillary effect [9].

There are several studies about washing method of heavy metals soil [10-12], or organic pollutants [13, 14].

The power of ultrasound has been used for soil release and removal of metals and metal compounds from the surface of soil particles instead of attrition technique.

Soil diluted with water was treated using 22 kHz ultrasound with power from 100 to 500 W. Ultrasound increasing the efficiency of soil remediation processes by 30% [15].

A new method for soils remediation is based on extraction with citrate under ultrasound conditions [16]. Citrate is an extracting substance that does not alter the environment and is successfully used to decontaminate soils with lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu). Application of ultrasound intensifies extraction of these metals after exposure for 30 min. at a frequency of 19.5 kHz, equivalent to a normal wash for 24 h.

Liu [17] and Mukherjee [18] showed that ultrasonic can dislodge organic matter adsorbed on a specific area of aquatic sediments and, therefore, significantly increase the bio-availability of sorbent.

Newman [19] conducted similar studies on granular pieces of brick impregnated with copper oxide as a model for the decontamination of polluted soils. He noted a 40%

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reduction of the copper content by washing the impregnated pellets with a stream of water in a tank at an ultrasonic frequency of 20 kHz.

These studies suggest that ultrasonic radiation can be an effective way to improve the extraction of ionic species in polluted soils [20-23].

The aim of the research presented in this paper was to determine how ultrasound helps to improve the extraction of uranium from radioactive contaminated soils.

### Experimental part

Laboratory tests were performed on four soil types characterized in terms of particle size, texture and chemical composition; these are the key factors in determining the performance and limits of the used decontamination process. 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 (0.385g/L uranium content, pH = 9) from mine water.

Decontamination kinetics was analyzed for each type of soil using three different reagents for decontamination of soil polluted with uranium: water, a 0.1 M solution of sulfuric acid ( $H_2SO_4$ ), and a chlorine solution 100 g/L sodium chloride (NaCl) + 10 g/L sodium carbonate ( $Na_2CO_3$ ) in 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.

For decontamination tests in ultrasonic field was used an ultrasonic generator, type UP400S Hielscher, at a frequency of 24 kHz, and a power of 400 W. The experimental conditions were: the mass ratio solid:liquid 1:2, the operating time 30 min., and the temperature 20 °C ( $\pm 2$ ).

In order to maintain the temperature of the reaction, the vessel is equipped with a mantle through which water circulates in a bath thermostat-type B12 (fig. 1).

Soils texture was made using a validated method (simplified Pipette method), 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). 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 h. 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 to one of 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 to the organic substances, either by



Fig. 1. Experimental installation

adsorption to complex formation, or through redox processes. The main organic components are humic substances; their concentration was established by dry combustion method [25]. Their determination was made by dry combustion method. This method involves heating the soil at 400°C, when the organic matter content is oxidized to carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ) and the most of minerals in the soil remain intact. The organic substances are removed in the form of gas; mass loss can be used to estimate organic matter content.

The soil samples were chemically characterized, in terms of the content of uranium, total iron oxide ( $Fe_2O_3$  total), ferric oxide ( $Fe_2O_3$ ), and ferrous oxide (FeO) before contamination. It is important to know the content of iron as  $Fe^{3+}$  and  $Fe^{2+}$  ions because they participate in uranium dissolution kinetics in the acidic environment.

Analytical method 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) was 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  $\gamma$  radiation (0-3MeV)-ORTEC was used.

### Results and discussions

An important criterion for application of wet soil processing is content of small particles and of organic matter. Therefore, it is important the characterization of soil which will be treated.

Particle size distribution of soils has a great importance to establish the applicability of the selected process. A soil with 25-30% content of small particles (less than 20 $\mu$ m) corresponds to the upper limit for soil washing method. On the other hand, soil with a high content of large-sized particles can be easily decontaminated. Experimental results for the four soil types, highlighting the size composition are shown in table 1.

Mesh size (mm)	SIEVE								
	0.056	0.075	0.1	0.16	0.2	0.25	0.5	1	2.5
Soil type									
1	79.32	3.92	6.53	1.63	1.46	3.26	1.48	0.75	1.65
2	8.55	3.08	12.55	11.40	19.42	19.62	6.08	4.67	14.63
3	88.28	0.45	0.68	0.32	0.51	2.48	1.93	1.08	4.27
4	74.95	7.81	7.22	4.55	0.60	0.32	1.75	1.25	1.55

Table 1  
PARTICLE SIZE DISTRIBUTION  
OF SOILS (%) DEPENDING ON  
THE MESH SIZE SIEVE

Soil sample	Sand %	Silt %	Clay %
1	29.90	50.83	19.27
2	95.28	1.75	2.97
3	6.36	42.38	51.26
4	32.83	31.77	35.40

As seen, in the samples soil 1, 3 and 4 prevail classes < 0.056 mm, and in sample of soil 2, 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

The experimental results on the structure of the four types of soils are shown in table 2.

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%) are in the terms of a potential remediation by washing. Sample of soil 2 has a low clay content, being suitable for this remediation method.

The experimental results for organic matter content of soil samples, determined by dry combustion method, are shown in table 3.

**Table 3**  
ORGANIC MATTER CONTENT OF SOIL SAMPLES

Soil sample	Organic matter content %
1	3.875
2	0.293
3	5.181
4	2.543

It can be seen that the soil sample 3 has the highest content of organic matter, which is also confirmed by the color of this soil sample (fig. 2).



Fig. 2. Soil samples

The results concerning the chemical composition of soil samples are shown in table 4.

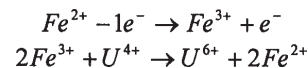
As shown uranium content of the soil samples are at the level of ppm (g/t), and the rate of dissolution of uranium in the acid is determined by the ratio  $Fe^{3+}/Fe^{2+}$ . Hexavalent uranium is slightly soluble in sulfuric acid (one of extraction reagents used), but in the form tetravalent uranium must be oxidized in order to be dissolved. Oxidizing agents act indirectly by conversion of ferrous sulfate to ferric sulfate.

Iron ion in valence state III oxidizes the tetravalent uranium through an electrochemical mechanism in which

Sample	Uranium ppm	Fe <sub>2</sub> O <sub>3</sub> total %	Fe <sub>2</sub> O <sub>3</sub> %	FeO %
1	3.98	3.92	3.17	0.75
2	2.15	1.37	0.46	0.91
3	5.74	5.98	4.67	1.31
4	3.21	4.51	3.83	0.68

**Table 2**  
SOIL SAMPLES STRUCTURE

the concentration of  $Fe^{3+}$  ions adsorbed on the particles surface determines the value of the reaction rate.



Divalent iron resulting from oxidation and dissolution of uranium is capable, in the presence of oxygen in the air, to be oxidized to  $Fe^{3+}$  again, and the process is repeated according to the same scheme.

For the initiation of the dissolution of uranium, it is generally considered suitable a  $Fe^{3+}$  concentration of about 1-2 g/L.

Decontamination of soils in the presence of ultrasound revealed the experimental results shown in figures 3 and 4.

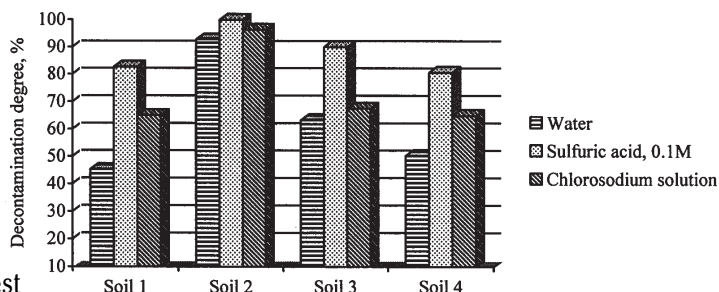


Fig. 3. Decontamination degrees of soils under ultrasound

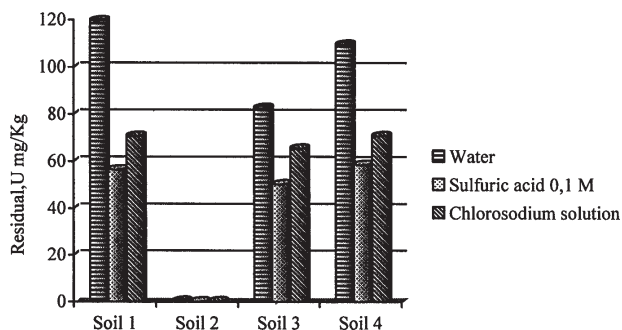


Fig. 4. Residual uranium content in decontaminated soils under ultrasound influence

Washing with pure water does not lead to a satisfactory soils decontamination. Soils 1, 3 and 4 have a higher residual content of 100 mg/kg, but in case of soil 2 it was realized an effective decontamination. Instead, usage of sulfuric acid and chloro-sodium solution leads for soils 1, 3 and 4 to a decontamination degree of 64-96% and for soil 2 to a practical total decontamination.

As expected, the higher decontamination degree was achieved for soil 2, which contains 96% sand and has an organic content of 0.19%; so all three reagents are effective for decontamination.

**Table 4**  
CHEMICAL COMPOSITION OF SOIL SAMPLES



Comparing the results obtained in the same conditions without ultrasonic action [26] (figs. 5, 6 and 7) and those obtained by the action of ultrasonic field, it was obtained comparable or greater values for the decontamination degree in the case of the use of the ultrasonic field; using ultrasounds the process takes place in 30 min, instead of 2 h in normal conditions.

This effect is found especially in case of difficult soils to decontaminate (soils 1, 3 and 4) which shows the role of cavitations in the uranium extraction from the fine fraction of the soil. These cavitations cause micro turbulence within the particle and solid-fluid interface, improving the speed of uranium diffusion.

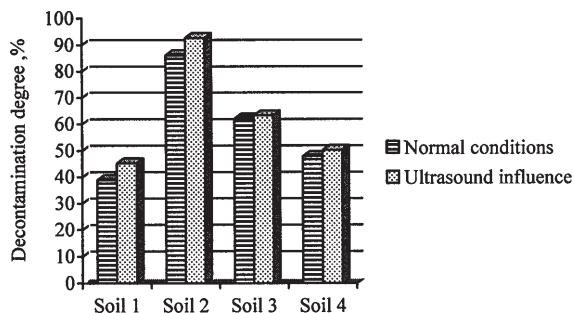


Fig. 5. Decontamination degrees of soils through washing with water in normal conditions and under ultrasound influence

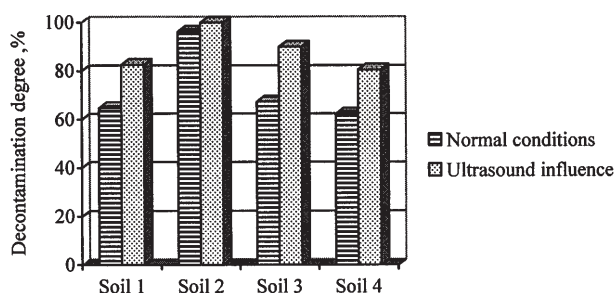


Fig. 6. Decontamination degrees of soils through washing with 0.1 M sulfuric acid in normal conditions and under ultrasound influence

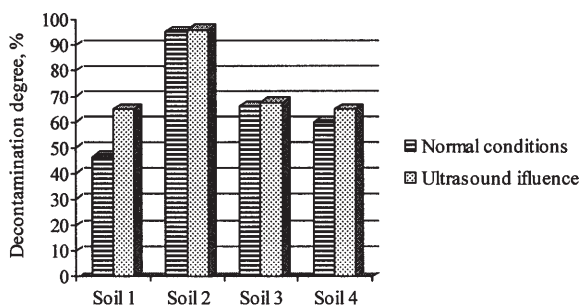


Fig. 7. Decontamination degrees of soils through washing with chlorosodium solution in normal conditions and under ultrasound influence

As can be seen, in the case of decontamination in normal conditions the higher decontamination degree was approx. 80%; the use of ultrasound field led to a decontamination degree of almost 100%, practically a total decontamination in a shorter period of time (30 min). The use of ultrasound field led to values of results comparable or higher degree of decontamination of soils with approx. 15-20% compared to classical decontamination by chemical cleaning. That makes the decontamination under ultrasound field using ultrasonic generator type UP400S Hielscher a rapid and appropriate method for uranium contaminated soils.

## Conclusions

Experimental investigations of uranium soils decontamination with an ultrasonic field indicate how the four soil types studied responded to the action of extraction reagent.

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.

Particle size distribution indicates that in the samples soil 1, 3 and 4 prevail classes < 0.056 mm, and in sample of soil 2 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.

Soil structure revealed three major classes namely granular sand (2.0 - 0.05 mm), silt (0.05 - 0.002 mm) and clay (<0.002 mm). It was found that the soil sample 3 has the highest content of clay, which indicates a soil hard to decontaminate.

Organic content (humic substances) is a very important factor because uranium and other pollutants have an affinity to bind them. Soil 3 has the highest content of organic matter (5.181%) which makes it most difficult to be decontaminated.

The ions Fe (III) - Fe (II) are involved in the kinetics of the uranium extraction in an acid medium; therefore it is important to know the original content of the soil in these components.

Decontamination tests using an ultrasonic field have revealed comparable levels or higher decontamination degree compared to classical decontamination by chemical cleaning. For soils 1, 3 and 4 the decontamination degree (acid extraction reagent) can reach values of 80% and about 100% for soil 2, an increase of approx. 20% compared to classic decontamination for a reaction time less than four times.

The economic effects of applying ultrasound to decontaminate radioactive soils are found in lowering operating life, in increasing of decontamination degree, and in the result of a clean soil. Decontamination of polluted soils using ultrasonic field can be a promising alternative to other methods.

The use of the ultrasound field for radioactive soils decontamination is an expensive method, compared to chemical cleaning method, but this method can be used when it is required a fast decontamination. In the future we will consider cheaper methods to obtain comparable or even better results.

## References

- GOSSOW, V., ZARBOK, P., Treatment of Contaminated Soil, *Aufbereitungs-Technik*, **33**, nr. 5, 1992, p. 248.
- NEEBE, T., Wet Processing of Contaminated Soil, *Aufbereitungs-Technik*, **31**, nr.10, 1990, p. 563.
- MASON, T.J., *Sonochemistry*, Oxford University Press, New York, 1999.
- TEKIN, T., *Hydrometallurgy*, **59**, 2001, p. 46.
- SUSLICK, K. S., PRICE, G. J., *Ann. Rev. Mater. Sci.*, **29**, 1999, p. 295.
- PANȚURU, E., JINESCU, G., RĂDULESCU, R., FILIP, G., *Rev. Chim. (Bucharest)*, **58**, nr. 6, 2007, p. 551.
- FLOAREA, O., JINESCU, G., *Procedee intensive în operațiile unitare de transfer*, Ed.Tehnică, București, 1975.
- MASON, T.J., PETERS, D., *Practical Sonochemistry. Power Ultrasound Uses and Applications*, second ed., Horwood Publishing Limited, Chichester, 2002.
- TEKIN, T., *Hydrometallurgy*, **64**, 2002, p. 46.

- 10.MEEGODA J. N., PERERA R., *Journal of Hazardous Materials*, **85**, nr. 1-2, 2001, p. 73.
- 11.GAVRILESCU M., PAVEL L. V., CRETESCU I., *Journal of Hazardous Materials*, **163**, nr. 2-3, 2009, p. 475.
- 12.PANTURU E., JINESCU G., RADULESCU R., *Rev. Chim. (Bucharest)*, **59**, no. 9, 2008, p. 1036.
- 13.KIM Y. U., WANG M. C., *Ultrasonics*, **41**, nr. 7, 2003, p. 539.
- 14.SHRESTHA R. A., PHAM T. D., SILLANPÄ M., *Journal of Hazardous Materials*, **170**, nr. 2-3, 2009, p. 871.
- 15.YAKUBOVICH, I. A., AGRANAT B. A., KIRILOV O. D., KHAVSKII N., *Izvest. VUZ, Tsvet. Metall.*, **4**, 1964, p. 23.
- 16.FURUKAWA, M., TOKUNAGAS., *Environ. Eng.*, **39**, nr. 3, 2004, p.627.
- 17.LIU, D., AOYAMA, I., OKAMURA, H., DUTKA, B.I., *Environ. Toxicol. Water Qual.*, **11**, 1996, p. 195.
- 18.MUKHERJEE, S., MATTHEW, R., HSIEH, H. N., *Geotech. Spec. Publ., ASCE, New York*, **65**, 1997, p. 122.
- 19.NEWMAN, A. P., LORMER, J. P., MASON, T. J., HUTT, K. R., *Ultrason. Sonochem.*, **4**, 1997, p. 153.
- 20.COLLINGS, A. F., *Proceeding Minerals Engineering '02, Perth, Australia*, 2002.
- 21.SUSLICK, K. S., *Ultrasound - Chemical, Physical, and Biological Effects*, VCH Publishers, New York, 1988.
- 22.MASON, T. J., LORIMER, J. P., *Applied Sonochemistry*, Wiley VCH, 2002.
- 23.FEUNG, D., ALDRICH, C., *Hydrometallurgy*, **55**, 2000, p. 201.
- 24.KETTLER, T. A., and oth., *Soil Sci. Soc. Am. J.*, **65**, 2001, p. 849.
- 25.WALKLEY, A., BLACK, I. A., *Soil Sci.*, **37**, 1999, p. 29.
- 26.RADU A. D., WOINAROSCHY A., PANTURU E., *UPB Sci. Bull., Series B*, **76**, 2014, in press

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