THERMOCHEMICAL METHODS OF SOIL DECONTAMINATION

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Abstract

Soil contaminated by various radionuclides is now one of the important environmental problems. The problem is caused especially by the medium- and long-lived radionuclides that are released during accidents or malfunctions of nuclear facilities, one of which is cesium-137. This radionuclide diffuses into the soil matrix where it is embedded. This bond is very strong and it is rather difficult to separate the cesium from the soil. Possibility of cesium separation was studied in high temperature thermochemical experiments in an electric furnace. Thermodesoption makes use of the fact, that alkaline metals may be volatilized from the material at high temperature. Three series of experiments were performed with a set of real cesium-137 contaminated soils. In the first of them, cesium release was studied at temperatures not exceeding 900 °C. In the second series, high temperature (up to 1180 °C) experiments were performed in a special electric furnace with kanthal wire heating elements. Cesium release not exceeding 0.5 % was achieved in these experiments. In the last series of experiments, interaction of the soil with a sodium meta– or tetraborate flux was investigated. The reaction was carried on at temperatures above 900 °C, the time necessary to produce homogeneous compound was found to be 5-20 minutes. The metaborate based glass is well soluble in mineral acids (HCl, HNO_3). This step allowed to transfer the activity from the insoluble soil into the solution. For quantitative separation of cesium from the solution, selective composite inorganic-organic ion-exchanger was used.

Introduction

The presence of cesium in the nature, namely the presence of its radioactive isotopes is a non-natural and unwanted phenomenon. Average abundance of cesium in lithosphere is close to zero (as low as 2,6 ppb) (1). However, significant quantity of radiocesium (^{134,137}Cs) was spread to the nature in the second half of 20th century as a result of neclear weapons tests and nuclear installations malfunction. Most of this radiocesium is now deposited in the soils. Thanks to the half-life of ^{137}Cs (cca 30 years), in some cases its contribution to the total dose to men may be significant.

The cesium cation (Cs^+) is strongly bound in soils, namely in the soil minerals. It diffuses through the crystals (even with its hydration shell) with the velocity of approximately 1 cm/year and it is incorporates in the dumbbell (2) points and in the crystal-lattice defects of silicates and aluminosilicates. The ion stabilization of cesium in these points results from charge re-distribution of the anionic group SiO_4^{4-}. In addition, the cesium ion can also replace other ions like K^+, Na^+, NH_4^+, Ca^{2+} or Fe^{3+} crystalline materials (3).

The fact that Cs is really strongly bound in the soils, may be illustrated by its resistance to leaching - no more than 60 - 75 % of cesium can be leached, regardless of the used leachant composition, leaching conditions or soil type (4). The cesium intrusion into the soil, caused by diffusion, soil mixing or washing and transport by precipitaion does not usually exceed the depth of 10 cm. Typically, more than 99 % of cesium can be found in the uppermost 2,5 cm of the soil (5).

There exist several methods for radioactively contaminated soils decontamination. Widely used are namely the leaching or electrochemical methods, among the new developments, the phytoremediation methods may be listed. The thermochemical method represents another prospective method that has not been studied in much detail, yet. That were these thermochemical methods that this project aimed to study.

The thermochemical methods make use of physico-chemical principles of increased temperature action on the studied materials. In the case of separation of elements or individual components of soil, the most straightforward possibility is to make use of differeces in boiling or melting points of these components. In the case of separation of cesium, that was transferred to the gas phase, from the soil, which remains in the solid state, we speak about the "direct thermodesorption". Another possibility offer the melting methods, which are based on transfer of the whole sample, including the cesium, into the solution and subsequent cesium separation by solid of liquid extractants.

Methods

The experimental execution of thermochemical methods is generally rather demanding because of the necessity to operate a suitable apparatus, which eanbles heating the studied sample up to the requested temperature on one hand, and separation of the fused or vaporized component by a suitable device on the other hand. In addition, resistance of the crucibles against the fluxing agents must be guranteed.

Direct thermodesorption

The application of this method on contaminated soils was based on the hypothesis that cesium could be removed from the sample by vaporizing it to its gas state by heating the sample above the cesium boiling point (705 °C), whereas the mineral matrix of the soil would not undergo any changes (would not be melted). The cesium vapor should then be captured in a suitable device, e.g. by condensation on a cooled surface.

The apparatus used was based on that designed earlier by M. Nemec (see Figure 1) (3). The sample was heated in a crucible in an electric furnace and the volatilized vapors of cesium were condensed on a cap, which was cooled by means of a coolers. Air was used as the cooling medium. The experiments were performed with 9 different soil samples from the area of the former Czechoslovak nuclear power plant A-1, that were contaminated by leaks from the decay tanks.

Figure 1: Design of the fusion apparatus
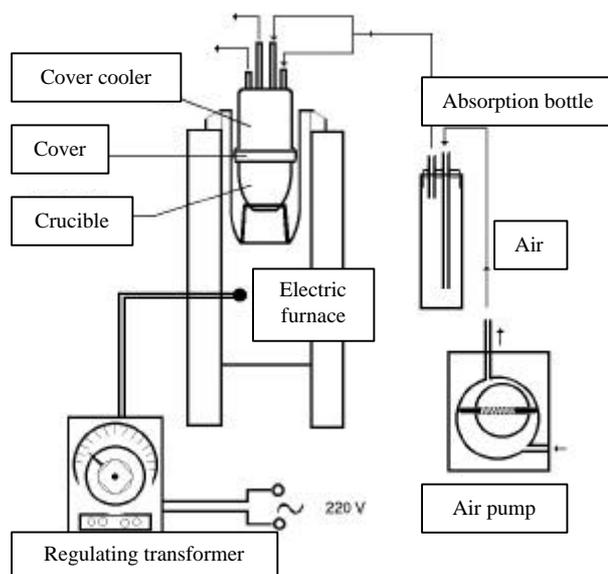
Electric furnace CLASIC 0412G (Clasic s.r.o., Lety, Revnice, Czech Republic) with temperature regulator Claro 4.0, equipped by Kanthal A1 heating elements, was used for the experiments. The soil samples (3 g) were weighed into a ceramic crucible (volume 70 ml), which was made from sintered corundum Oxal (Brisk Tabor, Czech Republic). The following annealing regimes were used:
- 30, 30+90, or 120 minutes at the temperature of 900 °C,
- 60 minutes at the temperature of 1200 °C

During the experiment, the crucible condensation cap was cooled by the air to the temperatures below 600 °C. After the annealing experiment, the cap was measured on a gamma-ray spectrometer ORTEC with coaxial HPGe detector (efficiency 22 %, resolution 1.9 keV for ^{60}Co with E_γ= 1332 keV). The total activity of cesium deposited on the cap was determined relatively to a standard sample prepared in the same geometry from the solution with know ^{137}Cs specific activity.

Leaching of cesium from the sample of annealed soil was studied relative to that from the original soil sample. 1M HCl + 0,5M CH$_3$COONH$_4$ + 0,5M Ca(NO$_3$)$_2$ leachant was used.

Soil decomposition by fusion with borates fluxing agents

Silicates and aluminosilicates are the major components of soils. It is known, that these materials are not difficult to convert into smelts. Efficient fluxing agents are metaborates or tetraborates of alkaline metals. They are typically used in the form of anhydrous salts, formed by dehydration at the temperatures 700 - 800 °C. These salts can be used alone, or in mixtures with different additives that facilitate the fusion. For the preparation of homogenous glasses, the fluxing agent choice depends always on the sample composition. Generally, it can be said that for materials exhibiting alkaline character (like Al$_2$O$_3$), acidic fluxing agent based namely on tetraborate should be used, while for the acidic materials (like SiO$_2$), alkaline mixtures with prevailing metaborates are preferable (6).

The use of both tetraborates and metaborates was tested for fusing the soils. In the initial phases, the fusion process should be executed at lower temperatures, then the temperature is increased up to 1000 °C and it is maintained at this value until a transparent mass is formed. Very resistant materials (e.g. some Al, Ti, Nb and Ta compounds) need to be treated for up to 1 or 2 hours, in the case of less resistant materials, 5 - 20 minutes usually suffices (6). By the fusion, black-colored tetraborate or dark green colored metaborate glasses are formed.

To keep the melting process running even, it is important to observe the recommended sample-to-flux ratio and homogenize the components well before the start of the fusion process. The soil homogenization was realized in an agate grinding mortar, mixing with the fluxing agent was realized right in the crucible, where both the components were carefully mixed by a glass rod. The same type of the crucibles and the same furnace were used as described above for the thermodesorption studies. The fusion process was visually controlled to prevent overboil of the mixture and the furnace contamination. The maximum time of fusion of approx. 15 min was used.

With the aim to find optimum conditions of the fusion process, the role of the soil/fluxing agent ratio was studied, and the temperature modes were modified on the basis of mixture behavior. Both the tetraborate and metaborate glasses produced were dissolved directly in the crucibles. Diluted mineral acids were used for the dissolution that was carried on for up to 14 days under occasional stirring.

Sorption experiments

From the solutions formed by dissolution of borate glasses, cesium separation was studied. Two selective inorganic absorbers were used: ammonium molybdophosphate (AMP) and potassium-cobalt ferrocyanide (FC 411). With these materials, static batch experiments were performed aimed at the distribution coefficients (K$_D$) determination. The absorbers used for the K$_D$ determination were pure powdered active components with grain size below 0.1 mm. The experiments were performed at the V/m (volume of the solution/mass of sorbents) ratio V/m = 100 ml/g (10 ml of the solution with 100 mg of the absorber), the suspensions were contacted by shaking on a KS 250 basic (IKA Labortechnic, Germany) shaker set at speed 400 for 23 hours. The distribution coefficients were calculated from the activities of aliquots of the initial solution (a_s) and the solution after contact with the absorber (a_r) following to the equation:

$$K_D = \frac{a_s - a_r}{a_r} \cdot \frac{V}{m}$$

The dynamic column experiments were performed in a SUPELCO polypropylene Rezorian™ A161 luer lock syringe cartridge (SUPELCO, USA, Cat.No. 852685) with bed volume (BV) of 1.2 ml, equipped with polypropylene frits at the top and bottom of the bed. The column was loaded with composite absorber FC411–PAN composed of the potassium-cobalt ferrocyanide active component in a binding matrix of polyacrylonitrile (7). The grain size of the absorber used was 0.1 - 0.3 mm, the contents of the active component in dry material was 85.7 % (w/w). The column was connected to a peristaltic pump PCD 22 (Kouril Kyjov, Czech Republic) equipped by thin silicon tube and set to the flow rate of 0.7 ml/min. In this setting, the actual flow rate was 12 ml/hour (10 BV/hour). Upward direction of the flow of the solution was used. The fractions were collected automatically after each 45.5 min. Count rates of the aliquots of the fractions were measured in standard conditions on the ORTEC gamma-ray spectrometer and related to the count rate of an aliquot of the initial solution.

Results and discussion

In the first step, experiments at conventional temperatures (up to 900 °C) were performed. Contrary to the earlier published data (3), no thermodesorption of ^{137}Cs from the soils was observed. Therefore, the next series of experiments was performed at the temperature as high as 1180 °C. In these conditions, small thermodesorption of ^{137}Cs from the soil and its deposition on the cooled cap was observed. After 1 hour of annealing treatment, the deposited ^{137}Cs activity was not higher than 12 Bq, which corresponds to the decontamination yield of no more than 0.4 % (see Table 1). After annealing at temperatures higher than 900 °C, the soil was sintered in the crucible and could not be removed. These experiments proved that the concept of direct thermodesorption failed, cesium cannot be removed from the soil by this method to a significant extent and for this reason this method cannot be used to treat real contaminated soils.

Table 1: Results of direct thermodesorption experiments
(temperature 1 180°C, annealing time 120 min)

Soil sample	Mass of soil	Cesium desorption
F1	3.09 g	ND
F2	3.01 g	ND
F3	3.03 g	ND
F4	3.04 g	ND
F5	3.00 g	ND
L1	3.01 g	0.15 %
L2	2.97 g	0.28 %
L3	3.03 g	0.05 %
L4	2.96 g	0,41 %

ND = not detected

Leaching of cesium from the sample of annealed soil was studied relative to that from the original soil sample. 1M HCl + 0,5M CH_3COONH_4 + 0,5M $Ca(NO_3)_2$ leachant was used. The results obtained are summarized in Table 2. From these data, it follows that cesium is released from the annealed soil almost five times less then from the original sample. Hence, it can be concluded that during the soil annealing cesium is incorporated into the soil matrix even stronger. This interesting phenomenon offers a potential new route to contaminated soils conditioning prior their final disposal to the repositories. More detailed study of the annealed soils leachability would be needed to confirm this option.

Table 2: Soil (sample No. L4) leaching by 1M HCl + 0.5M CH_3COONH_4 + 0.5M $Ca(NO_3)_2$ solution.
(mass of soil 2.96 g, leaching time 26 days, volume of solution/mass of soil ratio V/m=3)

Soil	Activity of the leachate	Cesium leached [%]
Annealed	5.5 Bq/ml	2.2
Original	20 Bq/ml	9.2

The studies of soil fusion with borate fluxing agents were performed with both sodium tetraborate and metaborate. Both these agents were found to efficiently decompose any of the studied soils regardless of their composition. An important pre-requisite of a successful decomposition was found to be execution of the processes at optimum conditions and after very good homogenization of the soil - fluxing agent mixture. A detailed study of the fusion conditions revealed that the optimum soil/flux ratio is 1/5, the optimum temperature program is shown in Figure 2. The behavior of mixtures with different soil/flux ratios is shown in Table 3. When non-optimum treatment conditions are used, the reaction gets either vigorous and the mixture overboils, or the formed borate glasses are non-homogenous and they are difficult to dissolve.
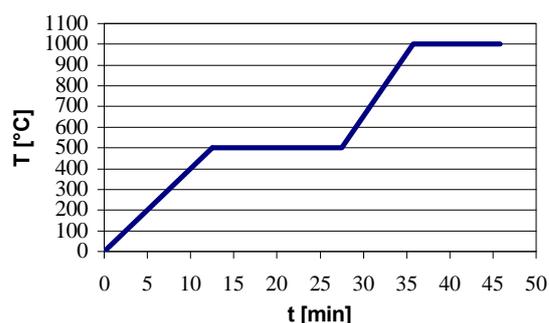
Figure 2: Optimum mode of fusion

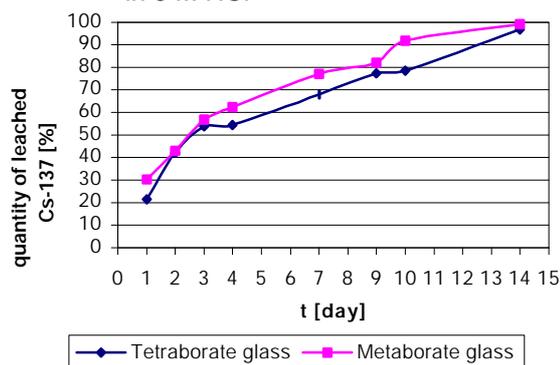Figure 3: Dissolution curves of borate glasses in 5 M HCl

Table 3: Results of fusion experiments

Soil/flux ratio	1/3	1/5	1/8
Temperature mode	100°C/min, 20 min at T~1200°C	40°C/min up to 500°C, 15 min at 500°C, 60°C/min up to 1000°C, 10 min at 1000°C	100°C/min, 20 min at T~1200°C
Characteristics of the products	Final product not homogeneous and it has dregs of soil	Good quality homogeneous final product	Experiment stopped at 350°C – overboil of the mixture

The study of the borate glasses dissolution revealed that 5M HCl was optimum for quantitative dissolution of the material. For the uncrushed samples of the original size (approx. 3 g of soil) the dissolution process took 14 days. After this time 99 % of ^{137}Cs was transferred into the solution from the metaborate glass. In the case of tetraborate glass, the dissolution was slightly less quantitative, some 97 % of ^{137}Cs was dissolved under the same conditions. The respective glass dissolution curves are shown in Figure 3. The solutions of the dissolved glasses were lemon-yellow colored and contained a lot of silicagel that gave them jelly-like appearance. The silicagel could be easily removed by centrifugation for 5 minutes at 4000 rpm. It was confirmed that no cesium is removed from the solution in silicagel removal step.

The static batch sorption experiments were performed with the solution of metaborate glass. The performance of both the inorganic absorbers (AMP, FC 411) was tested for both the initial solution and the same solution diluted with distilled water in the ratio 1:1. The results of these experiments are summarized in Table 4. From the results of the batch experiments, it could have been concluded that, for the respective acidity of the solution, the use of the FC 411 absorber is preferable because of its better chemical stability (the AMP absorber decomposed at the original non-diluted solution).

In the dynamic column experiments performed, upward direction of the flow of solution was used. The preliminary scouting experiments revealed that the use of the original 5M HCl solution is not feasible (the column was clogged shortly after the start of the experiments). Therefore, the diluted solutions (2.5M HCl) were used. A total of 100.6 ml (83.3 BV) of the dissolved metaborate glass solution was treated on the column of the FC411–PAN composite absorber. The measurements of the collected fractions showed, that the total ^{137}Cs activity in the effluent was not higher than 1 % of the initial activity. That means, that the separation of ^{137}Cs from the solution proceeded quantitatively (separation > 99%).

Table 4: Results of static experiments with absorbers

Adsorber	Acidity of solution	K_D (ml/g)
AMP	5 M HCl	9 120
	2.5 M HCl	21 603
FC 411	5 M HCl	7 059
	2.5 M HCl	6 390

Conclusions

The studies of thermochemical decontamination methods of soils showed, that the thermal methods can be successfully used for radionuclides separation. A process for soil decontamination was developed that is based on soil fusion with borate fluxing agents, dissolution of the resulting glasses in diluted mineral acids and subsequent cesium separation from the solutions by selective inorganic-organic composite absorbers. Even though this method is energetically demanding and does not allow for decontamination of large quantities of soil, it has one great advantage when compared to the currently available soil decontamination methods – the almost quantitative radionuclides separation, which reached up to 99 % in this study.

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