

ELECTROCHEMICAL DECONTAMINATION OF SOILS DEBASED BY ^{137}Cs

M. Nemeč^{1,2}, J. John^{1,2}, J. Rezbarik³, M. Prazska³

¹Department of Nuclear Chemistry, Czech Technical University in Prague,
Brehova 7, 115 19 Prague 1, Czech Republic, mojmir.nemec@jfifi.cvut.cz

²Center for Radiochemistry and Radiation Chemistry, Czech Technical University in Prague,
Brehova 7, 115 19 Prague 1, Czech Republic, jan.john@crrc.cvut.cz

³AllDeco s.r.o., Jiraskova 24, 917 01 Trnava, Slovak Republic, rezbarik@alldeco.sk

Abstract

After the accident in the Jaslovské Bohunice nuclear power plant (NPP) in 1977, some leaks from liquid waste tanks occurred and fission products, mainly cesium 137, contaminated the soil. Because soils and sediments are the natural ion-exchangers and the environmental “waste depots” for radioactive contaminants, the aim of this study was to find simple and efficient method for the decontamination of these soils debased by radionuclides, namely by ^{137}Cs . The studied method was the electrolytic decontamination, which allows disruption of the soil matrix and separation of the released cesium. In the experiments performed, the soil was electrolyzed at various conditions and the level of decontamination was determined by α -ray spectrometry. It was found, that electrolysis is an efficient method which could release more than 97% of cesium.

Introduction

During operation or malfunctions of nuclear facilities and development or testing of nuclear weapons, the environment was contaminated by fission nuclides on many places all over the world. The processes for the remediation of contaminated soils can be divided into two categories (1). The first one is “in situ” decontamination and it is used mainly for remediation of large areas. The second category groups techniques for treatment of soil, that has been removed from its original location, in special treatment devices. These techniques are used namely for high active soils from local contaminations; they are also appropriate for the soils from NPP Jaslovské Bohunice, which have been collected and moved to nuclear waste depots.

Cesium is a reactive, mobile and also volatile alkaline metal. Its radioactive isotopes, namely ^{137}Cs with a relatively long half-life (30,07 years), belong among the most problematic nuclear contaminants. It is produced in nuclear fission process with a very high yield (about 6 %). The migration mechanisms in nature lead cesium to the soils, where it is very strongly bound. To release it of the soil is not an easy problem.

Several methods were designed and tested for this purpose (1), but at present none of them can remove all cesium at reasonable costs and efficiency. Among the promising methods for soil decontamination, the electrochemical methods (2,3) play an important role. In these methods, it is assumed that cesium is bound in the soil by electrostatic interactions and electric field should be able to remove or migrate the Cs ions out of the soil to the electrolyte and then to the cathode, and thus enable the separation. The advantages of electrolytic mode of decontamination are: the very chemically aggressive environment formed near the electrodes, very high flux of the ions at higher currents, and also the temperature increase caused by the passage of the current. These conditions are able to break the soil matrix and to release even the cesium incorporated in it. The released cesium is then concentrated in the cathodic electrolyte. The aim of this study was to design, test and optimize electrolytic decontamination method for soils contaminated long time ago by ^{137}Cs .

Methods

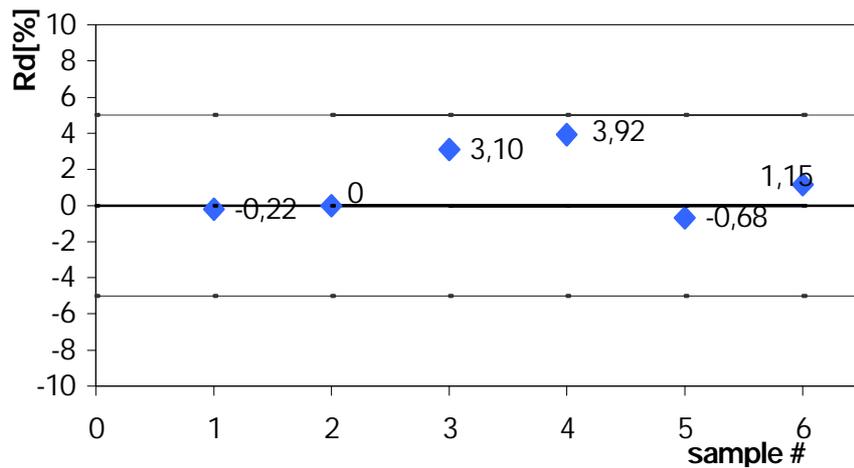
Soil samples with specific activities from 700 to 900 Bq/g from Jaslovské Bohunice NPP waste storage depots were used for the experiments. The soil was dried, homogenized and powdered; the activity and the degree of decontamination of the samples were determined by γ -spectrometry in standard geometry with HPGe semiconductor detector PGT PIGC-22 (Priceton Gamma Technologies, USA) with the ORTEC 919 (EG&G ORTEC, USA) multichannel analyzer.

For the electrolytic experiments, small soil samples (about 3 g) were prepared. The homogeneity of activity distribution in the samples was evaluated as a relative difference (Rd) of the specific activity of a series of samples with masses of 3-4 g relative to a selected standard sample. The following equation was used to calculate the differences:

$$Rd = \left(1 - \frac{A_2}{m_2} \cdot \frac{m_n}{A_n}\right) \cdot 100$$

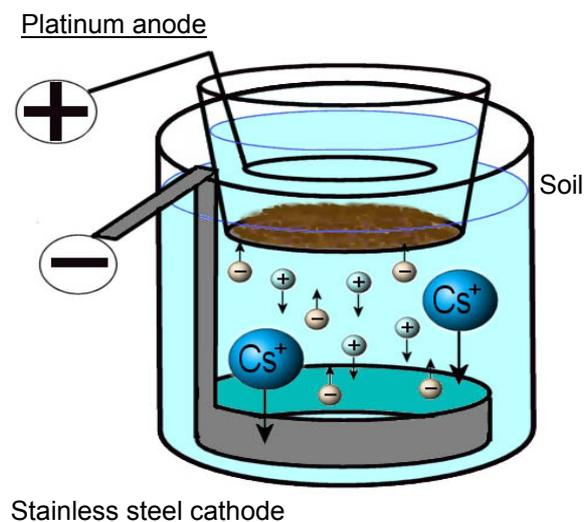
where A_i are count rates of the soil samples and m_i are their respective masses. The homogeneity of the prepared samples was found to be better than 5% on the 3-4 g sample size level (see Figure 1).

Figure 1: Homogeneity of the soil samples



The samples were electrolyzed in a glass crucible with porous glass frit bottom (Figure 2) inside an electrolytic cell. The anode electrode was placed as close as possible to the soil surface, to enable the action of the aggressive environment on the soil and gaseous mixing of the suspension. The soil was electrolyzed in a batch mode at different currents and in the presence of different electrolytes. As a power source, the constant current and voltage source SP150 20V / 7A (S PowerR product s.r.o., Bratislava, Slovakia) was used.

Figure 2: Schematic diagram of the set up for electrochemical decontamination



In the “standard” procedure, the process of the electrolysis was carried out in a “repetitive batch” mode, where the soil was always electrolyzed for 6 – 10 hours and after each electrolysis step the soil was dried at the room temperature (overnight) and measured. The spent electrolyte was stored and used again in the next electrolysis step; any loss of the electrolyte was compensated for only by refills of distilled water. From the soil activity decrements, the level of decontamination was calculated. All the samples were electrolyzed at least for 32 hours.

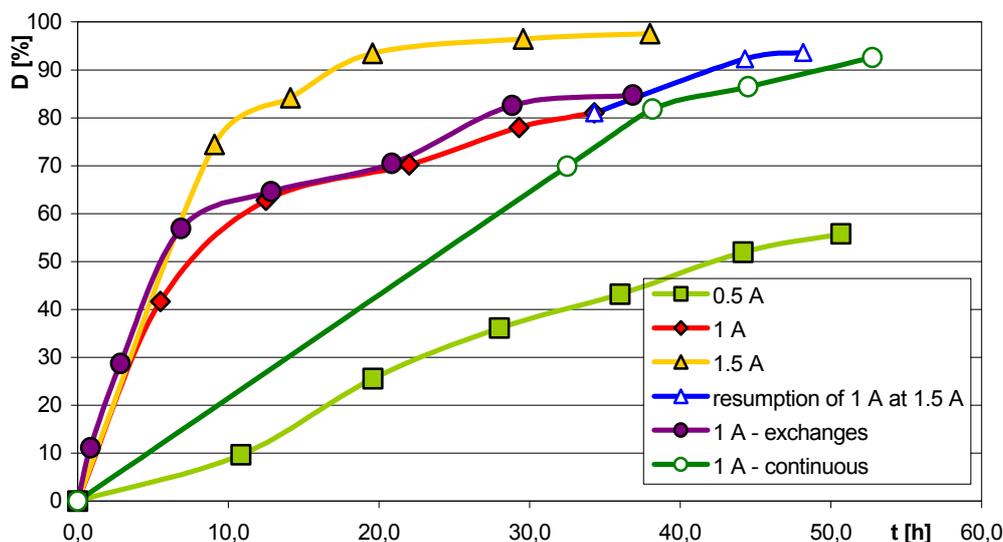
In the experiment series, several parameters of the process were studied:

- *Currents used in electrolysis.* The dependence of the decontamination factor on the current used was thereafter tested at three different values 0,5 – 1 – 1,5 A. The sample treated at 1 A current was thereafter electrolyzed again at higher current (1.5 A) to check the influence of the current used on the decontamination. Energy input per 1g of the soil was calculated from the current values, voltages applied and masses of the samples.
- *The influence of the electrolysis mode.* The soil was electrolyzed continuously for 32 hours, and then measured. For better estimation of the influence of soil relaxation, the sample from continuous treatment was electrolyzed 3 times again after 14, 7, and 20 days relaxation in dry state at room temperature. The result was compared to the standard “repetitive batch” experiment with identical experimental parameters but the total electrolysis time (34 hours) divided into 5 intervals.
- *The influence of electrolyte exchange.* To solve the precipitation problem and to facilitate the determination of cesium release, the possibility to use fresh electrolyte for each electrolysis step was tested.

Results and Discussion

Influence of the current: The current increase from 0.5 A to 1 A, and then to 1.5 A caused the decontamination increase after 32 hours of electrolysis to approximately 40, 80, and 97%, respectively (see Fig. 3). These values are very high for this type of contaminated soil, because in earlier aggressive soil leaching experiments (6 mol/L HNO₃ as a leaching solution, intensive shaking) no more than 45% of ¹³⁷Cs could have been released after 14 days of leaching (4). The comparison of time (Figure 3) and energy (Figure 4) curves shows that the decontamination process is faster and more efficient at higher currents. From the shape of these dependencies, it can be assumed that the release of cesium is influenced not only by the total energy absorbed by the system, but also by the incoming power. This result is not unexpected; it is similar to other processes, as e.g. in radiation chemistry, where the effects of the dose often depend on the dose rate. The importance of the current value is also shown in graphs as a curve “resumption of 1 A at 1.5 A”, where the decontamination level raised by about 12% after the current increase.

Figure 3: Dependence of the decontamination D [%] on the time of electrolysis t [hours]. For the explanation of conditions see the text



Electrolysis mode: Comparison of the curves “1 A – continuous” and “1 A” (in Figures 3 and/or 4) shows that the decontamination process is significantly influenced by breaks between the successive electrolysis steps. In the continuous electrolysis experiment, only 70% desorption of cesium was achieved after 32 hours of electrolysis, while in the repetitive batch experiment the level of decontamination was by 10% higher; or, if expressed in other way, the 70% level of cesium decontamination was achieved approximately by 10 hours sooner. Moreover, the next 3 electrolysis experiments on the same sample, performed after 14, 7 and 20 days of soil relaxation (stored after drying at room temperature) in the same conditions enabled to desorb about 93% of cesium, what is almost equal to the value achieved by electrolysis at 1.5 A (see Figures 3 and/or 4). It is supposed that this effect is caused by cesium speciation re-distribution during the relaxation period – part of the cesium relatively easily diffuses from the partially damaged crystalline structures and stabilizes in weaker bound forms.

Figure 4: Dependence of the decontamination D [%] on the absorbed energy E [Wh/g]. For the explanation of conditions see the text.

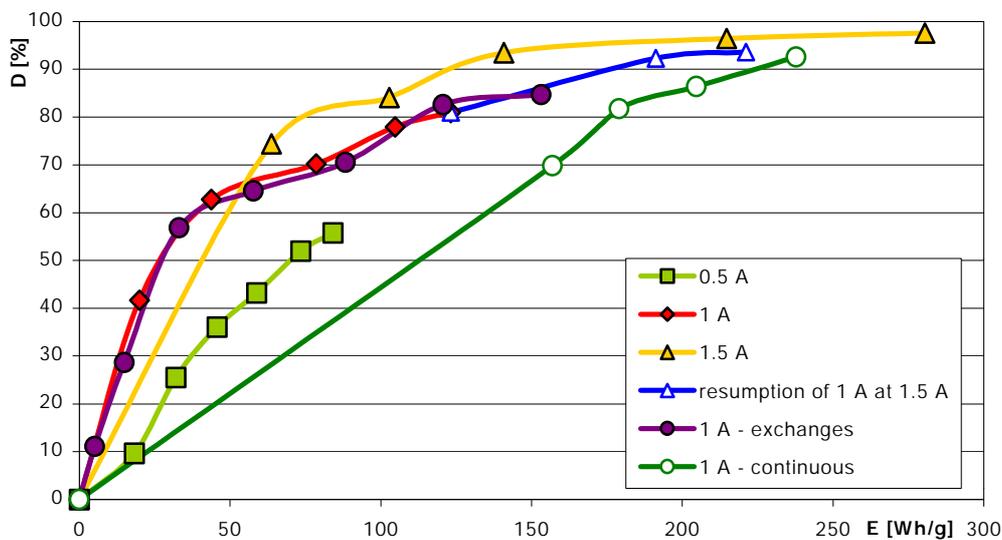
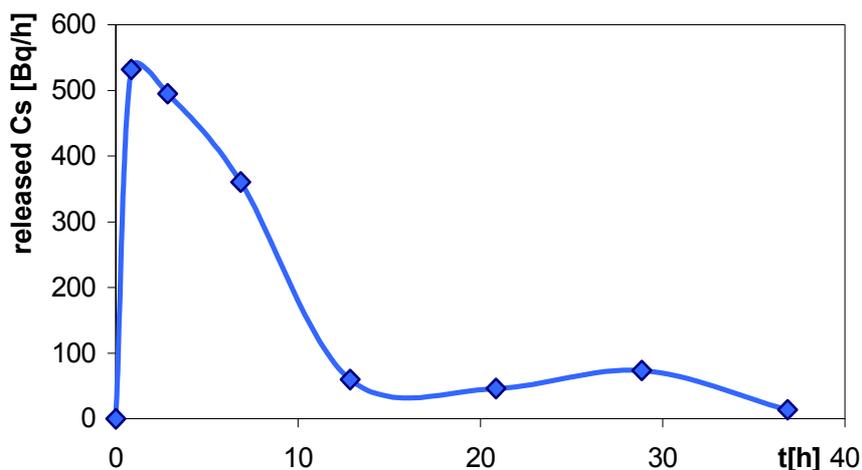


Figure 5: Release of cesium [Bq/h] from the soil as a function of the electrolysis time t [hours] in the electrolyte exchange experiment



Electrolyte exchange: The decontamination factors obtained by the standard procedure were compared to the results obtained in a similar experiment, where fresh electrolyte was used for each successive electrolysis step. From the dependencies shown in Figures 3 and 4, it can be seen that the curves “1 A” and “1 A - changes” are practically identical; the changes of electrolyte do not seem

to influence the release of cesium significantly. After 32 hours of electrolysis, the cesium desorption differed only by about 4% in the experiments with and without electrolyte exchange. The important conclusions of these findings could be summarized to these points:

- The efficiency of cesium release cannot be improved by the electrolyte exchange.
- During the method development, the electrolyte exchanges enable study of radionuclides and also major soil elements behavior, e.g. as is shown on Figure 5, the main part of cesium is released during the first 13 hours of electrolysis (almost 65 %); the remaining cesium is then released only slowly.
- In the industrial scale, the exchanges of electrolyte can suppress the precipitation of major soil elements in the cathodic part of the system. In addition the exchanges enable a batch-wise treatment of the electrolyte – separation of radionuclides (^{137}Cs) and e.g. heavy or toxic elements in a systems, where the continuous treatment may not be possible.

Conclusions

In the experiments performed, the possibility of electrochemical decontamination of soils was verified. The results have shown, that the almost quantitative removal of cesium from soils contaminated a long time ago is possible in cheap and easy conditions. The efficiency of this process is very high (up to 97%) and can be further optimized.

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