

A New Backfill Material for Repackaging Corroded Waste Drums - 9366

Heidi Sjølin Thomsen and Anne Sørensen
Dansk Dekommissionering
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ABSTRACT

The Waste Management Plant, Danish Decommissioning has developed a new backfill material for repackaging corroded waste drums. The drums contain, among other things, strongly corroding salts and varying radionuclides mixed and solidified with bitumen. The following criteria were set for the development of the backfill material:

- The backfill material must be able to absorb water and steam without any substantial swelling
- The material must be able to ensure a high pH in the considered environment in order to moderate any further corrosion of the waste items and to expand the lifetime of the new waste containers.
- The material must be able to retain selected radionuclides.
- The material must allow gas from the corroding units to escape.
- The material must allow for a possible increase in volume of the corroding units.
- The material must have a low angle of subsidence in order to easily fill up the space between waste items when being poured into a container.
- Furthermore it is considered an advantage if the material can be produced from well known, relatively cheap, and easily accessible materials.

The newly developed backfill material consists of mm-sized carbonate balls covered with concrete. The preparation, selected physical properties and the results of experiments investigating the new materials ability to maintain selected radionuclides are reported.

INTRODUCTION

For the repackaging of about 100 corroded drums containing historical waste the Waste Management Plant, Danish Decommissioning has developed a new backfill material. The material was developed in order to address a number of issues arising from current problems in the storage of the corroded drums. This paper presents some preliminary results on the characterization of the new backfill material.

BACKGROUND

Concentrate from the Waste Management Plant's distillation facility traditionally has been poured into 210 l concrete lined steel barrels and mixed with bitumen. In the seventies the barrels were stored in storages consisting of uninsulated concrete rings stacked on top of each other (Figure 1). The concrete 'tower' rings were covered by a roof, but humid air was able to enter the storage. The storage method combined with a content of strongly corroding salts in the drums resulted in corrosion of the steel drums.



Fig. 1 Storages consisting of stacked concrete rings. The storages contained concrete-lined steel drums filled with a mixture of concentrate from the distillation facility and bitumen.

In the mid nineties the 210 l drums were repackaged into new 280 l drums with a reinforced plastic membrane between the old and the new drums in an attempt to prevent further corrosion. However, in spite of these efforts, the repackaged drums are now corroded and are due to be repackaged in a way suited for long-term storage. For this purpose a new backfill material has been developed.

DESIRED PHYSICAL PROPERTIES FOR THE NEW BACKFILL MATERIAL

In order to deal with the specific problems related to the corroded steel drums a number of criteria were set for the wanted backfill material:

- The backfill material must be able to absorb water and steam without any substantial swelling
- The material must be able to ensure a high pH in the considered environment in order to moderate any further corrosion of the waste items and to expand the lifetime of the new waste containers.
- The material must be able to retain selected radionuclides.
- The material must allow gas from the corroding units to escape.
- The material must allow for a possible increase in volume of the corroding units.
- The material must have a low angle of subsidence in order to easily fill up the space between waste items when being poured into a container.
- Furthermore it is considered an advantage can be produced from well known, relatively cheap, and easily accessible materials.

Crushed concrete was considered as a possible candidate for backfill material, and an experiment was carried out in which the concrete rings from the circular storages mentioned above were used as raw material for crushing. The concrete rings were crushed into a particle size of about 4 cm but the resulting material contained large amounts of sand and fine dust as well. The material consisted of angular, irregular particles resulting in a high angle of subsidence. The crushing process turned out to be difficult to control and the experiments were abandoned.

Other experiments have been carried out attempting to produce backfill material consisting of granules of various materials mixed with cement [1], but the products turned out difficult and expensive to produce.

Instead it was decided to develop a material consisting of cement-coated carbonate balls for the desired backfill purposes. The ball-shaped carbonate acts as 'seeds' for the shaping of the final product, ensures a high pH value and furthermore acts as a 'sponge' when the final product is exposed to moisture. The cement adds capacity for the retention of radionuclides and pH- buffer-capacity. In the following the preparation and testing of the selected material is described.

PREPARATION OF THE BACKFILL MATERIAL

The preparation process for the backfill material is quite simple: A known amount of mm-sized carbonate balls is mixed with water while stirring. When the mixture is even cement is added. The mixture is stirred for about 3.5 hours. Finally the backfill is dried for about two weeks.

Table I shows the relative amounts of carbonate, cement and water used. The water-cement (w/c) ratio of this most successful mixture is 0.4. During the preparation-experiments it was observed that the order of mixing affects the quality and homogeneity of the product. The best result is achieved when, first, carbonate is mixed with water until all the water is absorbed by the carbonate. Secondly the cement is added. When the cement is added it draws water from the carbonate and during the process deposits nicely as a shell around the carbonate particles.

Table I. The relative amounts of carbonate, water and cement used for the preparation of the backfill material.

Carbonate	Water	Cement
100	20	50

The carbonate starting material was delivered as relatively rounded particles which good ability to roll (Dankalk Mineralkridt F12). The cement used was standard Portland cement.

CHARACTERISATION OF THE BACKFILL MATERIAL

The moisture content of the material is measured by weighing a sample before and after drying in a furnace at 80 °C for two days. The free moisture content of newly prepared backfill material is 5-7%. Stored at normal room conditions the humidity can drop to 2-3%.

The particle size of the produced backfill material is determined by passing through a sieve. The particle size distribution is shown in Table II.

Table II. The particle size distribution of the produced backfill material.

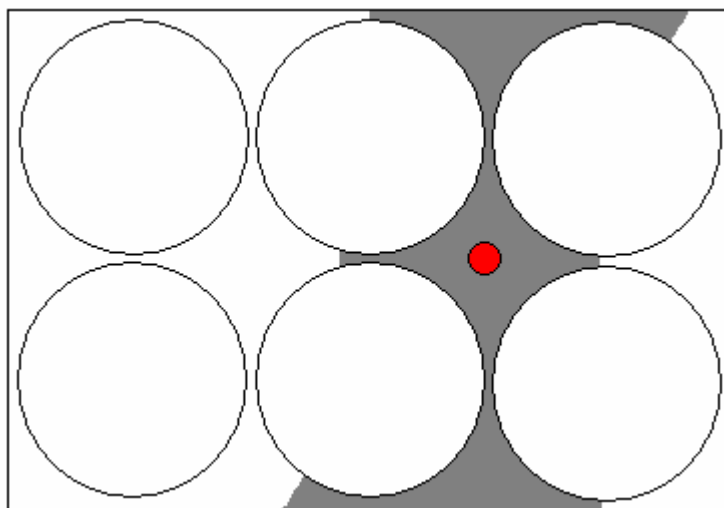
Particle size (mm)	Percentage of the material
0-0.5	10
0.5 – 1.0	26
1.0 – 1.6	22
1.6 – 3.2	17
> 3.2	25

In order to investigate the ability of the material to flow and fill cavities between waste items the angle of subsidence has been measured by pouring the material onto a surface from a height of ca. 50 cm. The angle of subsidence obtained from these experiments was measured to ca. 20°. For comparison the angle of subsidence of natural gravel was measured by the same method to ca. 30°.

Liquids in assumed equilibrium with the backfill material were extracted during the absorption-desorption experiments described below. The liquids had pH values between 9 and 12.

INVESTIGATING THE BACKFILL MATERIAL'S ABILITY TO FLOW

Dummy experiments were carried out in order to describe the new materials ability to flow. For these experiments backfill material was filled into a 100 l drum mounted with an open pipe in the bottom (imagine a large funnel). The drum was held over a ca. 200 cm x150 cmx140 cm steel container loaded with six waste-drums. Figure 2 a) and b) shows the distribution of the backfill material after 2 and 3 loads, respectively, of backfill material had been added to the container. The white areas in Fig. 2b are areas where the backfill material was not able to enter when pouring from one central location only. The drums were placed too close to the container rims for the material to fill the cavities. By moving the filler pipe it was possible to fill the container fully. A sum of 818 kg of backfill material was added to the container. The work of pouring the backfill material into the container took 2 persons for 1 hour, including the work of repeatedly refilling the 100 l 'funnel' barrel. After these investigations it was concluded that the backfill had sufficiently good abilities to flow to ensure a quick and easy repackaging of the waste-drums into the steel containers.



(a)

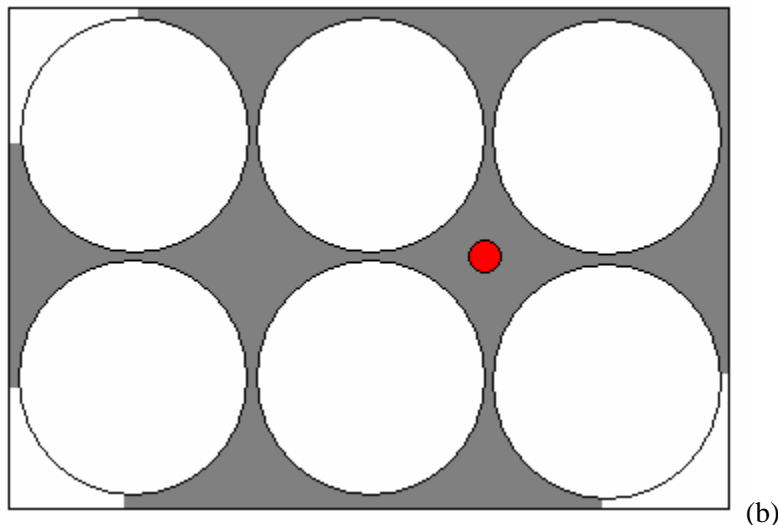


Fig. 2. A steel container with six waste drums seen from above. The dark areas show the extent of the backfill material after pouring two (a) and three (b) batches, respectively, of the material into the container from a height of ca. 140 cm. (Each batch is ca. 100 l, see text). The location of the ‘funnel’ used for pouring is shown as the red dot.

ABSORPTION OF SELECTED NUCLIDES

In order to investigate the ability of the backfill material to retain selected radionuclides a number of absorption-desorption experiments was planned.

The first series of experiments addresses the ability of the backfill material to absorb nuclides of Eu and Cs. The results of these experiments are presented here. In later series of experiments the ability to absorb nuclides of Ni, Co and possibly selected actinoids will be investigated.

EXPERIMENTAL PROCEDURES

The experimental procedures are designed to simulate the ability of the backfill material to retain nuclides that may leak from the waste-drums in the case of penetrating rain- or ground water into the waste repository.

Three different experiments have been carried out. In the first experiment (Exp. 1) 1 a 0,001M NaCl solution was added to the backfill material in order to simulate penetrating rainwater. After two hours the free amount of the NaCl solution was removed from the backfill. The backfill was now allowed to absorb a mixture of a 0,002 M Na solution and a ca. 4800 Bq/ml ¹⁵²-Eu tracer for two hours to obtain an assumed equilibrium between solids and liquid. Following the absorption a sample of the liquid was extracted. The absorption was followed by three desorptions in each of which the backfill material was added a 0,001M Na solution and let to equilibrate for two hours. After each desorption the free liquid was extracted. After the absorption and each of the three desorptions the activity of the liquid was measured and the activity remaining in the backfill material calculated.

The experiment was carried out on three different samples of the backfill material (run#1, #2 and #3) in order to confirm the reproducibility of the experiment.

Experiment 2 (Exp. 2) addresses the backfill materials ability to absorb Cs. The experiment was carried out using the same procedure as for Exp. 1, except that ¹⁵²-Eu tracer was replaced with a ¹³⁴-Cs tracer.

In the third experiment (Exp. 3) the added NaCl solutions (Exp. 1 and 2) were replaced with real concentrate from the Waste Management Plants distillation facility. This was done in order to, as closely as possible, simulate the event that penetrating water will wash out the concentrate into the backfill material. By all other means the experiment was carried out following the same procedures as above.

The experimental solutions and procedures are summed up in Table III.

Table III. The experimental solutions and procedures (Exp.1, 2 and 3)

<p>Exp. 1 The following solutions were used: A) NaCl, 0.001 M B) Eu-152 ~4842 Bq/ml C)NaCl 0.002 M</p> <p>Procedure:</p> <ul style="list-style-type: none">▪ Ca 15 g of backfill material is added to NUNC beaker.▪ First the backfill material is saturated with sodium by shaking for two hours with 20 ml solution A▪ Spin the NUNC beaker and sample the liquid.▪ Add 10 g of C and 10 g of B. Shake for 2 hours to obtain an assumed equilibrium.▪ Spin and sample the liquid. (Absorption).▪ Add as much A as the liquid just sampled above. Shake for two hours. Spin and sample the liquid. (1st desorption).▪ Repeat until liquids have sampled from four desorptions.▪ Analyze the liquids using gamma spectrometry. Calculate the specific activities of liquids and solids (Bq/g).
<p>Exp. 2 The following solutions were used: A) NaCl, 0.001 M B) 134-Cs ~968.88 Bq/ml C)NaCl 0.002 M</p> <p>Procedure: Same procedure as above.</p>
<p>Exp. 3 The following solutions were used: A1) Concentrate from the distillation facility B) Eu-152 ~4800 Bq/ml</p> <p>Procedure: Same procedure as above, with the exception that A1 replaces A and C in the description above.</p>

EXPERIMENTAL RESULTS

The experimental results of Exp.1, 2 and 3 are plotted in the figures 2, 3 and 4, respectively. Figure 2 shows the specific activities of 152-Eu in the solid phases versus the specific activities of 152-Eu in the liquid phases. As can be seen from the figure the specific activity of 152-Eu in the solid phase varies little

with varying liquid composition. This suggests that the absorption of 152-Eu in the backfill material is close to an irreversible sorption.

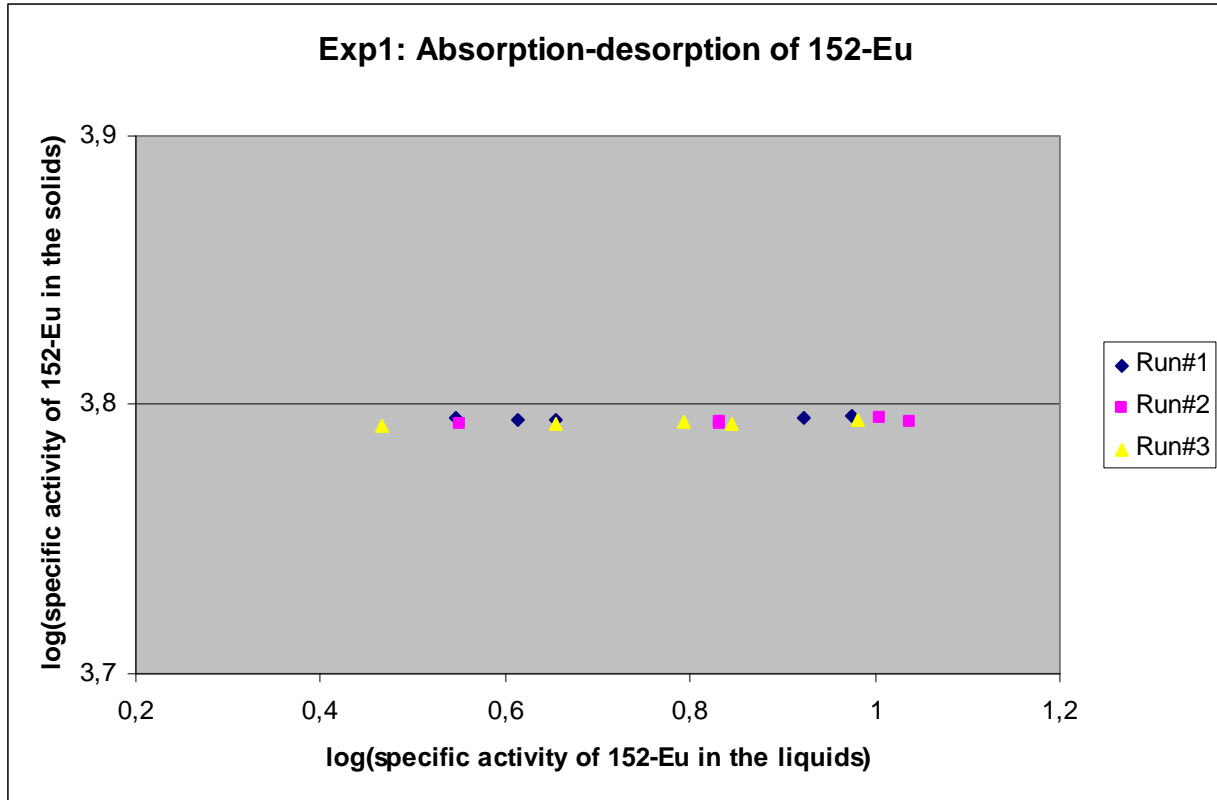


Fig. 2 The specific activity of 152-Eu in the solids plotted versus the specific activity of 152-Eu in the liquids for Exp. 1.

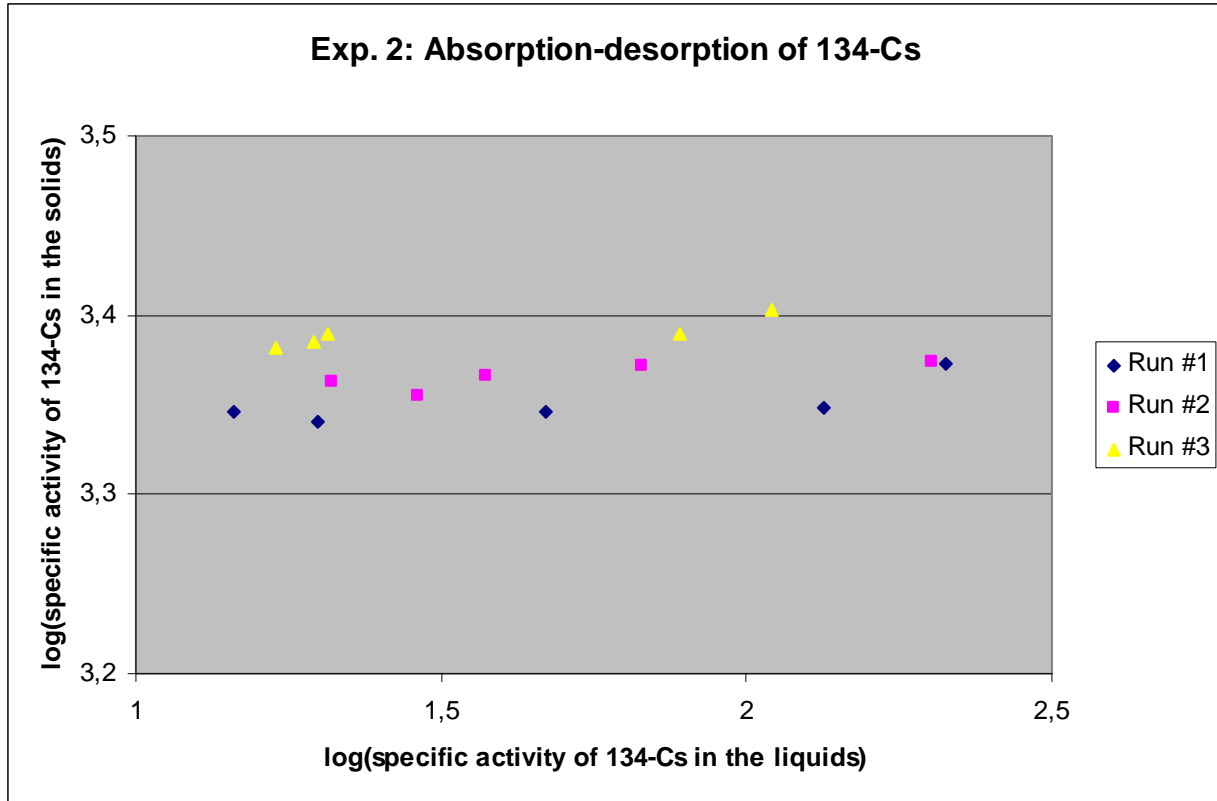


Fig. 3. The specific activity of ¹³⁴Cs in the solids plotted versus the specific activity of ¹³⁴Cs in the liquids for Exp. 2.

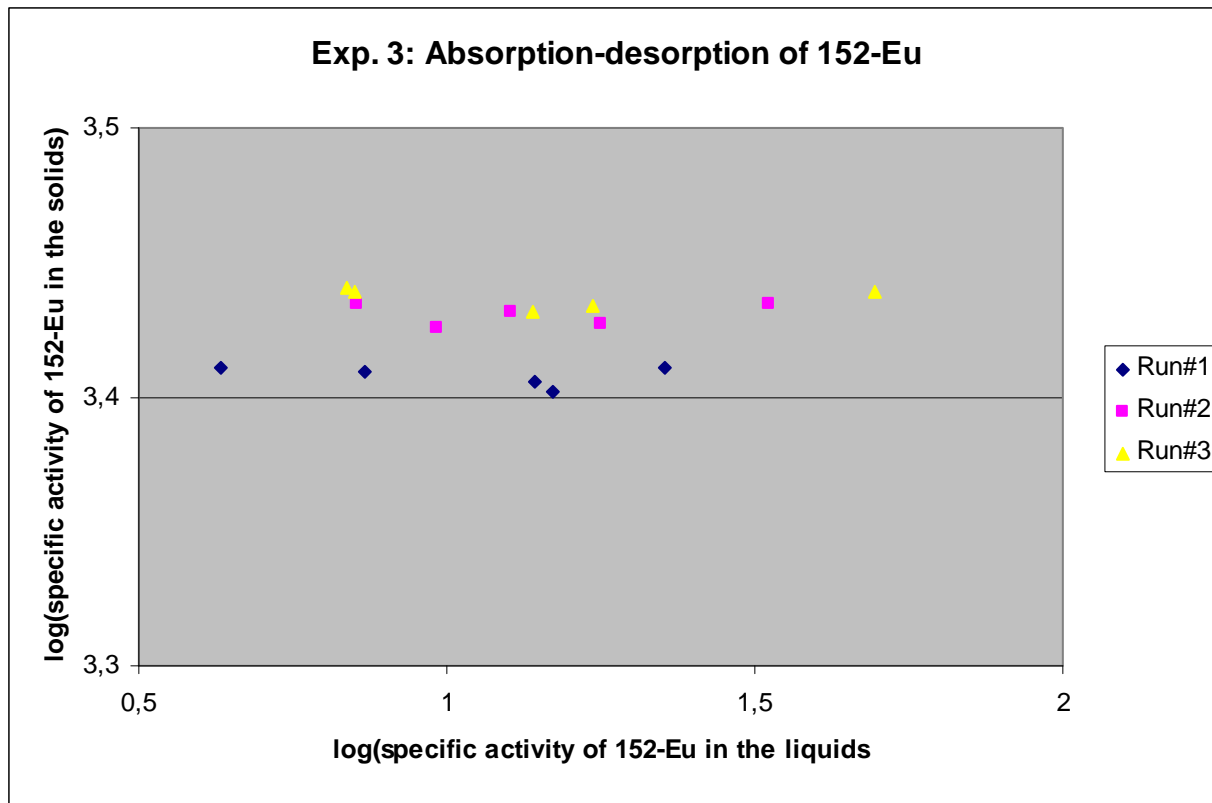


Fig. 4. The specific activity of 152-Eu in the solids plotted versus the specific activity of 152-Eu in the liquids for Exp. 3 where ‘artificial’ NaCl solutions are replaced with ‘real’ concentrate from the distillation facility.

Figure 3 shows the activities of 134-Cs in the solid phases versus the activities of 134-Cs in the liquid phases for Exp. 2 where the absorption-desorption of Cs in the backfill material is addressed. Like in Exp. 1 the activity of 134-Cs in the solid phase varies little with varying liquid composition, again suggesting that the absorption of 134-Cs in the backfill material is close to an irreversible sorption.

Figure 4 shows the activities of 152-Eu in the solid phases versus the activities of 152-Eu in the liquid phases for Exp. 3 where ‘real’ concentrate from the distillation facility replaces the simulated rain-water used in Exp. 1. As in Exp. 1 the activity of 152-Eu in the solid phase varies little with varying liquid composition in Exp. 3, suggesting that the absorption of 152-Eu in the backfill material is close to an irreversible sorption.

No swelling of the backfill material was observed when adding liquids during the experiments. However, specific experiments addressing possible volume changes will be carried out later.

CONCLUSIONS

The preliminary investigations of the newly developed backfill material show that the material has indeed a number of the desired characteristics for the needed backfill material. The material has the ability to flow easily and thus make packaging of the waste items quick and easy. No bulk volume increase of the backfill material has been observed during the experiments. This is probably due to a combination of the built-in porosity of the backfill particles combined with the fact that the material consists of separate, rounded grains with space in between. This suggests that a possible volume increase of a potential waste

item corroding may be accommodated by the backfill material. Also, a possible gas release may be accommodated within the backfill material. The composition of the backfill material ensures a high pH in the storage. Absorption-desorption experiments suggest a high capacity for retention of selected radionuclides. Thus the material is very promising as backfill material. Further experiments on the retention on selected radionuclides are planned.

REFERENCES

1. Barrier Performance of cements and concretes in nuclear waste repositories in F.P. Glasser ed. Project report for EU contract F14V-CT96-0030, EUR 19780 En, Knud Brodersen, Risø Contributions pp. 123-183.

ACKNOWLEDGMENTS

Knud Brodersen, former head of the Waste Management Plant, initiated the development of the new backfill material.

Kenn Skjørringe and Katja Rosschou. are greatly acknowledged for carrying out the experiments.