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Immobilization of natural radionuclides as a solution for large volume wastes from Non-Nuclear industries

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IMMOBILIZATION OF NATURAL RADIONUCLIDES AS A SOLUTION FOR LARGE VOLUME WASTES ORIGINATING FROM NON-NUCLEAR INDUSTRIES

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ABSTRACT

The European Commission has recently published a council directive in which the accepted exemption levels of radionuclides are given. These exemption levels for the natural occurring radionuclides are in general lower than in the former directive. As a result of this directive a new type of waste stream in the non-nuclear industry, characterized by its large volumes and its slightly enhanced radioactivity, occur. At this moment hardly any repository is available for this kind of wastes, and much too expensive when present.

A solution for large quantities wastes to be stored in nuclear repositories has been described. Immobilization of the radionuclides in a solidified matrix seems a possibility for storage into alternative storage for nuclear repositories.

Preliminary immobilization tests were studied in conformity with technologies and standard test procedures which are used for the immobilizaton of wastes contaminated with heavy metals. The measured availability of ^{238}U, ^{232}Th and ^{226}Ra were in the range of respectively <0.008-0.066%, <0.005-0.013% and 0.1-1%. With the used gammaspectrometry only tracers of ^{214}Bi, ^{214}Pb,^{212}Pb and ^{40}K were determined in the leachates. The results have demonstrated that the leaching percentages are of the same magnitude compared to the leaching of non-radioactive isotopes of the same element (0.04-0.44%).

INTRODUCTION

Over the last years there has been growing awareness that natural occuring radionuclides can be an important source of external and internal exposure for workers and population. Several industrial processes enhance the concentrations of these nuclides in waste streams which may lead to significant radiation protection problems.

Some of these industries already produce large quantities of waste materials which exceed their national exemption levels. In general, these waste materials have to be stored in repositories for nuclear wastes. These repositories are very expensive and not equipped for the disposal of large quantities. In addition, even if the storage capacity of the repositories will be enlarged, it is still a very expensive disposal treatment for the industries.

The new EC exemption levels for natural radionuclides are more strict compared with the existing national exemption levels. Implementation of these exemption levels in the national legislation of EU member states will therefore result in an enlargement of the waste stream characterized by its large volumes and slightly enhanced radioactivity. Strategies for solutions have to be developed in order to prevent full nuclear waste repositories, high costs for the involved industries or undesired long-term storage on industrial plant sites.

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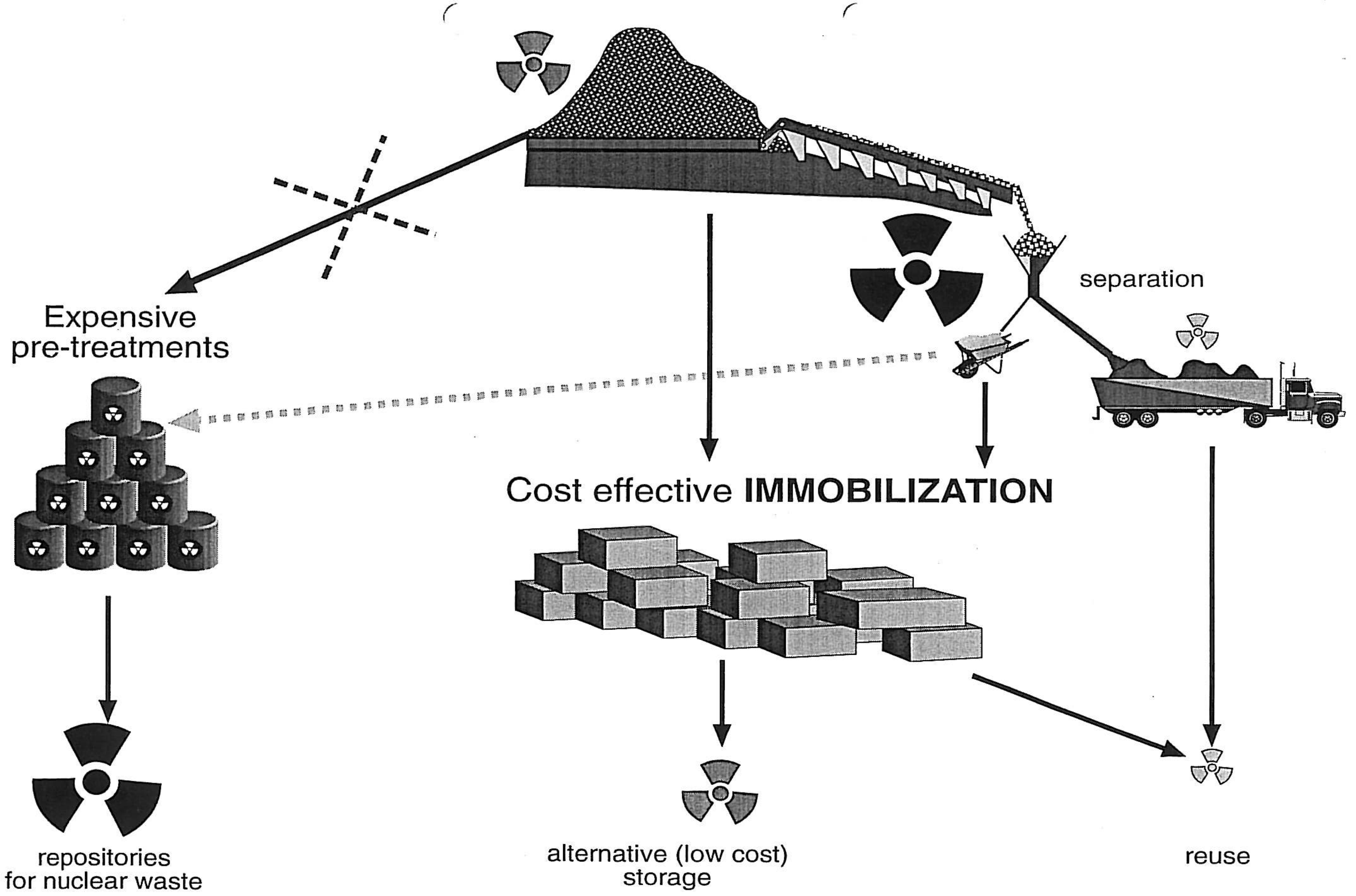

Fig. 1 Strategy for large volumes with slightly enhanced (natural) radioactivity

OPTIONS FOR SOLUTIONS

One possible strategy for solution for these types of waste streams might be the immobilization of the radionuclides in a solid matrix in order to store it into alternative nuclear wastes repositories (Roelofs and Wiegers, 1994). If it is sure that the radionuclides are stabilized in the matrix and do not reach the environment, even re-use of the materials may be considered as an option. The large volume of the waste streams can also be reduced by separation technologies which produce waste with a more increased content of radionuclides and "radionuclide free" waste. The reduced amount of waste with the high content of radionuclides should as next step be immobilized for other lower costs alternative disposal facilities. The remaining volume with a radioactive content below exemption levels can be used for recycling or standard disposal treatment (Fig. 1).

The choice of the treatments of the materials for the most feasible solution depends on the EC and national legislation, the specific properties of the waste materials, the content of the radionuclides and the half-lifes of the involved nuclides. In addition, economical and logistical aspects should also be considered. The treatment approach of the materials based on the radioactive content and half-lifes, is schematized in Fig. 2.

Technologies for the immobilization of radionuclides in non-nuclear wastes are essential for this strategy. Immobilization technologies can be classified in cold-bonded and thermal treatment processes. In the cold-bonded technology a mixture of binders and the material which has to be immobilized, are moulded and hardened. Melting techniques use more complicated installations for the required high temperature and the prevention of all kinds of emissions (CUR, 1995, Roelofs and Wiegers, 1995[a]).

Fig. 2 Treatments and storage of waste materials with enhanced concentrations of radionuclides depending on the activity content and half-lifes.

	Half-life	
content radionuclides	short	long
low (slightly enhanced)	separation and/or immobilization and/or temporary storage on plant-sites	separation and immobilization
high	immobilization	nuclear waste repositories

Nuclear wastes are, in general, immobilized in special (costly) containers before storage in repositories (Ghattas et al., 1992 and Glasser, 1992). In addition, these repositories are very expensive due to the pre-treatment, the particularly long-life time of the wastes and the health physics facilities. After alternative treatment of wastes with enhanced radionuclide content (Fig. 2) special containers will generally be not necessary and the waste can be moulded in desired shape before storage.

CRITERIA AND REQUIREMENTS FOR IMMOBILIZATION

Storage of wastes with enhanced levels of natural radionuclides in alternative less expensive repositories is only reasonable if the radionuclides are chemically or physically stabilized and thus preventing from reaching the environment. In order to test this, it is necessary to have (i) a measurement method available for the determination of the leachability of the radionuclides, and (ii) legislation on the permitted leachability. If the leachability of the radionuclides exceeds the permitted levels, immobilization techniques can be used to reduce the leachability. A test method for the determination of the leachability and the existence of leachability limits are thus essential factors for the development of appropriate immobilization techniques for radionuclides in non-nuclear wastes. Untill now neither test methods nor accepted limits are available. This regulatory framework has yet to be developed and based on the risks for the ecological system and workers.

A regulatory framework and standard test have been developed for non-radioactive inorganic components in soil, stony building material or wastes in the Netherlands and other EU-member states (van der Sloot, 1991). Because of similarities between the inorganic compounds and radionuclides it is likely that the development of a regulatory framework and standard test for radioactive inorganic compounds can follow a similar route. During this stage it is expected that adaption is necessary for radioactive nuclides in waste material.

The allowable limits of leachability of radionuclides (in produced immobilisates) could be based on limits of soil contamination with radionuclides. In standard leachability tests several main factors, like pH and liquid/solid ratio, are set on rather extreme values in order to shorten the test period, and thus only partly simulates reality (Van der Sloot et al. 1992). Therefore, a procedure has to be developed in which the release of different radionuclides in the environment over a long-term period can be simulated. Most natural radionuclides are heavy atoms, or even heavy metals and similarities between the leaching behaviour of heavy metals and radionuclides are thus likely. Some relevant differences between the leaching of radionuclides and heavy metals have, however, to be taken into account. The most important are: (i) the involved concentrations (% by weight) of radionuclides in the leachates can be extremely low, (ii) the ingrowth and decay of radionuclides in the material and leachates result in fluctuations in concentration in material as well as in leachates and (iii) the unknown long-term effect of radiation damage on the leachability. These aspects makes the interpretation of the results of leaching tests more complex compared with "standard" leaching tests.

Legislation on permitted levels of the leachability of inorganic compounds from building materials and waste materials has already been established in the Netherlands. The two most relevant standards of this framework of standards for non-radioactive inorganic compounds are experimentally adjusted to the specific radionuclide situation (NEN 7340). These standards are a test to simulate the availability for leaching of certain components (NEN 7341) and the diffusion test which simulates the leaching behaviour of products and monolithic materials (NEN 7345).

PRELIMINARY EXPERIMENTS

A research programme has been set up as a first step to develop a measurement technique for the determination of the leachability of radionuclides. As a first step the availability of radionuclides from fly ash has been determined in order to test the standard procedure for inorganic compounds. In addition, an availability test was conducted on two types of immobilisates.

MATERIALS AND METHODS

Test of availability

Samples of fly ash with enhanced concentrations of natural radionuclides were exposed in conformity with the Dutch standard for the determination of the availability of inorganic compounds to leaching (NEN 7341). The availability is defined as the quantity of a certain component which can leach out of a material under an aerobic environment and relatively extreme conditions (such as desintegration of the material, full oxidation and/or elimination of the acid-neutralization capacity). In this test very fine-grained material (< 125 μm) was mechanically shaken during 4 hours at pH=7 and at pH=4. pH was adjusted with nitric acid and the liquid/solid (L/S) ratio was between 2-10. The extractions were analysed on radioactive nuclides. This procedure was done with an increased involved volume of the material to prevent radionuclide concentrations in the leachates below detection limits. By measuring the nuclide contents of the material before and after the testing period, the results are controlled with a nuclide balance (Roelofs and Wiegers, 1995[b]).

Test of leachability

Natural sand with high levels of natural radioactivity was pulverized, mixed with cement and additives and moulded. The mix proportions were 75 wt-% of the natural sand and 25 wt-% of (two types of) binder (sample 1 and 2). After a hardening period (> 28 days), the immobilisates were exposed in accordance with the Dutch leachability standard (NEN 7345). The two immobilised samples were kept in destilled water during 64 days. The water was refreshed 8 times and sampled on several times after the start of the experiment. In this experiment the eluates were analyzed on potassium (^{40}K) and nuclides within the uranium and thorium series.

RESULTS

Availability

The availability of uranium in the fly-ash samples varies between <0.008 and 0.066%and for thorium between <0.03 and 0.013%. The radium availability fluctuates between < 0.2 and

Table 1 Availability (%) of the radionuclides ^{238}U,^{232}Th and ^{226}Ra in fly-ash samples

	Availability		
fly-ash sample	^{238}U	^{232}Th	^{226}Ra
1	0.026 ± 0.008	< 0.006	< 0.6
2	< 0.02	< 0.005	0.6 ± 0.3
3	< 0.008	< 0.005	0.3 ± 0.2
4	0.066 ± 0.016	< 0.003	< 0.5
5	0.039 ± 0.005	0.013 ± 0.003	< 0.2
6	< 0.008	0.005 ± 0.002	0.2 ± 0.1

0.6% (Table 1). The measured values for ^{238}U availability (L/S=2-10) are clearly lower than the availability (0.1-1.0%, L/S=100) of the element uranium in fly ashes, as determined by van der Sloot et al. (1985). The availability of radium in our fly-ash samp-les are more or less in the same range as those (0.1-5%) quantified for the chemically similar barium (Van der Sloot et al., 1985, Meij and Krijt,1993).

Preliminary estimates of the radionuclide balances of the fly-ash samples sometimes indicate some missing amounts (5-12%) of radionuclides. At this moment it is not clear whether this is caused by the preliminary methode of the determination of the nuclide balance or by the unexpected processes which lead to losses of radionuclides. Further research is necessary to adjust and validate the test set-up in this respect.

Leaching

The total amounts of radionuclides in the leachates are very low. With gammaspectrometry most nuclides were therefore below the detection limits. The contents of radionuclides which could be measured are shown in Table 2. The interpretation of the results is complicated due to the very low amounts of radionuclides (low reliability) and the mentioned complexity. The determined leaching percentages of the radionuclides and eventually the leached parents are, however, of the same magnitude as has been found for the leachability of non-radioactive uranium (0.01-0.05% van der Sloot 1985). In addition, a consistent difference in leaching of the measured radionuclides from sample 1 and 2 have been found (Table 2). The leaching from sample 2 is twice as high as that from sample 1. This indicates an effect of the type of binder on leaching from test samples.

Table 2 The amount of radionuclides (Bq) in the sand samples and their leachates

nuclide	^{214}Pb (U-serie) (Bq)		^{214}Bi (U-serie) (Bq)		^{212}Pb (Th-serie) (Bq)		^{40}K (Bq)	
sample	1	2	1	2	1	2	1	2
activity in sample	1725	1440	2157	1800	400	333	?	?
activity in leachates after								
step 1 /0.25 d	0.07	0.2	0.2	<0.27	0.07	0.1	<2.3	<3.3
step 2/1,0 d	<0.23	0.1	<0.28	0.19	0.15	0.31	0.5	2.1
step 3/2.25 d	0.09	0.15	0.06	0.31	0.23	0.18	1.2	2.2
step 4/4 d	0.29	0.25	0.62	0.51	0.32	0.86	<2.1	1.7
step 5/ 9 d	<0.23	0.22	<0.29	0.29	<0.21	0.17	<2.0	2.5
step 6/16 d	0.11	0.19	0.13	0.37	0.03	0.25	0.19	0.7
step 7/36 d	<0.3	0.07	<0.3	0.12	<0.22	0.07	<2.6	4.2
step 8/64 d	0.22	<0.29	0.24	<0.32	0.54	0.09	<1.9	0.8
total amount of leached nuclides	0.78 - 1.54	1.18 - 1.47	1.25 - 2.12	1.79 - 2.38	1.34 - 1.77	2.03	1.89 - 12.8	14.2 - 17.5
leaching %	0.04 - 0.09	0.08 - 0.10	0.06 - 0.10	0.1 - 0.13	0.34 - 0.44	0.6	?	?

CONCLUDING REMARKS

To restrict the quantities of radioactive wastes from non-nuclear industries which have to be stored in repositories for nuclear wastes under present legislation, new legislations on leaching of radionuclides has to be developed. Within this regulation the leachability framework for inorganic components can be used as a base for the development of tests for the leachability of radionuclides. Specific factors, however, must be either adjusted or added to this framework.

Preliminary results showed that most concentrations of the radionuclides in the leachates were below or just slightly above the detection limits of the used method. However, these low concentrations does not necessarily indicate that there are no risks involved with this rate of leaching. In case that the leachates rate exceeds the risk limits, the detection limit has to be lowered. This could be lowered by either using other detection methods and/or adaptations of the procedure.

From the nuclides concentrations which could be determined it can be concluded that:

* The availability and leachability of the radionuclides are of the same magnitude as comparable non-radioactive elements. This indicates that the used method, though altered, gives comparable results as the standard method for inorganic compounds;
* some differences have been found between two cold-bonded immobilization types, which suggest that immobilization can be used to decrease the leachibility of radionuclides.

A solution for large waste volumes with enhanced radionuclides concentrations can be stabilization of these nuclides in solid matrix and storage in alternatives for nuclear repositories. For this approach a legislative and regulatory system is required. Furthermore, methods for the determination of radionuclides in leachants have to be optimized. The progress of immbilization techniques provides in a protection of the environment against the uncontrolled dispersion of radionuclides an a cost-effective solution for the non-nuclear industries dealing with radioactive waste.

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