LONG-TERM BEHAVIOR OF BITUMINIZED WASTE

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ABSTRACT

The long-term properties of bituminized ion exchange resins were studied in a repository environment with access of water equilibrated with concrete. In these circumstances the most important properties are related to the interactions of bituminized waste with the surrounding barriers. The most important phenomena are water uptake due to rehydration of the resins and subsequent swelling of the product.

BACKGROUND

Bitumen has been used in the Nordic countries for the solidification of radioactive waste since the late 1960s. The first bituminization plant was installed at the Risø National Laboratory (DK) to treat evaporator concentrates from the research laboratories. At nuclear power stations, bituminization plants have been installed in Barsebäck and Forsmark (S), and at Olkiluoto (SF), all of which are BWRs.

In the Nordic countries bituminization is used only to solidify wet wastes, i.e. sludges from precipitation or evaporation, ion exchange resins and filter materials. At the BWR power reactors almost all the wet wastes are ion exchange resins and filter materials.

Disposal facilities for bituminized wastes are now under construction or being planned in Sweden and Finland. In Denmark various conceptional designs of disposal facilities have been made. In all the concepts the safety of the repository is based on the proper performance of several barriers acting as a hindrance to the transport of radionuclides to the biosphere.

Joint Nordic studies concerning the compatibility of cement and bitumen with ion exchange resins have been performed since 1974[1,2,3].

The main purpose of the present project (AVF-2) has been to identify the factors of importance for the long- term behaviour of bituminized wastes and to collect and develop knowledge of these factors. The final report summarizing the results obtained in the AVF-2 project and data available from related work conducted in the Nordic countries is now available[4].

GENERAL ASPECTS OF THE LONG-TERM BEHAVIOR OF BITUMINIZED WASTES

Many of the earlier studies on conditioned radioactive waste concentrated on its leaching properties. It is now becoming more and more obvious, however, that the properties of conditioned waste, i.e. the waste form, have to be related to the properties of the repository. The long-term behavior of radioactive waste can only be assessed when the waste form is considered as a part of the repository itself, and especially of its barrier system.

The behavior of solidified waste is basically dependent on the geological conditions of the repository. A feature common to all the disposal concepts in the Nordic countries is that the transport of radionuclides to the biosphere is prevented by the use of a number of barriers, both engineered and natural.

At the outset of the AVF-2 project it was decided to limit the study to concern the present Finnish and Swedish concepts for final disposal of reactor wastes. These concepts include a limited access of groundwater into the repository, and as the main construction material of the silo is concrete, the groundwater will become equilibrated with cement.

To forecast the development of interactions between waste and other barriers, knowledge of the long-term behavior of the waste form is needed. What remains to be done is to define the properties and mechanisms that are actually involved. The knowledge most vitally needed was found to be the interactions that might possibly reduce the diffusional resistance of the surrounding concrete and clay barriers. Three kinds of such adverse interactions have been identified in the present study:

- chemical effects
- *microbial* effects, leading to gas evolution, and
- mechanical effects, such as swelling of dehydrated ion exchange resins.

The deterioration of barriers as a result of chemical interactions with bituminized waste did not seem to be a major problem, and anaerobic microbial attack on a monolithic bitumen block takes place extremely slowly.

When ion exchange resins are solidified into a bitumen matrix, the extent of the dehydration depends on the process conditions, especially the time and the temperature during the drying and mixing of the resins with bitumen. Different solidification processes might give very different dehydration results.

Dehydrated ion exchange resins swell when they come into contact with water. Expansions of up to about three times the dry volume have been reported for resins from reactor waste [5,6]. When water is absorbed at a constant volume, the forces acting on surrounding media correspond to pressures of up to at least 40 MPa [7]. Clearly, such swelling must not be allowed to occur in such a way that it leads to unacceptable disturbance of the barrier system. Preventive actions may be applied, such as the use of the empty space around waste in which swelling is likely. Another possibility is to restrict the resin to bitumen ratio of the waste.

If the barriers remain intact for a few hundred years, the radiological consequences of swelling may well be acceptable, even if the barrier system is later destroyed by swelling. This shows the importance of considering the swelling mechanisms and the rate of swelling when assessing the performance of a repository.

INITIAL PROPERTIES OF BITUMINIZED WASTES

Physically, bitumens are solid or semi-solid substances at room temperature and can easily be liquidized by heating. Bitumens are resistant, but not totally impermeable to water attack. Experiments show that the solubility of water in Mexphalte 40/50 at 25^0C is in the order of $(5\pm2)x10^{-3}$ g water/g bitumen. The solubility of about 0.5 % water in pure bitumen may seem surprisingly high but it is in reasonable agreement with values found elsewhere, Ref. 6. Experiments have revealed a diffusion coefficient for the water in bitumen of $2x10^{-12}$ m^2/s at 20^0C, Ref.6.

During bituminization the ion exchangers are thermally treated to some extent, depending on the method. The cation exchanger is resistant to moderate heat treatment and its water uptake remains reversible after drying and heat treatment periods. When mild heat-treatment is used, the anion exchanger swells even more than to the original moist volume, but it is thermally unstable and its hydrophilic nature is destroyed when high temperatures and prolonged heat-treatment are used.

Figure 1, Ref.4, gives the maximum swelling of unused granular resins after various periods of heat treatment. It can be seen that cation exchange resin is not markedly influenced by heat-treatment up to 160^0C, while there is a significant effect on the anion resins already at about 100^0C.

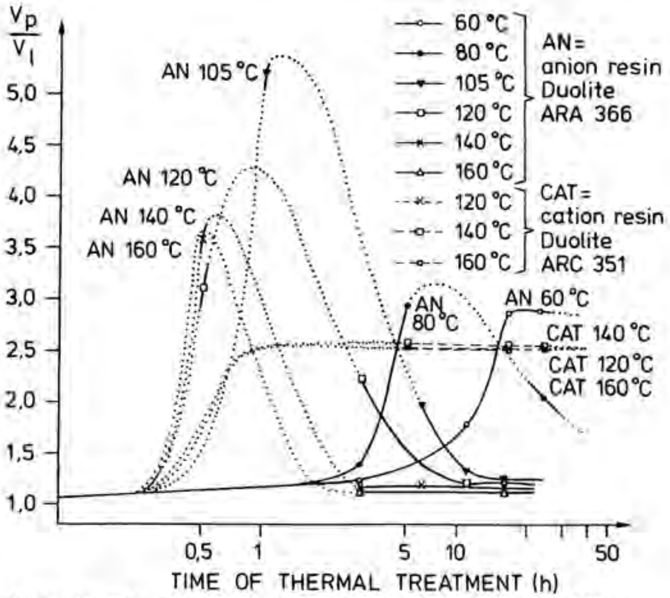

Fig. 1. The effect of heat treatment on the swelling of ion exhange resins. V_l: volume of heat-treated dry resin, V_p: volume of heat-treated resin after swelling in water[4].

Ideally, the result of the solidification process should be a monolith of a uniform material in which each ion exchange resin bead is surrounded by a layer of bitumen, the layer thickness depending on the waste loading, particle diameter, and the densities of bitumen and waste. Assuming tetrahedric close packing the thickness of the layer varies from 0.4xd to 0.15xd, where d is the waste particle diameter when the resin/bitumen ratio varies between 30% and 50%. This indicates a layer thickness of approximately 0.2 mm in a mixture containing 40% dry resin, (Fig. 2).

The waste particles in real bituminized waste are neither of uniform size nor spherical (except for grain-formed ion exchange resins), nor arranged in a regular lattice corresponding to theoretical close packing. This means that considerable variations must be expected in the distances between individual particles. There will also always be inhomogeneities in the product on account of segregation, sedimentation and swelling. Experiments in Sweden and Finland have shown that for bead resins the resin content increases towards the bottom of a drum. Moreover, some results (Olkiluoto BWR) indicate that the drums contain mainly anion resins in the top half and cation resins in the bottom half of the drum. Experiments with powdered resins show homogeneous products [4].

One way of monitoring any degradation of the product could be to characterize the inner structure of the bituminized wastes and to measure the water content of the product. This has been done for samples produced on laboratory scale at IFE. The water content of newly cast products varies between 1 and 10 %. After the products had been stored under humid conditions or immersed in water, their water content had risen to 3-25% [4]. This increase in water content, with its corresponding swelling, might lead to lead to cracks and pores throughout the product, thus expediting further water uptake and leaching of radionuclides.

To evaluate such cracking, a technique has been developed whereby the fracture surfaces of bituminized waste are examined by optical and sweep electron microscopy. However, it is not possible to see wheth-

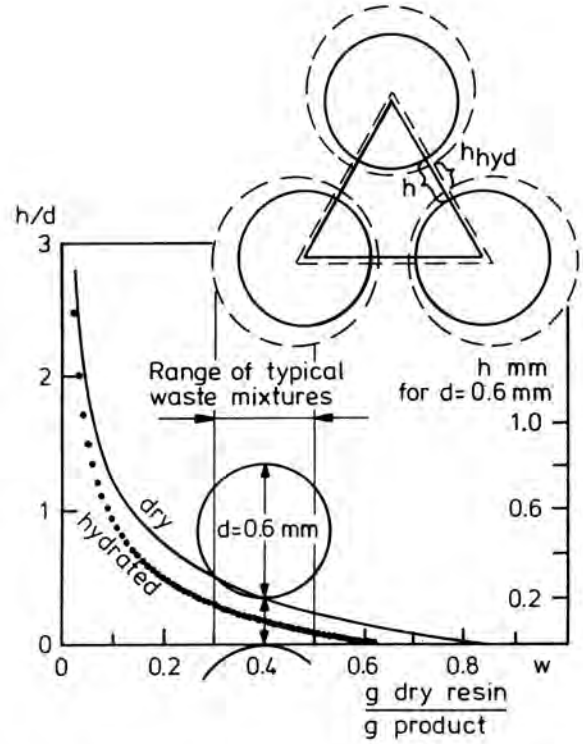

Fig. 2. Thickness of the bitumen layers between spherical resin particles of uniform size and distributed regularly in the corners of tetrahedric unit cells[8]. It is assumed, that the relative density of the IX-resin compared to bitumen is 1.5 and the volumetric swelling for IX-resin is 2.43 when the dried resin is allowed to absorb water.

er the cracks and pores detected are formed during fracturing of the product or not. Further investigations are needed.

Fig. 3. Mixed bed bead resin to bitumen ratio = 50:50 w%. Stored dry in a refrigerator for ca 4 years. Water content 4.9%. SEM 35x. The pictures show the preferential orientation of the cracks from bead to bead. Also the diameter of the relatively dry beads can be measured fairly accurately.

Figures 3 and 4, magnification 35x, show the swelling of ion exchange beads. Both pictures are of a specimen containing 50 %w mixed bed bead resins and 50 %w bitumen. The specimen in Fig. 3 has been stored dry after leaching, while the specimen in Fig. 4 has been stored in water. The relative volume expansion coefficient can be estimated, from these pictures, to be about 3x.

Generally, leached species of bituminzed ion exchange resin do show an extensive network of cracks and pores. The dimensions of the cracks are, lengths from 0.5 mm to above 5 mm and widths from 0.01 to about 0.04 mm. Pore diameters range from 0.1 mm to 1 mm with an estimated mean diameter of ca 0.4 mm.

Pictures of freshly cast specimens of the same composition do not exhibit any network of cracks or pores.

Fig. 4. A similar sample as in Fig. 3, but stored in contact with water. Water content 24.2%. Note the swelling of the beads and also the pores formed.

THE EFFECT OF DRY STORAGE

When bituminized wastes are stored dry for prolonged periods, various changes will occur in the properties of the materials. Some embrittlement must be expected, possibly together with stress generating phenomena such as bubble formation due to radiation damage. This may influence the behavior of the system if the packages are exposed to water at some later stage.

The viscosity of bitumen increases continuously with decreasing temperature, for example from values of about 10 Pa•sec at 100°C to 10^7 Pa•sec at 20°C [9]. Below 0°C, bitumen and bituminized wastes are brittle and likely to be cracked by accidental mechanical impact. Such cracks may heal again if the units containing the cracked material are reheated to room temperature. At such temperatures the freshly prepared materials are highly shock resistant, as demonstrated in drop tests[10].

It has also been shown that pure bitumen, like other polymers, will slowly become stiffer over a period of some months after casting. The effect is thought to be due to increased ordering of the large organic molecules. The change in viscosity at 20°C has been monitored for one year in samples of pure bitumen, bituminized ion exchange resin and bituminized sodium nitrate. Typically, the viscosity increased by a factor of 1.5 to 2. This is considerably less than the five to tenfold increase in viscosity obtained by introducing the waste particles into the pure bitumen.

The density variations in bitumen and bituminized wastes in (almost) dry storage were also monitored. It was found that whereas pure bitumen contracts slowly, 0.05-0.1 % in three months, probably because of the above mentioned ordering mechanism, a faster and larger contraction, ~1 to 2 %, may occur for bitumen containing suspended particles, for example ion exchange resin, various salt crystals or even an unreactive material such as quartz sand [9]. An example of a contraction curve for bituminized ion exchange resin is shown in Fig. 5.

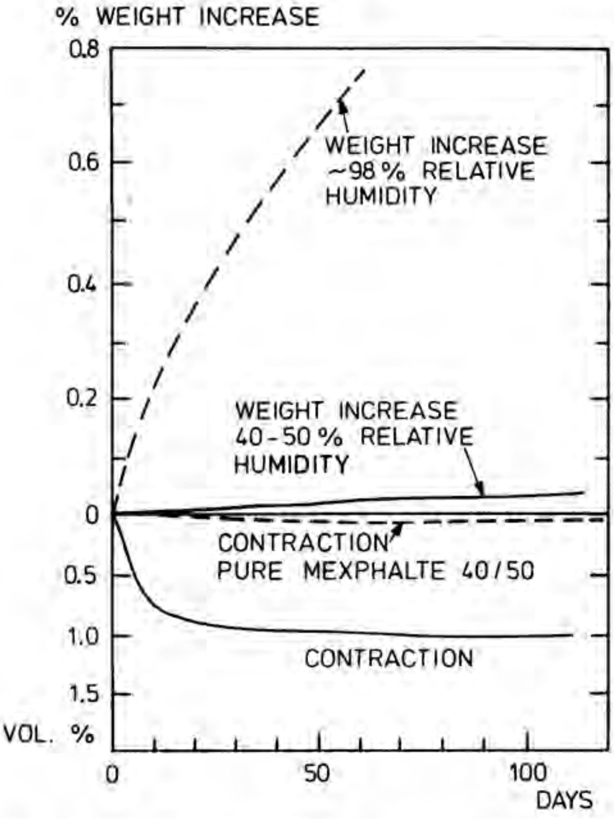

Fig. 5. Volume contraction and weight increase due to water uptake in a sample of dry bituminized cation exchange resin stored in ordinary laboratory air, compared with the weight increase for a similar sample stored in high humidity air, and with typical volume contraction of pure Mexphalte 40/50.
Sample material: 40% IR 120 on Na^+form/60% Mexphalte 40/50
data from Ref. 9,11.

Reviews of the extensive studies of the radiation stability of bituminized wastes are available[11,12]. The mechanisms are thought to be understood, and the experimental results are reasonably consistent. Bituminized ion exchange resins may contain from 4 GBq to 20 TBq/m^3, corresponding to maximum dose rates of up to 4 Gy/h and a maximum absorbed dose of less than 2 MGy (recalculated from Ref. 12). However, most reactor wastes will be exposed to considerably less radiation.

Radiolysis gas with a composition of more than 95% hydrogen is generated at a rate and in an amount proportional to the absorbed radiation dose. The oxygen present in the system is partly fixed in the bitumen and partly converted into CO_x and H_2O. The volume of radiolysis gas is approximately 0.1 l/kGy for a 200 l drum filled with bituminized ion exchange resin.

Another phenomenon that may cause swelling of bituminized waste materials is water uptake from moist air. It was shown early in the Nordic studies that bituminized ion exchange resin with high contents (>60 %) of dry resin swelled spectacularly when standing in ordinary air[1]. Later investigations have shown that water uptake from high humidity air also occurs relatively rapidly for bituminized ion exchange resin at low or moderate waste loading[13]. The rate of water uptake seems to be diffusion controlled with effective diffusion coefficients only slightly lower than for the same materials in direct contact with water. Uptake will probably continue until the vapour pressure in equilibrium with the moistened resin corresponds to the water content in the atmosphere. The associated swelling of the particles is likely to crack the bitumen films and increase the leach rate if the material is later exposed to water. In the example in Fig. 5, the water uptake from high humidity air eventually compensates for the contraction, but measurable swelling cannot be expected for two to three months. Slow water uptake from ordinary air with 40-50 % relative humidity has also been demonstrated for such materials[9].

THE EFFECT OF WATER CONTACT

In an idealized bituminization product each resin particle is surrounded by a bitumen layer. Diffusion of water into the product is caused by the gradient of water activity. This activity is greatest at the water-bitumen interface and is considerably lower in the interior of a waste package. If the ratio of waste to bitumen is high, clusters of resin particles will probably form. Water is diffused rapidly through the ion exchange material, and thus clusters of resin particles may form effective transport pathways of water in the product. In addition, an improperly made product may contain water-filled voids, which serve as direct pathways for additional water penetration.

A simplified model has been utilized when calculating effective diffusion coefficients for water absorption[14] from experimental data:

The transport of water through the heterogeneous mixture of bitumen and partially hydrated resins was assumed to be described by the diffusion equation

$$\frac{\delta C}{\delta t} = D\nabla^2 C \qquad (1)$$

where C is the bulk concentration of water and D a diffusion coefficient $_\rho$ for the composite material. This is an approximation, since in reality D is a function of C.

Using the simplest possible geometry, a one dimensional semi-infinite medium, the flow at the boundary surface is

$$J_o = C_o \left(\frac{D}{\pi t}\right)^{1/2} \qquad (2)$$

where C_o is the saturation concentration of water in the surface layer.

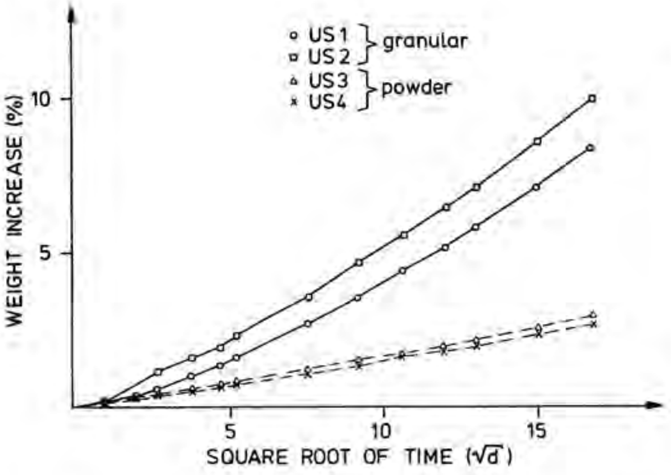

Fig. 6. Weight increase caused by water uptake during a leach test, Ref. 4. The samples contain mixed bed powdered or granular resin of 33 or 50 weight-%, respectively.

The accumulated amount of water Q per unit surface area is

$$Q = 2C_0 \left(\frac{Dt}{\pi}\right)^{1/2} \qquad (3)$$

In fact, the weight increase in the samples during leaching seems to be governed by a diffusion-like mechanism giving relatively straight lines when plotted as a function of the square root of time of Fig. 6. Thus an approximate diffusion coefficient can be obtained from the experimental data according to Eq. (3). If the material contains bubbles or voids, the surface of the material is not well defined, and the rate of water absorbtion is higher and cannot be fitted with a linear square root of time dependency.

Figure 7 presents some diffusion coefficients measured as a function of the weight fraction of a granular ion exchanger. Minimum and maximum values together with the mean value are shown. Several experimental results have been available for the same weight fraction.

The bituminization product can be described as a composite material, where the dispersed resin phase has much higher diffusivity than the continuous bitumen phase. The diffusion properties of such heterogenic media can be modelled in numerous ways[16]. When phase equilibria are taken into account, the diffusion coefficient of the composite material as a function of fraction dispersed phase might well have a minimum just as can be expected from the experimental data in Fig. 7 [17]. This behavior can most simply be explained by retention of water due to sorption in the resin phase. It should be noted, however, that since the saturation concentration is proportional to the resin content, the flow of water into the composite steadily increases with the fraction of dispersed phase of Eq. (2).

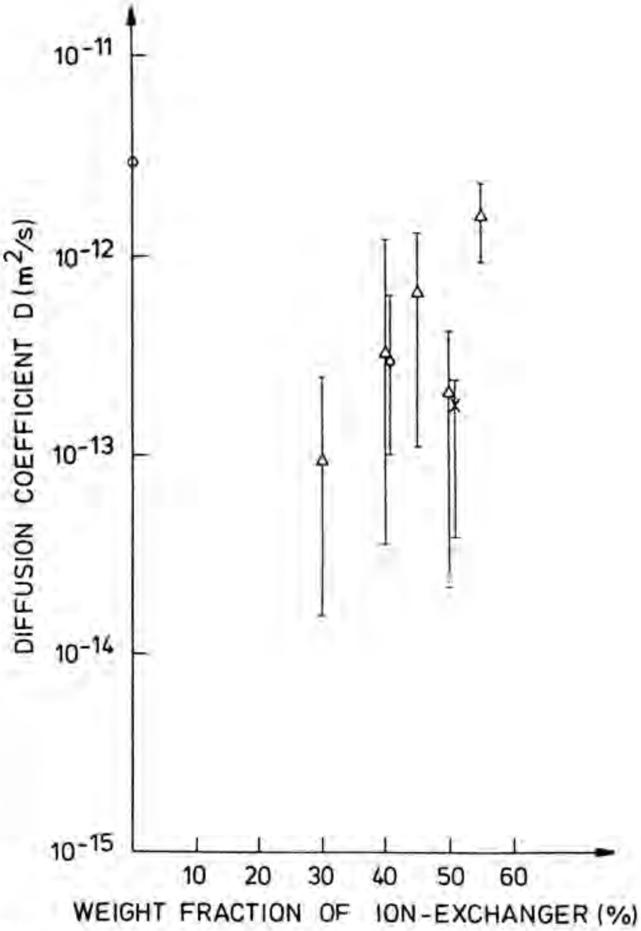

Fig. 7. Diffusion coefficients of water for bituminized granular ion-exchange resin.
Δ data from Aittola and Kleveland[14]
O data from Brodersen et al[6]
x data from Valkiainen and Uotila[15]

If the swelling of the bituminized ion exchange resin is restricted but the uptake of water is possible, considerable pressure may develop. Measurement of the swelling pressures for bituminized ion exchange resins leads to long follow-up periods. For rough evaluations of the pressure-volume characteristics, resins were mixed with inert powder to fill the voids between the grains, Table I.

TABLE I

Swelling pressures obtained with dried Duolite resins mixed with inert powder filling voids between the grains. ΔV is the volume increase allowed for the sample[4].

Sample	Drying	Swelling pressure, MPa ΔV=0%	ΔV=10%	ΔV=20%
ARA 366 40% + ARC 351 60% quartz powder 1:4	24h 105°C	31.0	2.5	0.3
ARA 366 67% + ARC 351 33% glass powder 1:0.9	16h 140°C	7.1	0.7	0.3

The use of glass powder cannot totally eliminate the possibility of some free swelling. Therefore the maximal swelling pressure measured could be lower than that which would be obtained with bituminized ion exchange resin.

LEACH TESTS

The influence of the ratios of waste to matrix and their types and qualities on the leachability and swelling of bituminized ion exchange resins has been examined within the framework of several joint Nordic projects[1,2,3].

Mainly granular mixed bed resins representing wastes from the primary reactor water purification system were assayed. An intermediate summary reviews swelling and leach data from prolonged water exposure (up to four years) of some 40 samples with such simulated waste[14].

The AVF-2 experiments concerning the influence of decontamination chemicals[18] were initiated as part of a study on the handling of reactor wastes from irregular or accident conditions. The presence of complexing agents from clean-up operations represents an extreme, but not unrealistic, case of chemical leach enhancement. To gain a better understanding of the mechanisms involved, the effects of different decontamination chemicals (citric acid, ascorbic acid and EDTA) on the leaching of representative waste nuclides (Cs-137 + Sr-85 + Co-60 and inactive Ni, resp.) from granular (strong OH-H) anion and cation exchangers were examined separately. Corresponding resin-free products served as types of reference samples. The ion exchange concentration (referred to the weight of dry resin) was 50% in all samples.

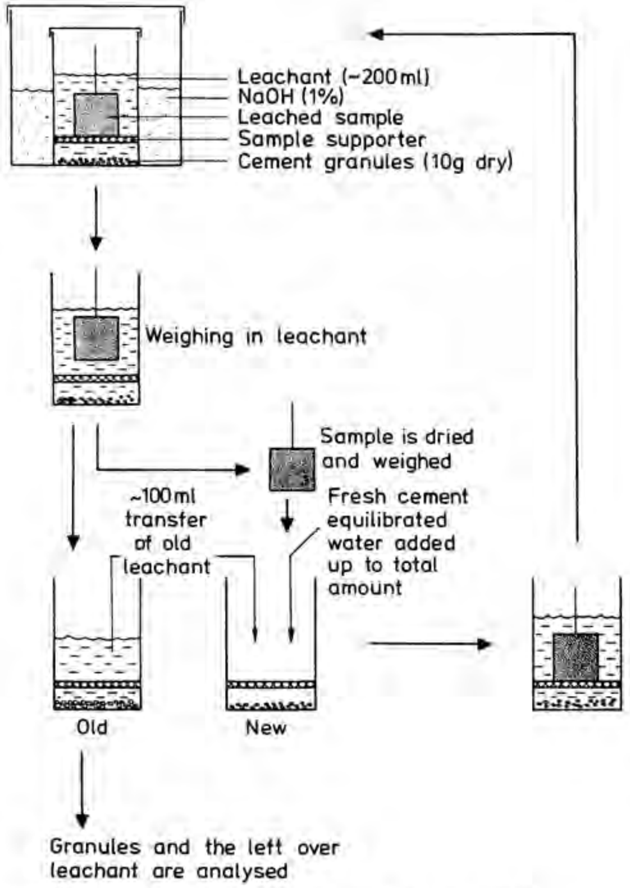

Fig. 8. A scheme featuring leaching and water uptake (weight increase and swelling) measurements for samples stored in cement equilibrated water[19].

Samples were dewatered, bituminized and cast with a laboratory scale "Werner & Pfleiderer LABOR LUK-4-X/A-2" mixing-kneading machine. Typical mixing temperatures were around 130°C. Leaching and swelling tests were performed both in cement-equilibrated and distilled water. The latter has been discussed in the context of earlier bituminization experiments, Ref. 3,14. The main features of the "cement water test" devised by K. Brodersen[19] are shown in Fig. 8. The distribution of leached nuclides between water and granules gives an indication of their mobility and any further spreading likely. Special precautions are needed to prevent CO_2 absorption from interfering.

The leach rates measured have been in the order of $<10^{-8}$ to 10^{-4} $gcm^{-2}d^{-1}$ for Co, 10^{-6} to 10^{-4} $gcm^{-2}d^{-1}$ for Cs and Sr, and still higher ($\sim 10^{-3}$) in some heterogeneous samples.

The effect of cement water varies for different nuclides and waste compositions. The bulk of the leached Co (50-90%) is immobilized by absorption on the cement granules, Fig. 9, while most Cs remains in the leachant. Sr is more evenly distributed between the two phases. Leaching tends to be much faster in "cement water" than in deionized water and is not delayed as in more dilute leachants. The ratio between the leach rates in the two leachants (R_{cem}/R_{de}) is by no means constant, but has varied between <1 (for resin-free reference samples) and >100 (for Co on anion and mixed bed resins).

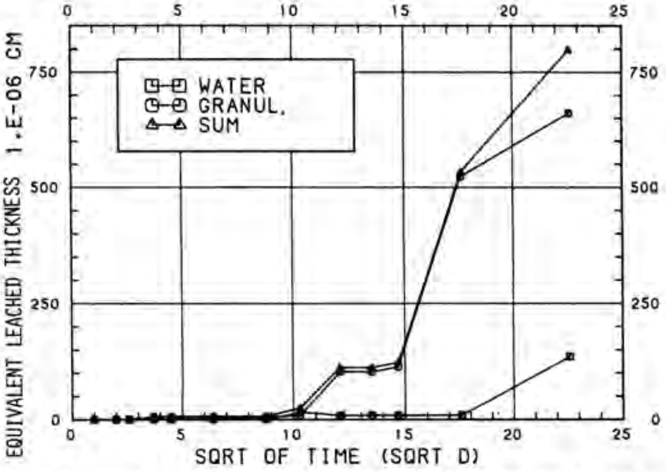

Fig. 9. The equivalent leached thickness of Co-60 in cement-conditioned water from bituminized granular mixed-bed ion exchange resin. Resin:bitumen = 50:50. (See Ref. 4)

The rate of swelling is highest for cation resins, somewhat lower for mixed-bed and significantly lower for anion resins.

CONCLUSIONS

For the Nordic disposal concepts the most important long-term properties of the bituminized wastes are those related to the interactions between the wastes and the surrounding barriers in the repository.

The bulk of the work within the AVF-2 project has been devoted to studies of the water uptake and subsequent swelling of the waste product and the connected question of leaching of radioactivity from the waste product. The following conclusions have been reached:

- the behavior of the waste product depends on the solidification process parameters, such as drying temperature, time and mixing method, and casting conditions;
- the dried resins, if unprotected, will absorb water and swell in contact with water. The maximum swelling depends on the resin type and the heat treatment during the solidification process. If the swelling is prevented, substantial pressure develops;
- the bitumen has a protecting capacity against water uptake. This capacity is dependent on the ratio of waste to bitumen. A simplified model of the water uptake and swelling has been studied. More elaborate models, however, such as those taking into account the interrelation between water transport and swelling, seem to be necessary;
- no physical aging of the bitumen matrix has been identified that will significantly affect the water uptake. If sedimentation of the ion exchange resins took place during casting of the product, however, it might have an important effect on water absorption;
- the leaching is based on water uptake and consequent transport of radionuclides through the hydrated layer of the bituminized product. In analogy with what has been said about water uptake, a simple diffusion model of leaching could be replaced by more elaborate models taking into account not only the factors relevant to water uptake but also water chemistry and the ionic state of the nuclides;

In the context of the AVF-2 study no unacceptable long-term effects have been found caused by bitumen itself, but swelling - or consequences thereof - must be taken into account when disposal of bituminized reactor waste with normal radionuclide content is planned.

ACKNOWLEDGEMENTS

This study is part of the safety program sponsored by NKA, the Nordic Liaison Committee for Atomic Energy, 1981-85. The project has been financed by the Nordic Council of Ministers and the participating national organizations.

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