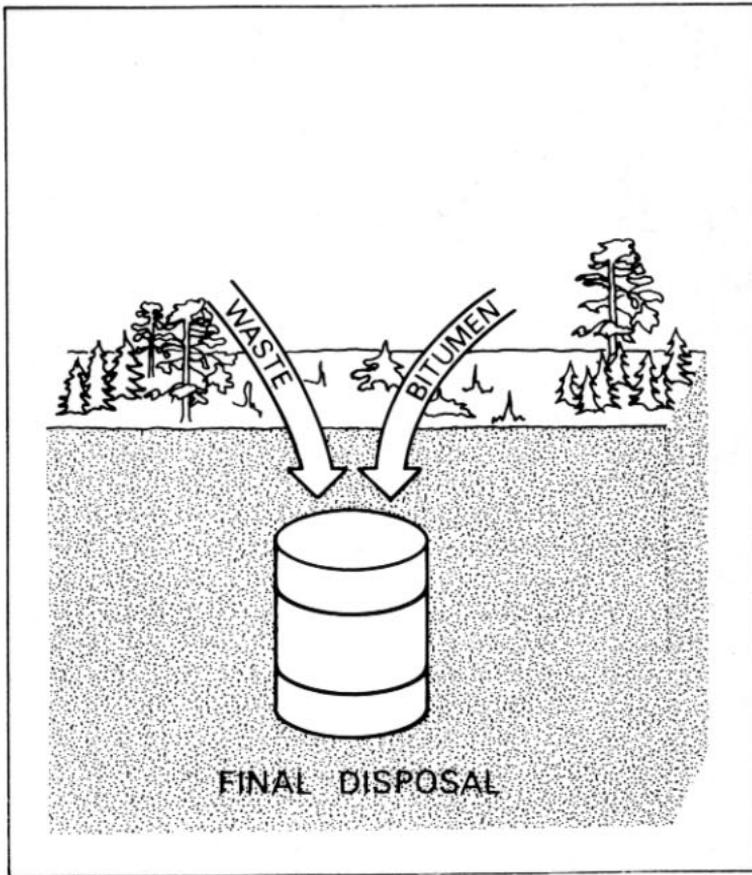


# LONG-TERM PROPERTIES OF BITUMINIZED WASTE PRODUCTS



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atomic energy

# **LONG-TERM PROPERTIES OF BITUMINIZED WASTE PRODUCTS**

SUMMARY REPORT OF THE NORDIC AVF-2 PROJECT

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## ABSTRACT

This study is a survey of the factors of importance for the long term behaviour of bituminized ion exchange resins. Phenomena occurring in bituminized waste products affected by the treatment, storage and disposal are identified. Test methods have been developed for characterizing product properties, which are important for the long-term behaviour.

The long-term properties of bituminized ion-exchange resins are 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.

### Key words

Asphalts - Bitumens - Denmark - Finland - Hydration - Immobilization - Ion-Exchange Materials - Leaching - Norway - Radioactive Waste Disposal - Radioactive Waste Processing - Radioactive Waste Storage - Sweden - Swelling - Underground Disposal

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## SUMMARY

The radioactivity released into process water in nuclear power plants is generally removed by ion exchange resins. These resins are subsequently solidified in concrete or bitumen. Bituminized wastes have been produced for several years in the Nordic countries. The radioactivity content of these products is typically such that the activity will decrease to a safe level within a few hundred years. Such "reactor waste" is intended to be disposed of in underground repositories surrounded by several barriers. For the assessment of performance and safety, knowledge concerning the long term properties of the waste products is required.

A Nordic project (AVF-2), financed in part by the Nordic Council of Ministers has studied this problem. The purpose of the project has been to identify factors of importance for the long-term behaviour of the bituminized wastes that may depend on the solidification process, the interim storage, or the disposal, and to collect and develop an understanding of the processes involved.

The waste products studied are ion exchange resins solidified in bitumen. The repository environment represents a typical Nordic concept which includes the use of concrete as one of the several barriers surrounding the waste units. This creates a chemical environment in equilibrium with concrete around the waste package.

The bituminized waste product consists in principle of waste particles embedded in a continuum of bitumen. The ion exchange resins in most cases become dehydrated in the course of the bituminization process, and the dry particles are surrounded by a protective layer of bitumen. The layer thickness depends on the fraction of resins in bitumen and on the resin particle diameter. The thickness will be approximately 0.2 mm in a mixture containing 40 % dried granular resin.

In practice, however, deviations from an ideal product structure may occur: mixtures may not be homogeneous and pores and cracks may develop. These deviations may be present already from the processing stage, or they can develop during dry storage and the subsequent disposal. During this project a method to study the inner structure of the product has been developed. When this method was applied, no cracks or pores were found in newly cast products, but after subsequent leach tests cracks were observed.

During interim dry storage of waste various changes in the properties of the materials will occur such as embrittlement and gas formation due to radiation effects, settling due to density differences, and swelling due to water uptake from moist air. These may influence the behaviour of the waste if it is exposed to water at some later stage. Some of these changes are described below.

For the large majority of waste packages with an activity content typical for Nordic reactor waste, gas formation due to radiation effects is negligible. For other kinds of waste, if there is an intense radiation field, radiolysis might lead to formation of gases and subsequent swelling of the waste packages.

Many bitumens behave like a viscous liquid at room temperature and above. If there are density differences between bitumen ( $1000 \text{ kg/m}^3$ ) and the embedded waste particles (for example dry cation exchange resin  $\sim 1300 \text{ kg/m}^3$ ) this could in theory lead to settling of the particles when the material is left standing for long periods of time. The effect of settling is primarily a depletion of waste particles in the top layer and an accumulation in the bottom layer of the waste package. Such an accumulation will make the product more permeable to water and increase the water uptake. However, at room temperature or below the settling is too slow to be of any significance during some hundreds of years. On the other hand, settling can be a problem during the casting of the material when the viscosity is lower.

Water uptake from moist air may cause swelling of bituminized waste materials. It was shown earlier in Nordic studies that bituminized ion exchange resin with high contents (above 60 %) of dry resin swelled spectacularly when standing in ordinary air. Later investigations have shown that the presence of humid air also leads to relatively fast water uptake in bituminized ion exchange resin even if the percentage of resins in the bitumen is much lower. The rate of water uptake seems to be diffusion controlled. Uptake will continue until the vapour pressure in equilibrium with the moistened resin equals the water content of the atmosphere.

Contact with water in the repository gives rise to a slow diffusion of water into the waste product. This may lead to different mechanisms affecting the integrity of the product such as swelling and build-up of swelling pressure. This in turn leads to a possible risk of degradation of surrounding barriers such as the concrete and of subsequent leaching of radionuclides and further transport by the groundwater.

The rate of water uptake depends on a number of factors such as the waste/bitumen ratio, particle size, and the homogeneity of the product.

For waste loadings less than 50 % the diffusion coefficient of water is low. However, the changes in the diffusion coefficient due to alterations in the product with time are possible.

Swelling is, in addition to the rate of water uptake, also dependent on such factors as the dimensions of the waste package, the waste loading and the volume ratio between dry and completely hydrated resin particles. The latter again depends on the solidification process parameters such as drying temperature, time and mixing method. The unprotected dry resins will absorb water and swell in contact with water. The maximum swelling has

been shown to be between 20 and 210 % depending on the resin type and the heat treatment. Anionic resins lose their swelling ability in the course of prolonged thermal treatment, while this is not the case for cationic resins.

The internal effects of swelling might lead to degradation of the waste product, e.g. formation of pores and channels. This can in turn enhance the water uptake and consequently affect the rate of swelling and leaching.

The external effects of swelling are important from the view-point of safety analysis. If space is not provided to allow free swelling, high pressures may develop and may cause damage to the repository constructions. In practice, there is a free volume (~10 %) in each drum. It is important to know whether this volume is big enough to keep the swelling pressure at a tolerable level. At present, however, the data on the pressure/volume characteristics of partially hydrated resins are incomplete. Direct measurements on the product would also be possible but they require long-term experiments.

Leaching of radionuclides from the waste products follows the water uptake and is dependent on the same factors as those affecting the water uptake. In addition, the water chemistry has a great influence on leaching.

In order to study the effect of the leachant composition on the leaching/swelling properties of the waste products, leaching with a strongly alkaline "cement" water in equilibrium with cement was done in order to simulate conditions that may occur in a repository with structural concrete materials.

The experiments showed that leaching is generally faster in the presence of concrete as compared to deionized water. On the other hand, swelling and deformation is somewhat suppressed in the presence of concrete.

A number of possible chemical interactions between the bituminized waste and surrounding barriers have been identified. It can be concluded, however, that the deterioration of the barriers due to such chemical interactions with the bituminized waste are unlikely. On the other hand, microbial attack on bitumen could lead to gas evolution that might impair the function of the barriers. The limited number of experiments and results available, however, does not give conclusive evidence about the appearance of such attack under anaerobic conditions.

In the context of the AVF-2 study it has been found that swelling - or consequences thereof - must be taken into account when disposal of bituminized reactor waste with normal radionuclide content is planned. The study has not revealed any other factor of similar importance.



## SAMMANFATTNING

För att rena reaktorvatten i kärnkraftverk och fånga upp frigjorda radioaktiva ämnen används ofta jonbytarmassor. Dessa gjuts sedan in i betong eller bitumen. Bitumeningjutet avfall har producerats under många år i Norden. Produkterna har vanligtvis ett lågt aktivitetsinnehåll och aktiviteten avklingar inom några hundra år till en sådan nivå att avfallet inte längre fordrar isolering. Denna typ av avfall planeras bli deponerad i slutförvar i berg, där det omges av flera barriärer. För att kunna genomföra en funktions- och säkerhetsanalys för slutförvaret behövs kunskaper om avfallsprodukternas långtidsegenskaper.

I det nordiska projektet NKA/AVF-2 har detta studerats. Målsättningen för projektet har varit att identifiera faktorer som är viktiga för långtidsbeteendet - faktorer som påverkas av ingjutningen, mellanlagringen eller slutförvaringen - och att samla och utveckla kunskapen om dessa faktorer.

De avfallsprodukter som studerats är jonbytarmassor ingjutna i bitumen. Slutförvarsmiljön är typisk för nordiska förhållanden. En av barriärerna som omsluter avfallsprodukterna är gjord av betong. Detta innebär att den kemiska miljön runt avfallsbehållaren bestäms av jämvikten med betong.

Den bitumeningjutna avfallsprodukten består i princip av avfallspartiklar jämnt fördelade i en kontinuerlig bitumenmatris. Jonbytarmassan torkas i de flesta fall under bitumeningjutningsprocessen och de torra partiklarna omges med ett skyddande lager av bitumen. Lagrets tjocklek bestäms av andelen jonbytarkorn i blandningen och av jonbytarpartikelarnas diameter. I en blandning med 40% torkad kornformig massa är lagrets tjocklek ca 0,2 mm.

I verkligheten kan emellertid avvikelser från den ideala produktstrukturen förekomma; blandningarna är kanske inte homogena och porer och sprickor kan bildas. Dessa avvikelser kan finnas redan efter ingjutningen eller bildas under mellanlagring och slutförvaring. Inom detta projekt har en metod utvecklats, med vars hjälp produktens inre struktur kan studeras. Sprickor och porer har ej upptäckts i färska bitumenprodukter men däremot har sprickor påvisats i bitumenprodukter som utsatts för utlakning.

Vid mellanlagring sker vissa förändringar i produkten. Produkten kan t ex bli sprödare och gas kan bildas på grund av strålning. Viss sedimentation kan ske på grund av skillnader i täthet, och produkten kan svälla på grund av vattenupptagning från fuktig luft. Dessa förändringar kan ha betydelse för produktens beteende i ett senare skede när den kommer i kontakt med vatten.

För de flesta avfallskollina med reaktoravfall från nordiska kärnkraftverk är aktivitetsnivån så låg att gasbildningen på grund av strålning är obetydlig. För andra avfallstyper med högre aktivitetsnivå kan radiolysen ge gasbildning och svällning av avfallsprodukten.

Bitumen är viskös vid rumstemperatur och högre temperaturer. Skillnader i densitet mellan bitumen ( $1000 \text{ kg/m}^3$ ) och den inbäddade avfallspartikeln (t ex torr katjonbytarmassa  $\sim 1300 \text{ kg/m}^3$ ) kan teoretiskt ge sedimentation av partiklarna efter lång tid. Sedimentation medför att det övre skiktet blir utarmat och att partiklarna ansamlas i botten av avfallskollit. En sådan ökning minskar motståndet mot vattenupptagning. Studien har dock visat att sedimentationen är för långsam vid rumstemperatur och lägre temperaturer för att vara av någon större betydelse. Å andra sidan kan sedimentation vara ett problem i samband med ingjutningen.

Vattenupptagning från fuktig luft kan förorsaka svällning av det bitumeningjutna materialet. I tidigare nordiska studier kunde man observera att bitumeningjutet jonbytaravfall med över 60 %

torr jonbytarmassa svällde märkbart i kontakt med luft. Senare undersökningar har visat att även produkter med lägre halt jonbytarmassa tar upp vatten i närvaro av luft med hög lufthalt. Vattenupptagningen tycks vara diffusionsstyrd. Den kommer att fortsätta tills ångtrycket över den fuktiga jonbytarmassan motsvarar vattenhalten i luften.

Om produkten i ett slutförvar kommer i kontakt med vatten, kommer en långsam diffusion av vatten att ske in i produkten. Detta kan ge olika effekter som påverkar produktens integritet, såsom svällning och uppkomst av svälltryck. Detta kan i sin tur leda till att omgivande barriärer försämras, t.ex. betongbarriären, och att en utlakning av radionuklider sker med därpå följande transport med grundvattnet.

Hastigheten för vattenupptagning beror på ett stort antal faktorer, såsom förhållandet avfall/bitumen, partikelstorlek och produktens homogenitet.

När halten jonbytarmassa är mindre än 50 %, är diffusionskoefficienten för vattenupptag låg. Det är dock inte känt hur diffusionskoefficienten ändras när produkten förändras med tiden.

Svällningsförloppet beror, förutom av hastigheten för vattenupptagningen, också av andra faktorer såsom avfallskollits dimensioner och dess innehåll av avfall, och av volymförhållandet mellan torra och vattenmättade jonbytarkorn. Det sistnämnda förhållandet är beroende av torkningstemperatur, tid och blandningsmetod vid ingjutningen. Ett torrt jonbytarkorn absorberar vatten och sväller i kontakt med vatten. Den observerade maximala svällningen har varit 20 till 210% beroende på typen av jonbytarmassa och på värmebehandlingen. Anjonbytare mister svällningsförmåga vid värmebehandling över 10 timmar medan detta inte är fallet med katjonbytare.

Inne i produkten kan svällningen ge upphov t.ex. till att porer och kanaler bildas, vilket kan leda till ökad vattenupptagning och följaktligen ökad svällning och utlakning.

Svällningens makroskopiska effekter är viktiga med hänsyn till säkerhetsanalysen. Om svällningen inte får ske fritt, skulle så höga tryck kunna uppstå att slutförvarkonstruktionen försämrats. I praktiken finns i varje fat fyllt med bitumen-jonbytarmassablandningen en fri volym på cirka 10%. Det är viktigt att veta om denna volym är tillräcklig för att minska svälltrycket till en acceptabel nivå. Detta kan undersökas genom att uppskatta jonbytarkornens svällning genom att utnyttja data för tryck/volympförändringar för jonbytare. Tillgängliga data är emellertid ofullständiga. Direkta mätningar på produkten skulle också vara möjliga, men dessa fordrar långtidsexperiment.

Efter vattenupptagningen kan radionuklider utlakas från produkten. Utlakningen är beroende av samma faktorer som påverkar vattenupptagningen. Därutöver har vattenkemin stor inverkan på utlakningens omfattning.

För att studera lakvätskans betydelse för utlaknings/svällningsegenskaperna hos produkten har lakförsök gjorts med ett starkt alkaliskt cementvatten i jämvikt med cementgranulat. Detta simulerar de förhållanden som råder i ett slutförvar byggt med betongkonstruktioner.

Experimenten visade att utlakningen är snabbare i närvaro av betong jämfört med rent (dejoniserat) vatten. Svällningen och deformationen är något mindre i närvaro av betong.

En rad olika former av kemisk växelverkan mellan bitumeningjutet avfall och omgivande barriärer har identifierats. Studierna visar emellertid att det är osannolikt att en sådan växelverkan skulle leda till en nedbrytning av barriärerna. A andra sidan

kan mikrobangrepp på bitumen leda till gasutveckling som kan försvaga barriärfunktionerna. De få experiment och resultat som finns att tillgå ger emellertid inte något slutgiltigt bevis för att ett angrepp kan äga rum i förhållanden där syre inte är tillgängligt.

AVF-2 projektet har visat att vattenupptagning med därpå följande svällning av avfallsprodukten är den viktigaste faktorn att ta hänsyn till i funktions- och säkerhetsanalyser för nordiska slutförvar.



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## 1. INTRODUCTION

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 conceptual 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.

Bituminization is also used at reprocessing plants. The Swedish utilities have contracts for reprocessing in France, which gives the French the option to send such wastes back to Sweden. The wastes from reprocessing will in general contain some long-lived radionuclides. The demands on the long-term behaviour and isolation of these wastes will thus be more stringent, and deep rock disposal is foreseen. The problems concerning the disposal of reprocessing wastes are not discussed in this report.

The knowledge required for assessment of low and medium active wastes from nuclear power stations has increased steadily, and this has resulted in waste products that in most cases fulfill reasonable demands on safe handling, intermediate storage and transport. The developing plans for final disposal have given the basis for evaluating the properties for waste products also from this point of view in the Nordic countries, and especially the spent ion exchange resins solidified in cement and bitumen have been studied. This report is mainly concerned with bituminized ion exchange resins.

Much work concerning the characteristics of cemented and bituminized wastes has been published internationally. Methods have been described to measure important characteristics such as stability, mechanical strength, leach rate and radiation resistance. Only a small fraction of this information deals with bituminized ion exchange resins. Experimental conditions have often been poorly described, which may be one explanation for the great deviations between results from different sources. However, the inherent micro-heterogeneity of the products is also likely to cause variation in the experimental results.

Joint Nordic studies concerning the compatibility of cement and bitumen with ion exchange resins have been performed since 1974 /1/. Under the coordination of NKA, several joint Nordic studies have been conducted, including research projects on nuclear waste management. A project (NKA/AO) dealing with a generic approach to the safety evaluation of an integrated waste management scheme for solidified reactor waste was completed in 1981 /2,3/. In the NKA/AO study, product properties were tested both in small scale and full-scale tests; guidelines were defined for relevant tests, which have been used as such or slightly modified in later work.

The joint Nordic research project (AVF-2) "Long-term properties of bituminized reactor waste" was initiated in 1982. The study has been run by a project group consisting of members from Risø

National Laboratory (Denmark) and SKB (Swedish Nuclear Fuel and Waste Management Co), SKI (Swedish Nuclear Power Inspectorate) and Studsvik Energiteknik AB (Sweden), IFE (Institute for Energy Technology, Norway), and VTT (Technical Research Centre of Finland).

The main purpose of the AVF-2 project 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 studies within the project include:

- characterization of the bituminized waste products
- basic studies concerning the behaviour of bituminized wastes in repository conditions (Figure 1-1).

The background of the studies initiated is described in Chapter 4.

The study got under way with a survey on the international status of current knowledge and with the search for an expert in the long-term properties of bitumen and bituminized waste products under repository conditions /4/. Simultaneously, a search was mounted for representative, old bitumen samples for comparative studies with fresh bitumen samples /5/. Neither "expert" nor suitable samples could be found, however.

The waste type chosen for experimental study consisted of bituminized ion exchange resins containing Co, Sr, Ni and Cs isotopes and decontamination chemicals. The incorporation of decontamination waste is closely connected with the AVF-1 research project (Management of radioactive waste resulting from nuclear fuel damage). The stability of the waste products was investigated by a special leach test procedure using cement conditioned water.

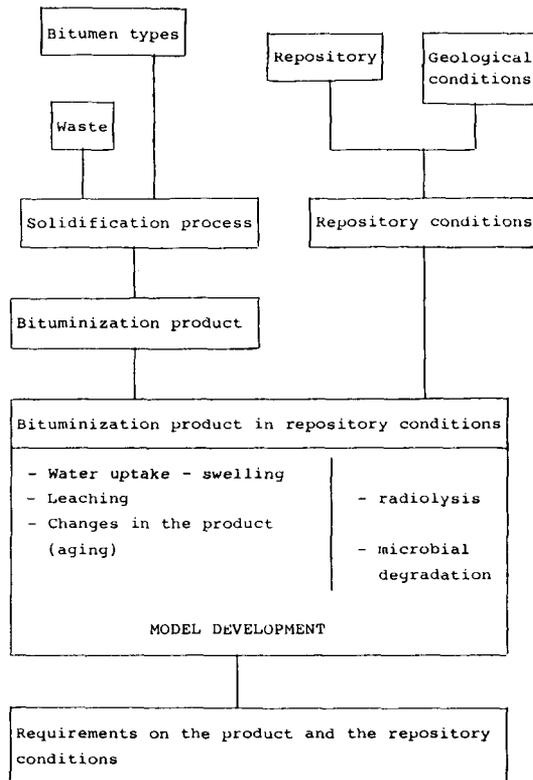


Figure 1-1. Assessment of the bituminization product under repository conditions.

This is in close accordance with the use of concrete as the construction material in the Finnish and Swedish concepts for disposal of reactor waste (Chapter 3).

Most of the studies concerning original waste properties, such as porosity and water content, were performed at Studsvik Energiteknik AB. The solidification processes in the Nordic bituminization plants differ in process parameters, such as drying temperature and time, and mixing method (Chapter 2). Some effects of the process parameters are also included in the characterization study of the waste products (Chapter 5).

Studies on the changes in the properties of bituminized wastes during prolonged storage or dry disposal were performed at Risø National Laboratory (Chapter 6).

Studies on the changes in bituminized wastes in contact with water have been carried out by all the participants in the project. Most of the previous work on the interactions between bituminized wastes and water has been devoted to determination of leach rates. The relevance of the results of these short-term leach tests for the actual long-term performance of industrial waste products is, however, questionable. There is a need for better understanding of the mechanisms involved. The AVF-2 project therefore deals with several aspects of waste-water interactions: theoretical evaluations, model development and experiments to predict the rate and final maximum water uptake. New test methods have been developed for fundamental studies of transport phenomena, swelling, structural changes and barrier interactions and parallel leach/swelling measurements on selected samples to investigate the effects of waste characteristics, process parameters and water chemistry (Chapter 7).

This report summarizes the results obtained in the project and data available from related work conducted in the Nordic countries.

## 2. BITUMINIZATION SYSTEMS IN THE NORDIC COUNTRIES

### 2.1 General

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 to treat evaporator concentrates from research laboratories. At nuclear power stations, bituminization plants have been installed at Barsebäck, Forsmark and Olkiluoto, all of which are BWRs. At the other Nordic nuclear power plants cementation is used. At one nuclear power plant, Loviisa, the solidification process has not yet been selected. A small experimental bituminization facility is installed at IFE, Kjeller, Norway.

This chapter gives a short description of the different Nordic bituminization processes, with the emphasis on factors that affect the characteristics of the waste products.

### 2.2 Wastes that are bituminized

In the Nordic countries, bituminization is used only to solidify wet wastes, i.e. sludges from precipitation or evaporation, ion-exchange resins and filter material. At the BWR power reactors almost all the wet wastes are ion-exchange resins and filter material /6/. Although the BWRs are also equipped with evaporators, these are seldom used.

The typical annual production of wet wastes from a BWR unit is:

- 2 - 5 metric tons bead resins
- 5 - 15 tons powder resins (incl. filter aid material)

The values are given as dry weights.

The bead resins are used in the reactor coolant clean-up system and in the waste water treatment system. Powder resins are used

together with filter aid material in the clean-up system for the spent fuel pond, in the condensate clean-up system and in the waste water treatment system. The highest activity is found in the wastes from the reactor coolant and spent fuel pond clean-up systems, typically 1-5 TBq/m<sup>3</sup> of waste; the specific activity of the wastes from the condensate clean-up system is lower by a factor of about ten. The most important radionuclides as measured by  $\gamma$ -spectrometry are Co-60, Zn-65, Cs-134 and Cs-137. The amount of cesium and other fission products is of course related to the integrity of the fuel.

Evaporator concentrates are bituminized at the Risø Research Establishment. The material contains soluble salts together with inorganic and organic sludges. The activity content is normally very low, 1 GBq/drum or less.

### 2.3 Description of the Nordic bituminization facilities

Table 2-1 gives some basic data on the Nordic bituminization facilities.

#### 2.3.1 Risø (DK)

The bituminization facility developed at Risø is of the pot evaporator type (Figure 2-1) /7/. A batch of primary evaporator concentrate with a solids content of about 14 - 20 % and pH slightly above 7 is fed from a storage tank to the concentrate feed tank. From there it flows by gravity to the electrically heated evaporator, where it is mixed with a batch of molten Mexphalte 40/50 added at the beginning of a run from the bitumen feed tank. The flow of concentrate is regulated so that the level in the evaporator is kept constant until the concentrate feed tank is empty. The temperature is about 105 °C throughout the period, which lasts about 18 hours. When the supply of concentrate stops, the last water is boiled off, the level in the evaporator decreases and the temperature increases to about

Table 2-1. The Nordic bituminization facilities.

	Bituminization process	Pretreatment of the waste			Mixing with bitumen			Total production Dec. 1984
		Treatment	Temperature	Time	Waste/Bitumen	Temperature	Time	
<u>Ion-exchange resin</u>								
Barsebäck	Continuous	Grinding of bead resins Addition of Na-sulphate	-	-	25/75	140°C	Minutes	960 m <sup>3</sup>
Forsmark 1 & 2	Batchwise	Grinding of bead resins and drying	130°C	Minutes	50/50	130°C	~1 h	220 m <sup>3</sup>
Forsmark 3	Batchwise	Corresponds to Olkiluoto						
Olkiluoto TVO I & II	Batchwise	Drying	140°C	~ 16 h	50/50	140°C	~15 min	390 m <sup>3</sup>
<u>Evaporator concentrates</u>								
Risø	Batchwise	-	-	-	40/60	I 105°C II 220°C	18 h 3 h	80 m <sup>3</sup>

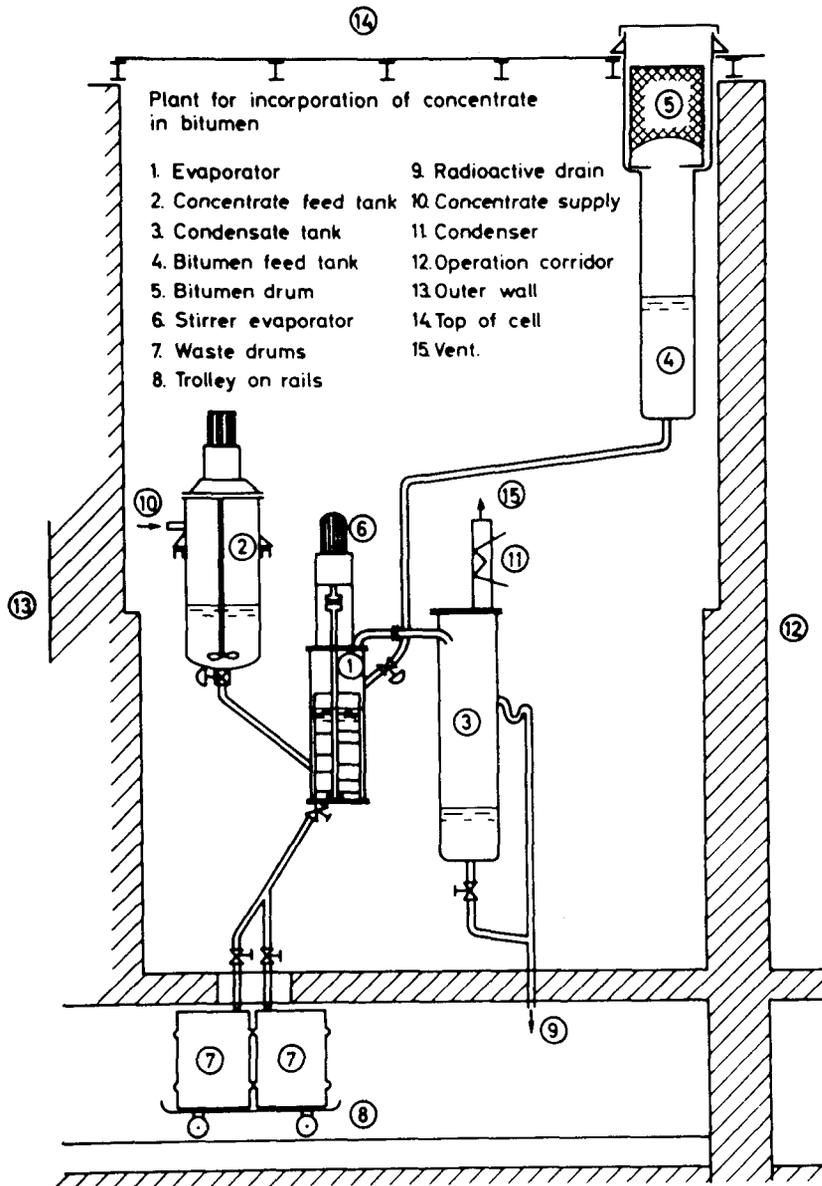


Fig. 2-1. Bituminization facility at the NRL Risø /7/.

220 °C, at which it is kept for about 3 hours. The product is therefore very dry, and some of the organic impurities are decomposed. Nonetheless, detergents and complexing compounds from the laboratories may still be present. The product normally contains about 40 % dry matter, mainly sodium sulphate and chloride together with a considerable amount of sludge material. There is no chemical pretreatment. Nitrates are present only in very low concentrations, thus minimizing fire hazards. Ion exchange resins are sometimes included, but only up to about 10 % and always in combination with evaporator concentrates. Since 1970 the plant has produced about 80 m<sup>3</sup> of waste product without any significant operational problems.

### 2.3.2 Barsebäck (S)

The bituminization plant at Barsebäck, which is of the thin film evaporator type, was built by SGN, France /8/. The flowsheet of the process is shown in Figure 2-2. The wastes to be bituminized are collected in a stainless steel feed tank. Bead resins are ground to a coarse powder before being fed to the feed tank. In the feed tank a slurry containing about 20 wt % dry matter is prepared, and sodium sulphate and an emulsifying agent are added. The function of the sodium sulphate is to saturate the ion-exchange resins and minimize thermal disintegration of the resin in the evaporator. Addition of an emulsifier to the slurry will improve the homogeneity of the bitumen-waste particle mixture in the evaporator.

The thin-film evaporator is a LUWA 210 (see Figure 2-3), which is heated by a circulating thermofluid at a temperature of about 220 °C.

Bitumen (Mexphalte 40/50) and slurry are fed continuously to the top part of the thin-film evaporator, where they are mixed, a thin film is formed and the water is evaporated.

The mixture flows from the bottom of the evaporator into a 220 l drum at a rate of about 45 kg/h, with a bitumen/waste ratio of about 75/25. The effective evaporation rate and therefore also the water content in the bituminized wastes is dependent on the residence time and temperature in the evaporator and on the film thickness. The normal residence time is a few minutes, and the temperature of the product from 130<sup>0</sup> to 180<sup>0</sup>C.

A test programme to measure the water and resin content in the waste product is in progress.

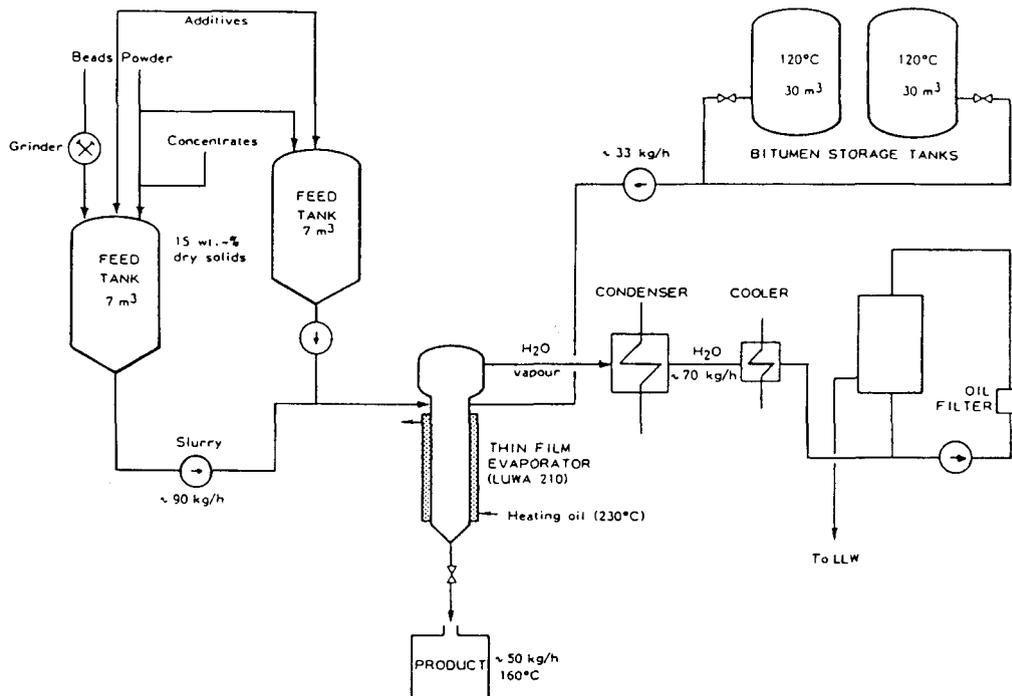


Fig. 2-2. Flowsheet of the bituminization system at the Barsebäck nuclear power station.

About 5000 drums were produced between 1975 and 1984.



### 2.3.3 Olkiluoto (SF)

A bituminization plant designed by Asea-Atom has been installed at Olkiluoto /9/. The general flow-sheet for the process is shown in Figure 2-4. The main parts of the system are a conical evaporator dryer with a planetary screw stirrer, and a conical mixer with a similar stirrer. Both the dryer and the mixer are heated with steam.

Before being fed to the evaporator/dryer, the waste is dewatered to about 20 wt % dry matter. The bead resins are not ground and there is no chemical pretreatment. In the evaporator/dryer the wastes are treated for about 16 h, during which time water is evaporated and a certain thermal degradation of the resins takes place. The temperature on the hot surface of the dryer is 150<sup>0</sup>C, and the final temperature in the ion-exchange resins will reach about 130<sup>0</sup>C. At this temperature, substantial destruction of the anion resins occurs (release of amines), but the cation resin is largely unaffected.

The dry powder is then fed into the mixer, where it is mixed with bitumen. A one-drum batch is mixed in one operation. The mixture is then fed into a 220 l drum. The ratio of bitumen to waste in the mixture can be varied within a fairly wide range. Normally, however, a mixture of around 50/50 is produced.

2000 drums were produced between 1979 and 1984.

### 2.3.4 Forsmark (S)

A similar system to that at Olkiluoto has been installed at Forsmark 3.

The bituminization system at Forsmark 1 and 2, which was delivered by Belgo Nucléaire, Belgium, is slightly different /10/. The flow sheet of the process is shown in Figure 2-5. It consists of a waste feed system, a rotary drum dryer and a mixing vessel.

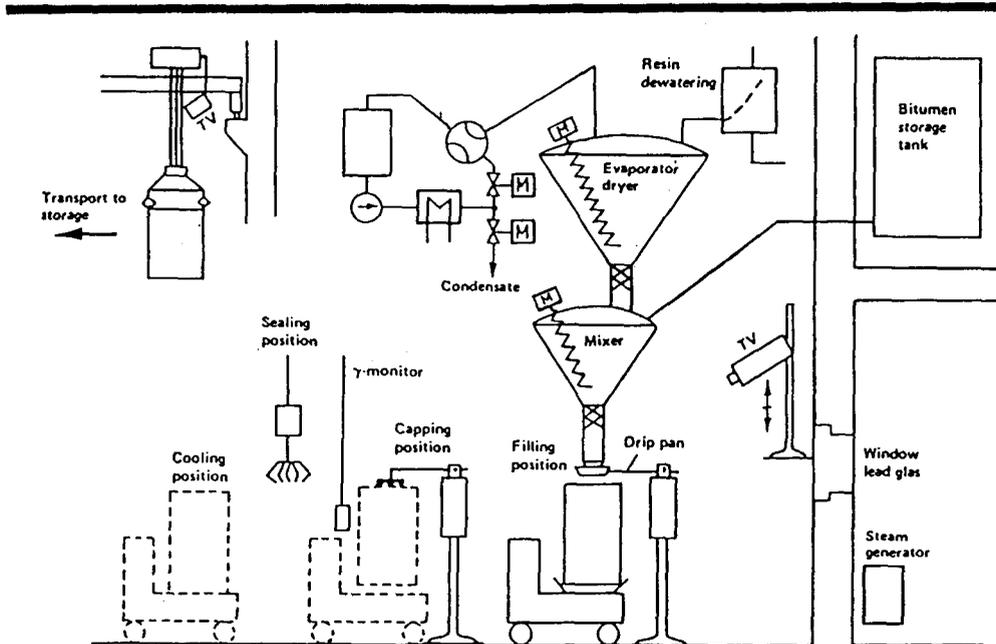


Fig. 2-4. Bitumization system at Olkiluoto.

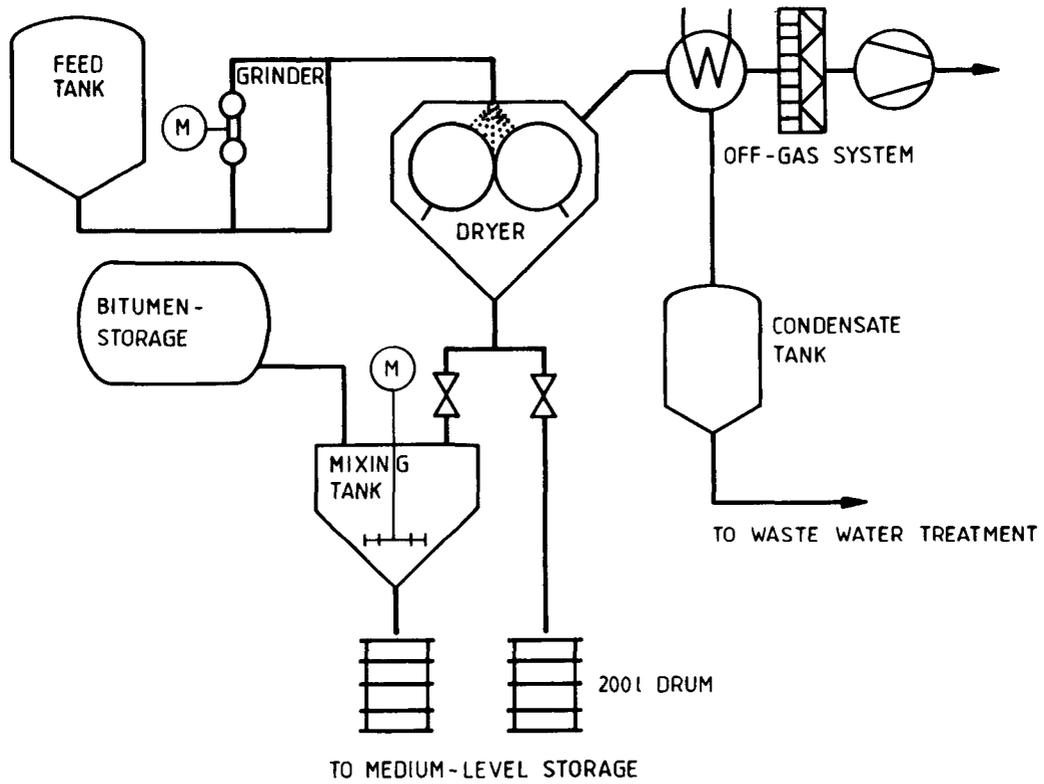


Fig. 2-5. Bituminization system at Forsmark 1 and 2.

Resin sludges containing 10-20 wt % dry matter are fed to the rotary drum dryer. Bead resins are ground before the drying step. After about half a minute in the dryer, the product is scraped off and fed to the mixer. The temperature on the surface of the drum dryer is about 160<sup>0</sup>C. The temperature of the resins, however, will not exceed about 80<sup>0</sup>C.

The dried resin and bitumen are mixed in the mixer. First the appropriate amount of bitumen for one drum is measured into the mixer and then ion-exchange resin is fed continuously from the drier. The feeding is stopped when enough waste /bitumen mixture for one drum is obtained. The mixture is then fed to a 220 l drum. The ratio of bitumen to waste in the mixture is about 50/50.

In this process, too, the drying will also lead to degradation of the anion resins. However, as the process time is shorter than at Olkiluoto and Forsmark 3, the degradation will only be partial. The water content in the waste has been measured for powder resins to be 5-10 %.

About 1200 drums had been produced by 1984.

### 3. REPOSITORY CONCEPTS

#### 3.1 General

In the Nordic countries, bituminized wastes are primarily obtained from nuclear power reactors. Disposal facilities are now under construction or being planned for these wastes in Sweden and Finland, and in Denmark various conceptional designs of disposal facilities have been made. In all the concepts the safety of the final disposal is based on the multibarrier principle, according to which water and dissolved radionuclides must penetrate several barriers before reaching the biosphere. The introduction of various barriers is based on the safety analysis of the whole disposal system.

#### 3.2 The final repository for reactor waste in Sweden (SFR)

In Sweden, a final repository for reactor waste, called SFR, is under construction near the Forsmark nuclear power station, on the Baltic coast /11/. SFR, which consists of a number of rock caverns in crystalline rock, is being excavated under the sea bottom about 1000 m from the shore. There will be at least 50 m of rock between the top of the caverns and the sea bottom.

The bituminized wastes will be placed in the silo repository (see Figure 3-1).

The silo repository has been designed in the form of rock caverns, 60 m high and 30 m in diameter, in which 50-m-high concrete silos will be built using the slip-form method. The concrete silos are 25 m in diameter and equipped with internal walls. These walls divide the silo into 2.5-m-wide squared shafts.

The concrete silo will be built on a bed of sand and bentonite, and the space between the walls and the rock will be filled with bentonite.

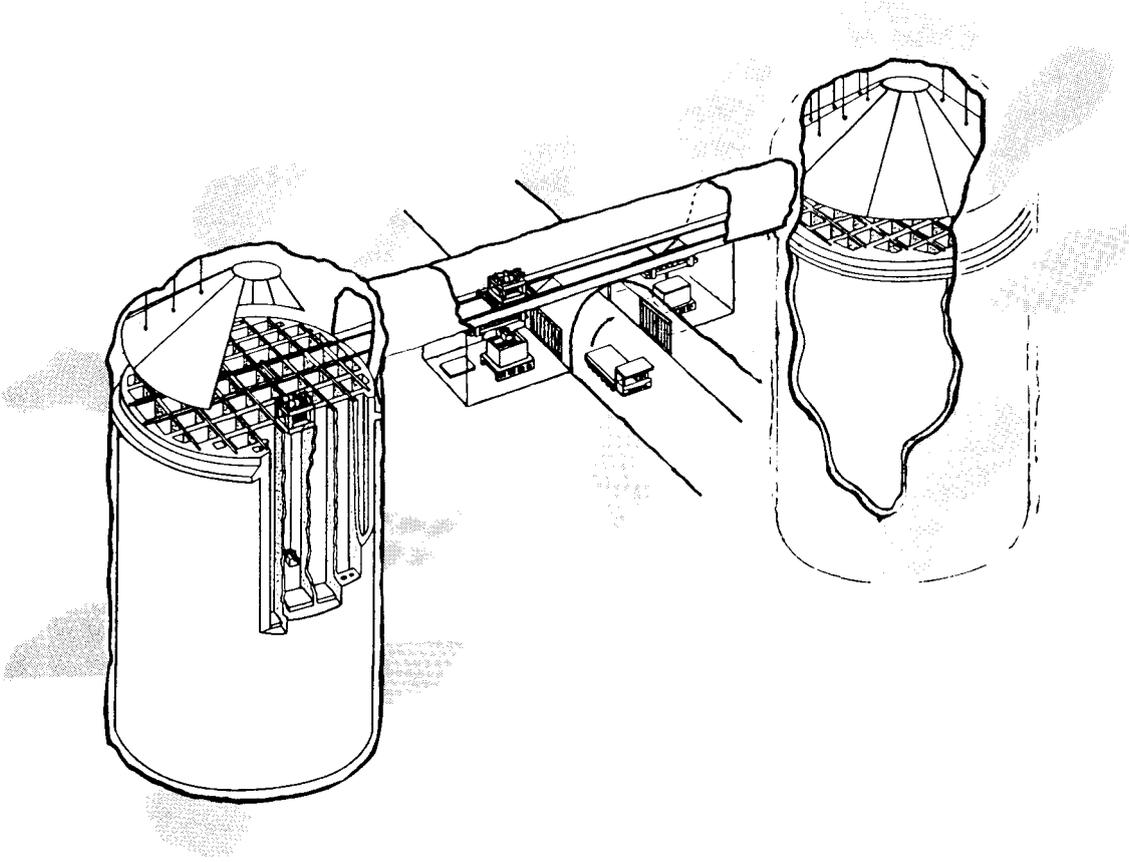


Fig. 3-1. Remote handling of waste packages in the silo repository (SFR)

The waste packages are placed in the shafts and subsequently surrounded by concrete grout.

Once a silo has been filled, a concrete lid will be cast on the top and covered with a layer of sand and bentonite, which will be compacted. The concrete silo is then completely surrounded by buffer material. The space above the buffer will finally be filled in order to stabilize the rock.

The concrete walls of the silo are primarily a necessary structural element for the disposal operations. After closure they will also act as barriers against the release of radionuclides. The main barrier, however, is the clay buffer, which guarantees that transport of water and ions around and through the wastes will only take place by diffusion.

When the silo is closed the waste package will thus be surrounded by

- concrete grout
- concrete walls
- sand and bentonite

At the time of closing the repository water will start penetrating into the silo and eventually reach the waste. This process is very slow and it will take scores of years for the silo to be saturated.

The natural groundwater conditions at Forsmark, Olkiluoto and, for comparison, the Baltic Sea water in the Forsmark area are given in Table 3-1.

The environmental conditions in the silo are determined not only by the groundwater chemistry but also by the behaviour of the concrete in contact with groundwater. Concrete is an alkaline material and the water penetrating into the pores of the concrete gains a high pH value. In the long term the pH, which is estimated to be about 12.5, will be controlled by the dissolution of alkali hydroxides and free  $\text{Ca(OH)}_2$ .

Table 3-1. Groundwater compositions (average values) compared with the composition of water from the Baltic sea /12,13/.

	Forsmark	Olkiluoto	Baltic sea
pH	7,4	8,2	8,2
Cond mS/m	800	110	800
HCO <sub>3</sub> <sup>-</sup> mg/l	86	370	70
SO <sub>4</sub> <sup>2-</sup> "	300	210	400
HPO <sub>4</sub> <sup>2-</sup> "	<0,01	0,15	-
NO <sub>3</sub> <sup>2-</sup> "	0,1	0,2	-
NO <sub>2</sub> <sup>-</sup> "	0,01	0,04	-
Cl <sup>-</sup> "	3600	50	2860
F <sup>-</sup> "	-	0,1	-
Ca <sup>2+</sup> "	700	80	70
Mg <sup>2+</sup> "	180	50	180
K <sup>+</sup> "	10	20	50
Na <sup>+</sup> "	1400	80	1600
Fe <sub>tot</sub> "	2	5	-
Mn <sup>2+</sup> "	2	1,3	-
SiO <sub>2</sub> "	3	15	-

### 3.3 The final repository at Olkiluoto, Finland

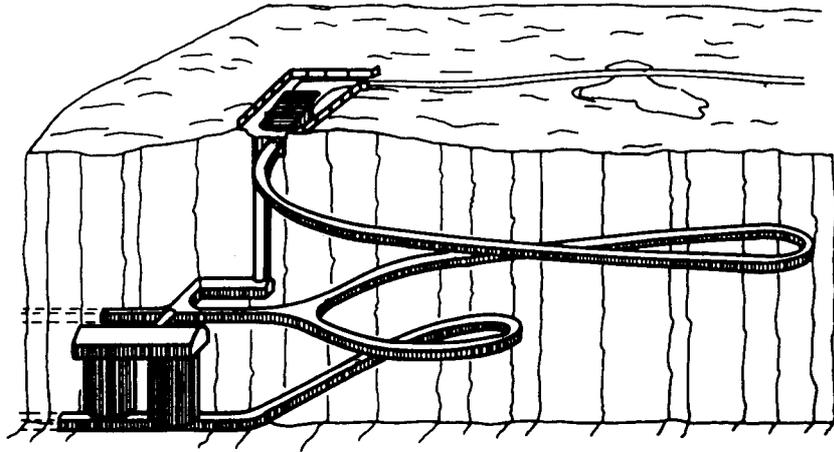
The Olkiluoto repository will be located on the Ulkopää peninsula, at the site of the Olkiluoto power plant. The general layout of the repository is shown in Figure 3-2a /14/. Waste packages will be placed in cylindrical caverns excavated in bedrock at a depth of 50-100 m.

The cavern for bituminized wastes is depicted in Figure 3-2b. The waste drums will be emplaced in layers in a reinforced concrete cylindrical silo 19 m in diameter and 27 m high. When a layer has been filled with drums, the spaces between the drums will be filled with concrete. Extra space will be provided around individual drums to accommodate any swelling of the waste, and thus any detrimental stresses in the backfill concrete will be avoided.

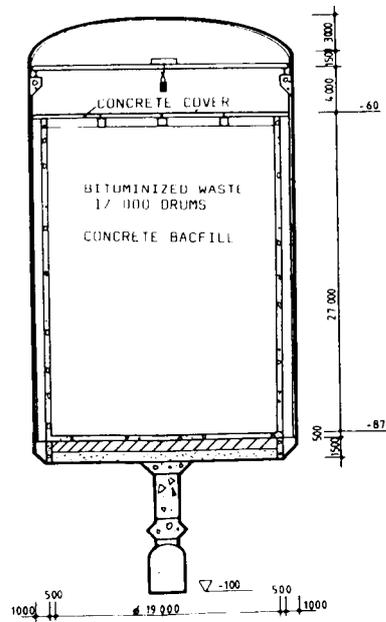
The annulus between the concrete wall and the bedrock surface will be filled with crushed rock aggregate during the shutdown and sealing of the repository. The crane hall above the waste caverns will be filled with cement-stabilized sand.

### 3.4 Potential repositories in Denmark

In Denmark a feasibility study has been produced on the final disposal of wastes in salt /15/. It is only concerned with high level wastes, but chambers similar to those of German design can probably be constructed for reactor waste. In such a disposal facility the waste packages will normally be exposed to a dry atmosphere, even after closure. Only in the unlikely event of water penetration will the waste come into contact with water in the form of brine. The composition of this brine solution can be expected to be similar to the Q-brine found in flooded salt mines, as reported in German safety studies (see Table 3-2). A saturated sodium chloride solution may also be feasible.



(a)



(b)

Fig. 3-2. The repository and silo for bituminized waste (TVO).

Table 3-2. Composition of Q solution corresponding to equilibrium in the system: NaCl-KCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O /16/.

At temperature	Mole/1000 mole H <sub>2</sub> O				Salt conc. Mole/kg
	NaCl	KCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>	
25 °C	6.8	12.8	68.3	5.1	5.2
55 °C	6.8	17.4	77.3	3.2	5.8

A conceptual study has also been made of disposal within a concrete structure built in an unconsolidated geological formation such as clay or sand /17/ (see Fig. 3-3). This is a further development of one of the reference designs in the Nordic Study on reactor waste /2/. A special feature of this concept is the proposal to use bitumen as a sealing material between individual waste units, taking advantage of the softness of bitumen, which effectively prevents the formation of water-conducting cracks. Water penetration into such a system is therefore expected to be very slow. The water chemistry will be dominated by the concrete and possibly by the waste.

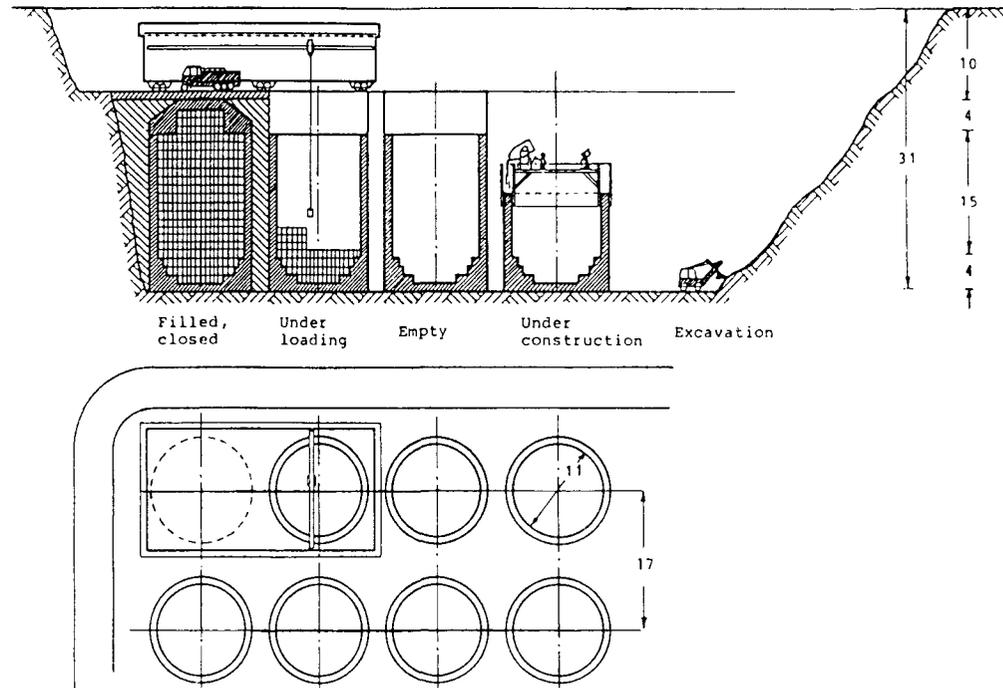


Fig. 3-4. Danish concept of cylindrical bunkers, 10 m soil cover.

#### 4. GENERAL ASPECTS OF THE LONG-TERM BEHAVIOUR 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, the waste form, have to be related to the properties of the repository. The long-term behaviour 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 need for this knowledge became even more apparent during the AVF-2 study and greatly influenced the study itself during its final stages and also the conclusions drawn from it. Investigation has shown that good leaching resistance in a specific environment in laboratory experiments is only one of several important parameters when judging the function of a waste form.

In the performance assessment of a repository, each of the various barriers is evaluated separately as a part of the entire barrier system, the goal being to enable the radionuclide transport to be calculated. As a repository is often designed with a system of multiple barriers, the interrelations between the various barriers and between the barriers and the waste form must be known if the transport and retention of the radionuclides is to be fully understood. To some extent, the barriers are dependent on each other and thus make a physically stable system. The long-term behaviour of waste forms should be studied and evaluated in terms of the waste package as a part of an integrated barrier system.

It may reasonably be assumed that a barrier can only be neglected when calculating the release of radionuclides from a repository if the behaviour of the total system is sufficiently well understood and if the investigators are confident that no adverse mechanisms have been overlooked that might threaten the

integrity of the barriers included in the calculation. It is not necessarily safe to conclude that several pessimistic assumptions, when added together, might not make an optimistic case.

#### 4.1 Interactions in a repository for reactor waste

The behaviour 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 concrete. Since the main concern of this study was the long-term behaviour of the waste form and the mutual influence of the waste form and the appropriate barriers, the study could thus be restricted to the immediate environment of the repository.

The transport of radionuclides from the solidified waste product through engineered barriers is governed mainly by three processes: solubility, diffusion of soluble species and sorption phenomena.

In earlier studies, the leach rate from a certain waste form was regarded as the only important property of the waste product as long as its physical integrity could be looked upon as satisfactory. Judged using these measures, bituminized wastes might fulfill high demands on retention properties. As shown in laboratory experiments the initial leach rates for most radionuclides in bituminized wastes are often better than the leach rates of similar cemented wastes by as much as one or more orders of magnitude /18/.

However, currently available knowledge on the degradation of certain waste matrices has been judged insufficient to permit these properties to be taken as a decisive factor in safety analyses for licensing purposes /19,20/. In addition, the actual leaching properties for the reactor waste produced to date are poorly understood.

The difficulty of assigning inherent retentional properties to reactor waste has caused a temporary switch of interest from study of the initial leaching properties of waste products to investigation of the retentional properties and long-term stability of the engineered barriers. However, there is still a question concerning the highly complex interactions leading to degradation of the waste products. To forecast the development of interactions between waste and other barriers, knowledge of the long-term behaviour of the waste itself is needed. When related to the surrounding barriers, the long-term properties of waste products must not be overlooked. What now remains to be done is to define the properties and mechanisms that are actually involved.

In the preliminary safety report the applicant for the Swedish SFR repository showed that the diffusional resistance in the pore water of the surrounding concrete and clay barriers provides sufficient transport resistance to most radionuclides /20,21/. Such a condition would imply that no restrictions on the chemical form (speciation) of the radionuclides would have to be considered in the safety analysis. As a consequence of this system property any degradation product from the waste itself or the waste matrix, i.e. complexing agents, could be accepted without an unacceptable increase in the leakage of radionuclides to the biosphere as calculated in the safety analysis. It follows that the knowledge most vitally needed concerns the interactions that might 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.

In this study, swelling and leaching experiments were run in parallel under as realistic conditions as possible, mainly on bituminized decontamination waste. For bituminized wastes other than those from normal reactor operation, such as waste produced during clean-up after severe fuel damages and reprocessing waste, it might be necessary to consider the retentional properties of the waste products as well as the barriers.

#### 4.2 Chemical interactions between wastes and barriers

It is possible that a clay barrier surrounding the repository might be affected by the presence of surface active agents. Any degradation products from microbial degradation or hydrolytic attack of concrete water on bitumen are presumably dominated by carboxylates. Since such species correspond to anionic surfactants this phenomenon should be of minor concern. The sulphate in the waste might cause the concrete barrier to crack. The amount of sulphate should therefore be limited or it should be shown that such additions do not influence the barrier integrity.

In the search for any other adverse chemical phenomena, a closer look should be taken at the waste matrix itself.

Although not in thermodynamic equilibrium with some of the surrounding materials, bitumen and resin should in fact be extremely resistant to chemical transformations in the repository over a very long period.

This is indicated by the presence of natural waxes in the fractures of igneous rocks, even though the origin and exact age of this material is largely unknown.

The long-term stability of the bitumen qualities employed for solidifying reactor wastes is still uncertain, however. Most studies on the degradation of bitumens and asphalts have been performed in aerated systems, and the observed effects might be due to oxidation. A search was conducted during the present study for samples of old bitumen stored under anaerobic conditions, but samples suitable for comparative studies could not be found /5/.

Radiolysis of waste might lead to some gas formation (and subsequent swelling of the waste packages in intense radiation fields), but it has been shown that this phenomenon is of negligible importance, at least for typical reactor waste /22,23,24/.

In summary, the deterioration of barriers as a result of chemical interactions with bituminized waste does not seem to be a problem.

#### 4.3 Influence of microbial activity on the barrier function

The presence of bacteria is always to be expected in a repository. Significant amounts of organic material in reactor wastes will contribute to microbial activity to a much greater extent than is generally encountered at repository depth. The likelihood of adverse effects of bacterial attack must therefore be included in the safety analysis. It has been found that the most important effect of microbial activity in a repository might be the formation of carbon dioxide, which in turn acts as a catalyst for the corrosion of iron during the formation of hydrogen gas. The subsequent gas flow from the repository could lead to an increased turnover of contaminated water and thus indirectly to an impaired function of the barriers.

However, with regard to the presence of bituminized wastes alone it has been shown /24/ that the likelihood of this happening is remote. Anaerobic microbial attack on a monolithic bitumen block takes place extremely slowly. The active groups of the ion exchange resins contain hexavalent sulphur (sulphonate) and amine nitrogen, which could act as nutrients for sulphate-reducing bacteria. The most probable end-products of such bacterial activity would be pyrite and carbon dioxide. For further details, see Chapter 7.

#### 4.4 Swelling of bituminized ion exchange resins

A barrier may be affected by mechanical phenomena emanating in the waste form, e.g. swelling, and leading in more severe cases to mechanical cracking or disruption of a barrier.

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. This is clearly shown in the description of the various processes in Chapter 2. The waste with the least residual water is apparently produced by the plants at Olkiluoto, Forsmark 3 and Risø, while waste containing considerable amounts of water is expected from the plant at Barsebäck.

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 /25,26/. When water is absorbed at a constant volume, the forces acting on surrounding media correspond to pressures of up to at least 40 MPa /27/. 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.

As will be shown in the following chapters, considerable efforts are currently being made in the Nordic countries to fully understand the swelling mechanisms and related phenomena /28,29,30/. Diffusion models for the uptake of water into bituminized waste have been found to be of great value in defining what properties and mechanisms should be examined in particular. Such work is now under way in Finland and Sweden, where experimental studies of the water sorption isotherms and compressibilities necessary for the calculation of effective diffusion coefficients and swelling pressures are in progress. Part of that work is described in Chapter 7.

The ultimate goal of all these studies is to simulate the swelling in a way that permits barrier stability to be predicted, and the quality requirements of bituminized wastes to be defined in the future. A model with such characteristics should take into account the conditions of newly produced wastes with respect to resin properties, sedimentation, structure and initial water content (see Chapter 5) and also aging phenomena in the bitumen matrix (Chapter 6). These problems are examined more closely in Ref. /31/.

#### 4.5 Leaching

A wealth of data concerning leaching resistance of bituminized waste has been produced in earlier studies. In the present Nordic project, combined leaching and swelling experiments have been conducted under the conditions expected in the repository environment. No effort has been made, however, to simulate the leaching mechanism. These studies are described in detail in Chapter 7.

## 5. INITIAL PROPERTIES OF BITUMINIZED WASTES

In the Nordic study, reference bituminized waste material was manufactured at IFE, Kjeller. In their laboratory process, resin and bitumen are mixed in a heated chamber in a Werner & Pfleiderer type kneading machine. After evaporation of excess water the mixture is heated to about 150°C for some 15 minutes and the material is cast into aluminium dies. Process parameters that can be varied include product water content, heating and casting temperatures and mixing times.

The main reason for using this process was to obtain well characterized test samples and thus make it easy to detect any subsequent changes in the product as a result of handling or storage or both.

### 5.1 Properties of pure bitumen

Physically, bitumens are solid or semi-solid substances at room temperature and can easily be liquidized by heating. The mean values of some physical properties of bitumen are summarized in Table 5-1 /32/.

Chemically, bitumen consists of a mixture of rather high molecular aliphatic, aromatic and heterocyclic hydrocarbons. The aromatic and heterocyclic components are mainly present as asphaltenes (M = 1000 to 100 000) in the form of colloids dispersed in a softer matrix of mainly aliphatic hydrocarbons (M = 500 to 5000). A third type of material, the resins, of intermediate molecular sizes is also present as part of the bitumen.

The chemical composition of typical bitumens lies within the following ranges:

C	80-88 %
H	8-11 %
O	1-12 % as hydroxy, carbonyl or ester groups
S	1- 7 % as thiophene, benzothiophene groups
N	0- 1½ % as pyridine, pyrrole groups

Table 5-1. Physical data of bitumen /32/.

Property	Value
Density	$1.04 \pm 0.03 \text{ g/cm}^3$ at $25^\circ\text{C}$
Coeff. of cub. expansion	0.00061 per $^\circ\text{C}$ (in the range $15\text{-}200^\circ\text{C}$ )
Specific heat	1.90 J/gK
Thermal conductivity	0.15 W/mK
Permeability to $\text{H}_2\text{O}$ vapour	$2.7 \cdot 10^{-15} \text{ kg/m}\cdot\text{s}\cdot\text{Pa}$ (at $25^\circ\text{C}$ )
Surface tension	$0.029 \pm 0.001 \text{ N/m}$
Total surface energy	$0.051 \pm 0.001 \text{ J/m}^2$
Resistivity	$10^{16} \text{ ohm/m}$ (at $30^\circ\text{C}$ )
Dielectric strength	2-3 MV/m (at $20^\circ\text{C}$ , flat electrodes)
Dielectric constant	2.7 (at $20^\circ\text{C}$ )
Dielectric loss	$\tan \delta$ 0.015 (50 Hz, $20^\circ\text{C}$ )
Radiation resistance	ca $10^7 \text{ Gy}$
Viscosity	$10^2\text{-}10^{19} \text{ Pa}\cdot\text{s}$ (in the range $50\text{-}0^\circ\text{C}$ )
Combustion heat	40 MJ/kg
Compressibility	$4 \cdot 10^{-4} \text{ MPa}^{-1}$
Permeability to $\text{O}_2$ (blown bitumen, penetr = 16, R+B = $116^\circ\text{C}$ )	$\sim 8 \cdot 10^{-17} \text{ kg/m}\cdot\text{s}\cdot\text{Pa}$

In a steady-state situation, the rate of water transport through undamaged films of bitumen is expected to be proportional to the solubility of water in bitumen and to the diffusion coefficient for water in the bitumen.

Experiments show that the solubility of water in Mexphalte 40/50 at 25°C is in the order of  $(5 \pm 2) \times 10^{-3}$  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 /26/. The experiment revealed a diffusion coefficient for the water in bitumen of  $2 \times 10^{-12}$  m<sup>2</sup>/s at 20°C /26/.

## 5.2 Hygroscopic properties of resins

The majority of the ion exchangers used for water purification in nuclear power plants are either strongly acidic cation exchangers or strongly basic anion exchangers. They consist of a polystyrene skeleton crosslinked with divinyl-benzene. The chemically active ionogenic groups are sulphonic acid and quaternary amine, respectively. 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 5-1 /33/ 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°C, while there is a significant effect on the anion resins already at about 100°C.

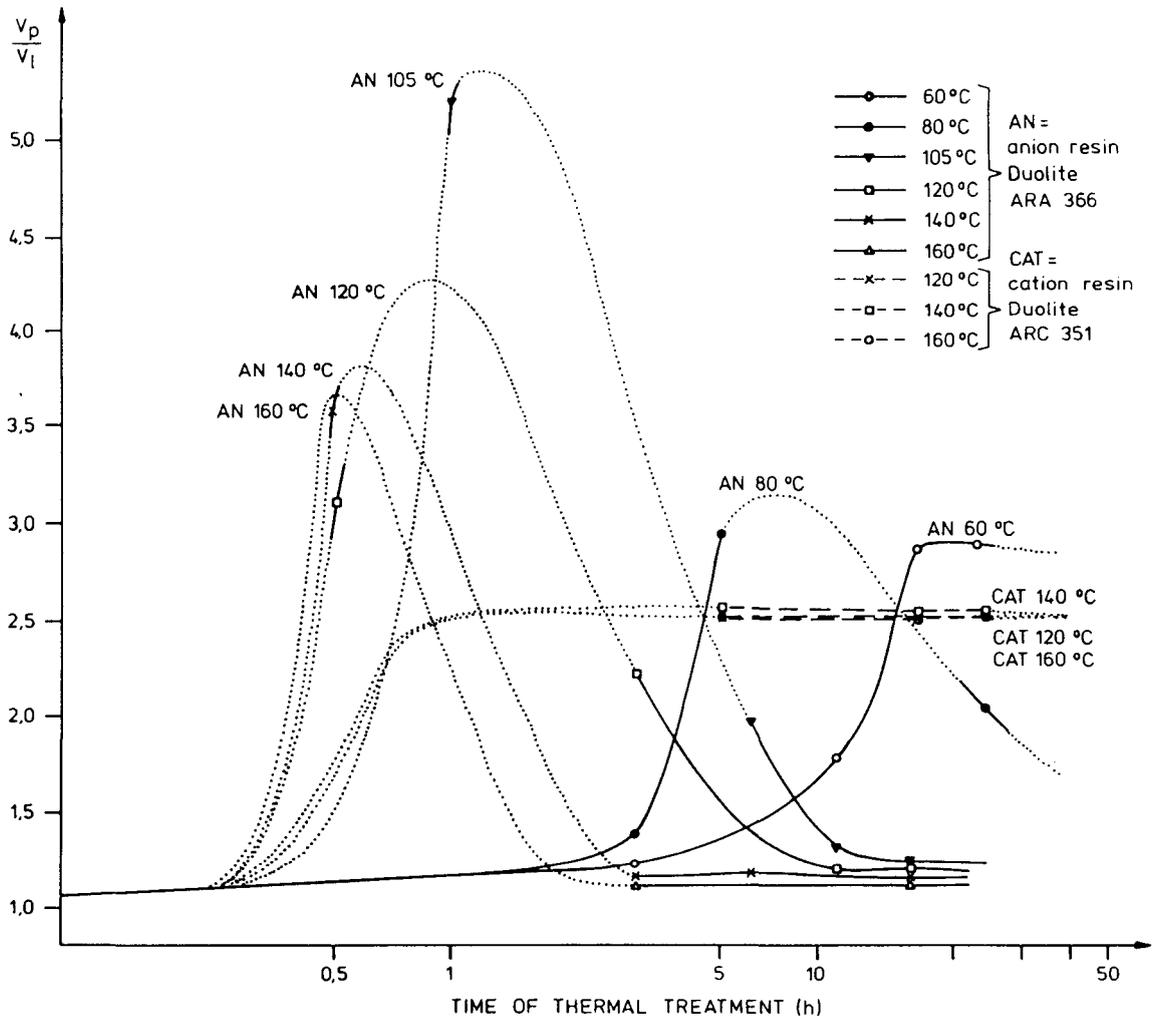


Figure 5-1. The effect of heat treatment on the swelling of ion exchange resins.  $V_l$ : volume of the heat-treated dry resin,  $V_p$ : volume of heat-treated resin after swelling in water /33/.

When thermal treatment is applied at 300<sup>0</sup>-400<sup>0</sup>C /26/, cation resin decomposes, but some swelling capacity still remains.

The ionic state affects the size of swollen resin particles, ionic states H<sup>+</sup> and OH<sup>-</sup> generally giving the largest volumes. The treatment of unused resins with Na<sub>2</sub>SO<sub>4</sub> reduces the swelling ability and the effect of the thermal treatment /25/.

Considerable pressures can build up if dried ion exchange resin comes into contact with water and its swelling is prevented, /33, 34/; this is discussed in Chapter 7.

### 5.3 Properties of bituminized wastes

Spent resins are normally bituminized batchwise in a process in which pre-dried ion exchange resins are mixed with hot bitumen for a specified period, after which the hot mixture is discharged into steel drums, as described in Chapter 2.

#### 5.3.1 Bitumen layer thickness

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.

Calculations /35/ have shown that 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.

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.

Small particles will be positioned between the larger particles to some degree, resulting in a somewhat more efficient use of the available bitumen than in the case of monodisperse particles /35/.

Calculations of particle distances by the idealized model, as shown in Fig. 5-2, can therefore only give an indication of the mean thickness of the bitumen film surrounding the particles /35/.

### 5.3.2 Segregation and sedimentation

Depending on the bituminization process used, however, any one of several phenomena may cause inhomogeneities in the products. One is the separation or settling of the resins in the hot bitumen during and immediately after the casting of the product. The likelihood of the segregation of anionic and cationic resins should also be considered.

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) indicate that the drums contain mainly anionic resins in the top half and cationic resins in the bottom half of the drum. Experiments with powdered resins show homogeneous products /33,36,37/.

Attempts to model the sedimentation process mathematically have also been made. The results obtained show that for the bitumen grades normally used for the solidification of resins, sedimentation varies with temperature and grain size during the first few hours after casting but that thereafter sedimentation is negligible. No attempt to validate this model has been made, however /38/.

EXAMPLE OF TETRAHEDRIC  
UNIT CELL

Parameter values  
for IR 120

$$\varphi_w / \varphi_{\text{bit}} = 1.5$$

$$F = (d_{\text{hyd}} / d) = 2.43$$

$$d = 0.6 \text{ mm}$$

$$w = 0.4 \text{ (40 \% dry resin)}$$

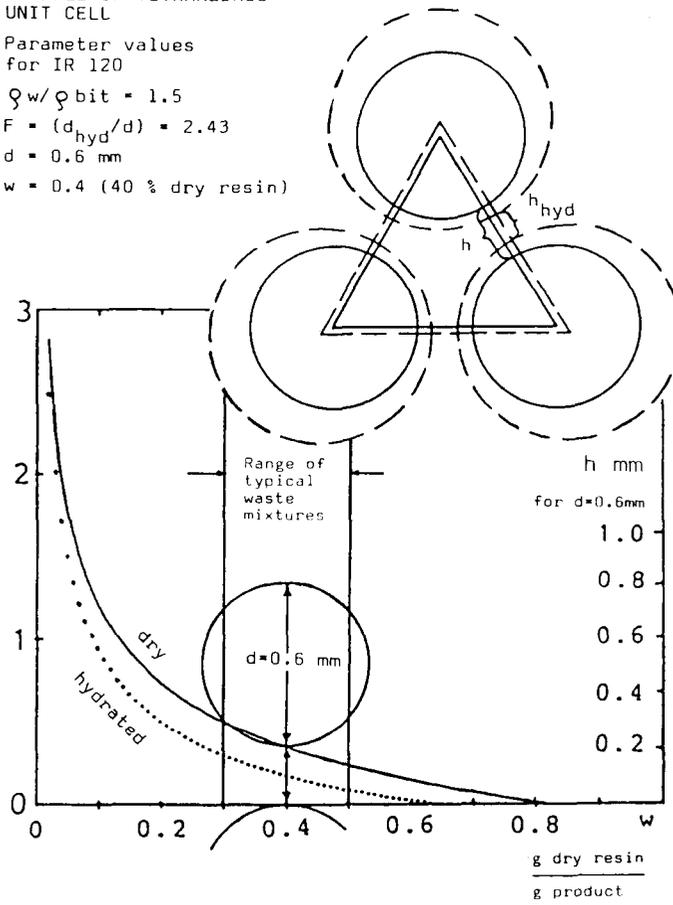


Figure 5-2. Thickness of the bitumen layers between spherical resin particles of uniform size and distributed regularly in the corners of tetrahedric unit cells  
/35/

### 5.3.3 Inner structure of bituminized wastes

As described earlier, the product should ideally consist of waste particles embedded in a continuum of bitumen, but owing to processing and handling this is not possible in practice. There will always be inhomogeneities on account of segregation, sedimentation and swelling. 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 products produced 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% /39/. This increase in water content, with its corresponding swelling, is expected 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 whether the cracks and pores detected are formed during fracturing of the product or not. Further investigations are needed.

Another source of cracking and pore formation is the dose absorbed through alpha, beta and gamma radiation. Experiments with external gamma irradiation have shown that no appreciable effects are observed until the absorbed dose amounts to about 500 kGy or more /40/.

Examples of the inner structure of some bituminized waste products are shown in Figures 5-3 - 5-5. These figures are sweep electron microscope (SEM) photographs of fracture surfaces.

Figure 5-3 at a magnification of 75x is a detail view of the fractures encountered in a leached sample containing 50 w% anion exchange resin and 50 w% bitumen.

Figures 5-4 and 5-5, 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 5-4 has been stored dry after leaching, while the specimen in 5-5 has been stored in water. The relative volume expansion coefficient can be estimated, from these pictures, to be about 3x.

Generally, leached species of bituminized 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.

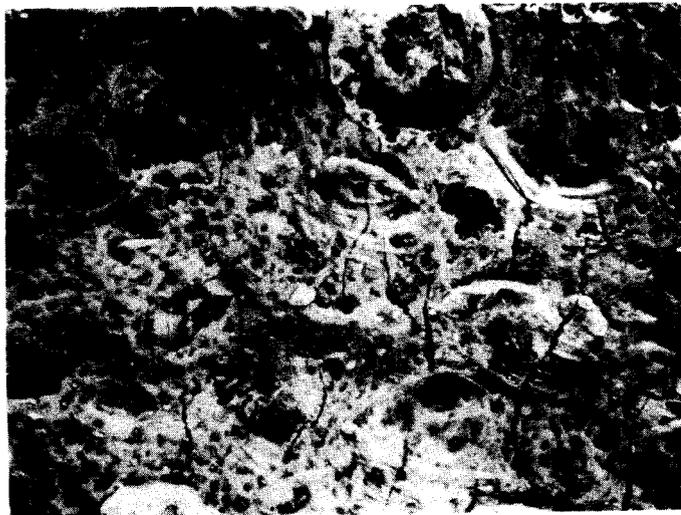


Figure 5-3. Anion resin to bitumen ratio = 50:50 w%. Stored dry after leaching. Water content 11.6%. SEM 75x. Detail view showing the extensive net of cracks formed.



Figure 5-4. 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.



Figure 5-5. A similar sample as in 5-4, but stored in contact with water. Water content 24.2%. Please note the swelling of the beads, and also the pores formed.

#### 5.4 Quality assurance

The properties of special interest for QA/QC for the assessment of the long-term behaviour of bituminized waste, are homogeneity, waste loading, water content (free and total) and swelling ability. Most of these properties are interdependent.

As a consequence of the process dependence of the product properties, relevant to long term stability and safety, no generally applicable QA/QC rules can be established. Each process and each repository concept generates its own set of requirements to be considered separately by the authorities.

QC will probably be based on the control of raw materials, waste composition, radionuclide inventory and process control. Sufficient work must also be done on the characterization of the product.

## 6. CHANGES IN PROPERTIES OF BITUMINIZED WASTES DURING STORAGE OR DRY DISPOSAL

Containers holding bituminized waste products will be stored for shorter or longer periods before being transported to the disposal site. Storage at or near room temperature in air with low relative humidity can be ensured by using high-quality engineered storage systems. Under more primitive conditions the packages may be exposed to frost, fluctuations in temperature or high humidity. The temperature may also vary during transport, which, moreover, may expose the packages to mechanical stress. Severe accidents involving high temperatures or large mechanical forces will be infrequent and only involve a minor fraction of the total number of units. The material may or may not be changed significantly by such accidents. This will not be discussed here.

During and after emplacement of the waste packages in a disposal facility the bituminized material will remain dry for a period depending on the quality of the container and the type and design of the facility. Dry conditions may last indefinitely when disposal is in a salt formation. The temperature of the disposed low- and medium-level active material will be almost constant and determined by the ambient temperature of the site. Geological disposal of large amounts of medium level wastes in a compact manner may, however, result in slight temperature increases due to decay heat /59/. This will obviously depend very much on the layout of the repository.

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 behaviour of the system if the packages are exposed to water at some later stage.

## 6.1 Thermal effects, sedimentation

The viscosity of bitumen increases continuously with decreasing temperature, for example from values of about 10 Pa·sec at 100°C to 10<sup>7</sup> Pa·sec at 20°C /41/. 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 /42/.

The thermal expansion of bitumen is relatively high, about 0.00015 cm/cm·°C at 20°C /41/. Differential expansion between bitumen and embedded waste particles (especially large particles) may therefore influence the mechanical stability of such products. However, the effect of thermal cycling between -20° and 0°C on dry bituminized ion exchange resins has been found to be negligible /3/.

The viscous behaviour of bitumen at room temperature and above means that density differences between bitumen (~1.0 g/cm<sup>3</sup>) and the embedded waste particles (for example dry cation exchange resins ~1.3 g/cm<sup>3</sup>) may lead to settling of the particles, when the material is left standing for long periods. The phenomenon has been studied both theoretically and experimentally /32,38/. In all cases the conclusion is that the sedimentation is too slow to be of any significance at room temperature and below. If the units are stored (exposed to strong sunshine) or emplaced (deep geological disposal) at higher ambient temperatures, sedimentation may become important. Sedimentation can also be a big problem in quality assurance in connection with casting of the material (see Chapter 5). The effect is primarily a depletion of waste particles in the top layer and an accumulation in the bottom layer of the units, leading to reduced resistance to the uptake of water (see Chapter 7).

## 6.2 Physical aging

It can be demonstrated 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<sup>0</sup>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 rate of increase in viscosity decreases with time, but it is difficult on the basis of these relatively short experiments to say anything definite about material properties after a period of many years /41/.

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 /41/. An example of a contraction curve for bituminized ion exchange resin is shown in Fig. 6-1.

The phenomenon is highly variable and probably due to the presence of small air inclusions in the matrices. A period of contraction lasting for some months is important when interpreting the measurements of swelling forces due to water uptake, since contraction may compensate for swelling for a long time, especially in the case of thick samples.

A physical aging phenomena should be reversible, i.e. the effect should disappear when the material is reheated. This is only partly so with the contraction phenomena and not at all with other types of aging reaction.

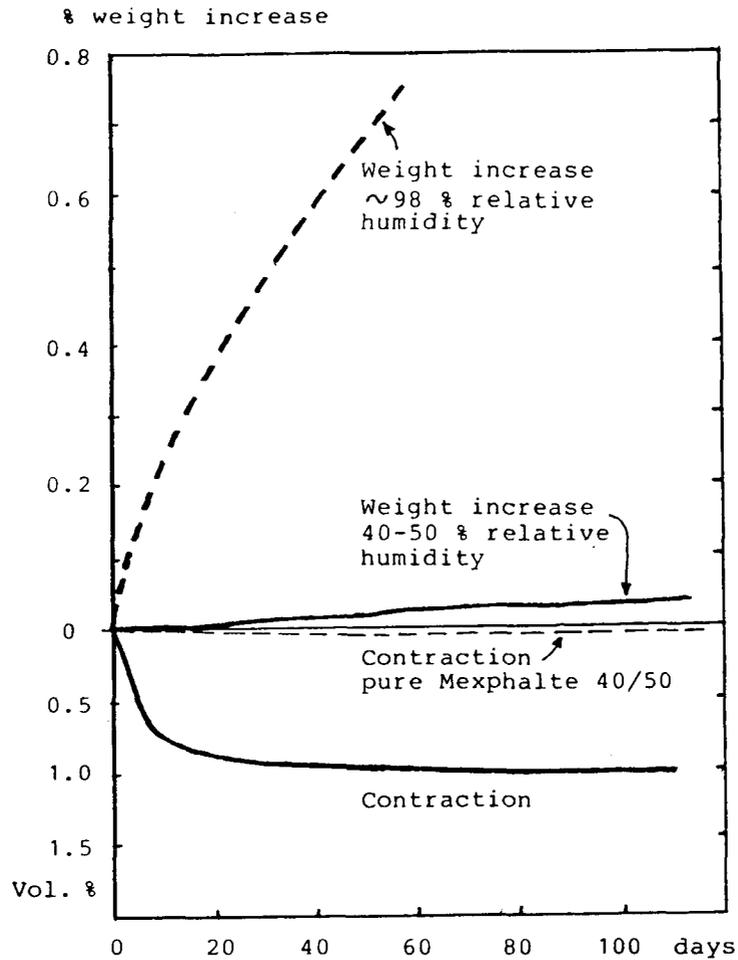


Figure 6-1. Volume contraction and weight increase due to water uptake in a sample of dry bituminized cation exchange resin stored in ordinary laboratory air, compared with the weight increase for a similar sample stored in high humidity air, and with typical volume contraction for pure Mexphalte 40/50.

Sample material:

40 % IR 120 on  $\text{Na}^+$  form / 60 % Mexphalte 40/50  
data from /28,41/.

### 6.3 Chemical aging

It should be remembered that slow reactions probably take place between bitumen and components from the embedded waste particles even in completely sealed systems stored at room temperature. However, specific experimental evidence is lacking.

A special type of chemical aging contributing to embrittlement is the evaporation of volatile organic components from the material. This is usually insignificant since the bitumen types commonly employed are more or less weight-stable at reasonable storage temperatures.

It is well known from investigations of other applications of bitumen that the material reacts with oxygen from the atmosphere /32,43/. The process is slow in the dark but relatively fast when samples are exposed to sunlight. The result is the formation of a hard and brittle surface layer. This mechanism is irrelevant for bituminized wastes, which will not normally be exposed to sunlight, but internal radiation may result in similar photolytic reactions with oxygen from the environment.

### 6.4 Radiation aging

Reviews of the extensive studies of the radiation stability of bituminized wastes are available /22,32/. 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<sup>3</sup>, corresponding to maximum dose rates of up to 4 Gy/h and a maximum absorbed dose of less than 2 MGy (recalculated from Ref. 22). 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  $\text{CO}_x$  and  $\text{H}_2\text{O}$ . The volume of radiolysis gas is approximately 0.1 l/kGy for a 200 l drum filled with bituminized ion exchange resin.

When the amount of radiolysis gas exceeds the solubility of the hydrogen in bitumen (about 1/2 l for a 200 l drum), swelling due to bubble formation can be initiated. In practice, significant swelling only occurs above 100 kGy, but the limiting dose is largely a function of the dose rate and of the size, container geometry and temperature of the unit since these determine the rate of out-diffusion of the hydrogen. It has been shown /44,45/ that roughly the same degree of swelling is obtained for samples with typical dimensions  $L$  and exposed to dose rates  $I$  provided the product  $I \cdot L^2$  is the same. This provides a tool for extrapolating experimental results obtained with high dose rates to real storage conditions.

Besides the safety aspects (cracked containers) associated with swelling as such, bubble formation may strain the material and lead to micro-cracks and impaired performance of the material in contact with water. However, experimental evidence indicates that moderate radiation may improve the properties of the material as far as leaching is concerned /45/. Fig. 6-2 shows an example of bubble formation in a small sample of bituminized ion exchange resin irradiated at a high dose rate to 500 kGy.

According to the above formula, a similar effect can be expected in a full-size drum irradiated to 500 kGy at a rate of  $\sim 10$  Gy/h, i.e. a factor 2 above the maximum dose rate for reactor waste mentioned above. In real wastes, the radiation will mainly be from internal sources, and this is likely to enhance the gas generation, especially if  $\alpha$ -radiation is involved. However, gas formation is not expected to be a problem for the wastes considered here.

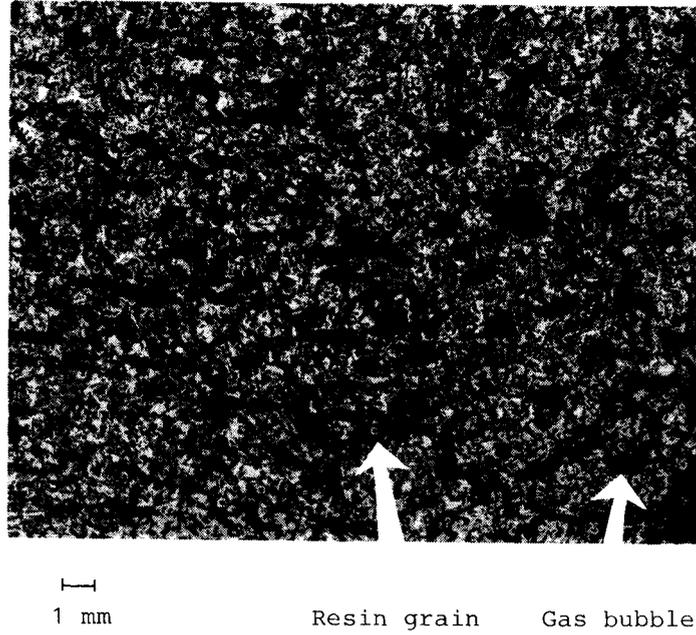


Fig. 6-2. 40 % cation exchange resin mainly on  $H^+$  form  
60 % Mexphalte 40/50

Sample size:  $d = 5.5 \text{ cm}^\phi$   
Irradiated with external  $\gamma$ -rays to 500 kGy at  
28.4 kGy/day at room temperature. /39/

### 6.5 Water uptake from moist air

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 /28/. 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. 6-1, 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 /41/.

## 7. CHANGES IN BITUMINIZATION PRODUCTS IN CONTACT WITH WATER

Waste products will come into contact with water that is gradually filtering into the disposal silo. There is also a risk of accidental water contact if long-distance transport to the disposal site is needed. In the latter case, short-term leaching effects before retrieval of the waste packages are of importance.

Contact with water gives rise to a slow diffusion of water into the waste product, which provides a basis for

- leaching of radionuclides from the wastes and eventual transport of released activities by diffusion or with flowing groundwater
- swelling and build up of swelling pressure with risk of mechanical impairment of external barriers
- degradation of the waste product, pore formation and channelling, which may enhance the water uptake and consequently even the rate of swelling and leaching.

The extent to which such processes will lead to the release of radionuclides into the biosphere will depend on various system properties, on waste and matrix characteristics and history (see Chapter 5 and 6), on water chemistry and on flow rates relative to exposed surfaces. Most work on interactions between bituminized wastes and water has been focused on the determination of leach rates. The relevance of results from these short-term leach tests to the actual long-term performance of industrial waste products is, however, questionable. There is still a need for a better understanding of and more versatile investigations into the mechanisms involved. For this reason the AVF-2 project has dealt with several different aspects of the interactions between waste and water:

- Theoretical evaluations and model development to predict the rate and final maximum water uptake /35,46,47/.

- Development of test methods for fundamental studies of transport phenomena, swelling, leaching /48/, structural changes /30/ and barrier interactions.
- Prolonged parallel measurements on leaching and swelling in selected samples to investigate effects of waste characteristics, process parameters and water chemistry /3,49/.

Under wet disposal conditions, the following properties of the system are likely to be of importance for the stability of the waste material and for the rate of release of activity /35/:

- Waste and matrix type, waste/matrix ratio, homogeneity and initial water content of the solidified waste as determined by process parameters.
- Chemical conditions in the leachant.
- Temperature.
- Removal rate of the leached material from the exposed surface area of the barrier system.
- Conditions influencing microbial growth: nutrients, pH, toxic materials, etc.

Internal or external influences may cause the properties of the waste and also the repository environment to change considerably with time. Some of these have been investigated in the project.

#### 7.1. Transport of water in the product

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.

If we assume that no voids were originally present in the product, the water transport can be described as follows:

- At low resin to bitumen ratios, all particles are surrounded by a film of bitumen and water uptake can be described by a diffusion model and the diffusion coefficient can be measured. When the bituminized resin particles swell they may damage the bitumen film, and so water transport proceeds at a faster rate than that corresponding to diffusion-controlled water uptake.
- When the resin to bitumen ratio is higher, clusters or connected strings of resin particles, which conduct water through the whole waste monolith, will probably be formed. This phenomenon can be studied with the aid of the percolation theory /50/.

Theoretical models of the transport mechanism of water should take the following into account:

- Initial water content.
- The isotherm for sorption of water by ion exchange resins.
- The effect of resin concentration.
- The effect of thermal treatment of resins.
- Swelling.
- Pressure build-up.

A simplified model has been utilized when calculating diffusion coefficients for water absorption /46/ 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

$$\frac{\delta C}{\delta t} = D \nabla^2 C \quad (7-1)$$

where C is the bulk concentration of water and D a diffusion coefficient 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

$$\hat{J}_0 = C_0 \left( \frac{D}{\pi t} \right)^{1/2} \quad (7-2)$$

where  $C_0$  is the saturation concentration of water in the surface layer.

An example of measurement of water uptake is shown in Fig. 7-1 /33/. The time is drawn in square root scale to linearize the behaviour according to the diffusion law.

The accumulated amount of water Q per unit surface area is

$$Q = 2C_0 \left( \frac{Dt}{\pi} \right)^{1/2} \quad (7-3)$$

The equation (7-3) is fitted to the experimental data to obtain D.

The weight increase in the samples during leaching is often governed by a diffusion-like mechanism giving relatively straight lines when plotted as a function of the square root of time. Thus an approximate diffusion coefficient can be obtained from the experimental data. If the material contains bubbles or

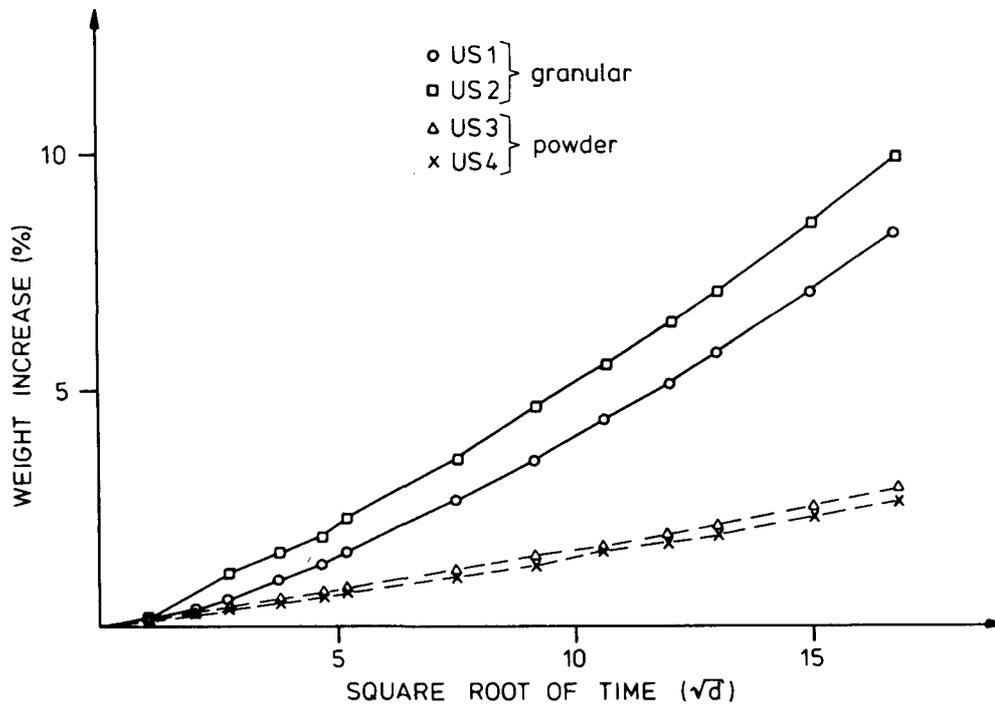


Figure 7-1. Weight increase caused by water uptake during a leach test /33/. The samples contain mixed bed powdered or granular resin of 33 or 50 weight-%, respectively.

voids, the surface of the material is not well defined, and the rate of water absorption is higher and cannot be fitted with a linear square root of time dependency.

Figure 7-2 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.

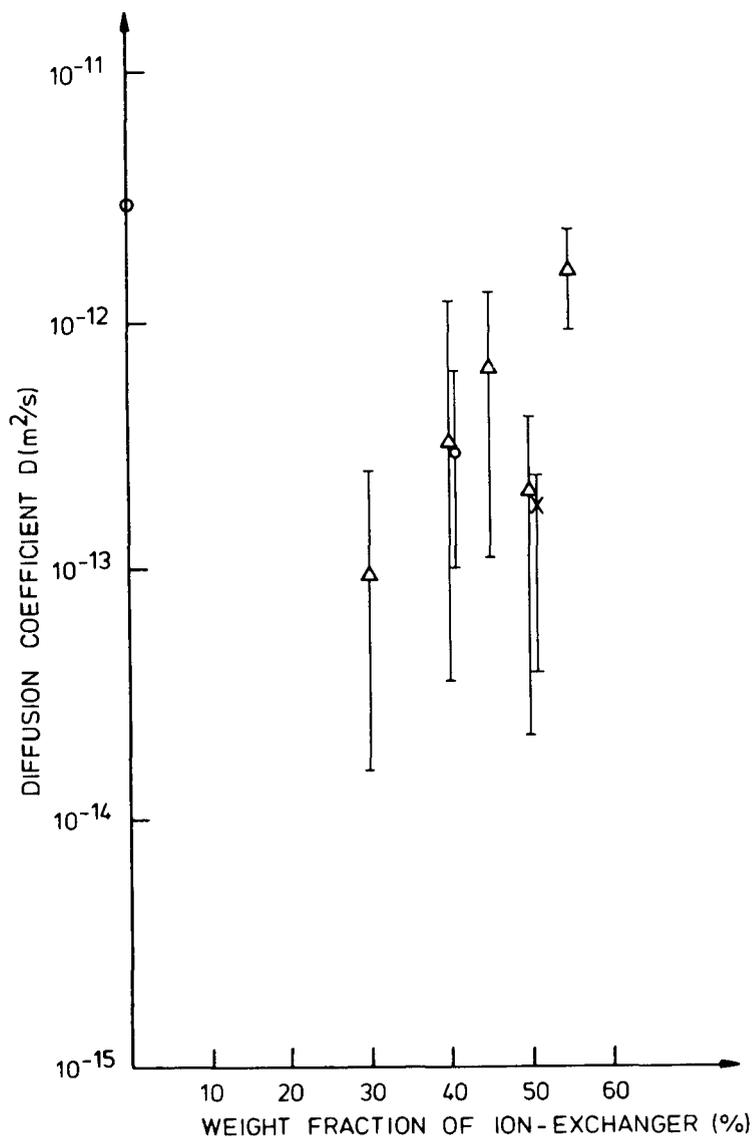


Figure 7-2. Diffusion coefficients of water for bituminized granular ion-exchange resin.

△ data from Aittola and Kleveland /46/

○ data from Brodersen et al. /26/

x data from Valkiainen and Uotila /51/

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 /52/. 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. 7-2 /60/. This behaviour 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. 7-2.

As mentioned above, percolation-like phenomena can influence the transport mechanism of water in a product containing water-conducting ion exchange particles of sufficiently random distribution. Numerical studies have shown that a volume fraction of 0.29 and more of a conducting medium dispersed in a non-conducting medium will give a continuously conducting composite /50/. An attempt should be made to simulate percolative conduction for bituminized ion-exchangers. The experimental data points in Fig. 7-2 cover the region of practical resin to bitumen mixtures from 30 % of resin upwards, showing a simultaneous increase in the diffusion coefficient. A data point around 10 % would be needed to verify the decrease in  $D$  experimentally.

## 7.2 Swelling of the bituminization product

The rate of swelling depends on the rate of water diffusion in the material and on the sample dimensions, but, if all the water is taken up by the particles, the final maximum swelling is only dependent on the waste loading, the swelling capacity of the waste and the initial water content. Various possibilities in swelling behaviour have been discussed by Brodersen et al /35/.

In the simplest case the swelling is due to rehydration of the dried and bituminized resin particles without the additional formation of water-filled voids. If the ratio of volumes of resin before and after rehydration is  $S$ , the fractional volume increase of the product containing a weight fraction  $W$  of resin is given by  $S'$  /35/.

$$S' = \frac{S - 1}{1 - W + \frac{W \rho_d}{\rho_{bit}}} \quad (7-4)$$

$\rho_d$  and  $\rho_{bit}$  are the densities of dry resin and bitumen, respectively. If the amount  $Q$  of water is absorbed in the bituminization product so that the corresponding amount of resin is completely saturated, a volume increase of  $\Delta V$  is obtained.

$$\Delta V = \frac{Q}{\rho_W} \left[ 1 + \frac{\rho_d}{\rho_W \left( S - \frac{\rho_d}{\rho_W} \right)} \right] - \frac{Q}{\rho_d} \left[ \frac{\rho_d}{\rho_W \left( S - \frac{\rho_d}{\rho_W} \right)} \right] \quad (7-5)$$

where  $\rho_W$  is the density of the wet, swollen resin.

The rate of volume increase of unrestricted swelling can be roughly obtained by applying (7-3) and (7-5). If the resin densities (dry and wet) are close to the density of water, the volume increase is almost equal to the water volumes absorbed. However, any contraction phenomena, as discussed in Section 6.2, should also be taken into account.

If the swelling of the bituminized ion exchange resin is restricted but the uptake of water is possible, considerable pressure may develop. Swelling pressures have been estimated both theoretically /29,30,53/ and experimentally /33,34,54/.

Measurement of the swelling properties of 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 7-1.

Table 7-1. Swelling pressures obtained with dried Duolite resins mixed with inert powder filling voids between the grains.  $\Delta V$  is the volume increase allowed for the sample.

Sample	Drying	Swelling pressure, MPa			Ref.
		$\Delta V=0\%$	$\Delta V=10\%$	$\Delta V=20\%$	
ARA 366 40% + ARC 351 60% quartz powder 1:4	24h 105 <sup>0</sup> C	31.0	2.5	0.3	/34/
ARA 366 67% + ARC 351 33% glass powder 1:0.9	16h 140 <sup>0</sup> C	7.1	0.7	0.3	/33/

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. However, swelling pressure has also been measured with mixtures of cationic resin and bitumen containing 50-60 % resin /34,54/. A measurement using a constant volume ("zero swelling") showed a stabilized maximum swelling pressure of 2.3 MPa after 50 days /54/, while another measurement with a constant load of 1 MPa showed a saturation of swelling of 20 % after 400 d /34/.

According to present understanding, the repository design should allow for the swelling caused by rehydration of ion exchange resins.

If swelling is restricted, it is important to estimate the residual swelling pressure after the available free volume is used up. This could be done by applying Eq. (7-4) to obtain the maximum allowable  $S$ . There is, however, a certain lack of reliable pressure-versus-volume data for restricted swelling.

### 7.3 Leaching

The term "leaching" is mostly used to refer to the release of radioactive components, but there will always be a simultaneous leaching of inactive materials (salts, organics) from the waste and the matrix. This may influence the leaching and mobility of the radioactive components. Effects on external barriers may also have to be considered.

It has been shown that small amounts of organic material (typically 1-3 mg  $\text{CH}_2$ /l at equilibrium) can be leached from pure bitumen in contact with water with a different pH /56/. It has still not been possible to identify the extracted components, but nevertheless the investigations furnish an experimental basis for further studies concerning the leaching of organic materials from bitumen products.

#### 7.3.1 Leaching and source terms /35/

Many results are available from investigations of the leaching of radio-isotopes from various types of bituminized waste under different conditions. Unfortunately the experiments have normally been of relatively short duration: from a few months, to a few years at the most. In most of them no attempt was made to investigate what is actually happening in the material during the leaching process. Direct extrapolation of measured leach

rates for use in safety analyses covering long periods is therefore a somewhat questionable practice.

Measured leach rates from bituminized waste products can often be described with reasonable accuracy to be governed by diffusion, i.e. for flat samples of semi-infinite thickness they follow (after a short initial period) a relationship in the form:

$$R = \sqrt{\frac{D}{\pi \cdot t}} \quad \text{cm/day} \quad (7-6)$$

which, introducing the product density,  $\rho$  g/cm<sup>3</sup>, and the specific activity,  $a = a_0 \cdot \exp - (\ln 2 \cdot t/t_{1/2})$  Ci/g, gives a release rate:

$$R \cdot \rho \cdot a = \sqrt{\frac{D}{\pi \cdot t}} \cdot \rho \cdot a_0 \cdot \exp - (\ln 2 \cdot t/t_{1/2}) \quad \text{Ci/cm}^2/\text{day} \quad (7-7)$$

Multiplication by the water-exposed specific surface of the bituminized waste,  $A(t)$  cm<sup>2</sup>/g, and the amount of waste that has been disposed of:  $M$  g, gives a source term for the release of activity to the environment.

Such formulas can be used to extrapolate the leach rates measured and to obtain source terms for future situations, but it should always be kept in mind that the conditions determining the shape of the leach curve are not necessarily constant and may change with time. This can happen in the form of changes in the bituminized material, in the leached layers or in the environment where the leaching takes place:

- The presence of water in the bituminized material is thought to be a prerequisite for the leaching of radioactive isotopes and other components from the waste. This statement is supported by the fact that no or very little activity is associated with the bitumen if it is extracted from a dry mixture of waste and bitumen using a suitable organic solvent, i.e. there is no tendency for the radioisotopes to migrate out in bitumen as such. A possible exception could be components not of the ionic type.

If water must penetrate into the material before leaching can take place - and in cases investigated /35/ it has been possible to demonstrate that water always penetrates deeper into the material than the thickness of the leached layer - it follows that mechanisms influencing water uptake, as described in previous sections, may also influence leach rates. However, if the experimentally measured leach rates always represent a situation with leaching from already fully water-saturated layers, they may also be fairly representative of leaching from deeper layers, which at a later stage are changed by water uptake. The condition for this is, of course, that the development of water-saturated layers must always be faster than the increase in thickness of the leached layer.

- Leach rates can only be expected to follow the  $\sqrt{t}$  law typical of diffusion governed leaching when there is no dissolution or disintegration of the leached layers. A further requirement is that there must be no significant changes with time in the properties of leached layers. Such changes, if they occur, represent a type of aging reaction but the situation is very different from the aging of the unleached bulk material in the interior of the waste package.
  
- Changes in external conditions, such as temperature, pressure, water flow rate and water chemistry, will influence the leach rate in various ways. Some of these effects can be taken into account in the form of parameter variations of the diffusion coefficient  $D$ , but it is by no means certain that samples with different histories will behave in the same way when placed under identical external conditions.

A phenomenon that will change the source term, even if the leach rate is unchanged, is an increase in the water exposed surface of the waste. This might occur if:

- The originally monolithic waste units are cracking into smaller pieces. (This is not very probable with the generally very tough bituminized waste products.)
- The outer container, which protects the surface of the waste, is corroding or cracking.
- The waste is flowing out of corroded or cracked containers. However, this is probably not possible in an efficiently back-filled repository. The main questions as far as the exposed surface is concerned are therefore when, how fast and to what extent the outer containers corrode or crack.

Leaching performed with large amounts of frequently changed or continuously fast flowing water will result in very low concentrations of leached components in the water. Under such conditions, the simple leach rate and source term formulas on page 61 can be used to calculate the release.

If the water is stagnant or slow flowing, leaching will result in increased concentrations of leached materials near the surface of the waste. This will retard or even prevent further diffusion out of the material. Simple use of the leach rate and source term formulas will then give an excessively high estimate of the release. More realistic calculations require mathematical simulation of the combined system of waste plus surroundings, including water flow rates, diffusion and retardation of the leached materials.

The leaching of radionuclides can be enhanced or retarded by chemical processes, e.g. by complex formation, hydrolysis or ion exchange reactions. The (leachant) water chemistry is of vital

importance in this respect - as illustrated by systematic single-component experiments made at NRL, Risø /55/ - but interactions with other waste constituents (salts, organic materials, complexing agents) must also be considered.

Comparisons of data for products prepared in the laboratory and from different technical bituminization processes are hampered by a lack of information about the influence of deviating process parameters /3/.

It is not likely to be easy to disentangle the many partly interdependent and overlapping effects of all the variables in a real waste system. Fundamental work with simplified systems may be needed to understand more realistic simulation experiments with "real" wastes /26/.

Leach data from different sources may vary considerably owing to the influence of experimental parameters /2/. It is therefore important to choose relevant test conditions. B. Allard /57/ has reviewed standard leach methods (Hespe, ISO, MCC-1) with respect to their suitability for simulation of leaching from bituminized ion exchange resins in a repository in granite bedrock. In conclusion he recommends a modified ISO/Hespe test with two standard waters, supplemented by tests to control the effects of certain corrosive agents, micro organisms and organic materials.

### 7.3.2 Leach measurements and waste variables

To provide leach data that are representative for real, often poorly defined, technical wastes, the major impact of the variations expected in waste composition and process conditions must be taken into account.

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 frame work 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 on the from prolonged water exposure (up to four years) of some 40 samples with such simulated waste /46/.

The AVF-2 experiments concerning the influence of decontamination chemicals /58/ 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.

Samples were dewatered, bituminized and cast with a laboratory scale "Werner & Pfleiderer LABOR LUK-4-X/A-2" mixing-kneading machine /49/. Typical mixing temperatures were around 130°C. Additional experiments with varying bituminization temperatures, modes and degrees of dewatering /49/ give some impression of the impact of typical process parameters.

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 /3,46/. The main features of the "cement water test" devised by K. Brodersen /48/ are shown in Figure 7-3. Leaching with strongly alkaline "cement water" and hardened cement granules in the leachant simulates conditions in a repository where concrete is used as structural material. 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  $\text{CO}_2$  absorption from interfering.

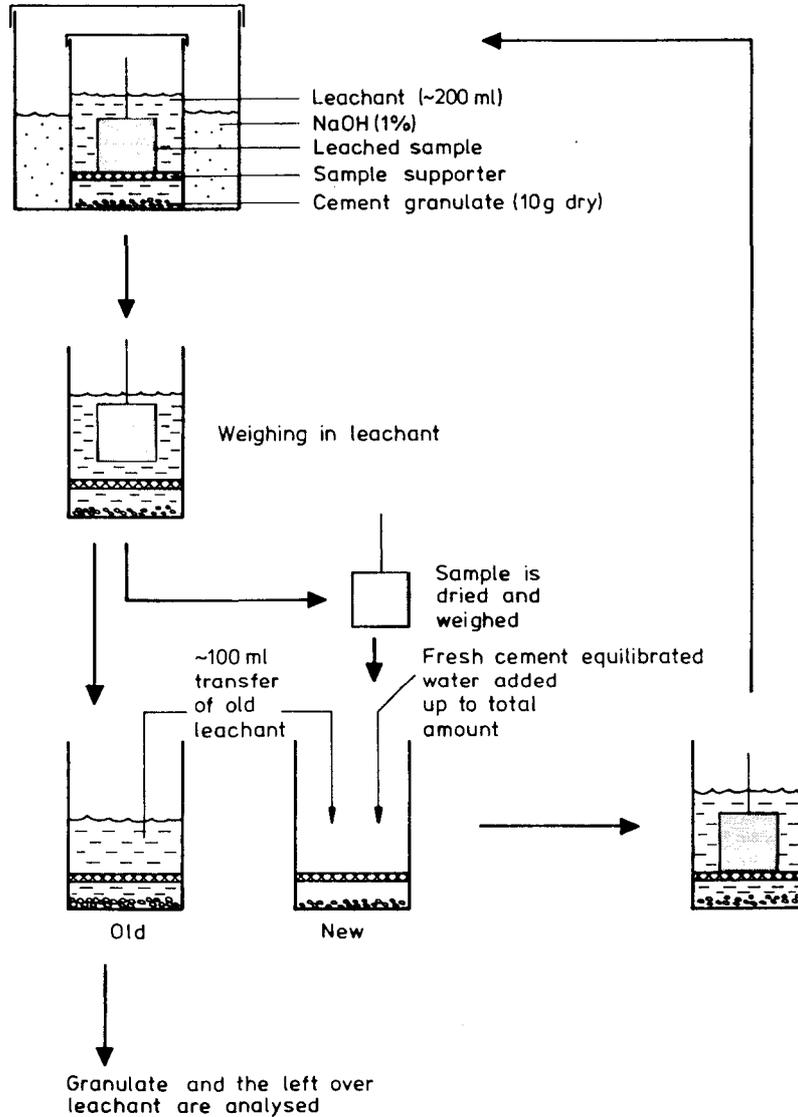


Figure 7-3. A schema featuring leaching and water uptake (weight increase and swelling) measurements for samples stored in cement equilibrated water /49/.

The reproducibility of leach measurements on bituminized granular resins is impeded by the (micro)heterogeneity of a material with relatively large resin beads dispersed in a bitumen matrix. It may even be difficult to avoid macroheterogeneities due to sedimentation of the heavier cation resin beads. A frequently observed initial phase with an exceptionally low (but occasionally even high) leach rate is also typical of this material.

Simultaneous measurement of three nuclides (Cs, Sr and Co) in the same sample and in two different leachants helps to control such effects and to demonstrate the main effects of the system variables. The leach rates measured have been in the order of  $<10^{-8}$  to  $10^{-4}$   $\text{gcm}^{-2}\text{d}^{-1}$  for Co,  $10^{-6}$  to  $10^{-4}$   $\text{gcm}^{-2}\text{d}^{-1}$  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. 7-4, 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 ( $R_{\text{cem}}/R_{\text{de}}$ ) 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). Conditions for Cs are illustrated by Fig. 7-5. The impact of decontamination chemicals may be fundamentally different in the two media.

Swelling and deformation, see Fig. 7-5, are somewhat suppressed for samples soaked in cement-conditioned water.

Overlapping ion exchange reactions make it difficult to derive quantitative correlations between leaching and swelling.

The rate of swelling is highest for cation resins, somewhat lower for mixed-bed and significantly lower for anion resins (e.g. CAT:AN ~ 3:1 as shown in Fig. 7-5). A corresponding trend (AN<CAT) is observed in "cement water" leach rates.

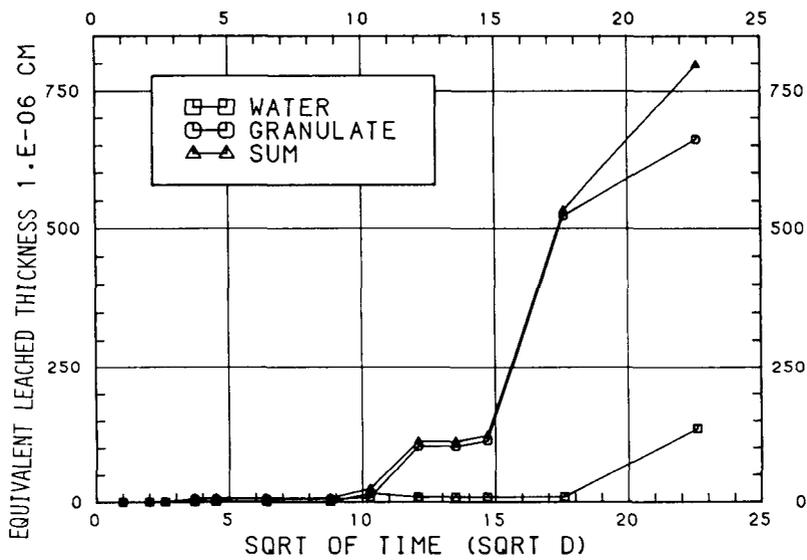


Figure 7-4. The equivalent leached thickness of Co-60 in cement-conditioned water from bituminized granular mixed-bed ion exchange resin. The time scale is the square root of days. Resin:bitumen = 50:50 /49/. (Granulate, see Figure 7-3)

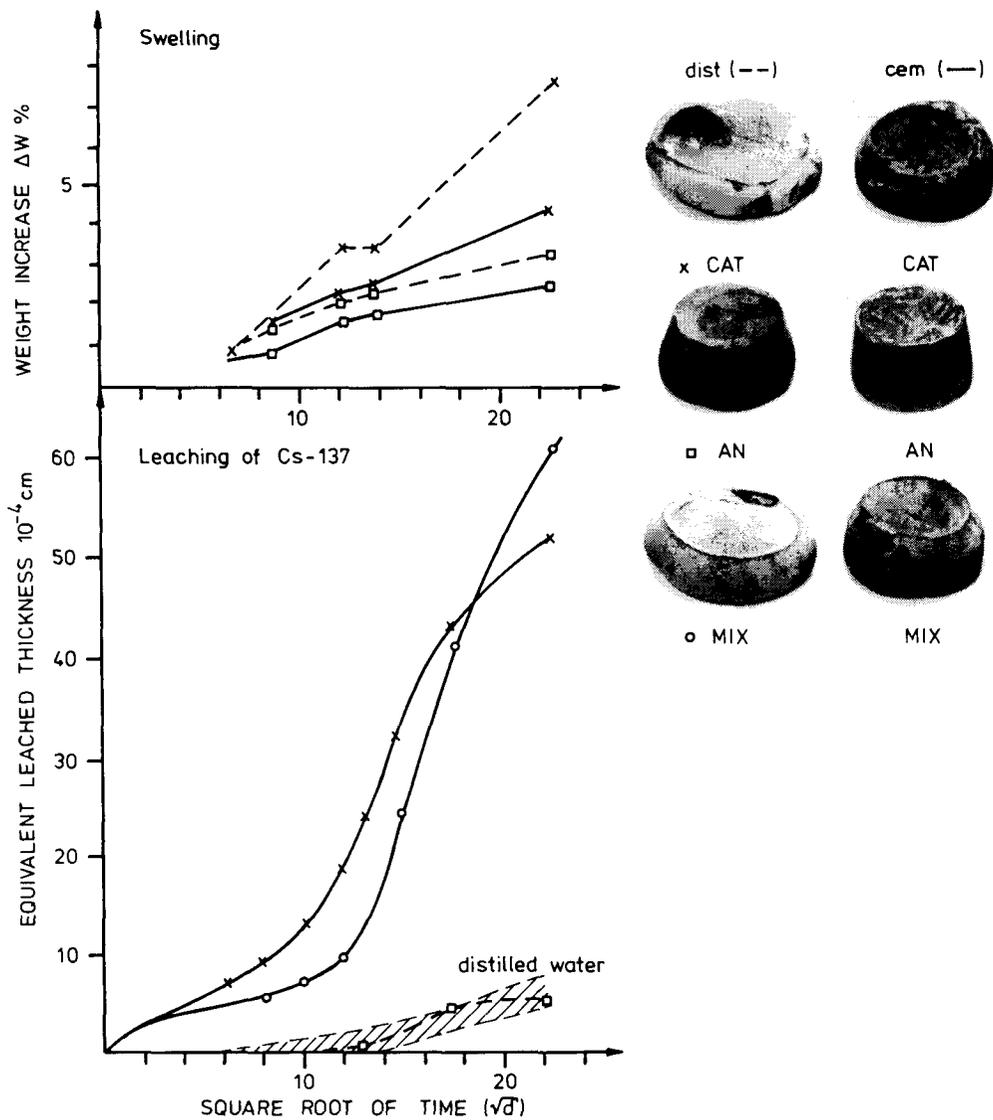


Figure 7-5. Effect of cement conditioned water on swelling and leachability of cation (CAT), anion (AN) and mixed bed (MIX) resins. 512 d exposure in distilled (dist) and cement conditioned (cem) water /49/.

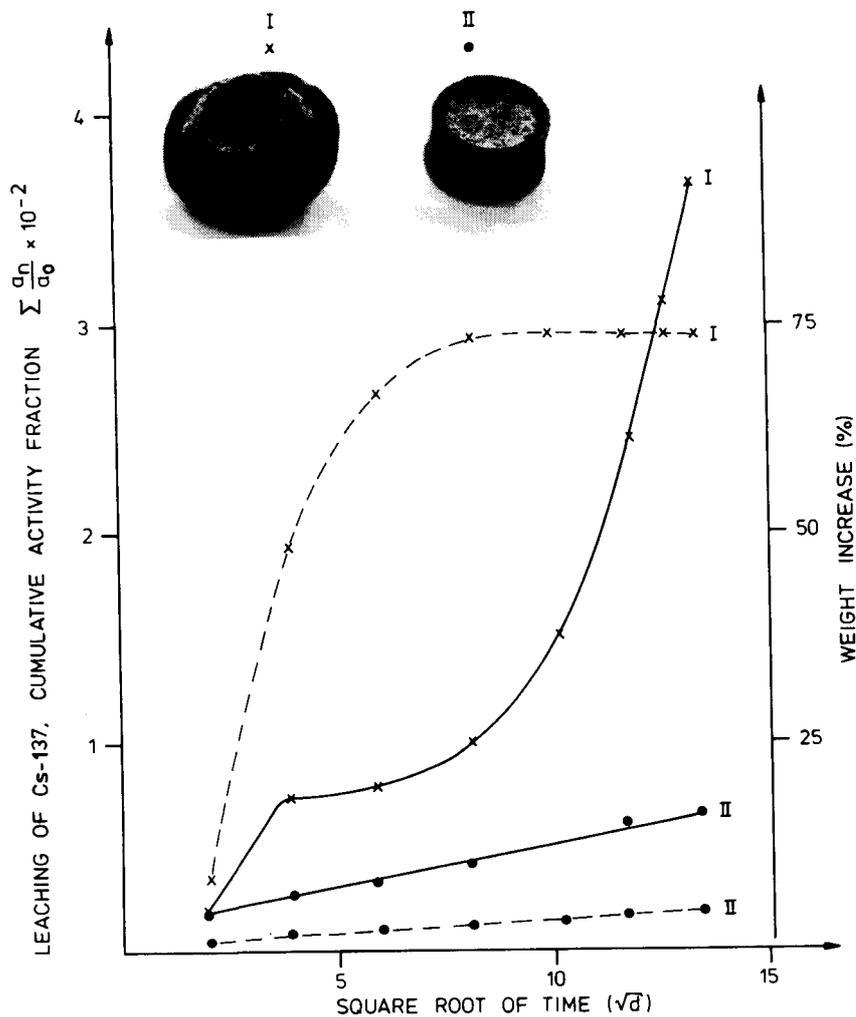


Figure 7-6. Enhanced swelling (---) and "cement water" leaching of Cs-137 (—) from heterogeneous cation exchange product. Effect of drying conditions. I. Resin pre-dried to const. weight at 105°C. II. Wet (even level) resin dewatered in bituminization machine (standard procedure). Both bituminized at 160°C /49/.

The most drastic leach enhancements are observed at high (>60 w-%) resin concentrations /1,3/. Normal waste loadings of up to 40-50% are well below this critical concentration range, but sedimentation or incomplete homogenization may introduce risks of local critical concentrations, enhanced leaching and swelling, as illustrated by Fig. 7-6.

The observed impact of bitumen qualities /3,46/ can probably be ascribed to such effects. An excessively soft and light matrix will favour sedimentation of the heavier cation resin beads. Bitumen density, viscosity and softening point, resin concentration and particle size are important in this respect.

The presence of decontamination chemicals may lead to severe swelling and enhanced leaching of Co /46/.

The effects of swelling are governed mainly by decomposition of the organic chemicals and by the interaction between the resultant decomposition products and the bitumen matrix. They are strongly affected by minor variations in process temperature profiles, and decomposition is further enhanced in the presence of nitrates. This has caused interference in experiments with macroconcentrations of Ni nitrates /49/, but could be kept under control in the radioactive (Cs-Sr-Co) tracer experiments, where only minor effects on swelling were observed.

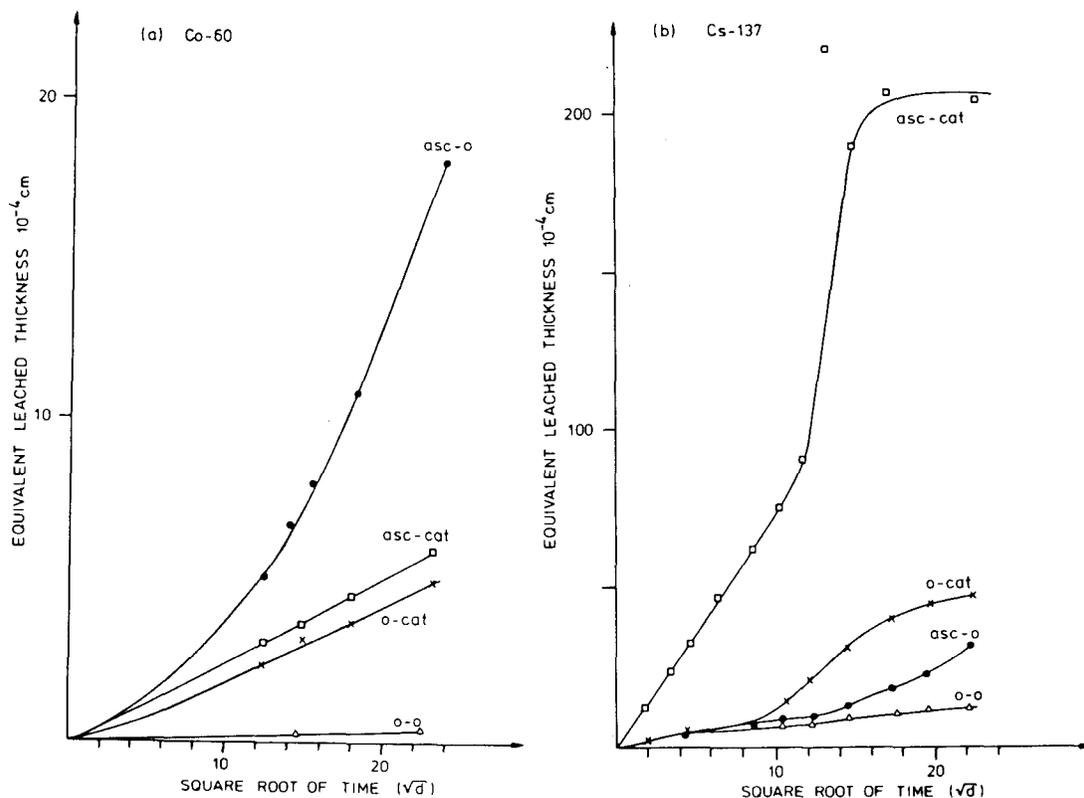
The rather complex influence of decontamination chemicals on the leaching of these nuclides can be illustrated by two representative cases, Figs 7-7.

- a. Strongly enhanced leaching from resin-free samples. Elimination or reduction of this effect in the presence of ion exchange resins. Observed in Co (and Ni) in both leachants, partly also for Cs and Sr in dist. water.
- b. Enhanced leaching from bituminized resins. Typical of Cs and Sr in "cement water". Only minor effects on leaching from resin-free samples.

Absorption on ion exchange resins may extend the tolerance limits for the incorporation of organic decontamination chemicals. Drastic effects of complex formation are often moderated or eliminated (a). Additional effects, such as enhanced leaching of Cs (b) and Sr in "cement water", however, must be taken into account. This may be associated with increased water uptake and swelling caused by the decomposition products of the decontamination chemicals and their possible interactions with the bitumen matrix, as demonstrated by the Ni-nitrate experiments /49/.

Increasing bituminization temperatures (110<sup>0</sup>C, 135<sup>0</sup>C and 160<sup>0</sup>C) appear to reduce the leachability and swelling of anion resin products, Fig. 7-8(a), which is consistent with the reduced swelling tendency of the free resins owing to the thermal degradation of functional groups. The opposite trend observed in cation exchange samples, Fig. 7-8 (b) may be due partly to a parallel increase in the casting temperature and resultant sedimentation.

The mode of dewatering may have significant effects on product homogeneities. Fig. 7-6 illustrates the drastic effects of altered drying conditions on sample homogeneity, swelling and leaching, further exacerbated by high casting temperatures. Such effects can probably be overcome by adaptation of other process parameters (contact time, mixing efficiency, temperature profiles).



ASC-O = ASCORBIC ACID + BITUMEN + TRACER NUCLIDES  
 ASC-CAT = ASCORBIC ACID + BITUMEN + CATION RESIN + TRACER  
 NUCLIDES  
 O-CAT = CATION RESIN + BITUMEN + TRACER NUCLIDES  
 O-O = BITUMEN + TRACER NUCLIDES

Figure 7-7. Effects of decontamination chemicals. Cumulative leach rates for (a) Co-60, (b) Cs-137 in "cement water" /49/.

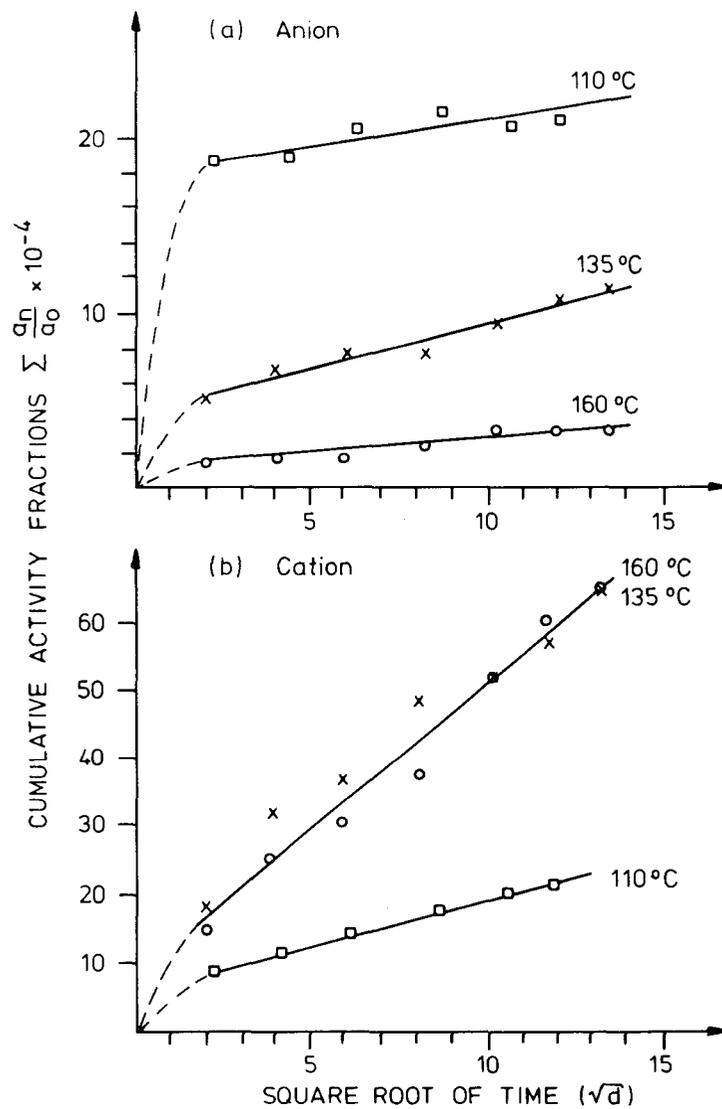


Figure 7-8. Effects of bituminization temperatures on the rate of leaching of Cs-137 from bituminized (a) anion and (b) cation exchange resins in "cement water" /49/.

The water content was found to have some effect on swelling and leaching. Because of the overlapping effects of other process parameters (mainly temperature profiles) consistent trends could not be demonstrated.

The following conclusions can be drawn from these leaching experiments

- Product homogeneity is of major importance. Bituminization of granular resins may involve risks for sedimentation leading to local critical concentrations, enhanced swelling and leaching. There is a need for control and optimization of the parameters that may affect sedimentation: resin concentration and particle size, bitumen viscosity, density and softening point, bituminization and mixing efficiencies, casting temperatures and conditions.
- Cation exchangers lead to most problems: the free resins have a large swelling capacity after drying and there is a risk of sedimentation due to high specific weight.
- Swelling introduced by decontamination chemicals is not dominated by effects on the resins, but mainly by the interactions between the decomposition products and the bitumen matrix. Drastic effects of complexing agents on the leaching of Co and Ni are moderated or eliminated by absorption on ion exchangers.

#### 7.4 Degradation of bitumen by micro-organisms

The effects of micro-organisms on bitumen and bituminized wastes were not investigated during the Nordic studies, but elsewhere it has been shown beyond doubt /26/ that under aerobic conditions bitumen is attacked by a variety of micro-organisms, including bacteria and fungi. A mixed culture growing on Mexphalte 40/50 is shown in Fig. 7-9. The rate of attack depends on the availability of nutrients, mainly N, P and S, and probably also on oxygen pressure.



Figure 7-9. Colonies of micro-organisms on the surface of pure Mexphalte 40/50 four months after inoculation. The sample was kept under aerobic conditions in a nutrient solution /28/.

Nitrogen and sulphur and the necessary micronutrients will often be present in bituminized wastes in sufficient amounts, but lack of phosphorus could be a limiting factor. High pH values, due to factors such as the presence of concrete, tend to diminish the rate of attack but seem not to prevent it.

Under anaerobic conditions, i.e. very low oxygen pressures, bitumen may also be attacked by micro-organisms, provided nitrates, sulphates or other materials that can act as electron acceptor in the energy supplying process of the micro-organism are present. There are indications that this is possible, but quantitative aspects cannot yet be evaluated.

The direct influence of micro-organisms on leaching from bituminized materials is likely to be small, since the rate of attack, even under optimum aerobic conditions, is low or comparable to the rate of increase of the leached layer owing to ordinary leaching. Under certain anaerobic conditions, the leach rate for  $^{60}\text{Co}$ , for example, can be reduced considerably perhaps as a result of precipitation of sulphides /21/.

Pressurization due to the carbon dioxide or other gases, or both, produced by the microbiological activity may be of importance for safety assessments.

The water chemistry of the systems will be influenced by the presence of micro-organisms. They may change the redox conditions and the pH, and degradation products from their metabolism are likely to form complexes with some leached ions, thus influencing the speciation of the released activity. However, this is probably a very local phenomenon since many complexes will split again relatively rapidly once the concentration of the ligand decreases with increasing distance from the source. Some model calculations illustrating this phenomenon have been made using the migration programme COLUMN /56/.

## 8. CONCLUSIONS

Significant amounts of bituminized low- and intermediate level wastes have been produced on a full-scale basis for several years in the Nordic countries. The intention is to dispose of these wastes in underground repositories. For the assessment of the performance and safety of the disposal, knowledge is required of the long-term properties of the waste form in the repository environment.

The purpose of the AVF-2 project has been to identify the factors of importance for the long-term behaviour of the wastes and to augment knowledge about these factors.

In the concepts for the final disposal of low- and intermediate-level wastes in Finland and Sweden the drums containing the bituminized wastes are surrounded by a concrete structure, thus limiting the empty space around the drum and creating a chemical environment in equilibrium with concrete. Fundamentally different chemical conditions will occur for disposal under conditions such as prevail in a Danish salt formation.

Under these conditions 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. A number of chemical interactions have been identified. It can be concluded, however, that the deterioration of the barriers caused by these interactions with the bituminized wastes is not likely to be a problem.

Microbial attack on bitumen could lead to gas evolution that could impair the function of the barriers. The limited number of experiments, however, does not provide conclusive evidence as to whether such an attack would be significant under anaerobic conditions or not.

For the Nordic disposal concepts the most important factor to be considered in the performance and safety assessment is the water uptake and subsequent swelling of the waste product. The bulk of the work within the AVF-2 project has been devoted to studies of these phenomena and the connected question of leaching of radioactivity from the waste product. The work has focused mainly on the ion exchange resins incorporated in bitumen. The following conclusions have been reached:

- the behaviour 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 it has been found that swelling - or consequences thereof - must be taken into account when disposal of bituminized reactor waste with normal radionuclide content is planned. The study has not revealed any other factor of similar importance.

The study shows that any restrictions in the use of bitumen as a waste matrix seem to result more from insufficient knowledge than from established detrimental or unacceptable long-term properties.

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