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Preparation of titanates and zeolites and their uses in radioactive waste management, particulary in the treatment of spent resins

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University of Lund, May 1983

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PREPARATION OF TITANATES AND ZEOLITES AND THEIR USES IN RADIOACTIVE WASTE MANAGEMENT, PARTICULARLY IN THE TREATMENT OF SPENT RESINS

A summary of efforts in Sweden until 1982

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SUMMARY

Work on the preparation of titanates and zeolites was started and their possible uses in the management of radioactive wastes proposed in the first years of the 1970's by the Department of Nuclear Chemistry at the Royal Institute of Technology in Stockholm and the Chemical Center of the University of Lund, respectively. The major part of these efforts was sponsored by the National Council for Radioactive Waste (Prav), while the concluding phase including an over-all system design study adapted to the Swedish nuclear power programme for an economic evaluation was sponsored by the KBS Division of the Swedish Nuclear Fuel Supply Co.

The preparation work resulted in processes ready for industrial scale production of sorbents of qualities adequate for applications in radioactive waste treatment. The essential effort was devoted to the treatment of spent resins from nuclear power plants by transfer of their radioactive contents to titanates and zeolites, which can then be sintered to stable ceramic bodies (the PILO process). The economic evaluation indicated a significant economic incentive for the introduction of the PILO process if an incineration step is included for all types of spent resins.

The essential efforts and results from this programme are summarized in this report.

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May 1983

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1. INTRODUCTION

1.1 Background

Spent ion exchange resins from the purification of water in reactor cooling circuits and spent fuel storage pools constitute a major fraction of low and medium level waste from the operation of nuclear reactors. With presently applied technology the spent resins are immobilized in cement or in bitumen, or, for the most low active fraction, just drained and stored in concrete tanks. These waste forms will account for about 70% of the total volume of operating low and medium level wastes from the Swedish nuclear power programme.

During the first years of the 1970's an interest was developed in Sweden on the possible use of titanates and zeolites as solidification matrices for radioactive wastes. Processes were developed for the preparation of these materials at the Royal Institute of Technology in Stockholm and the University of Lund, respectively. The original efforts were supported by the Board for Technical Development and the Atomic Research Council. In 1976 this responsibility was transferred to the National Council for Radioactive Waste which defined the application mainly to concern the management of low and medium level operating wastes. As the council was dissolved in mid 1981, the concluding phase of this programme was taken over by the KBS Division of the Swedish Nuclear Fuel Supply Co (SKBF).

1.2 Scope

Direct replacement of organic resins by inorganic sorbents was first tried without success in sampling loops of the Oskarshamn I reactor. The aim of the programme was subsequently changed to the development of a system for the transfer of more than 99% of Cs and Sr and most of remaining nuclides from the spent resins to inorganic sorbents, titanates, zeolites, that could be given a stable final form by drying and heat treatment. Such a system was finally demonstrated in laboratory scale using actual spent radioactive resins.

The development of sorbent preparation continued during the whole programme in order to obtain non-expensive sorbents of qualities suitable for use in column operations.

Some efforts were aimed at direct sorption from reactor station drainage water and from a fission product solution from the reprocessing of low burn-up fuel (at Kjeller, Norway). Studies on resin incineration and resin pyrolysis were also given attention.

An over-all study of a centralized system for the treatment of spent resins from all the Swedish nuclear power plants with a preliminary cost estimate concluded the programme.

Essential efforts and results, based mainly on previous publications from this programme (1-9) besides special contributions from the authors, are summarized in this report.

1.3 Proposed treatment system

A block diagram of a possible new scheme for the treatment of spent resins is shown in figure 1.

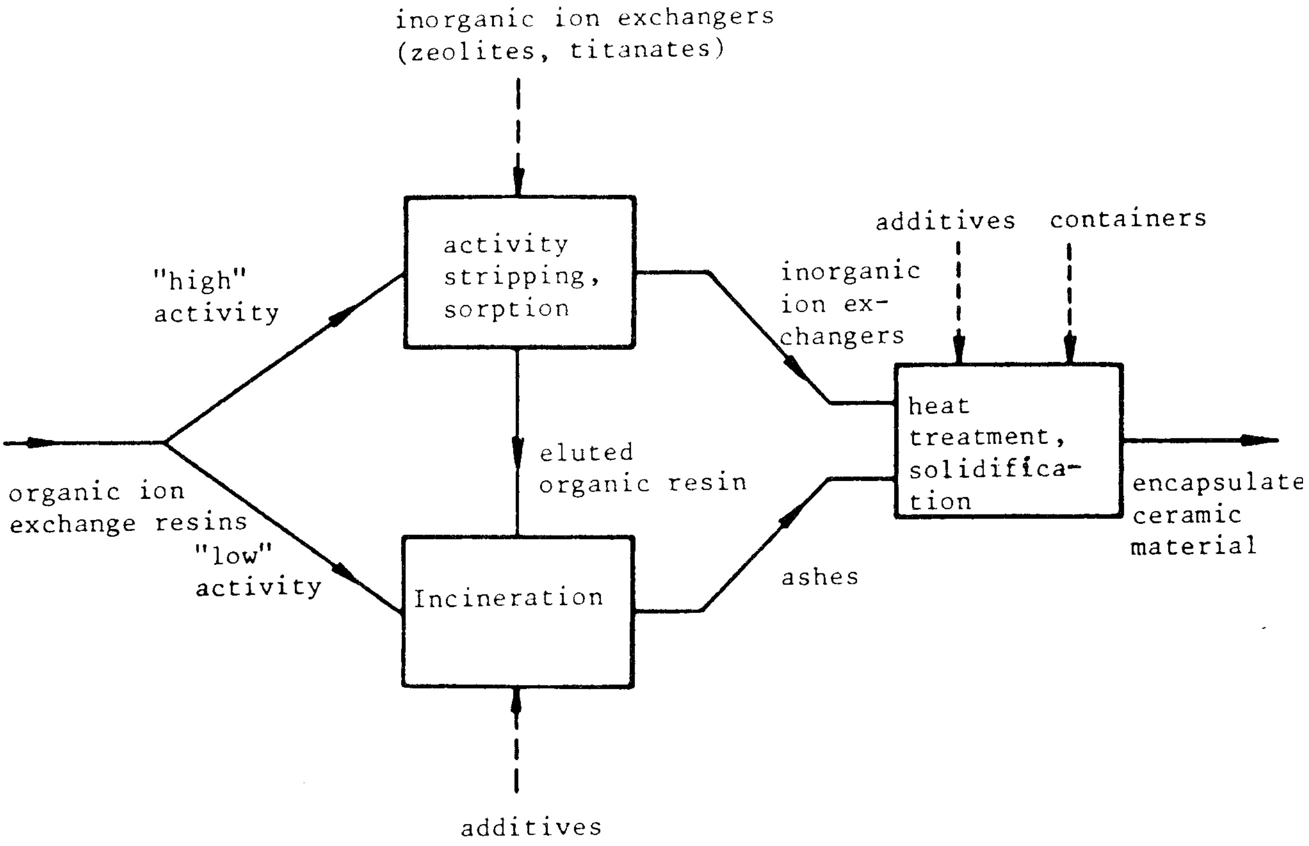


Figure 1 Block diagram of a new system for the treatment of spent organic ion exchange resins.

The basic idea is to transfer the long-lived activity of significance, mainly Cs-137 and Sr-90, and the main part of other active nuclides from the resins to inorganic ion exchangers (zeolites and titanates) that are sintered to leach resistant final products. A simplified incineration of the stripped resins is then possible. Resins of low activity may be incinerated directly. The integrated process would reduce initial waste volumes by a factor of 10, to compare with a volume increase by a factor of 2 for bituminization and 4-20 for cementation.

2. CHOICE OF SORBENTS

2.1 Background

As in other nuclear countries also in Sweden inorganic ion exchangers were studied already in the 1950's as decontaminating agents for radioactive waste solutions with potential applications for reactor cooling circuits. A number of such materials were prepared and tried for such applications in cooperation between AB Atomenergi and the University of Lund. However, as commercial purification systems based on organic ion exchange resins became technically established, these studies were concluded during the 1960's (10).

In view of new preparation techniques for inorganic sorbents developed at the beginning of the 1970's and the economic potential in volume reduction technology for radioactive wastes becoming visible, new incentives were found. The purpose of the work was to develop ion exchanging materials which can selectively sorb toxic long-lived waste nuclides, such as Cs-137 and Sr-90, and which can be transformed to stable ceramic or glass materials. Titanates and zeolites seemed promising for these aims.

2.2 Titanates

In 1974 T Westermark suggested ceramic materials such a TiO_2 as host matrices for high level radioactive waste with potential durability superior to borosilicate glass (11). The stability of strontium titanate, the long-term durability of naturally occuring rutile as a mineral and experiences from use of titanium dioxide as a dye pigment in paints for road markings supported this assumption. Preliminary tests on hot isostatic pressing of sodium titanate also gave very dense and stable bodies which encouraged continued work, as did the publication on advanced work along this line elsewhere (12).

2.3 Zeolites

Naturally occuring zeolites were first found in 1756 by the Swedish mineralogist Axel Fredrik Cronstedt, who also gave them their name (13). Today more than 300 000 tonnes of zeolitic tuff are mined each year for commercial uses. Natural zeolites are used for filler in paper industry, in pozzolanic cements and concrete, in fertilizer and soil conditioners, as ion exchanger in waste water treatment (such a plant is now under construction (14) at the Sellafield reprocessing plant in UK) in the separation of oxygen and nitrogen from air, as reforming petroleum catalysts, and as acid resistent adsorbents in gas drying and purification. Over the last 20 years the production of synthetic zeolites has, however, developed into a multi-million dollar business, mainly for applications as molecular sieves.

Zeolites are crystalline, hydrated aluminosilicates. Structurally the zeolites are framework aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygens. The framework contains channels and interconnected voids (35) which are occupied by the cations and water molecules as illustrated in figure 2.

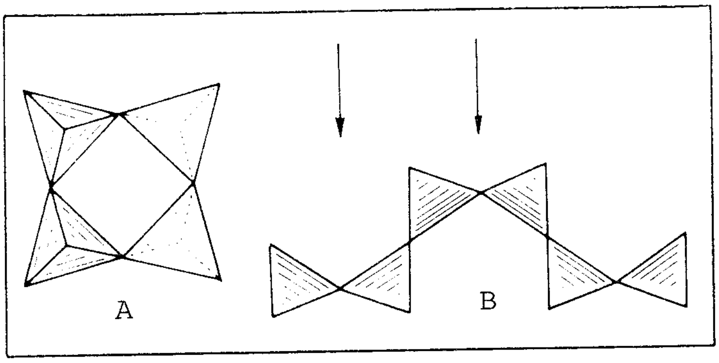


Figure 2 Figure 2A shows an element of a zeolite structure composed of four interconnected (Si, Al)O_4-tetrahedra.

Figure 2B shows such elements forming a chain structure, where figure 2A is a projection limited by the arrows. Three-dimensional structures may be obtained by interconnecting these chains.

The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. The diameter of the channels varies in size from about 2 Å and up. Depending on the channel size and the crystal structure it is possible for the zeolites to adsorb water and to act as molecular sieves and as selective exchangers.

Characteristic for most of the inorganic ion exchangers are their tunnel structures. Well known examples of such compounds are pyrochlor and pharmacosiderite. Zirconium phosphates and other Me(IV) phosphates and arsenates are also wellknown as ion exchangers. Different alkali-alumino-phosphates and germanates are examples of inorganic ion exchangers, stable at low pH-values. The drawback of the zeolites is their low stability in acid solutions. Zirconium phosphate and other Me(IV) phosphates, on the other hand, show a leakage of phosphate at higher pH-values.

The previous discussion explains why it is feasible to sorb various fission products as cations on a zeolite column. This sorption can, by a suitable choice of zeolite, be made selective. E.g. chabazite and faujazite may be used to remove Cs-137 and Sr-90 from a solution of mixed fission products.

Many zeolites have typical ceramic or glass compositions and it is thus possible to make a direct transition from zeolite to a stable ceramic or glass material by simply heating the material. The vapour pressure of the sorbed fission products is very low in this process because the exchanged ions are locked into the channels of the three-dimensional framework structure. This indicates that sorption of fission products on zeolites may offer a way to convert a liquid radioactive waste solution to a stable solid.

3. PREPARATION AND PRODUCTION OF SORBENTS

The desired characteristics of inorganic sorbents to be used in a column system for the decontamination of aqueous solutions may be defined as good sorption properties, ease of handling in the charging and discharging of columns, and low costs for their production. These characteristics were the guidance for the preparation of titanates and zeolites in this programme.

3.1 Titanates

The titanates used during most of the programme were prepared by precipitation from solutions of titanium tetrachloride. This is an intermediate product in industrial production of TiO_2 pigments, and was thus considered a possible basis for an economic large-scale production of titanate ion exchangers. Precipitation from aqueous solutions always yielded precipitates too fine-grained for use in columns, while precipitation from organic solutions almost always yielded coarse-grained precipitates. Ethanol was thus chosen as the solvent. Although sodium was considered to be the counter-ion of choice for titanate ion exchangers, several other basic agents were tried as precipitants, in the search for special effects from structural conditions determined by the agent itself. The following bases were tried: sodium and potassium hydroxide, ammonia in aqueous or alcoholic solution, mono-, di- or trimethylamine supplied in aqueous solutions, and hydrazine. Other bases. e.g. lithium hydroxide, ethylamine, ethylendiamine, quaternary methylamine and aromatic amines were considered but never tested systematically.

Batch precipitation of gram amounts of titanates in small beakers was repeatedly performed. Precipitates with no visible fraction finer than 30 µm were easily obtained, the largest grains approaching 1 mm. The heat from exothermic reactions dissipated without severe heating, but had to be considered for larger amounts.

For that reason, and in order to prepare for possible future large-scale production, a semi-continuous route was tried. In a first step, a stream of titanium tetrachloride was mixed with ethanol. In a second step, alcoholic solutions of the chloride and of the precipitating base were reacted. The first reaction developed so much heat when the chloride was fed through a polyethylene tube in counter-current with the solvent inside a narrow, cooled glass tube, that the ethanol occasionally came to boiling and the mouth of the plastic tube melted.

In order to cope with those problems, the glass apparatus shown in figure 3 was designed, making possible a smooth production of a few hundred grams of titanate ion exchanger per day. The viscosity of the slurry precipitated limited possible flow rate and optimum concentration, thus decreasing the total production capacity. For that reason a preneutralization step was introduced, comprising precipitation of ammonium chloride by the addition of ammonia, either as an aqueous solution or as a dry gas. A flowsheet for the preparation process is shown in figure 4.

As shown in table 1, this step allowed at least 90% of the chloride to be reacted with ammonia and at least 80% to be precipitated in the form of ammonium chloride and separated without

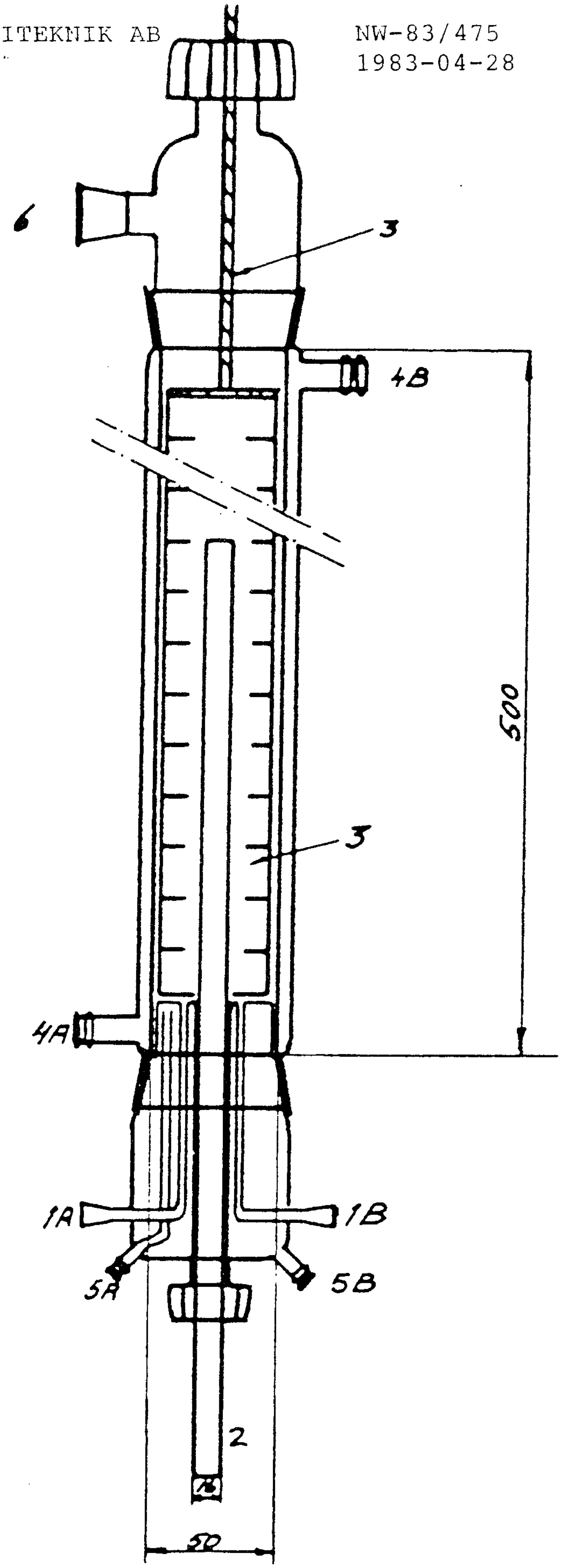


Figure 3 Glass apparatus used for the preparation of titanates from $TiCl_4$. 1A and 1B are inlets for $TiCl_4$ and base solutions, 2 is outlet for the slurried product, 3 is a steel stirrer with shaft, 4-5 are ports for cooling water, 6 is a vent.

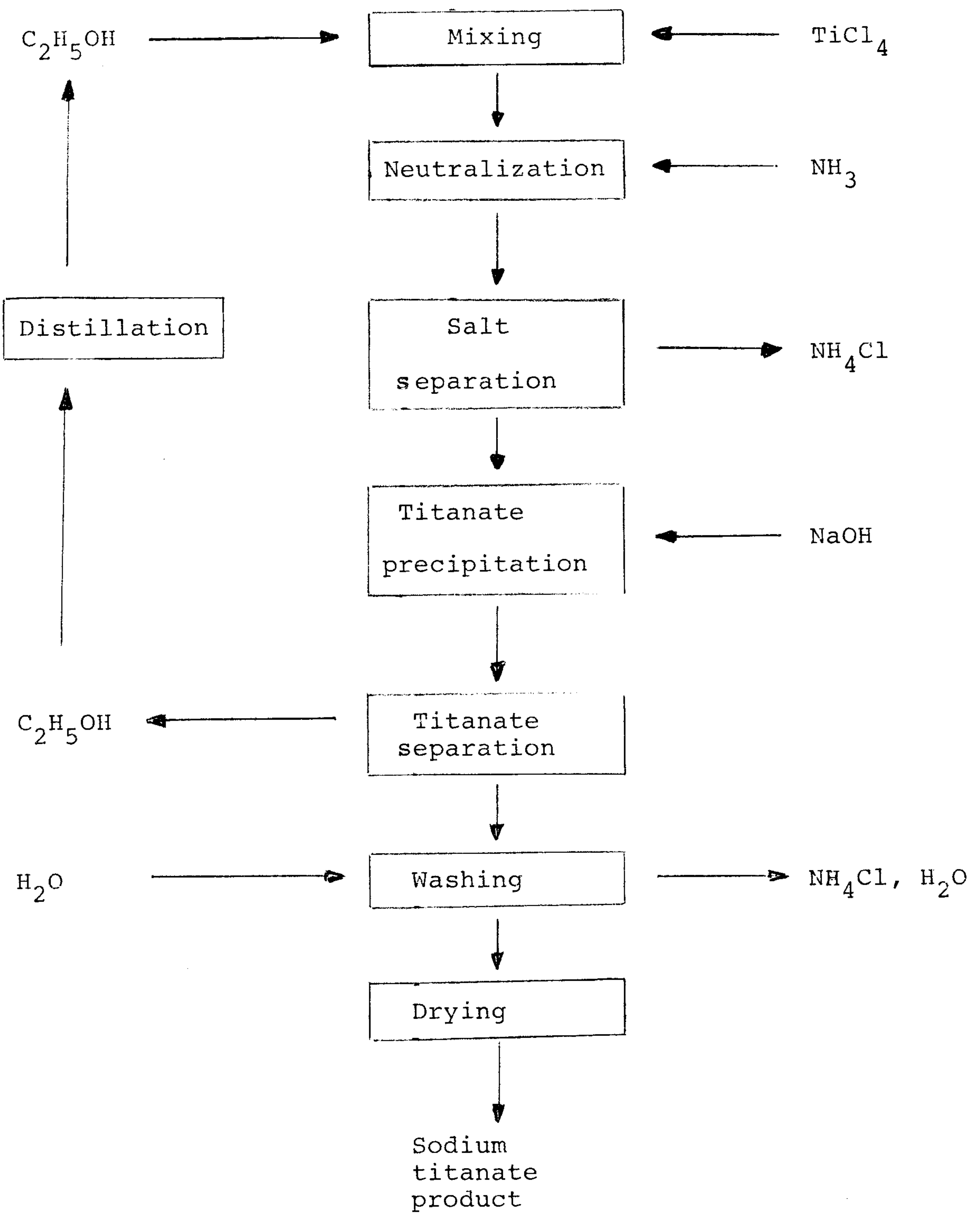


Figure 4 Flow sheet for the preparation of sodium titanate from $TiCl_4$ with a preneutralization step.

Table 1 Effects of preneutralization of a solution of 10 ml of $TiCl_4$ in 99.5% ethanol (10% by volume) by the addition of solutions of ammonia (1.6 M).

Mole NH_3 added per mole Cl	Dry precipitates: Soluble in H_2O (NH_4Cl) g	Dry precipitates: Insoluble in H_2O mg	Fraction of NH_4Cl removed by washing %
0.3	0.511	20	85
0.6	1.069	26	89
0.9	1.558	24	87
1.2	1.662	358	85

substantial losses of titanate. The slurry of ammonium chloride had a low viscosity, permitting efficient cooling and high flow rates in that step. The final precipitation of the titanate ion exchanger could benefit from much lower heat released, representing only a fraction of the total possible exothermic energy of the reactions. A second advantage was that only 20% or less of the chloride remained and had to be washed out of the product slurry. Also much less sodium hydroxide had to be dissolved in ethanol for the formation of sodium titanate, a rather slow reaction. On the negative side the need for an additional solidus/liquidus separation must be noted.

The final alcoholic slurry obtained was curd-like and not crystalline. The best product was obtained after filtering off the solvent for recovery, suspending the filter cake in a considerable amount of water and leaving it for several hours (i.e. overnight) before filtering. After drying by hot air, the filter cakes were hard and strong. They were ground and sieved to any grain size, limited upwards only by the thickness of the dry filter cakes. Noteworthy was the strong abrasive action of this product. The grain sizes most frequently used were, in order, 125-250, 250-500, 63-125 and 500-1000 µm.

A patent for the preparation process was applied for and accepted (15).

All titanate ion exchangers used in the process development were, until 1981, prepared from titanium tetrachloride. The product had a good mechanical stability, and could also be prepared to meet more exceptional requirements with respect to attrition.

However, even on the scale corresponding to the demand of a full-scale Swedish plant, 40 tonnes per year, this titanate product turned out to be too expensive. No supporting large market was found, in which case radical simplifications and cost reductions might have been obtained in the processing of titanium tetrachloride (16).

In order to find less expensive production routes other alternatives were considered (17, 18).

As stable filter cakes could easily be formed by drying, it was anticipated that this step could be used for tailoring each grain separately, dismissing crushing and sieving. Two methods were considered, extrusion and moulding. The abrasive action of the product was a contraindication to the former method, leaving casting or moulding as the method of choice. The drying of rinsed sodium titanate in small boreholes in sheets of different plastics yielded promising results. At this stage it appeared that this technique had been successfully applied on a large scale for the production of uniformly sized grains of hydrous titanium dioxide (19). A very fine-grain quality of sodium titanate, that is obtained as an intermediate product in the production of 25 000 tonnes per year of rutile pigments from ilmenite in Norway (20) was acquired and shown to give very encouraging results. A thick slurry of this titanate, with 28% dry substance, was filled in the holes of perforated steel plates and dried in hot air. During drying, the material shrinked and the cylinder shaped grains, of 1 mm height and 1 mm diameter, were easily loosened from the plates. The mechanical stability of the product obtained was inferior to that of the products from the process described previously. With careful handling it was found sufficiently stable for its application, however, and more than 60 l of this quality were prepared in the laboratory.

Air dried sodium titanate contained 20-30% of water, depending on the preparation conditions. Most of the water was lost by heating the titanate up to 500°C, lewing a very hygroscopic residue. The hygroscopicity was found to disappear at heating above 600°C.

The exchange capacity of prepared titanates were in the region of 2.5 equivalents per kg of air dried titanate. When air dried titanate was soaked in water, the water became alkaline and the exchange capacity of the titanate decreased slowly.

3.2 Zeolites

Synthetic zeolites have been prepared in many places for the last thirty years and about forty different synthetic zeolites have been presented (21). The common method used is the crystallization from hydrogels, which gives fast reactions and crystalline products of uniform size. However, the crystal size in these products is generally very small, less than about a few μm, and therefore these products are not directly useful in many applications. Thus methods for the preparation or larger crystals or aggregates are required.

Some general conditions have to be fulfilled in zeolite crystallization:

1. Reactive starting materials such as freshly coprecipitated gels, or amorphous solids.
2. Relatively high pH introduced in the form of an alkali hydroxide or other strong base.
3. Low temperature hydrothermal conditions at low autogeneous pressure and saturated water pressure.
4. A high degree of supersaturation of the components of the gel leading to the nucleation of a large number of crystals.

A gel is defined as a hydrous metal aluminosilicate which is prepared from aqueous solutions, reactive solids, colloidal sols, or from reactive aluminosilicates such as the residual structure from metakaolin and glass.

The gels crystallize in a closed hydrothermal system at temperatures varying from room temperature to about 350°C. The time for the complete crystallization varies from a few hours to several weeks for different zeolites.

From the choice of raw materials the preparation methods may be divided into three different groups:

1. Preparation by hydrogel processes.
2. Preparation of zeolites from clays.
3. Preparation of zeolites from other raw materials.

3.2.1 Preparation by hydrogel processes

In the hydrogel processes a freshly prepared, highly reactive water-rich aluminosilicate gel is crystallized to a zeolite in a hydrothermal system. Common raw materials in the gel preparation are $Al(OH)_3$, amorphous silica, NaOH and water, or the combination NaOH, Na_2SiO_3 and $NaAlO_2$. The gel consists of a polymer of aluminate and silicate groups. When the temperature is increased a depolymerization of the gel takes place followed by nucleation and crystallization. The crystal growth is very moderate in this kind of crystallization and the final crystal size is almost exclusively below 5 microns. During the crystallization it is necessary to agitate the reaction mixture to avoid inhomogeneous products.

The hydrogel process is shown schematically in figure 5 with the system $Na_2O - Al_2O_3 - SiO_2 - H_2O$ used as an example.

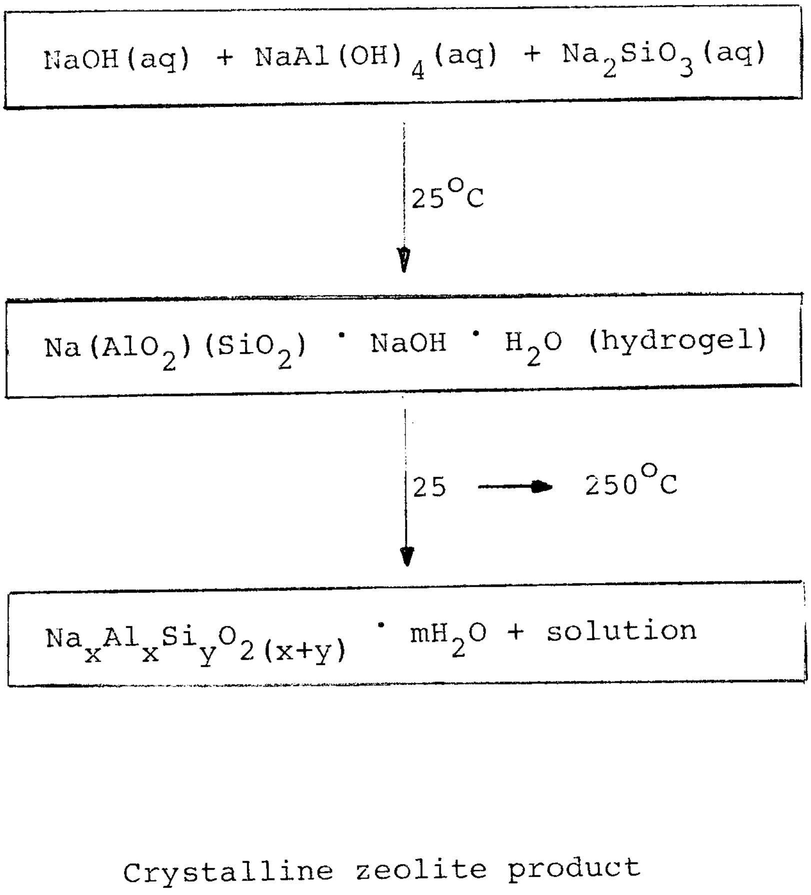


Figure 5 Preparation of crystalline zeolite by the hydrogel process.

Many different zeolites were prepared with the hydrogel method in this programme, in the later part of which the work was more or less concentrated on the zeolites 13X, P_c and Na-D, a zeolite of the mordenite type. The zeolite 13X has a good selectivity for divalent ions and is therefore suitable for the sorption of Sr^{2+}. Both P_c and Na-D have extremely good selectivities for Cs. Zeolites are fairly simple to prepare in a pure form but has a rather low stability in acidic solutions. Na-D can be easily transformed to its H^+ form and it has compared to other zeolites a very good resistance in acidic solutions. Much effort was made to find crystallization methods yielding crystals big enough for column experiments. After many attempts 3 kg of the zeolite Na-D were successfully prepared for the column experiments in bench scale at STUDSVIK. The average crystal size was about 30 microns and the whole lot was prepared in 50 gram portions each with a crystallization time of two weeks. After that work has continued in cooperation with EKA AB and the process is ready for industrial production.

The preparation parameters for the zeolites 13X, P_c and Na-D were studied in detail and some preparation data are presented in table 2.

Table 2 Data for the preparation of zeolites.

ZEOLITE	PREPARATION TIME h	PREPARATION TEMPERATURE °C	AVERAGE PARTICLE SIZE microns
13X	5	95	10
P_c	24	120	20
Na-D	48	150	30

Much effort was devoted to obtain particle sizes suitable for use in full scale columns. The general route to granulate zeolites is the introduction of a binder such as a clay mineral followed by sintering. The commercially available zeolites Linde A and 13X are for instance available in granulated form containing about 20% clay material. This non-zeolitic part of the ion exchanger has some drawbacks in the actual application. The ion exchange capacity is deteriorated and as the material is not a pure phase the ceramization may be more difficult to control.

For these reasons efforts were made in two different directions: to make granules without binders and to prepare larger crystals or crystalline aggregates. Both methods were quite successful. To prepare granules without binders we introduced a double crystallization, the first one in the normal way which yields a crystal size of about 30 microns, followed by granulation together with new raw material and a new rapid crystallization which yields small crystals cementing the granules together.

The process is illustrated in figure 6.

3.2.2 Preparation from clays

Synthetic zeolites may be crystallized from clay minerals such as montmorillonite and kaolin. The most important process uses minerals from the kaolin group, which can be represented chemically as $Al_2O_3 \cdot 2\ SiO_2 \cdot 2H_2O$. In order to activate the clay for the reaction, it is most often necessary to convert the kaolin to metakaolin by a thermal treatment at about 550°C. After this calcination the material has become amorphous and by a hydrothermal treatment at a normal zeolite crystallization temperature zeolites are formed. For example, if only NaOH is added to the metakaolin, the zeolite Linde A is formed.

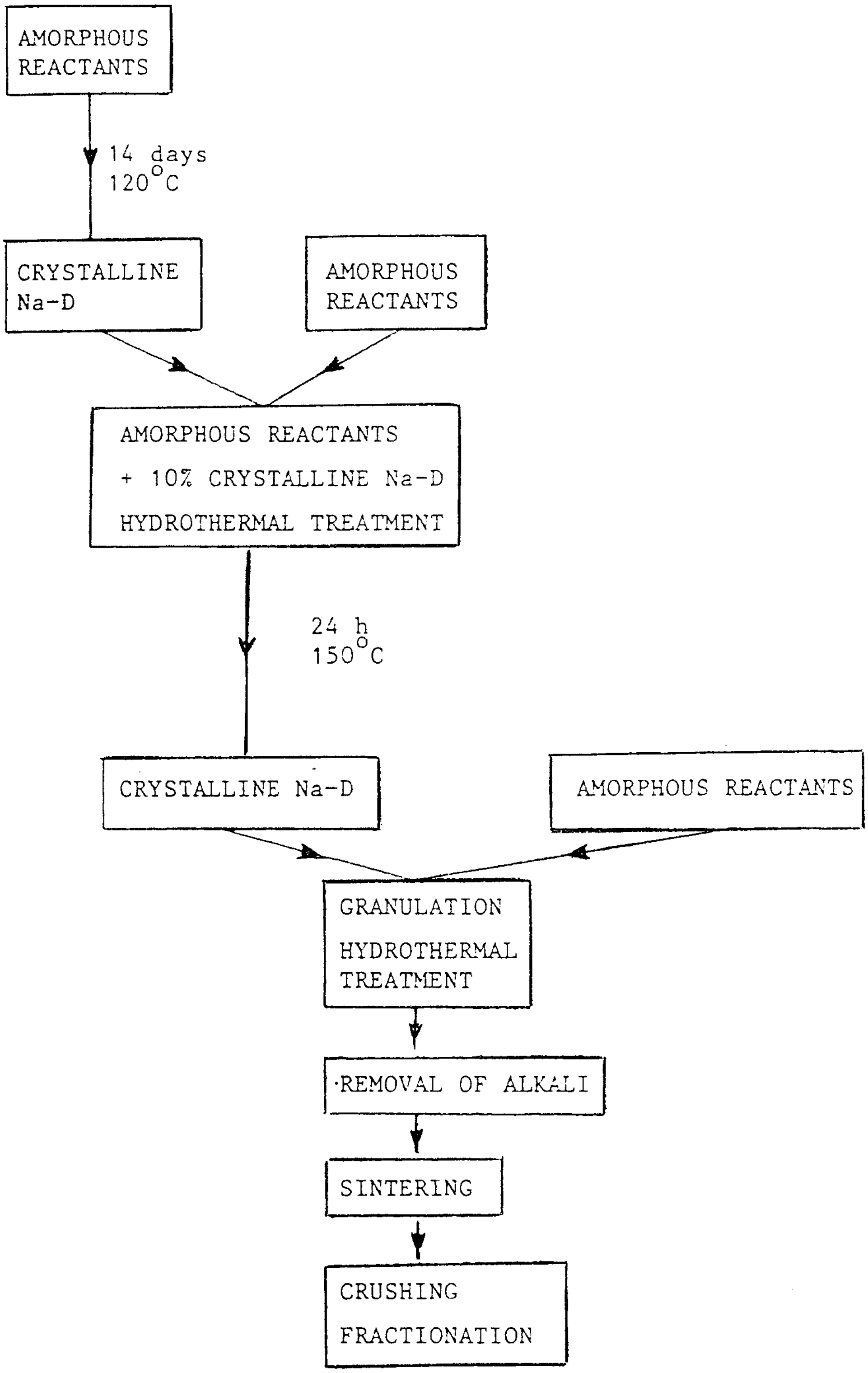


Figure 6 Scheme for the preparation of granular zeolite Na-D without binder.

This is illustrated in the following scheme:

1) Conversion of kaolin to metakaolin

$$2Al_2Si_2O_5(OH)_4 \xrightarrow{550^{\circ}C} 2Al_2Si_2O_7 + 4H_2O$$

2) Crystallization of the zeolite

$$6Al_2Si_2O_7 + 12NaOH \xrightarrow{100^{\circ}C} Na_{12}(AlO_2)_{12}(SiO_2)_{12} \cdot 27H_2O + 6H_2O$$

This crystallization is easily made and it is also possible to pre-form the zeolite particles. Disadvantages of the method include very limited ranges of compositions of the raw material which means that only a few different zeolites may be prepared, and resulting impurities in the zeolites, such as contamination with iron which affects the zeolite quality.

3.2.3 Preparation from glasses

Many attempts to form large crystals and crystalline aggregates of zeolites have been made, but very few useful methods have been presented. Charnell (22) presented a method using incorporation of an organic base as a buffering component. This was quite useful for the zeolites Linde A and 13X of which crystals of up to 100 microns were prepared.

Ciric (23) introduced transport reactions in carbopolgels and had some success with the zeolite P_c.

In both these methods reaction rates are very low requiring long crystallization times, up to six weeks which is expensive and a hindrance to their commercial use. Sand and Dodwell (24) produced rather large crystals of synthetic mordenite from dry hydrogels rich in silica. Also their method requires a rather long reaction time.

More economic processes have been developed by industry. This has been achieved by granulation and pelletization of the powders from the hydrogel processes, commonly with the use of binders, such as clays, which are added in amounts of up to about 20%. This results, however, in product properties not equal to those of the pure zeolite, which may obstruct use and further treatment. It seems obvious that a new, economically reasonable method for the preparation of large crystals or crystalline aggregates would be very useful, commercially as well as for scientific studies of the zeolites.

Other authors have reported zeolite preparation by crystallization from natural or synthetic glasses (25, 26). They were successful in the zeolite crystallization but not in the growth of crystals. The question was why the crystals did not grow, when it is well known that many large natural zeolite crystals originate from vulcanic glasses.

After two years of studies we became quite sure that a small number of critical conditions control the crystallization as well as the crystal growth of the zeolites from glasses:

1. Glass composition and homogeneity.
2. Composition of solution and vapour in the hydrothermal system.
3. Temperature and pressure during the hydrothermal reaction.
4. Particle size of the glass.

During the crystallization a gel is formed at the surface of the glass particles. The nucleation takes place in this gel and the crystals grow when the gel is "consuming" the glass particle. It is obvious that the single crystal cannot grow to a larger size than the original glass particle.

If the conditions are optimized for a certain zeolite the crystallization rate will be at its maximum and if the glass particles are large enough the crystals will continue to grow. The process is illustrated in figure 7.

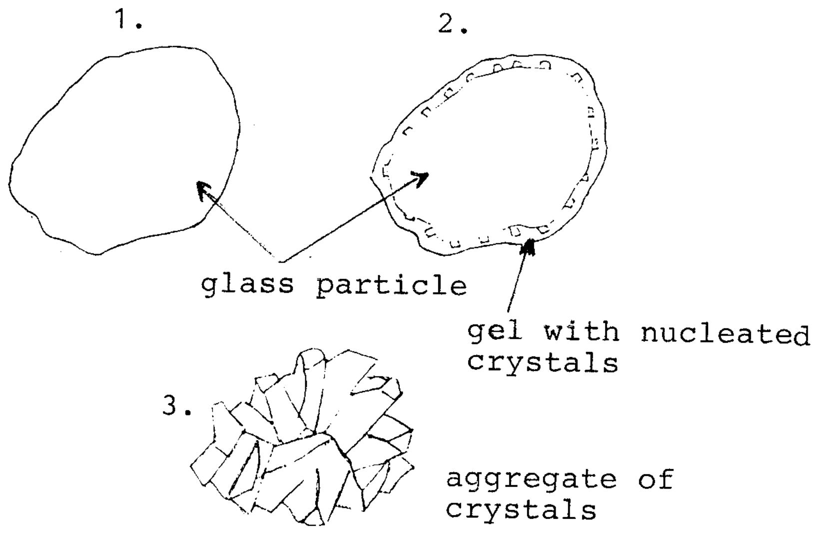


Figure 7 Illustration of zeolite crystallization from glass under hydrothermal conditions.

3.2.4 Examples of crystallized products

A large number of different glasses in the system

$$MAlO_2 - SiO_2 - M_2CO_3$$

where M = Na, K, Ca, Mg, Cs, Rb

were used for hydrothermal preparation of zeolites.

The glasses were prepared by melting at temperatures between 1300 and 1600°C and hydrothermally treated at temperatures between 70 and 350°C, with the actual hydroxide solution as well as organic amine solutions of different concentrations in plastic containers (below 100°C) or stainless steel autoclaves. The crystallization time was varied between 8 h and 6 weeks.

Crystalline zeolites prepared by hydrothermal synthesis from glasses are illustrated in figures 8 - 11.

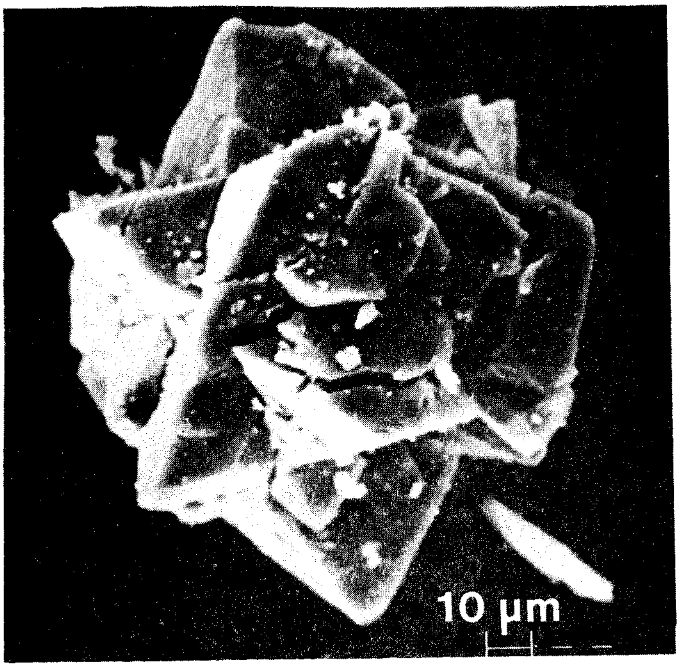


Figure 8 A low silica variety of zeolite P, grown from a glass with an Si to Al ratio of 1:1 in 0.25 M NaOH-solution for 2 weeks at 150°C. The cracks are caused by water loss of the zeolite in the evacuated microscope.

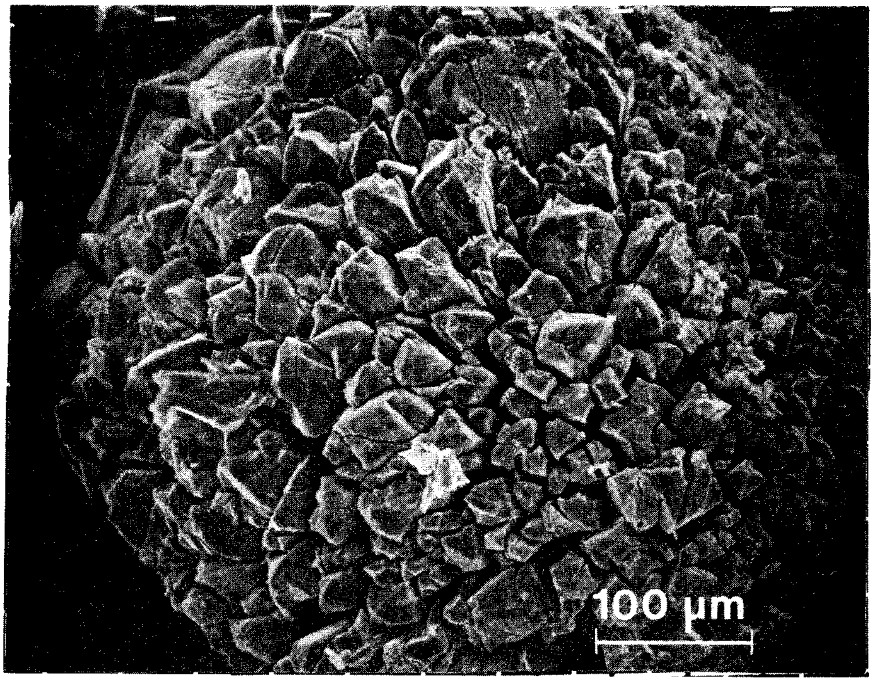


Figure 9 A variety of zeolite P grown from a glass with an Si to Al ratio of 3:1 in 1M NaOH-solution for 48 hours at 150°C. The cracks are caused by water loss of the zeolite in the evacuated microscope.

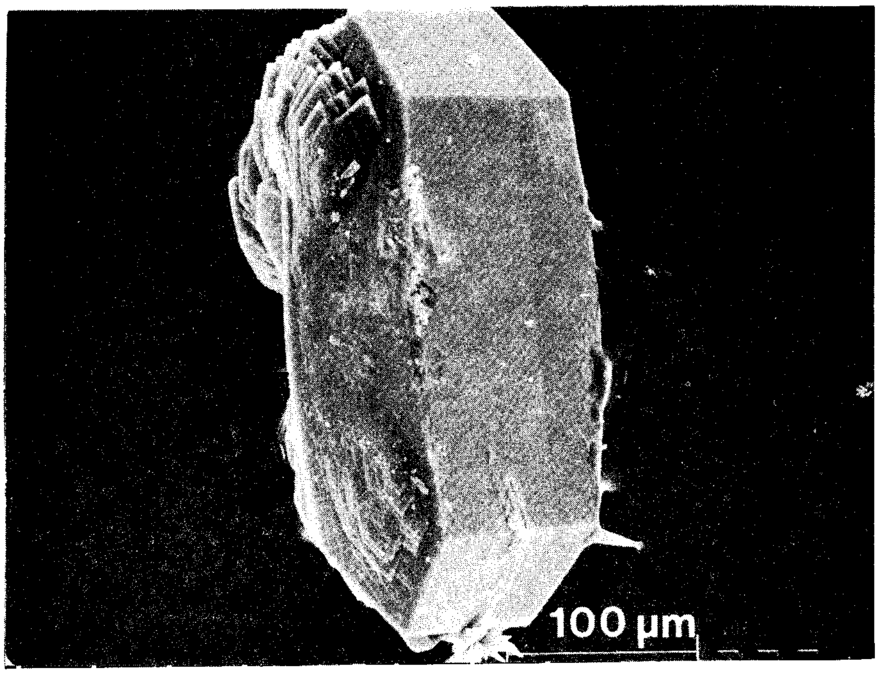


Figure 10 Synthetic mordenite grown from a glass with an Si to Al ratio of 11:1 in 0.25 M NaOH-solution for 48 hours at 200°C.

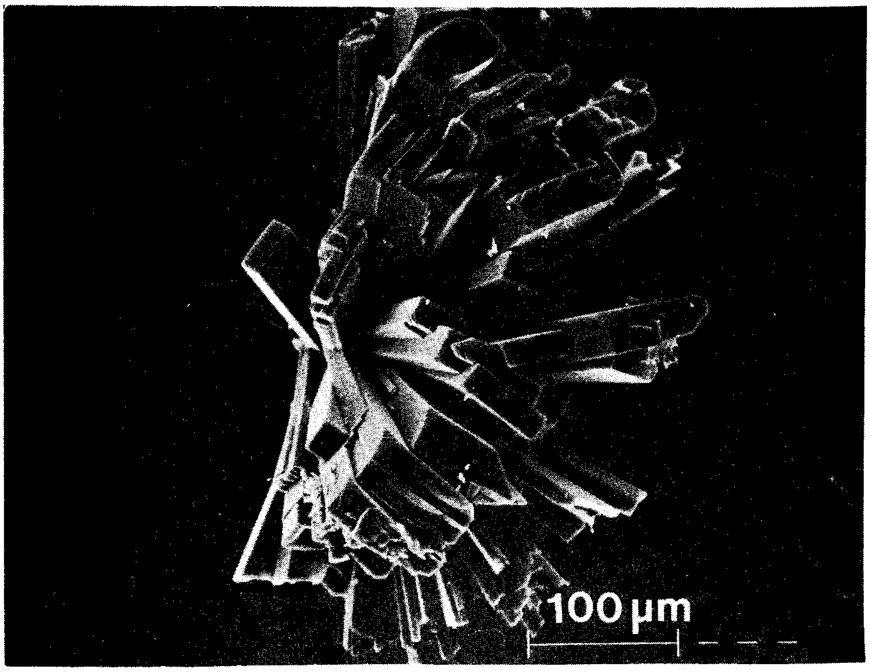


Figure 11 Synthetic mordenite grown from a glass with an Si to Al ratio of 6:1 in 0.1 M NaOH-solution for 20 hours at 300°C.

4. PROCESS DEVELOPMENTS

4.1 Direct applications

4.1.1 At a nuclear power plant

The original idea to replace the organic ion exchange resins by a zeolite-titanate system was tested in 1977 at the Oskarshamn nuclear power station. In one experiment parallell sampling columns of about 1 l volume were charged separately with zeolite 13X in Na-form and normally used organic resin Duolite 20H for comparison of their removal efficiency. In a 5 hour run average removal of nuclides were obtained (28) as given in table 3.

Table 3 Sorption of different nuclides in sampling columns containing Duolite 20H and zeolite 13X, respectively, in a 5 hour test run.

Nuclide	Average percent sorption in	
	Duolite 20H	Zeolite x13X
Co-58	91	97
Co-60	90	96
Zn-65	92	97
Ag-110m	96	93
Cs-134	88	63
Cs-137	85	69
Ce-141	73	88

The sorption efficiency of zeolite 13X is, except for Cs, comparable to, or better than, in Duolite 20H. The unexpectedly low Cs-removal efficiency is partly explained by high flow rates (>90 l/h per liter resin). However, the leakage of Na, Al and Si from the zeolite was unacceptably high. In a test with sodium titanate in a second run the purification efficiency was equally good but the leakage of Na unacceptable. After this experience the efforts were reoriented to find a system for the transfer of nuclides from the spent resins to the inorganic sorbents in a separate system.

Small scale experiments were performed also for another application at a nuclear power plant. Floor drainage water spiked with 100 ppm inactive Sr and 200 ppm inactive Cs was passed through a small column containing zeolite P_c. Breakthrough of Sr occurred after about 500 bed volumes, while Cs was not detected in the effluent after more than 600 bed volumes, when the experiment was stopped. No efficient retention was found for Co and Cr for zeolite P_c.

4.1.2 At a reprocessing plant

A possible application is sorption of radioactive nuclides from the high level liquid waste from the reprocessing of spent nuclear fuel. During 1980 a cooperative effort was made at the Institute for Energy Technology at Kjeller, Norway on sorption in a system of titanate columns from a product solution obtained in extraction campaigns on low-burn up fuel during the 1960's. Problems that had to be solved were connected to the need to neutralize the nitric acid feed solution and some clogging of the columns. Decontamination factors obtained were

$\sim 10^8$ for Sr, 10^7 for Cs, 10^5 for Pu, 10^4 for U and Am and ~ 1 for Tc at a volume reduction factor of 2 from liquid to wet sorbent, equivalent to about 10 from liquid to titanate solidified by hot isostatic pressing (29).

4.2 Treatment of spent resins

As noted in section 4.1.1, the work was finally oriented towards transfer of nuclides from the spent resins to the inorganic sorbents by elution - sorption in a separate system.
After elution of the radioactive nuclides from the organic resins and sorption on titanates and zeolites, the resins may be incinerated or eventually disposed without immobilization, while the inorganic sorbents may be heat treated to a stable form for disposal.

The goal also included

- an effective utilization of the sorbents
- a good stability and leach resistance of the final inorganic products
- a competitive process with regard to safety and costs.

The principle of the use of inorganic ion exchangers in the treatment of spent resins is illustrated in figure 12. The designation PILO was given this process in the continued development work.

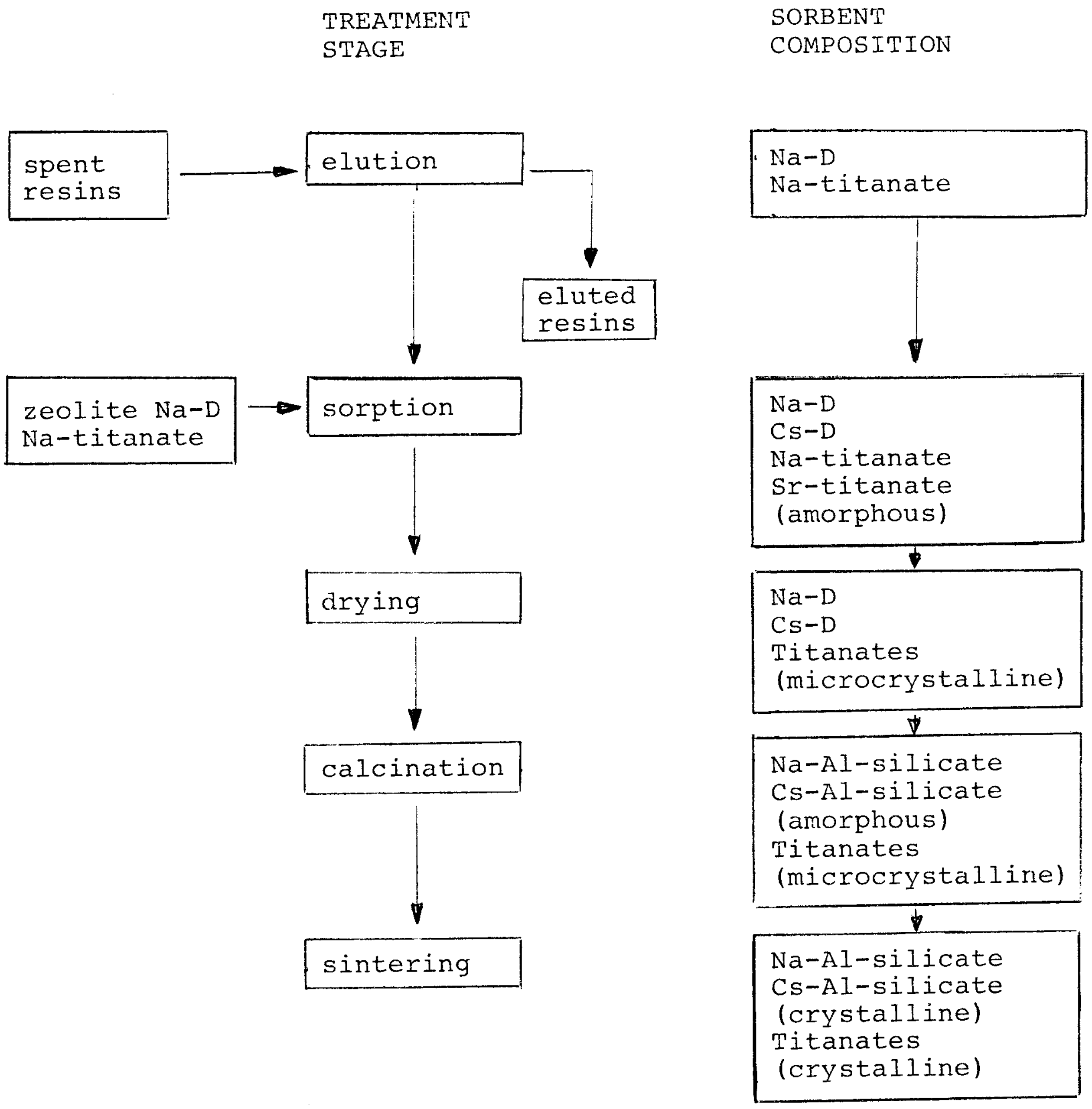


Figure 12 Principal scheme illustrating sorption of Cs and Sr on zeolite Na-D and Na-titanate after their elution from spent resins, and appearing phases in the following heat treatment stages.

Essential points from the development effort along this line is given in the following. Most of these experiments used spent mixed-bed BWR bead resins from the Oskarshamn nuclear power plant; some experiments were performed also on spent PWR bead resins from the Ringhals nuclear power plant.

4.2.1 Elution of resins

A series of elution experiments were performed with mineral acids (H_2SO_4, HNO_3 and HCl) as eluants. Cesium and strontium could mostly be eluted quantitatively with one molar acid. The residual activity of the resin was , however, significant, with Co-60, Zn-65, Ag-110 and Mn-54 dominating, probably due to crud in the resin. Elution at 90°C by 5 M acid HCl : HNO_3 1:1 reduced the remaining activity to 1.8% Co-60, 1.1% Zn-65 and 0.5% Mn-54. This acid concentration would, however, require a neutralization step and give rise to undesirable secondary waste.

A number of complexing agents were then tried as eluting agents: citrate, oxalate, malonate, thioglycollate, tartrate and EDTA. The optimum choice, with regard to both elution and subsequent sorption, was found to be sodium tartrate. Its concentration was not critical and 0.3 M was chosen for system development. Most of the cation exchange sites remain in hydrogen form at the time of resin discharge at the nuclear power plant, and the tartrate solution turned acid in contact with the spent resin. Gas bubbles of carbon dioxide are thus released which has to be taken into consideration in system design.

The PWR resins contain also lithium and borate. Laboratory scale experiments indicated that 99% of the lithium would be eluted by 1 M nitric acid, if recovery for re-utilization were considered desirable. The presence of borate was found not to have any negative effects in the following steps.

4.2.2 Sorption on titanates-zeolites

Titanates

With the fine-grained titanate materials precipitated in the first precipitation experiments, sorption of strontium exceeding 99.99% was easily obtained. The exchange capacity of the titanate quality mostly used in this programme was estimated to be in the region of 2.5 meq per g air dried titanate containing 20-30% of water. Although most other radionuclides of interest were sorbed fairly well, cesium was one exception. Three methods to increase cesium sorption were tried

1. Mixing sodium titanate with titanium phosphate. Column experiments showed that although cesium sorption increased the sorption of other nuclides such as Sr-90 and Co-60 decreased at the same time.
2. Mixing sodium titanate with titanium arsenate. Although sorption experiments were encouraging, sorbent preparation was complicated and hot isostatic pressing yielded powders rather than solid bodies.
3. Mixing sodium titanate with mordenite. 20% mordenite was sufficient to have a cesium retention on level with other nuclides. The heat treatment stage yielded bodies significantly less leach resistant than if the titanate and the zeolite were sintered separately (see tables 13-14).

From these results it was decided to design a sorption system with titanate and zeolite kept separately.

Zeolites

Ion exchangers of the zeolite type in contact with a solution containing several species exhibit a varied preference of exchange with different ionic species. The sorption of cesium, strontium and europium on a number of different zeolites was investigated. Europium was used as a model substance for the trivalent lanthanide and actinide ions in the waste solutions.

Determination of selectivity coefficients for Cs^+, Sr^{2+} and Eu^{3+} were carried out by a series of equilibration experiments with known amounts of zeolites and solutions of varying compositions. Weighed, sodium based zeolite samples in glass vessels were contacted with solutions containing Cs^+, Sr^{2+} or Eu^{3+} in the concentration range 10^{-1} - 10^{-4} M. The distribution between solution and zeolite was determined by tracer technique or atomic absorption. From the sorption data the selectivity for the different ions were determined. The following zeolitic materials were investigated: F, P_c, L, W, A, 13X (synthetic); analcime, chabazite, clinoptilolite, mordenite, erionite and phillipsite (minerals). All the zeolites investigated had, to varying degree, ability to sorb the ions investigated. Cesium was sorbed practically completely on all the zeolites at concentrations less than 10^{-2} M. The sorption of strontium and europium, on the other hand, exhibited large variations among the different zeolites. The most satisfactory sorption properties were shown by zeolites 13X, F and P_c. At concentrations less than about 10^{-2} M the ions studied were sorbed almost quantitatively on zeolite 13X. The distribution coefficient, K_D, for cesium was determined for the zeolites P_c and 13X and for the commercial mordenite quality zeolon 100. The results obtained from neutral water of low ionic strength are given in table 4.

Table 4 Distribution coefficients for Cs between neutral water of low ionic strength and 3 different zeolites.

ZEOLITE	K_D, ml/g
zeolite P_c	$K_D = 2.1 \times 10^4$
zeolite 13X	$K_D = 2.1 \times 10^4$
zeolon 100	$K_D = 3 \times 10^4$

The kinetics of ion exchange was investigated on some of the zeolites. Information about the kinetics is essential to judge the possibility for continous sorption on columns. For the materials investigated, the attainment of equilibrium was practically instantaneous.

Also the sorption of some corrosion products such as Mn, Fe, Co, Ni, Zn on zeolites were studied. In the concentration range $5 \cdot 10^{-3}$ - 10^{-4} M all the ions were sorbed on e.g. zeolite 13X. Furthermore, the sorption was not markedly affected if the solutions contained Na^+ as excess competing ion which could be of importance in anticipated application.

4.2.3 Elution - sorption system

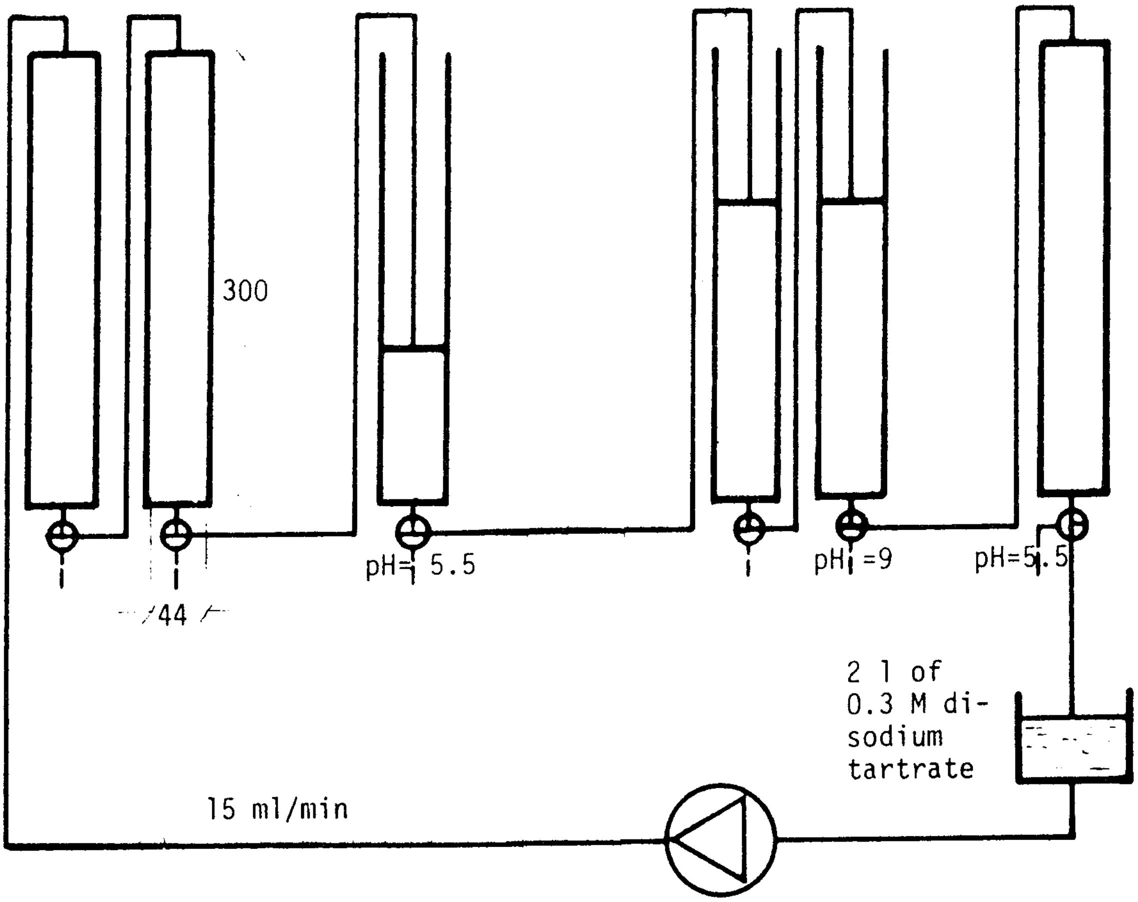
The zeolite Na-D (mordenite), $NaAlSi_5 \cdot O_{12} \cdot 3H_2O$, exhibited the best stability in acid solutions. It has a good Cs-selectivity and may be prepared in H^+-form. It was decided to use this zeolite and titanate in the laboratory scale development of a elution -sorption system for the transfer of radionuclides from spent resins to inorganic sorbents, with a sodium tartrate solution as the transfer medium.

A laboratory scale system of consecutive columns is shown in figure 13. A 0.3 M disodium tartrate solution is recirculated until at least 99.9% of the radioactive cesium isotopes are transferred from the mixed-bed resin to the zeolite, requiring about 20 bed volumes of recirculation. As the pH of the effluent from the second titanate column rises to above 9 and some active corrosion products are less easily eluted at this pH, a continuous pH adjustment was introduced in the system by a weak cation exchange resin column. This reconstituted the pH of the solution to about 5.5.

Typical elution efficiency of a 0.3 M sodium tartrate solution is shown for the main nuclides in table 5.

Spent resin columns (mixed bed) Grain size 300 - 1200 μm	Zeolite column (mordenite) Grain size < 63 μm	Titanate columns Grain size 250 - 500 μm		Weak cation exchange resin column, in H^+/Na^+-form for control of pH

	Eluted	Sorbed	Sorbed	
			A	B
Sr	99.9%	Traces	99.9%	0.1%
Cs	99.9%	99.9%	N.d.	N.d.
Co	90 %	Traces	80 %	10 %
Zn	95 %	Traces	90 %	5 %



The columns and beds are drawn to scale, with connections and circulating system. The flow rate in the beds is ~ 1 $ml/cm^2 \cdot min$. Dimensions are in mm.

Figure 13 Column system for the transfer of radionuclides from spent resins to zeolites and titanates.

N.d. = not detected

Table 5 Main radioactive nuclides in a 0.5 l bed of BWR spent mixed-bed resin, before and after elution with 20 l 0.3 M sodium tartrate solution. Nuclide activities are given in MBq/kg dried resin. (From ref 6)

Nuclide	Cs-137	Sr-90	Co-60	Mn-54	Zn-65
Before elution	900	40	1 900	79	3 600
After elution	< 2	< 0.01	200	5	150

The elution of Co-60 varied according to the amount of crud present; in some experiments only 2% of Co-60 remained in the spent resin.

Typical axial distribution of Cs, Zn and Co in the mordenite column is shown in table 6. Table 7 shows the axial profiles of Co, Mn, Ag and Zn in the first titanate column. No cesium passed on to the titanate columns.

As further illustrations the sorption of Cs from 0.3 M sodium tartrate solution on different zeolites is shown i figure 14, and the sorption of Sr, Cs, Co and Zn on titanate in figure 15, as obtained by gamma spectrometric measurements on small scale columns (3).

It was found that the process is not sensitive to the concentration of tartrate. A somewhat lower tartrate concentration and a slightly higher temperature might be of advantage for the total process.

Most experiments were performed in this system with spent BWR resins. Some experiments with spent PWR resins indicated no hindrance from the borate present.

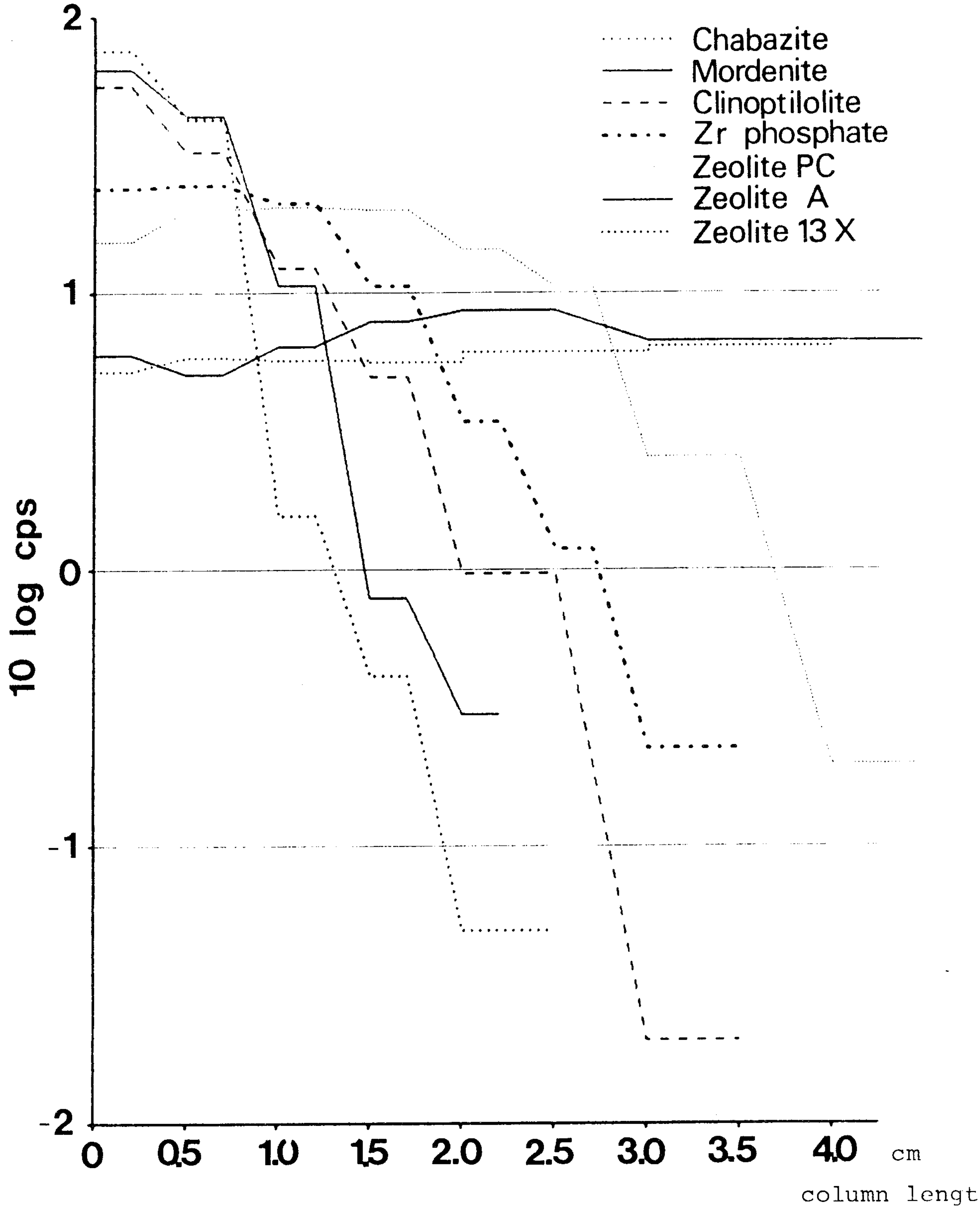


Figure 14 Sorption of Cs from 0.3 M sodium tartrate solution on different zeolites in small scale columns.

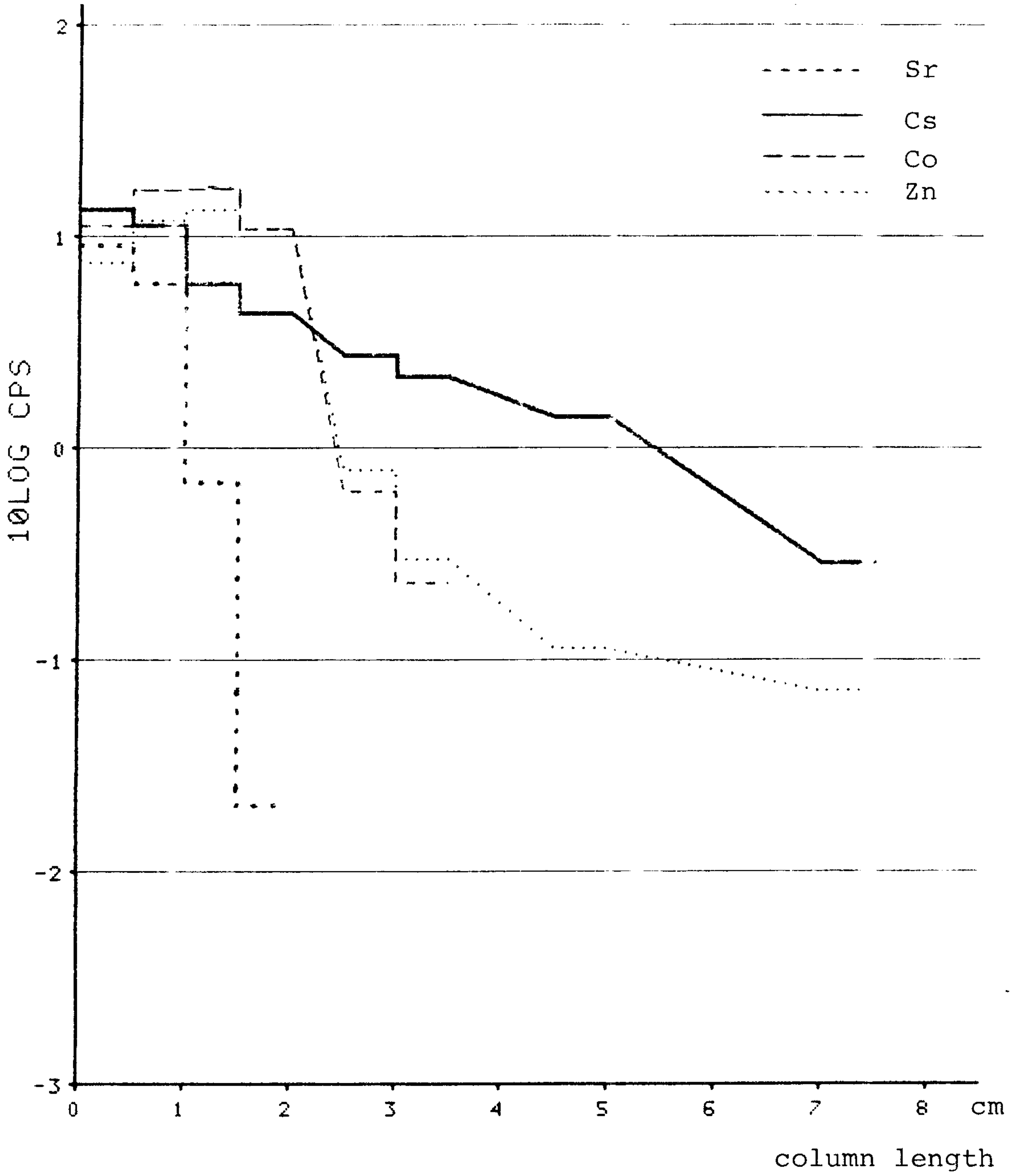


Figure 15 Sorption of Sr, Cs, Co and Zn from 0.3 M sodium tartrate solutions on a small scale sodium titanate column.

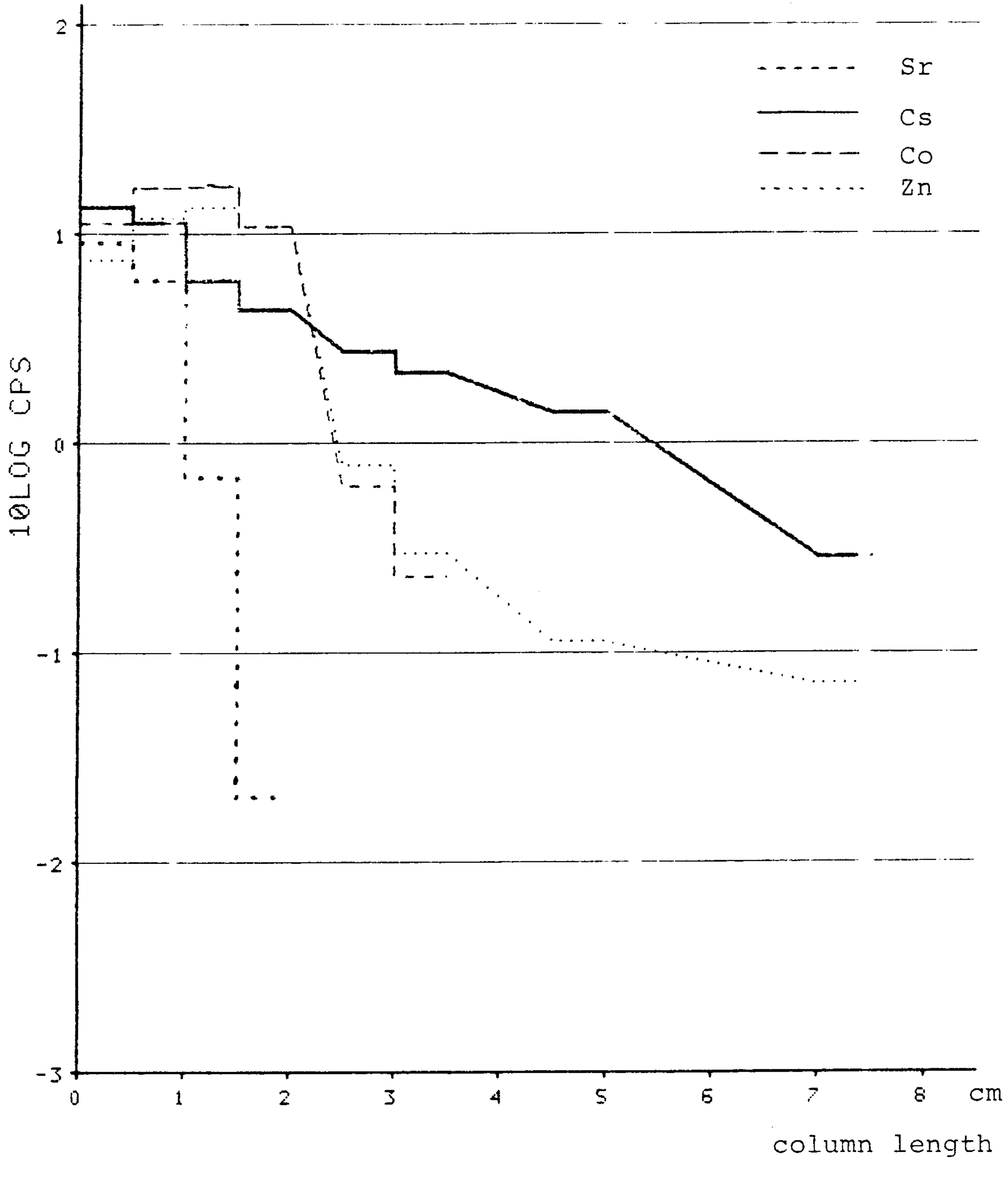


Figure 15 Sorption of Sr, Cs, Co and Zn from 0.3 M sodium tartrate solutions on a small scale sodium titanate column.

Table 6 Relative count rates from a bed of mordenite.

Distance from top, cm	Radioactive element Cs	Zn	Co
0 - 2.5	15 000	170	220
3.5 - 6	7 300	45	96
8.5 - 11	104	32	15

Table 7 Axial nuclide distribution in the titanate column. Activities are given in MBq/kg dried titanate. Strontium was not detected below 10 cm from the top. No cesium was detected.
nd = not detected.

Titanate bed fraction in cm from the top	Nuclides Co-60	Mn-54	Ag-110m	Zn-65
0	3 200	700	400	10 000
0 - 10	6 400	nd	nd	15 800
10	2 300	"	"	1 380
10 - 20	1 160	"	"	670
20	21	2.6	2	6

4.2.4 Large scale column experiments

To evaluate sorbent behaviour in large scale columns, some experiments were performed in a 0.25 x 0.97 m, 48 dm^3, column. The granular sodium titanate quality prepared by drying 1 x 1 mm cylindrical grains was used. No production of fines was observed during the packing step. A solution of 0.3 M disodium tartrate was pumped downstream through the column at a rate of 10 $ml/cm^2 \cdot min$. The pressure drop over the column was constant at 3 m of water. A pertechnetate solution containing Tc-99m was injected at intervals in the influent and the flow stopped just before any activity appeared in the effluent. Monitoring of the activity distribution in the column showed no deviations from a symmetrical distribution. The activity break-through in the effluent is shown in figure 16, where also the break-through in a small column of 0.29 dm^3 volume is given. The difference is evidently not significant which indicates that no channelling accurred in the larger column.

4.3 Sintering of inorganic sorbents and product characterization

4.3.1 Introductory studies

The crystallization and recrystallization during increasing temperature were followed for zeolite P, mordenite and sodium titanate loaded with ∿ 5% by weight of corrosion products. In two samples of titanate their contents of sodium was displaced with stoichiometric amounts of acid and ammonium respectively. The acid did also displace some of the corrosion products. Later displacements of sodium were performed solely with ammonium.

Crystalline phases, formed after heating to successively higher temperatures, are presented in table 8. Due to low concentrations, the fate of individual elements could not be followed, however. In order to study possible elemental behaviour, a series of titanates saturated with important single elements was prepared. The crystal structures formed in the heat treatment of this series are shown in table 9.

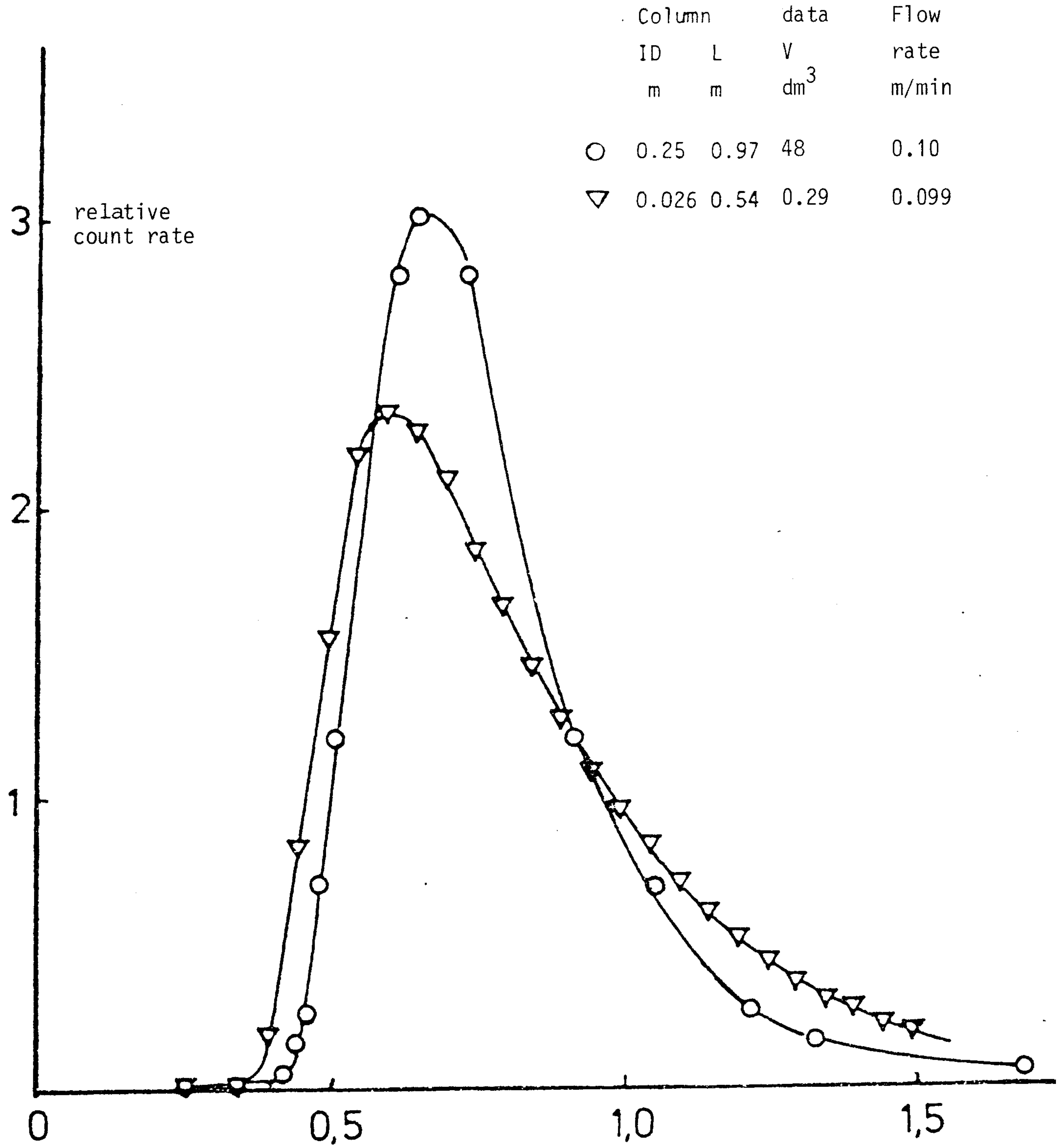


Figure 16 Distribution of Tc-99m in the effluent from sodium titanate columns, grain size 1 mm long, 1 mm diameter. The activity is given as the relative count rate versus bed volumes of effluent after the injection of TcO_4^- to the influent, 0.3 M sodium tartrate solution.

Table 8

Crystalline phases identified by means of a Guinier-Hägg powder camera after heating for two hours in open platinum crucibles. The abundances were judged from the intensity of diffraction lines.

A = anatase, R = rutile, X = unidentified

Starting material	(Surplus) counter-ion	Temperature °C	Type of structure w-%
Synthetic	Na^+	∿ 900	amorphous
mordenite	Cs^+	∿1000	amorphous
		∿1200	$CsAlSi_5O_{12}$ (new phase)
Zeolite P	Na^+	∿ 900	nepheline
	Cs^+	∿ 600	plagioclase
		∿1100	pollucite + quartz
Titanate	Na^+	∿ 400	amorphous
with ∿ 5 %		∿ 700	A 30, R 20, $NaFeTi_3O_8$ 50
corrosion		800-1200	R 50, $NaFeTi_3O_8$ 50, X
products	H^+	500- 600	A
		700- 800	R 85, $Sr_{0.2}Cu_{0.8}Ti_{1.1}O_3$
		900-1200	R 85, perovskite 15, X
	NH_4^+	∿ 500	A
		600- 700	A 50, R 50
		900-1200	R 85, perovskite 15, X

Table 9

Appearance and disappearance of crystalline phases during heating of single-element titanates to successive, higher temperatures for two hours in open platinum crucibles (Guinier-Hägg powder camera). A = Anatas, R = rutile. CPI = corrosion product ion at the exchange. The numerals at 1200 °C indicate relative abundances of phases.

CPI	Mn^{2+}		Fe^{2+}		Co^{2+}		Cu^{2+}		Zn^{2+}	
Temperature										
1200 °C	R	7	R	7	R	7	R	6	R	6
	$MnTiO_3$	3	Fe_2TiO_5	3	$CoTi_2O_5$	3	Cu_2TiO_3	3	Zn_2TiO_4	4
							Cu_3TiO_5	1		
1000 °C							Cu_2TiO_3			
900 °C	$MnTiO_3$									
800 °C										
700 °C			R		$CoTiO_3$				R	
			Fe_2TiO_5							
600 °C	R		A		R		CuO		$ZnTiO_3$	
	Mn_2O_3									
500 °C	A				A		R		A	
400 °C							A			

4.3.2 Sintering techniques

In order to guide the choice of sintering process, the resulting materials from four different sintering routes were studied:

- Hot Uniaxial Pressing, HUP
- Hot Isostatic Pressing, HIP
- Cold Pressing and atmospheric Sintering, CPS.
- Direct Sintering with Additives, DSA.

The sorbents studied in the first three routes were mordenite in its sodium form, containing radioactive cesium, and titanate loaded with corrosion products. Two series of titanates were prepared for sintering experiments, one containing about twice the concentration of corrosion products anticipated in an applied process and one series containing about half that concentration, i.e. about 5% and 1% by weight in the dried titanate. In some samples sodium was replaced by ammonium. (32)

The samples prepared were characterized by SEM and optical microscopy, diffraction analysis, specific surface analysis, density determinations, and leach testing.

The direct sintering route was tried out in preliminary tests at the end of the programme. The samples were in this case only characterized by visual inspection and density determinations.

Hot uniaxial pressing, HUP

The hot pressing was performed in graphite cylinders of 25 mm internal diameter under nitrogen at atmospheric pressure. The materials were axially compressed at 0.5 MPa while heating to 1070°C for 2 hours, resulting in 2-4 mm thick pellets.

Hot isostatic pressing, HIP

For hot isostatic pressing the dried materials were packed in cylindrical steel containers of 20 mm diameter and compacted with a piston at room temperature. Lids with central steel tubes were welded on the filled containers. The containers were placed in a furnace, heated and kept at 600°C for 4 hours with evacuation through the piping. After control of the tightness, the tubes were closed by squeezing, cut, and welded.

As an extra measure against contamination of the press, each sample was provided with a similar, tightly fitting outer container.

The isostatic pressing was performed by ASEAs High Pressure Laboratory at Robertsfors, Sweden. In a first series the temperature was kept at 1200°C for 2 hours at an argon pressure of 150 MPa. Most of the containers failed during the pressing, probably due to welding deficiencies. At proper functioning, the steel containers are heavily compressed and deformed. Many containers were hardly deformed, revealing leakage at an early stage of the pressing cycle.

For a second HIP series new containers were prepared. The material was thoroughly packed and precompacted with the container in a die at a pressure of 100 MPa. The material was then pretreated at 700°C for 14 hours under vacuum before hot isostatic pressing at 1300°C for 6 hours.

The final product should be sufficiently dense and homogenous. SEM analysis and the determinations of matrix density showed that there is an optimal pretreatment temperature.

If the pretreatment temperature is too low water vapour may be formed in the HIP stage. This risk prevails up to temperatures above 600°C. At temperatures between 7-800°C rutile nucleation takes place. At still higher temperatures, the rutile nuclei will grow into crystals. The rutile crystals are structurally very stable and will not change during continued heat treatment thus hindering continued densification.

Other mineral phases formed will only partially fill the voids between the rutile crystals, and thus a porous and mechanically weak matrix is formed. One further disadvantage will be that this matrix has a large specific area exposed to leaching.

Therefore pretreatment should be done preferentially at temperatures around or slightly below 700°C. Some experimental results supporting this conclusion are shown in table 10.

Cold pressing and atmospheric sintering, CPS

Atmospheric sintering was performed on cylindrical pellets of 11.3 mm diameter obtained by uniaxial cold pressing in a die at a pressure of 100 MPa. The pellets were sintered in a tube furnace in a nitrogen or air atmosphere at a temperature of 1070°C or 1300°C. Sintering at 1070°C was found not to yield pellets of sufficient strength for handling, while sintering at 1300°C yielded pellets comparable to those obtained by hot isostatic pressing (37).

Direct sintering with additives, DSA

Uncompacted sodium titanate was shown not to sinter at temperatures up to 1250°C. If intimately mixed with 20% borosilicate glass, a mixture of titanate and zeolite in proportion 1:1 yielded, however, a dense body after 3 hours sintering at 1200-1250°C.

Table 10

Density and structure of titanates, only preheated to different temperatures, or HIP-treated after preheating to different temperatures

cp = contains corrosion products
HIP = Hot Isostatic Pressing at 1 300°C and 150 MPa for 2 h

Material	Pretreatment temperature °C	Density g/cm^3	Phases after treatment
NH_4^+-tit cp	500	3.95	80 % Anatase 20 % Rutile
"	600	3.96	"
"	700	4.19	80 % Rutile 20 % Spinel
"	800	4.29	70 % Rutile 30 % Spinel
"	900	4.19	"
" HIP	500	4.13	70 % Rutile 20 % Chrichtonite 10 % Unidentified
" "	600	4.33	" + Ilmenite
" "	700	4.40	not determined
" "	800	4.24	90 % Rutile 10 % Chrichtonite
" "	900	4.25	70 % Rutile 30 % Fe_2TiO_5 (pseudobrookite)
Na-tit cp	500	3.80	100 % Anatase
"	600	3.92	80 % Anatase 20 % Ilmenite
"	700	4.16	70 % Rutile 20 % $NaFeTi_3O_8$-type 10 % Anatase
"	800	4.24	70 % Rutile 30 % $NaFeTi_3O_8$-type
"	900	4.23	70 % Rutile 25 % $NaFeTi_3O_8$-type 5 % Chrichtonite
" HIP	500	3.95	50 % Rutile 30 % $NaFeTi_3O_8$-type 15 % Chrichtonite 5 % Unidentified ev Ilmenite
Na-tit HIP	600	not determined	not determined
"	700	4.23	60 % Rutile 20 % $NaFeTi_3O_8$-type 15 % Chrichtonite 5 % Unidentified
"	800	4.25	40 % Rutile 30 % $NaFeTi_3O_8$-type 25 % Chrichtonite 5 % Unidentified
"	900	4.22	60 % Rutile 20 % $NaFeTi_3O_8$-type 15 % Chrichtonite 5 % Unidentified

Guinier analysis of sintered bodies from two HIP series, at 1200°C and 1300°C (150 MPa), one HUP series at 1070°C (5 MPa) and CPS tests up to 1300°C (100 MPa cold pressing) were performed. Main crystalline phases as determined by Guinier analysis of the sintered material are exemplified in table 11. No essential differences in crystalline structure of materials sintered above 1000°C by the three different routes could be detected.

The CPS treated titanates exhibited, however, low mechanical stability, especially when sintered below 1200°C. The original grains remain with voids between grains and between crystals in the grains. To illustrate the dense body produced by HIP technique, ammonium titanate, heat treated at 900°C and HIP treated at 1300°C, is shown in figure 17 and figure 18.

Table 11

Crystalline phases and their abundances in materials HUP treated at 1070°C for 2 hours or HIP treated at 1200°C for 2 hours.

Material	Phases formed			
	HUP		HIP	
Radioactive ST	$Na_2Ti_6O_{13}$ $NaFeTi_3O_8$-type	70% 30%	$Na_2Ti_6O_{13}$ $NaFeTi_3O_8$-type	70% 30%
Radioactive M	Amorphous		Amorphous	
AT with 5% CP	Rutile Crichtonite-type Ilmenite-type	90% 5% 5%	Rutile Crichtonite-type Ilmenite-type	90% 5% 5%
AT with 1% CP	Rutile Crichtonite-type	95% 5%	Rutile Crichtonite-type Ilmenite-type	90% 5% 5%
ST with 5% CP	Rutile $NaFeTi_3O_8$-type Crichtonite-type	60% 30% 10%	Rutile $NaFeTi_3O_8$-type Crichtonite-type Ilmenite	60% 30% 10% traces
ST with 1% CP	$Na_2Ti_6O_{13}$ Rutile $NaFeTi_3O_8$-type	60% 20% 20%	$Na_2Ti_6O_{13}$ Rutile $NaFeTi_3O_8$-type Ilmenite	50% 30% 20% traces
Zeolite P	Nepheline type		Nepheline type	

Abbreviations

ST = sodium titanate
M = mordenite
AT = ammonium titanate
CP = corrosion products

Figure 17 Ammonium titanate heat treated at 900 °C. 3 500X

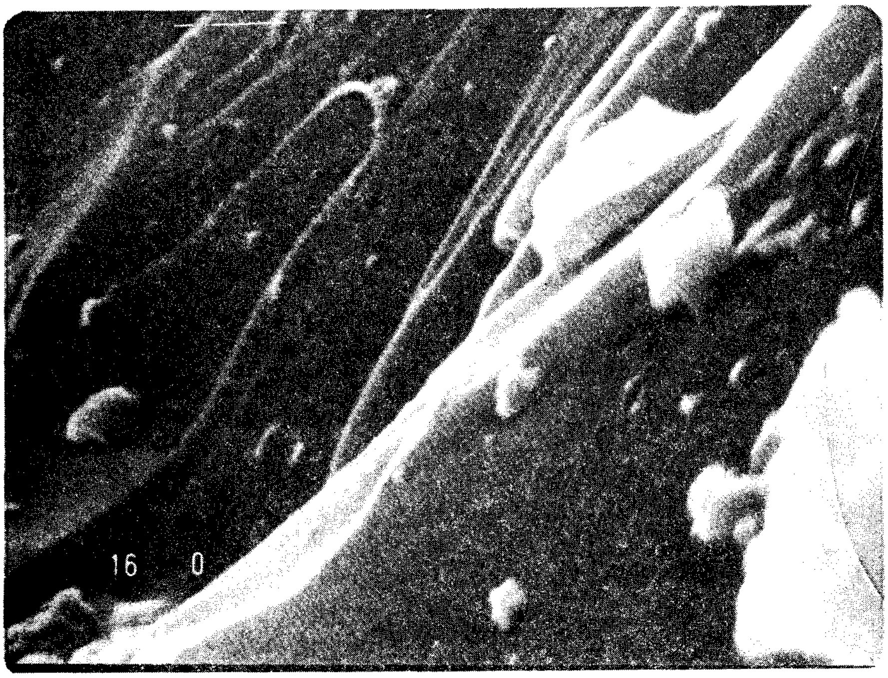


Figure 18 The same ammonium titanate after hot isostatic pressing at 1300 °C, 150 MPa 3 500 X

4.3.3 Leach testing

The sintered materials were leach tested by different methods:

- 72 h Soxhlet leach test on crushed and sieved materials
- 14 days Soxhlet leach test on monoliths, cut with a diamond saw
- a static test at 40°C in ground water according to MCC-1 (33).

Surface determinations on crushed material were made by the BET-method. In all samples radioactive tracers were added and leach rates were calculated from the tracer activity appearing in the leachant.

For the purpose of screening, leaching in Soxhlet equipment by distilled water was the method of choice. Lacking an accepted international standard, the conditions were chosen from a modified ISO standard proposal. As too small pieces of material were available for monolithic leaching, the materials were crushed and sieved, and ∿ 1 g of the fractions 250-500 μm were placed in open steel cylinders with bottoms of stainless steel nets, and leached for 3 days. A few grains of the same fractions were studied topographically by means of SEM, somewhat larger amounts were ground for diffraction studies.

After leaching, the flask containing the leachate, 300 ml, was boiled for one day with carriers and nitric acid in order to decontaminate the glass walls. Cobalt and strontium were precipitated as carbonates, the centrifugate was evaporated to dryness, and the tracers were measured by means of a Ge(Li) detector. The gamma line of Sr-85 from the solid material could not be separated from the annihilation radiation from Na-22. Therefore, strontium was analysed by means of the $K_{\alpha}X$ radiation.

The static tests were performed in a tight plastic container with a volume to surface ratio of 10 cm. To avoid interactions with the container the monolith was suspended from a platinum wire in the leachant with a pathway of at least one cm to the nearest surface.

The containers were kept in a heating cupboard at 40^{o}C. No measurable loss of leachant was observed. Before leaching the monoliths were cleaned in an ultrasonic bath using absolute alcohol as the washing agent.

As leachant synthetic granitic groundwater was used, (composition in table 12). The changings of leachant were done according to standard test MCC-1. The leachates were collected and evaporated to a volume suitable for analysis.

Table 12 Composition of synthetic granitic groundwater according to Allard (38).

HCO_3^-	2.014×10^{-3} M	123	ppm
H_4SiO_4	2.056×10^{-4} M	12	"
SO_4^{2-}	1.000×10^{-4} M	9.6	"
Cl^-	1.973×10^{-3} M	70	"
Ca^{2+}	4.477×10^{-4} M	18	"
Mg^{2+}	1.774×10^{-4} M	4.3	"
K^+	1.000×10^{-4} M	3.9	"
Na^+	2.836×10^{-3} M	65	"
pH	8.0 - 8.2		

Ionic strength 0.0085

Some results are given in tables 13 - 15, for sodium titanate, mordenite and a mixture of sodium titanate and mordenite in proportion 4:1. It may be concluded from the leach tests that

1) Initial leach rates of different samples of the same material may vary with a factor of 10 for any of the sintering methods.

2) Initial leach rates in ground water at 40°C are not significantly lower than in Soxhlet tests using distilled water (at 100°C). The leach rates decrease at prolonged leaching.

3) Sintered samples of mixed mordenite-titanate exhibit considerably higher leach rates than materials sintered separately.

Table 13 Leach rates in µg · cm^{-2} · d^{-1} from 72 h Soxhlet tests on crushed samples, sieved to 250 - 500 µm.

Sample	Sintering route	Co	Sr	Na	Cs	BET-surface $cm^2 \cdot g^{-1}$
ST1	HIP	4.6	0.6	3	48	1 530
ST1	HIP	0.3	2.3	1.5	16	590
ST1	CPS	28	6	4		
ST5	HIP	2.3		8		1 450
	CPS	28	3	30		
ST aut	HIP	0.04			25	4 490
M	HIP				0.8	
M aut	HUP				2.5	170
M	CPS				0.7	
ST1 +M	HIP	4	40	130	130	
ST5 +M	HIP	70	80	240	140	

Explanations

ST1, ST5: sodium titanate with 1% resp 5% of corrosion products

M: Mordenite

ST +M: 80% ST + 20% M

HIP: hot isostatic pressing, 1300°C at 150 MPa for 6 h

HUP: hot uniaxial pressing, 1070°C at 5 MPa for 2 h

CPS: cold uniaxial pressing at 500 MPa, sintering at 1300°C

aut: samples from authentic activity transfer experiments.

Table 14 Leach rates in µg · cm^{-2} · d^{-1} from 14 d static leach test on monoliths at 40°C in ground water according to MCC-1 (32). Average leach rates over day 15-35 are also included. Other symbols as in table 13.

Sample	Sintering route	Co	Sr	Na	Cs
ST1, 14	HIP	2.4	4.2	300	
ST1, 15-35	HIP	0.3	2.3	120	
ST5, 14	HIP	2.5	3.4	50	
ST5, 15-35	HIP	3.5	13	nd	
ST5, 14	CPS	11	9	1	
ST5, 15-35	CPS	1.9	4	nd	
M 14	HIP				1.4
ST1+M, 14	HIP	20	19	150	21
ST1+M, 15-35	HIP	3.8	17	90	19
ST5+M, 14	HIP	110	63	300	120
ST5+M, 15-35	HIP	24	19	90	150

Table 15 Leach rates in µg · cm^{-2} · d^{-1} from 14 d Soxhlet test on monoliths. Symbols as in table 13.

Sample	Sintering route	Co	Sr	Na	Cs
ST1	HIP	5	4	830	
ST5	HIP	0.04	0.9	29	
M	HIP				1.6
ST1 +M	HIP	4.2	6.8	1 100	2 200
ST5 +M	HIP	21	140	420	520

4.4 Volume reduction of spent resins

4.4.1 Fluid bed incineration

With the system chosen in this programme, eluted resins appear as secondary waste, requiring immobilization and disposal. A number of methods have been studied by others to reduce the volume of spent resins, such as incineration, pyrolysis, acid digestion, and wet oxidation. In this programme some studies were performed on the feasibility of fluid bed incineration and of pyrolysis.

One effective way to reduce the volume of spent resin waste is by incineration, which may reduce the volume by at least a factor of 10. Inactive pilot plant studies on resin incineration in a fluidized bed were performed at the Institute of Technology in Lund. The experimental set-up is illustrated in figure 19.

Mainly powder resins were used. A slurry of spent inactive resins, water and ethanol was pumped into the fluidized bed. Different types of sand qualities were tested as bed materials. Special attention was given to the volatilization of cesium by different additives. The experiments demonstrated the feasibility of resin incineration in a fluidized bed but also that an extensive off-gas cleaning system would be needed (30). No effective cesium retention mechanism was found and the experiments were discontinued.

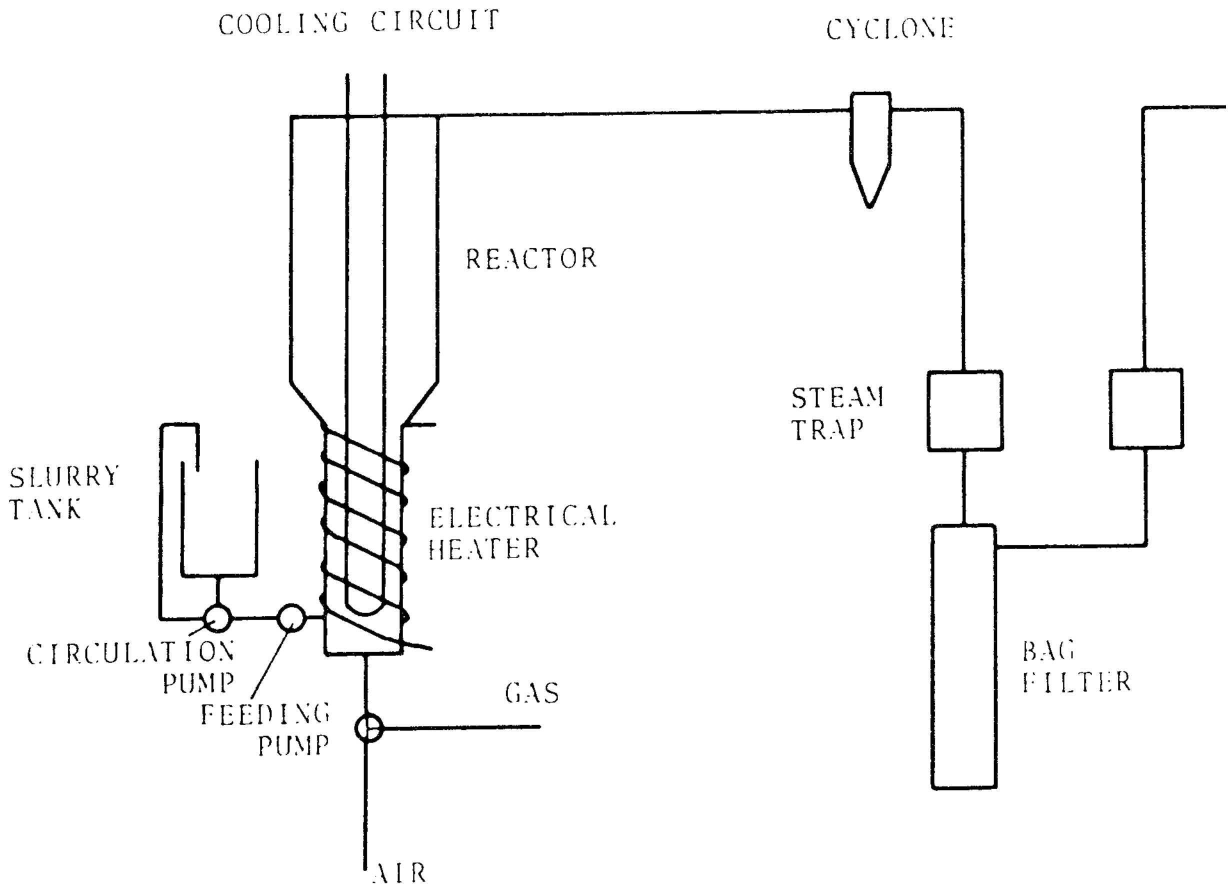


Figure 19 Experimental arrangement for studies of fluidized bed incineration of spent resins.

4.4.2 Pyrolysis

Small scale active pyrolysis and incineration studies were made in a tube furnace at Studsvik. During pyrolysis of granular resins in nitrogen at 300 - 500^{o}C no cesium was detected in the off-gas. The product from the pyrolysis step was then incinerated in a second step with a cesium volatilization of 20-30 ppm of original amount. A combined pyrolysis-incineration process may thus be the preferred solution in view of the off-gas problem. It may be concluded, however, that still a great deal of R & D work would be needed to get a good and reliable system (31, 36).

5. SYSTEM DESIGN

Based on the process development work engineering design studies of a pilot plant with a nominal capacity of 10 m^3/y of spent resins were performed for the wet part of a PILO plant in 1979-80 (39).

A study of a full-scale system dimensioned to meet the needs of the Swedish nuclear power programme was completed in 1982 (40, 41) and reported at the IAEA symposium on radioactive waste conditioning in Utrecht (9). The system design capacity was chosen to include:

- 180 m^3/a of medium level resins containing a maximum of 3700 GBq/m^3 Co-60 equivalents

and

- 700 m^3/a of low level resins containing a maximum of 70 GBq/m^3 of Co-60 equivalents.

The full-scale system study included the following parts (figure 20):

- transportation of spent organic resins from power plants to a central waste treatment plant
- elution of medium-level resins and sorption of eluted nuclides on zeolites and titanates
- heat treatment of radioactive zeolites/titanates to stable ceramic bodies
- treatment of eluted organic resins and other low level resins by drainage in transportable concrete containers or by incineration.

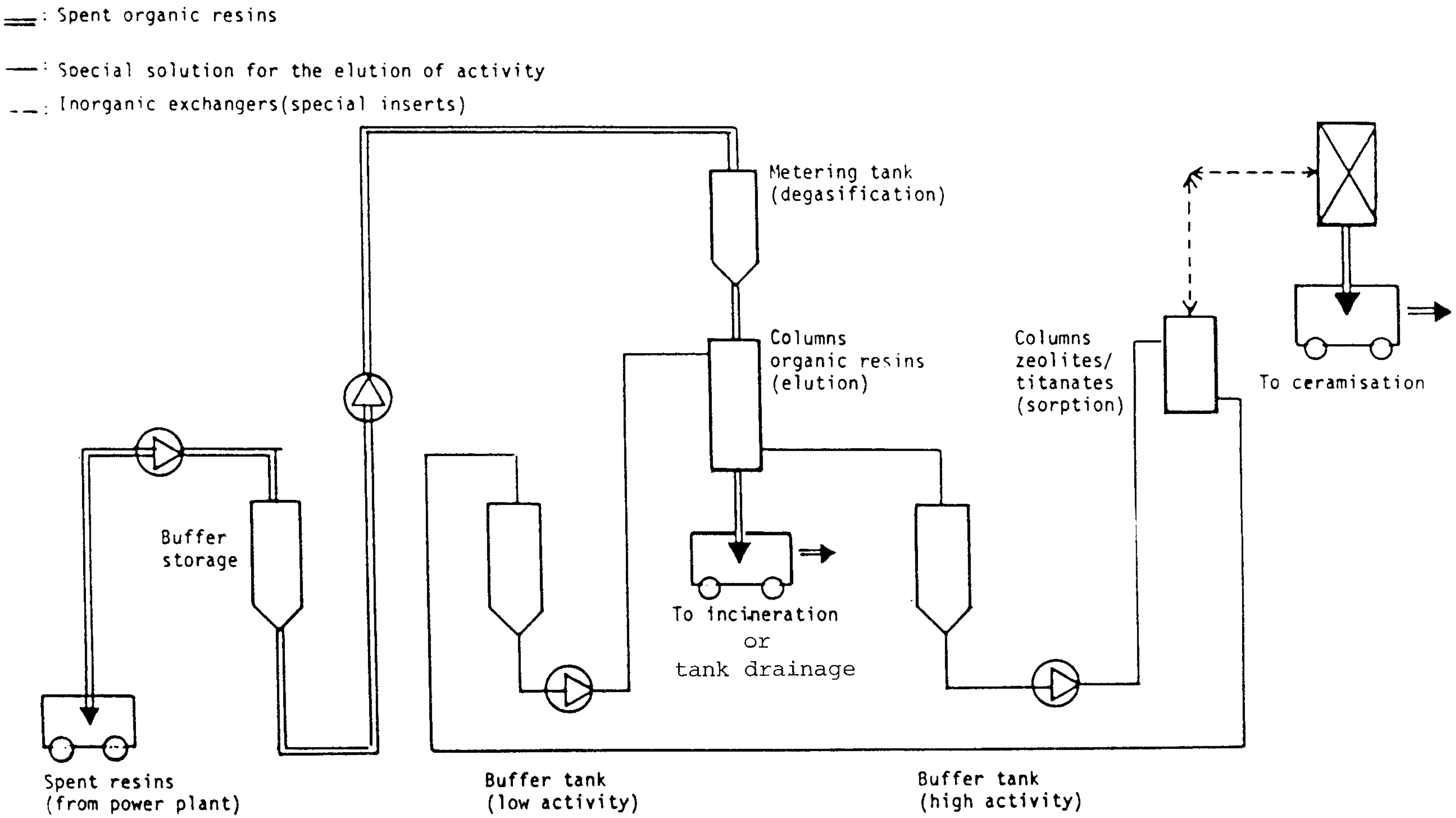


Figure 20 Simplified presentation of a PILO system.

If realized the system would offer the immobilization of critical nuclides in a very stable form and, if the low level resins are incinerated, also an efficient waste volume reduction.

5.1 Transportation

In a PILO system spent resins would be transported to a central treatment facility presumably co-located with the repository for low and medium level wastes, SFR, at the Forsmark nuclear power plant. The medium level resins would require type B transport containers while low level resins may use tank containers. All transportation would be by ship.

International experience was reviewed (34). Over-all experience is good but limited to Canada, USA and the Federal Republic of Germany. The containers TN 20 and TN 21 used in FRG are specially constructed for filling and discharge of slurries and resins. It is concluded that the transportation of spent resins is technically feasible and can be made in a safe manner.

5.2 Plant & flowsheet design

A preliminary engineering study was made of a central PILO plant for the treatment of medium level resins. It included two subsystems:

- process for the transfer of radionuclides from spent resins to inorganic sorbents by elution-sorption
- process for the solidification of radioactive inorganic sorbents by a sintering process.

The eluted resins may be simply dewatered in transportable concrete containers for further storage and disposal or, alternatively, incinerated together with other low-level resins.

A flowsheet is shown in figure 21.

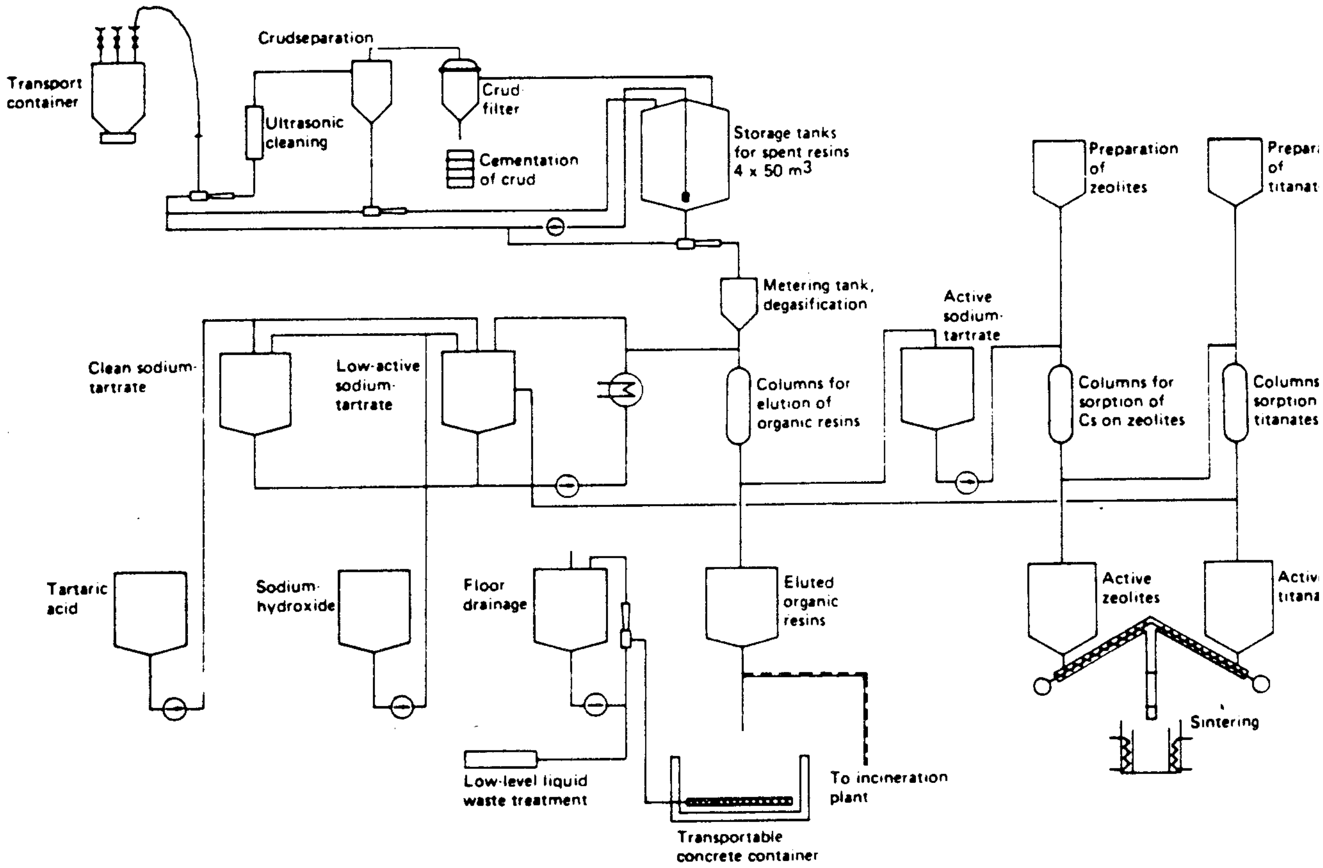


Figure 21 PILO flowsheet designed as a basis for a preliminary engineering study.

It was concluded that further experience would be desirable regarding i.a. secondary waste arisings and the consumption of process chemicals. However, the application of the PILO process on an industrial scale was considered feasible, with additional investigations needed for a detailed engineering design.

For the incineration of eluted resins foreign experience was reviewed. Firm operating experience from large scale incineration of spent resins seemed not to be available, although R&D work was found in progress in several countries and industrial plants were in the planning stage. Comprehensive experience was considered necessary before the technical and economic possibility of the large-scale incineration of spent resins could be further established.

5.3 Economics

The costs of the introduction and operation of a central PILO plant for the Swedish nuclear power programme were calculated.

The economic evaluation was based on the following assumptions:

- During the years 1985 - 2010 the average production of spent resins will be 180 m^3/a medium level resin and 700 m^3/a low level resin.
- The central treatment plant and the repository for reactor waste (SFR) will be in operation in 1988. They will both be located at the Forsmark power plant site.

It was found that central treatment only of medium level resins by elution/sorption/sintering would not be economic in the present Swedish nuclear programme. However, if this treatment is combined with incineration of all low level resins, including eluted resins, the cost estimates indicated that quite substantial savings could be made. A detailed analysis taking into account different assumptions of inflation and interest rates showed that the possible cost savings were in the order of 100 million Swedish crowns over a period of 20 years.

6. CONCLUSION

The potential use of titanates and zeolites in the treatment of low and intermediate level operating wastes has been evaluated by experimental investigations, system design and cost analyses. This report summarizes mainly the experimental work performed in Sweden from 1976 to 1982.

The conclusion is that technical feasibility and economic incentives exist for the use of titanates and zeolites in the treatment of spent resins from reactor operation and spent fuel pool cleaning. However, for a detailed process and plant design further experience would be desirable regarding i.a. secondary waste formation and resin incineration.

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