

TECHNICAL REPORTS SERIES NO. 408

Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 2002

APPLICATION OF ION EXCHANGE
PROCESSES FOR THE TREATMENT
OF RADIOACTIVE WASTE AND
MANAGEMENT OF
SPENT ION EXCHANGERS

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Printed by the IAEA in Austria
June 2002
DOC/010/408

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VIC Library Cataloguing in Publication Data

Application of ion exchange processes for the treatment of radioactive waste and management of spent ion exchangers. — Vienna : International Atomic Energy Agency, 2002.

p. ; 24 cm. — (Technical reports series, ISSN 0074-1914; no. 408)
STI/PUB/408

ISBN 92-0-112002-8

Includes bibliographical references.

1. Radioactive wastes — Management. 2. Ion exchange. I. International Atomic Energy Agency. II. Series: Technical reports series (International Atomic Energy Agency) ; 408.

VICL

02-00286

FOREWORD

Ion exchange is one of the most common and effective treatment methods for liquid radioactive waste. It is a well developed technique that has been employed for many years in both the nuclear industry and in other industries. In spite of its advanced stage of development, various aspects of ion exchange technology are being studied in many countries to improve its efficiency and economy in its application to radioactive waste management.

Spent ion exchangers are considered to be problematic waste that in many cases requires special approaches and precautions during its immobilization to meet the acceptance criteria for disposal. The subject of ion exchange processes and the treatment of spent ion exchange media has been covered in two IAEA Technical Reports, one published in 1967 (Technical Reports Series No. 78, Operation and Control of Ion-exchange Processes for Treatment of Radioactive Wastes), the other in 1985 (Technical Reports Series No. 254, Treatment of Spent Ion-exchange Resins for Storage and Disposal). Since the publication of those reports, many new developments have been reported for improving the efficiency of ion exchange process applications. Taking this into account, it was decided to review and update the IAEA's publications on these subjects and prepare a new report that would reflect the existing state of the art of the application of ion exchange processes for liquid radioactive waste treatments and of the management of spent ion exchange media.

The initial draft of this report was compiled by consultants from Canada, Germany and India in June 1997. The draft was discussed and revised by experts from 13 countries at a Technical Committee Meeting held in Vienna in February 1998. Based on contributions from Technical Committee members the report was revised in March 1999 by the IAEA Secretariat and consultants from Canada, the United Kingdom and the United States of America. The final report was prepared by the IAEA after a review of the information, data and comments received from the consultants and Technical Committee members.

The IAEA would like to express its thanks to all those who took part in the preparation and revision of the report. The officer responsible for the report at the IAEA was V.M. Efremkov of the Waste Technology Section, Division of Nuclear Fuel Cycle and Waste Technology.

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1. INTRODUCTION

1.1. BACKGROUND

There are a number of liquid processes and waste streams at nuclear facilities (i.e. nuclear power plants, fuel reprocessing plants, nuclear research centres, etc.) that require treatment for process chemistry control reasons and/or the removal of radioactive contaminants. These processes may be for reactor primary coolants, the cleanup of spent fuel pools, liquid radioactive waste management systems, etc. One of the most common treatment methods for such aqueous streams is the use of ion exchange, which is a well developed technique that has been employed for many years in both the nuclear industry and in other industries.

Nuclear power plant process water systems have typically used organic ion exchange resins to control system chemistry to minimize corrosion or the degradation of system components and to remove radioactive contaminants. Organic resins are also used in a number of chemical decontamination or cleaning processes for the regeneration of process water by reagents and for radionuclide removal.

In the past decade inorganic ion exchange materials have emerged as an increasingly important replacement or complement for conventional organic ion exchange resins, particularly in liquid radioactive waste treatment and spent fuel reprocessing applications. Inorganic ion exchangers often have the advantage of a much greater selectivity than organic resins for certain radiologically important species, such as caesium and strontium. These inorganic materials may also prove to have advantages with respect to immobilization and final disposal when compared with organic ion exchangers. However, in nuclear power plant operations the currently available inorganic exchangers cannot entirely replace conventional organic ion exchange resins, especially in high purity water applications or in operations in which the system chemistry must be controlled through the maintenance of dissolved species such as lithium ions or boric acid.

The ion exchange process is very effective at transferring the radioactive content of a large volume of liquid into a small volume of solid. The treatment and conditioning of radioactive spent ion exchange materials is a complex process encompassing a detailed consideration of the materials' characteristics and their compatibility with the various processing, storage and/or disposal options. The handling of spent ion exchange media also needs to be assessed in the context of an integrated waste management system for all the radioactive waste generated; for example, in some cases ion exchange waste may constitute such a relatively minor fraction of the total waste stream that a specialized treatment only for ion exchange media may not be cost effective. Conversely, the radiochemical characteristics of

spent ion exchange media may require specialized handling, even though the volumes may represent a small fraction of a facility's waste inventory.

Although inorganic ion exchange materials play an increasing role in the selective removal of specific radionuclides, organic ion exchange resins continue globally to represent the dominant form of ion exchange waste. This is largely because organic ion exchangers have proved to be reliable and effective for the control of both the chemistry and radiochemistry of water coolant systems at nuclear power plants and also for processing some liquid radioactive waste. Organic ion exchange resins have been developed over a much longer period of time than the selective inorganic ion exchangers that are now becoming available in commercial quantities and they can now meet the demands of the nuclear industry. In a number of cases, for specific physical and chemical reasons, organic resins cannot be replaced by inorganic ion exchangers.

The volumes of spent organic ion exchange resins that arise from typical nuclear power plant operations are shown in Table I.

1.2. OBJECTIVES

The primary objectives of this report are to analyse the current status of the applications of ion exchange processes for the treatment of particular liquid radioactive waste streams, to provide information on the selection of the appropriate organic or inorganic ion exchangers for waste processing, to discuss the different approaches for the treatment and conditioning of spent ion exchange media and to identify the appropriate strategies for dealing with the resulting spent ion exchangers.

TABLE I. SPENT ORGANIC ION EXCHANGE RESIN GENERATION BY REACTOR TYPE

| Reactor type | Spent ion exchange resin generation ($\text{m}^3 \cdot \text{unit}^{-1} \cdot \text{a}^{-1}$) |
|--------------|--|
| PWR | 4–7 |
| PHWR | 5–7 |
| BWR | 20 |

Note: The quantity of significantly greater waste arisings from the BWR plants is largely the result of the extensive use of resins for condensate polishing.

PWR: pressurized water reactor. **PHWR:** pressurized heavy water reactor. **BWR:** boiling water reactor.

This report should provide Member States and responsible organizations with information related to the selection of appropriate ion exchange media and the processes for liquid radioactive waste treatment, as well as information concerning the availability, advantages and limitations of various methods for the treatment and conditioning of spent ion exchange materials. These objectives will be addressed by reviewing:

- The characteristics of the different types of ion exchange media,
- Their applicability to the treatment of particular waste types,
- The specifics of the various ion exchange processes and techniques,
- The methods for processing spent ion exchange materials to meet the specific requirements for long term storage and/or disposal.

1.3. SCOPE AND STRUCTURE

This report describes the ion exchange technologies currently used and under development in the nuclear industry, in particular for waste management practices, along with the experience gained in their application and with the subsequent handling, treatment and conditioning of spent ion exchange media for long term storage and/or disposal. The focus will be on the ion exchange materials and processes that are currently used on an industrial scale or that are in an advanced stage of development.

The previous IAEA publications on these subjects include Technical Reports Series No. 78, Operation and Control of Ion-exchange Processes for Treatment of Radioactive Wastes [1], and Technical Reports Series No. 254, Treatment of Spent Ion-exchange Resins for Storage and Disposal [2], which was the compilation of several individual reports on research performed within the framework of an IAEA Co-ordinated Research Project. Since that time many new developments in ion exchange processes and methods for the conditioning of spent ion exchange media have been reported.

The increased role of inorganic ion exchangers for the treatment of radioactive liquid waste, both in nuclear power plant operations and in the fuel reprocessing sector, is recognized in this report. The intention of this report is to consolidate the previous publications, document recent developments and describe the state of the art in the application of ion exchange processes for the treatment of radioactive liquid waste and the management of spent ion exchange materials.

The report is organized by topics:

- Section 2 briefly describes the principles of ion exchange processes;
- Section 3 discusses the various types of ion exchange materials;

- Section 4 presents descriptions and examples of various ion exchange processes;
- Section 5 describes the preconditioning of spent ion exchangers, including destruction methods;
- Section 6 discusses the direct immobilization of spent ion exchangers for storage and/or disposal;
- Section 7 discusses the influence of storage and/or disposal requirements on the selection of treatment and conditioning options;
- Section 8 discusses the future trends in ion exchange media development, the application of ion exchange processes and the management of spent ion exchange media;
- Section 9 presents the conclusions;
- The Annex provides details of the test procedures for the direct comparison of different sorbents developed by the Novel Absorber Evaluation Club of AEA Technologies, United Kingdom, which are based on standard procedures and ‘benchmark’ materials.

2. PRINCIPLES OF ION EXCHANGE PROCESSES

2.1. GENERAL

Ion exchange is a process in which mobile ions from an external solution are exchanged for ions that are electrostatically bound to the functional groups contained within a solid matrix. When the functional groups are negatively charged the exchange will involve cations and when they are positively charged they involve anions. By taking advantage of the fact that, under certain conditions, ion exchange media have a greater affinity for certain ionic species than for others, a separation of these species can be made; for example, the hydrogen form of a cation exchanger will release its hydrogen ion into solution and pick up a caesium ion from the solution according to the following equation:



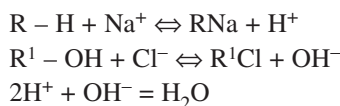
where R represents the insoluble matrix of the ion exchange resin. The negative counter ion of the caesium salt is not affected by the exchange since every caesium ion removed from solution is replaced by a hydrogen ion and electroneutrality is maintained.

TABLE II. pK VALUES FOR THE MOST COMMON FUNCTIONAL GROUPS OF ORGANIC ION EXCHANGERS

| Cation exchangers | | Anion exchangers | |
|------------------------------------|------|--------------------------------|------|
| Functional group | pK | Functional group | pK |
| -SO ₃ H (strong acidic) | 1-2 | ≡N ⁺ (strong basic) | 1-2 |
| -PO ₃ H ₂ | 2-5 | =N | 4-6 |
| -COOH | 4-6 | =NH | 6-8 |
| -OH (weak acidic) | 9-10 | -NH ₂ (weak basic) | 8-10 |

Depending on the type of the functional group, ion exchangers can be divided into several types: strong acidic, strong basic, weak acidic and weak basic. In Table II the negative logarithm of the dissociation constant (pK) is presented for different functional groups. Ion exchangers containing sulfo- and phospho-acidic groups and those containing tetraammonium basic groups are strong acidic and strong basic exchangers, respectively, whereas those containing phenolic and primary amino groups are weak acidic and weak basic exchangers, respectively. Exchangers with carboxy groups and tertiary amino groups take a medium position between strong and weak acidic and basic exchangers, respectively.

To achieve the removal of both positively and negatively charged ions from solution, a mixture of cation and anion resins in a mixed bed system is often used; for example, for a NaCl solution the ion exchange process will be:



Since H₂O is only weakly dissociated, the reactions of ion exchange are driven in this case to the right hand side of the equation.

2.2. ION EXCHANGE EQUILIBRIUM AND SELECTIVITY

Ion exchange equilibrium can be described in terms of any of the following:

- The ion exchange isotherm,
- The separation factor,
- The selectivity coefficient,

- The thermodynamic equilibrium constant,
- The distribution coefficient.

These terms are defined and described in Ref. [3]. It should be noted that selectivity coefficients are not constant and will vary with the experimental conditions of, for example, concentration, temperature and the presence of other ions in the solution. The determination of selectivity coefficients is a complicated task and is ordinarily not undertaken in the design of waste treatment systems; most of these parameters can be extracted from manufacturers' data or research literature. For general design purposes a few 'rules of thumb' can be applied: for cationic organic ion exchange resins at low concentrations and the temperatures normally encountered in waste processing, the affinity typically increases with (a) an increasing charge on the exchanging cation and (b) an increasing atomic number (decreasing hydrated ionic radii) of the exchanging cation; for example:

- (a) $\text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+ < \text{Mg}^{2+} < \text{Co}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ce}^{3+} < \text{La}^{3+} < \text{Th}^{4+}$
- (b) $\text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ (Li^+ is an exception, owing to its high hydration energy)

For anions a typical series is as follows:



Changes in physical parameters and of the concentration of functional groups affect the distribution coefficient and can affect the driving force for the ion exchange process. High values of the distribution coefficient are always desirable. Table III gives examples of the selectivities of different ion exchangers in specified experimental conditions, showing the wide range of values among different media.

TABLE III. SELECTIVITY OF DIFFERENT MEDIA FOR CAESIUM/SODIUM

| Ion exchange media | Concentration of sodium (mol/L) | Selectivity coefficient $k^{\text{Cs/Na}}$ |
|-------------------------|---------------------------------|--|
| Strong acid resin | 1.0 | <10 |
| Caesium-selective resin | 6.0 | 11 400 |
| Zeolite (mordenite) | 0.1 | 450 |
| Silico-titanate | 5.7 | 18 000 |
| Hexacyanoferrate | 5.0 | 1 500 000 |

2.3. ION EXCHANGE AND SORPTION

Sorption is a separation process involving two phases between which certain components can become differentially distributed. There are three types of sorption, classified according to the type of bonding involved:

- (a) Physical sorption. There is no exchange of electrons in physical sorption, rather intermolecular attractions occur between 'valency happy' sites and are therefore independent of the electronic properties of the molecules involved. The heat of adsorption, or activation energy, is low and therefore this type of adsorption is stable only at temperatures below about 150°C.
- (b) Chemical sorption. Chemical adsorption, or chemisorption, involves an exchange of electrons between specific surface sites and solute molecules, which results in the formation of a chemical bond. Chemisorption is typified by a much stronger adsorption energy than physical adsorption. Such a bond is therefore more stable at higher temperatures.
- (c) Electrostatic sorption (ion exchange). This is a term reserved for coulombic attractive forces between ions and charged functional groups and is more commonly classified as ion exchange.

In addition to being ion exchangers, ion exchange materials can also act as sorbents. When they are contacted with an electrolyte solution the dissolved ions are concentrated on both the surface and in the pores of the ion exchange media. In a solution of weak electrolytes or non-electrolytes, sorption by ion exchangers is similar to that of non-ionic adsorbents. In a solution of strong electrolytes a sorption equilibrium results, owing to the electrostatic attraction between the ions in solution and the fixed ionic groups on the ion exchange media. Sorption equilibrium is normally represented by 'sorption isotherm' curves.

Many forces and interactions have been found by experimentation to affect the sorption of non-electrolytes. Solutes may form complexes or chelates with the counter ions of the exchanger. Temperature variations may not only affect the state of the solute but also the condition of the exchanger. The molecular size of the solute and the degree of cross-linking of the exchanger will also affect the sorption kinetics.

2.4. ION EXCHANGE CAPACITY

The term 'ion exchange capacity' is intended to describe the total available exchange capacity of an ion exchange resin, as described by the number of functional groups on it. This value is constant for a given ion exchange material and is generally

given as milliequivalents per gram (meq/g), based on the dry weight of material in a given form (such as H^+ or Cl^-). For organic ion exchange resins it can be given as milliequivalents per millilitre (meq/mL), based on the wet fully swollen volume of a settled bed of resin. The numbers quoted in the literature vary widely for different resins. This number can be used to compare different resins or to calculate the total amount of resin to be added during a batch exchange process.

For the characterization of ion exchangers two capacity parameters are commonly used: the total static exchange capacity (which is determined under static conditions) and the dynamic exchange capacity (which is determined by passing a solution through a bed of the exchanger). The exchange capacity depends on the number of functional group per gram of exchanger. The extent of the use of the total exchange capacity depends on the level of ionization of the functional groups of the exchanger and on the chemical and physical conditions of the process.

The operating or breakthrough capacity of a column type ion exchange system (see also Sections 2.5 and 2.6) depends on its design and operating parameters, the concentration of the ions being removed and the effects of interference from other ions. In a column system this generally refers to the volume of the solution that can be treated before a sharp increase in the effluent concentration of the species being removed is observed. At this point the ion exchange medium is considered to be spent and must be replaced or regenerated. The operating or breakthrough capacity is the number of most interest in the design of a column type ion exchange system and is generally given as the number of bed volumes (the ratio of the volume of liquid processed before the breakthrough point to the volume of the settled bed of the exchanger).

Some important parameters that affect the breakthrough capacity are the:

- Nature of the functional group on the exchanger,
- Degree of cross-linking,
- Concentration of the solution,
- Ionic valence,
- Ionic size,
- Temperature.

2.5. KINETICS AND DYNAMICS

When designing an ion exchange processing system it is desirable to have an appreciation of the rate at which the reaction will occur. The required contact time will influence the physical size of the plant.

When an ion exchanger particle is brought in contact with a solution there is a static liquid film formed around it, the thickness of which may vary between

10 and 100 μm , depending on the rate of flow of liquid past the particle. The ion exchange reaction occurring between the resin particle and the solution will involve five distinct steps:

- (a) Diffusion of the ions through the bulk solution in order to reach the ion exchanger particle,
- (b) Diffusion of the ion through the hydrated film surrounding the particle,
- (c) Diffusion of the ion across the film–particle interface,
- (d) Diffusion of the ion through the particle,
- (e) The actual chemical reaction involving the exchange of ions.

Providing that the concentration of ions in the solution is not extremely low steps (a), (c) and (e) are generally fast and do not determine the rate of the reaction. It is only step (b) (diffusion through the hydration film) or step (d) (diffusion through the particle) that controls the kinetics of the overall process, although sometimes both may determine the rate simultaneously. This is a simplified picture of the mechanism of an ion exchange process and its kinetics. The kinetics may be affected by a number of parameters, such as the nature of the exchanger, the nature of the counter ions, the extent of agitation, the concentration of the counter ions, etc. As an example, the general effect of salt concentration on exchange kinetics is shown in Table IV.

The actual rates of ion exchange can vary over a wide range, requiring a few seconds to several months to reach equilibrium. Some additional factors affecting the exchange rate are given in Table V.

For a particular liquid–ion exchanger combination, the distribution coefficient (K_d) can be measured for each radionuclide and/or species present in the solution. The distribution coefficient can be used directly to calculate the amount of ion exchange medium that is needed to achieve a desired decontamination for a certain amount of liquid in a batch process.

Under dynamic conditions, in which the ion exchange medium is used in a packed bed or in a column, the distribution coefficient can be used to calculate the

TABLE IV. EFFECT OF SALT CONCENTRATION ON REACTION MECHANISMS

| Salt concentration (normal) | Rate controlling mechanism |
|-----------------------------|-----------------------------|
| <0.001 | Film diffusion |
| 0.3–0.001 | Film and particle diffusion |
| >0.3 | Particle diffusion |

TABLE V. FACTORS AFFECTING ION EXCHANGE RATES

| Parameter | Particle diffusion control | Film diffusion control |
|----------------------------------|--|--|
| Counter ion mobility | | |
| Solid phase | Proportional to D_e | No effect |
| Liquid phase | No effect | Proportional to D_f |
| Co-ion mobility | No effect | No effect |
| Particle size | Proportional to $1/r^2$ | Proportional to $1/r$ |
| Capacity of the ion exchanger | No effect | Proportional to $1/x$ |
| Nature of the fixed ionic groups | Slow when fixed ionic groups associate with mobile ions | No effect |
| Degree of cross-linking | Decreases with increasing cross-linking | No effect |
| Selectivity of the ion exchanger | Preferred counter ion is generally taken up at a higher rate and released at a lower rate, except under special conditions | |
| Concentration of the solution | No effect | Proportional to the concentration |
| Solution volume | Decreases with increasing solution volume | |
| Temperature | Increases with temperature, approximately 4 to 8% per °C | Increases with temperature, approximately 3 to 5% per °C |
| Rate of agitation or flow | No effect | Increases with the agitation rate |

D_e = interdiffusion coefficient in the ion exchange medium; D_f = interdiffusion coefficient in the static hydration film; r = particle radius; x = concentration of functional ionic groups.

theoretical maximum capacity of the ion exchange bed. If the bed includes m kg of ion exchange medium, the total capacity of the bed V_{tot} can be calculated as:

$$V_{\text{tot}} = K_d \times m$$

In column operation the total capacity can never be exploited, owing to interference from co-existing counter ions. In practice, the operator of the ion exchange system will set a requirement for the decontamination factor; for example, if the decontamination factor requirement is 100 the ion exchange bed has to be replaced when 1% breakthrough occurs. The capacity for which this set requirement is met is called the breakthrough capacity or the operation capacity of the ion exchange bed.

A typical breakthrough curve (also known as an effluent concentration history or exchange iso-plane) is shown in Fig. 1. Breakthrough begins at point c and the

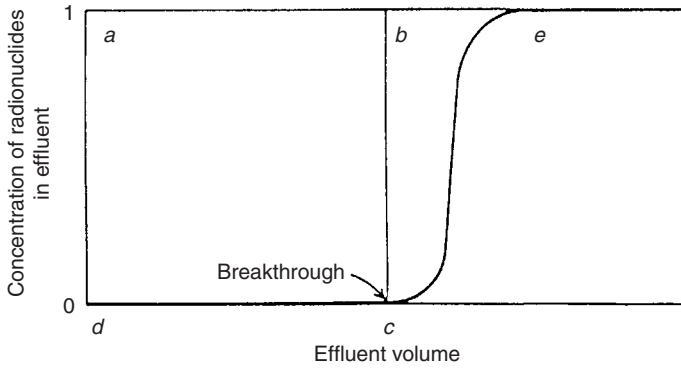


FIG. 1. Schematic breakthrough curve.

extent of breakthrough increases until, at point *e*, no further ion exchange occurs (i.e. the ion exchanger is saturated). The breakthrough capacity is proportional to the area *abcd* and the overall capacity to the area *aecd*.

The shape of the breakthrough curve and the breakthrough capacity (i.e. the total liquid volume treated up to a particular percentage breakthrough) will depend on the operational conditions (i.e. the ion exchange medium grain size and the liquid flow rate) and on the appropriate diffusion coefficients of the exchanging ions in the system.

In practical operations it is desirable to have the breakthrough curve as steep as possible. A steeper breakthrough curve will increase the extent of column utilization; that is, bring the ratio of the breakthrough capacity to the total capacity closer to unity. If the required decontamination factor is high the degree of column utilization can vary considerably for different ion exchange media.

2.6. LIMITATIONS OF ION EXCHANGER APPLICATIONS

Certain characteristics of ion exchange materials and processes limit their applicability and efficiency. When used as a packed bed in a column, the complete removal of a specific radionuclide is not normally possible, owing to leakage or breakthrough. This will cause the radionuclide to pass through without being captured. In a properly designed system this breakthrough may be very low, but will still be present. Leakage may be due to:

- Radionuclides in a colloidal form or attached to a finely divided particulate material (pseudo-colloidal);

- A portion of the radionuclide may be in a non-ionic or other non-exchangeable form;
- Mechanical problems, such as channelling in column systems, possibly due to a shrinkage of the resin beads or an uneven settling of the resin bed.

When used in a batch process, inadequate mixing will also limit the effectiveness of the ion exchange material. The total concentration of dissolved salts in solution must generally be low (<1 g/L). At high concentrations the exchange potentials for ions diminish and there is more competition for the available exchange sites between non-radioactive ions and the radioactive species. However, for specifically developed ion exchangers (usually inorganic) the tolerance for dissolved salts can be very high (e.g. up to 240 g/L [4]).

The breakthrough of radionuclides will cause some contamination of the effluent. In plant operation breakthrough will start when a certain preset level of ion concentration is reached. When breakthrough starts the column is removed from the system. The start of the breakthrough has to be detected and therefore it is necessary to have a sensitive measurement system that can indicate the breakthrough immediately.

When used in a downward flow mode the amount of suspended solids in the waste solution must be low to avoid the bed of ion exchanger blocking. In most cases prefiltration will extend the life of the ion exchange media, permit a closer control of the system operation, reduce ionic leakage and permit more efficient backwashing and regeneration.

Additional limitations specific to certain types of exchangers are discussed in Section 3.

3. ION EXCHANGE MATERIALS

3.1. GENERAL

A wide range of materials is available for the ion exchange treatment of radioactive liquids. These materials are available in a variety of forms, have widely differing chemical and physical properties and can be naturally occurring or synthetic. This section focuses on materials that are commercially available and that can be readily obtained and used for radioactive liquid treatments. Materials that are not suitable for the treatment of radioactive liquids, such as pharmaceutical ion exchange gels and liquid exchangers, are not described.

Ion exchange materials can be categorized according to their suitability for different applications. Nuclear grade organic ion exchange resins are normally used when liquids from primary circuits or fuel pools are purified. The type of material to be used is selected based on its ability to remove impurities and undesirable ions and to control pH. Nuclear grade ion exchangers are similar to commercial grade resins but have a tighter specification for particle size and composition. Organic resins are often used for a number of treatment cycles by eluting the absorbed radioisotopes with suitable solutions and then restoring the ion exchanger to its original ionic form before its reuse.

Inorganic materials are commonly used for the treatment of liquid waste streams for which very high chemical cleanliness is not required; for example, inorganic ion exchange media can be used in systems in which contaminated liquid is purified for certain recirculation purposes or to reduce the level of radionuclide concentration in the liquid to allow its reclassification. Highly selective inorganic materials also make it possible to utilize ion exchange in the event that very high concentrations of competing ions are present. Inorganic ion exchangers are almost entirely used on a once through basis only.

To minimize disposal costs, in any process for the removal of radionuclides from a liquid waste it is important to minimize the volume of the secondary waste to be conditioned and disposed of in a final repository. An intermediate goal in the treatment process is that the main waste stream after treatment can be discharged or recycled in a technically less demanding and less costly manner. Environmental aspects are also very important, since the regulations on discharges are becoming increasingly more stringent. Highly selective inorganic ion exchangers play an important role in solving these problems.

Even if an inorganic ion exchanger is highly selective for a certain radionuclide, it needs to meet several other requirements to become a product that can be used in industrial scale separation processes. Some inorganic ion exchangers can be produced in a granular form, but the granules are often of a low mechanical strength and when contacted with aqueous solutions they break down and may peptize to produce colloidal particles.

To overcome the problem of poor physical strength of the intrinsic exchanger granules, methods for incorporating inorganic ion exchangers into supporting binder materials, both inorganic and organic, have been developed.

Chemical stability, especially low solubility, is important for the usefulness of inorganic ion exchange materials. Most zeolites, for example, only work over a limited pH range (4–9), since they are soluble both in acidic and alkaline media. Of the inorganic ion exchange materials developed so far, those based on pure or mixed titanium oxides have been shown to be the most stable and capable of taking up radionuclides, even from highly alkaline waste effluents. There are some known categories of compounds that are stable in highly acidic solutions and that take up radionuclides such as caesium.

In nuclear waste treatments at reprocessing plants the stability of ion exchangers in nitric acid can be important, since concentrated nitric acid is used to dissolve spent fuel. In general, a single ion exchange material is unlikely to be able take up a particular radionuclide over the whole pH range found for waste streams. Radionuclides, especially those of transition metals, can be found in several hydrolysed and complexed forms at different pH values and in different media. The formation of complex ions often results in a reversal of the charge polarity of the ion containing the radionuclide. When this occurs the ion exchanger will not be able to take up the radionuclide. In addition, some exchangers, such as hydrous oxides, do not work in acidic solutions at all, as they act like weakly acidic exchangers and therefore will take up hydrogen ions in preference to any of the radionuclides present in the solution.

A modern trend among authorities and industry is to avoid using any organic based materials, owing to their limited radiation stability. Special concern should be paid to the possible radiation induced generation of gases, especially hydrogen, in long term storage and final disposal.

The cost of the ion exchanger should be reasonable. It is likely that the price of some new ion exchangers will be higher than those of conventional materials. Obviously, the cost of the ion exchanger has to be considered along with the savings in the waste treatment and disposal costs obtained from its use.

A general comparison between organic and inorganic ion exchangers is given Table VI.

3.2. NATURALLY OCCURRING ION EXCHANGERS

3.2.1. Natural inorganic ion exchangers

Many natural mineral compounds, such as clays (e.g. bentonite, kaolinite and illite), vermiculite and zeolites (e.g. analcite, chabazite, sodalite and clinoptilolite), exhibit ion exchange properties. Natural zeolites were the first materials to be used in ion exchange processes. Clay materials are often employed as backfill or buffer materials for radioactive waste disposal sites because of their ion exchange properties, low permeability and easy workability. Clays can also be used in batch ion exchange processes but are not generally suited to column operation because their physical properties restrict the flow through the bed.

In 1985 British Nuclear Fuels plc (BNFL) successfully commissioned the Site Ion Exchange Effluent Plant (SIXEP), which uses naturally occurring clinoptilolite to remove caesium and strontium from fuel cooling pond water [5].

Other natural aluminosilicate materials, such as green sand, are also used in some waste treatment applications, generally in column or large deep bed designs. In this capacity they can be used as a combination of an ion exchanger and a particulate filter.

TABLE VI. GENERAL COMPARISON OF ORGANIC AND INORGANIC ION EXCHANGERS

| | Organic exchangers | Inorganic exchangers | Comments |
|---------------------|--------------------|----------------------|--|
| Thermal stability | Fair to poor | Good | Inorganics are especially good for long term stability |
| Chemical stability | Good | Fair to good | Specific organics and inorganics are available for any given pH range |
| Radiation stability | Fair to poor | Good | Organics are very poor in combination with high temperatures and oxygen |
| Exchange capacity | High | Low to high | The exchange capacity will be a function of the nature of the ion being removed, its chemical environment and the experimental conditions |
| Selectivity | Available | Available | For some applications, such as caesium removal, inorganics can be much better than organics, owing to their greater selectivity Ion selective media are available in both organic and inorganic forms |
| Regeneration | Good | Uncertain | Most inorganics are sorption based, which limits regeneration |
| Mechanical strength | Good | Variable | Inorganics may be brittle or soft or may break down outside a limited pH range |
| Cost | Medium to high | Low to high | The more common inorganics are less costly than organics |
| Availability | Good | Good | Both types are available from a number of commercial sources |
| Immobilization | Good | Good | Inorganics can be converted to equivalent mineral structures, organics can be immobilized in a variety of matrices or can be incinerated |
| Handling | Good | Fair | Organics are generally tough spheres, inorganics may be brittle; angular particles are more friable |
| Ease of use | Good | Good | If available in a granulated form both types are easy to use in batch or column applications |

Clay minerals and natural zeolites, although replaced by synthetics to a large extent, continue to be used in some applications, owing to their low cost and wide availability. The main disadvantages of natural inorganic ion exchangers are:

- Their relatively low exchange capacities;
- Their relatively low abrasion resistance and mechanical durability;
- Their non-controllable pore size;
- That clay minerals tend to peptize (i.e. convert to a colloidal form);
- That zeolites are difficult to size mechanically;
- That they can be partially decomposed in acids or alkalis;
- That, owing to their limited chemical stability in many solutions, especially those with a very low salt content, they sometimes need a chemical or thermal pretreatment.

3.2.2. Natural organic ion exchangers

A large number of organic materials exhibit ion exchange properties; these include polysaccharides (such as cellulose, algic acid, straw and peat), proteins (such as casein, keratin and collagen) and carbonaceous materials (such as charcoals, lignites and coals). Of these, only charcoals, coal, lignite and peat are used commercially. Although they exhibit a very low ion exchange capacity compared with synthetics, they are widely available at a very low cost. They are normally used as general sorbents, with their ion exchange properties being a secondary consideration. Commercially available materials are often treated or stabilized with other additives to improve their uniformity or stability. Some materials, such as charcoals, can be doped with chemicals to improve their capacity or selectivity.

The main limitations of natural organic ion exchangers are:

- Their low exchange capacity compared with other materials,
- Their excessive swelling and tendency to peptize,
- The very limited radiation stability of cellulosic and protein materials,
- Their weak physical structures,
- Their non-uniform physical properties,
- That they are non-selective,
- That they are unstable outside a moderately neutral pH range.

3.2.3. Modified natural ion exchangers

To improve exchange capacity and selectivity, some naturally occurring organic ion exchangers are modified; for example, cellulose based cation exchangers may be modified by the introduction of phosphate, carbonic or other acidic functional groups.

The sorption parameters of natural materials can be modified by a chemical and/or thermal treatment; for example, by treating clinoptilolite with a dilute solution of acids or some salts a more selective form of sorbent can be developed for a particular radionuclide [6].

In Japan natural minerals treated with alkaline solutions under hydrothermal conditions have been proposed for the sorption of caesium and strontium from solution. These treatments have provided materials with distribution coefficients of 1000 to 10 000. Good results have been reported for the removal of caesium and strontium by neoline clays modified with phosphoric acid [7].

3.3. SYNTHETIC ION EXCHANGERS

Synthetic ion exchangers are produced by creating chemical compounds with the desired physical and chemical properties. They can be inorganic (mineral) or organic (generally polymer) based.

3.3.1. Synthetic inorganic ion exchangers

Some of the important synthetic inorganic ion exchangers are described below.

3.3.1.1. Zeolites

Zeolites were the first inorganic materials to be used for the large scale removal of radionuclides from nuclear waste effluents. Zeolites are crystalline aluminosilicate based materials and can be prepared as microcrystalline powders, pellets or beads.

The main advantages of synthetic zeolites when compared with naturally occurring zeolites are that they can be engineered with a wide variety of chemical properties and pore sizes, and that they are stable at higher temperatures.

The main limitations of synthetic zeolites are that:

- They have a relatively high cost compared with natural zeolites;
- They have a limited chemical stability at extreme pH ranges (either high or low);
- Their ion specificity is susceptible to interference from similar sized ions;
- The materials tend to be brittle, which limits their mechanical stability.

The selectivity and capacity of zeolites can provide a satisfactory processing of low strength salt solutions. The actual processing capacities obtained with zeolites are lower than their maximum capacities since the bed is changed at the early stages of breakthrough and because the waste streams usually contain other ions that will

occupy some of the exchange sites and therefore reduce the processing capacity. In particular, potassium interferes strongly with the exchange of caesium.

In high salt solutions, such as evaporator concentrates and fuel reprocessing effluents, the processing capacities of zeolites are very low. For instance, in the purification of high salt supernates (6.9M Na) the processing capacities of zeolites for ^{137}Cs were only of the order of 10 L/kg. In most cases such a low capacity is unacceptable, thus there is an ongoing need to develop more selective exchangers for the removal of ^{137}Cs (and ^{90}Sr) from high salt and medium salt waste streams.

Zeolite ion exchangers were used extensively in the cleanup of large volumes of contaminated water at Three Mile Island after the Unit 2 reactor accident. A mixture containing 60% Linde Ionsiv IE-96 and 40% Linde A-51 was used in columns to remove ^{137}Cs and ^{90}Sr with a high efficiency [8]. In India a systematic investigation has been carried out to evaluate the performance of locally available synthetic zeolites for the removal of caesium, strontium and thorium from solution [9–11]. The zeolites, after exchange with caesium, strontium or thorium, were thermally treated to fix the ions successfully in the same matrix [12]. A locally available synthetic mordenite was used recently in a campaign to reduce activity in spent fuel storage pool water [13]. A 120 L bed of sodium mordenite was able to remove nearly 10^{12} Bq of ^{137}Cs , which was the predominant radionuclide present.

3.3.1.2. Titanates and silico-titanates

For many years the oxide and hydroxide of titanium have been known to be effective in removing metal ions from solution. In 1955 studies in the UK and later in Germany and Japan identified a hydrous titanium oxide as the preferred exchange material for the large scale extraction of uranium from sea water. Subsequent studies found that this material also had a strong affinity for actinide metal ions and for ions with a charge of 2+ or more.

Titanates and hydrous titanium oxide (known both as HTiO or HTO) are known to be highly selective exchangers for strontium [14–16]. These materials have been prepared on a large scale and used for in-tank precipitation at the Savannah River Site in the United States of America [17].

A titanate product for the removal of radioactive strontium is manufactured by a Finnish company under the trade name SrTreat. It is a highly effective exchanger in an alkaline solution (i.e. for pH >9) [18]. This exchanger was used, in combination with a hexacyanoferrate absorber (CsTreat), at an industrial scale in Murmansk, Russian Federation, in autumn 1996 to purify process waters at a civil nuclear fleet base. The decontamination factors obtained for ^{137}Cs and ^{90}Sr were 1000 and 5000, respectively. This ion exchanger has also been used at the Japan Atomic Energy Research Institute and in the USA [19].

Titanates and hydrous titanium oxides are not efficient for the removal of caesium from solution. A new type of titanate exchanger, called crystalline silico-titanates, has recently been developed at the Sandia National Laboratory and at Texas A&M University [17]. These exchangers have a high selectivity both for ^{137}Cs and ^{90}Sr and they have been tested, for example, for the purification of tank waste at the United States Department of Energy's (US DOE) Hanford Site [20–21]. A silico-titanate is commercially available as IonSiv E-910 [22].

3.3.1.3. *Transition metal hexacyanoferrates*

Insoluble transition metal hexacyanoferrates have been known for decades as effective agents for the removal of radioactive caesium from solution [23]. Various forms of hexacyanoferrate are available for selective caesium removal; for example, in India potassium cobalt(II)–hexacyanoferrate(II) has emerged as a promising inorganic sorbent that can be prepared in a column-usable granular form that needs no resin support. A 5 L column of sorbent was recently used to reduce the ^{137}Cs activity in 12 000 L of ion exchange regeneration waste from 3.7×10^4 Bq/mL to 3.7 Bq/mL. The sorbent was also found suitable for removing ^{137}Cs from alkaline reprocessing waste containing a high concentration of sodium salts [24].

A freshly precipitated cupric hexacyanoferrate has been also examined in India for the removal of caesium from aqueous solutions [25].

In 1996 a total of 760 m³ of various wastewaters accumulated during the operation of ex-Soviet naval training reactors in Paldiski, Estonia, was purified using a column of CsTreat, a hexacyanoferrate based exchanger. No sign of bed exhaustion was observed after the treatment of 60 000 bed volumes of waste [19].

The Enhanced Actinide Removal Plant (EARP) at the BNFL reprocessing plant at Sellafield, UK, uses a floc treatment process with a solid–liquid separation by membrane filtration [26]. The plant has provision for the addition of finely divided inorganic exchange materials, such as a transition metal hexacyanoferrate, to reduce the levels of certain radionuclides even further than the levels achieved by the floc treatment alone.

3.3.2. **Synthetic organic ion exchangers**

The largest group of ion exchangers available today are synthetic organic resins in a powdered (5–150 μm) or bead (0.5–2 mm diameter) form. The framework, or matrix, of the resins is a flexible random network of hydrocarbon chains. This matrix carries fixed ionic charges at various locations. The resins are made insoluble by cross-linking the various hydrocarbon chains. The degree of cross-linking determines the mesh width of the matrix, swelling ability, movement of mobile ions, hardness

and mechanical durability. Highly cross-linked resins are harder, more resistant to mechanical degradation, less porous and swell less in solvents.

When an organic ion exchanger is placed in a solvent or solution it will expand or swell. The degree of swelling depends both on the characteristics of the solution/solvent and the exchanger itself and is influenced by a number of conditions, such as:

- The solvent's polarity,
- The degree of cross-linking,
- The exchange capacity,
- A strong or weak solvation tendency of the fixed ion groups,
- The size and extent of the solvation of counter ions,
- The concentration of the external solution,
- The extent of the ionic dissociation of functional groups.

The main advantages of synthetic organic ion exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic media. The main limitations are their limited radiation and thermal stabilities.

At a total absorbed radiation dose of 10^9 to 10^{10} rads most organic resins will exhibit a severe reduction in their ion exchange capacity (a 10 to 100% capacity loss), owing to physical degradation at both the molecular and macroscopic level.

Cation exchange resins are generally limited to operational temperatures below about 150°C , while anion exchange resins are usually limited to less than 70°C . This requires that some streams, such as reactor coolant water, be precooled substantially before their introduction to the ion exchange media.

The main groups of synthetic organic ion exchange resins are described below.

3.3.2.1. *Polystyrene divinylbenzene*

The most common form of ion exchange resin is based on a copolymer of styrene and divinylbenzene. The degree of cross-linking is adjusted by varying the divinylbenzene content and is expressed as the percentage of divinylbenzene in the matrix; for example, 5% cross-linking means 5 mol % divinylbenzene in the matrix. Low divinylbenzene content resins are soft and gelatinous and swell strongly in solvents.

Fixed ionic groups are introduced into resin matrices, for example by sulphonation, to create an ion exchanger. In sulphonation eight to ten $-\text{SO}_3\text{H}$ groups are added for every ten benzene rings in the structure. The H^+ of the $-\text{SO}_3\text{H}$ group then becomes the mobile or counter ion. It can be replaced by a treatment with a solution containing another cation; for example, a solution of NaOH will produce the $-\text{SO}_3\text{Na}$ group, with Na^+ as the mobile ion.

Anion exchangers can be produced by creating $-\text{NH}_3^+$ or $-\text{N}_2^+$ functional groups on the matrix with OH^- , Cl^- or other anions as the counter ion.

3.3.2.2. *Phenolic*

Phenol-formaldehyde condensation products, with the phenolic $-\text{OH}$ groups as the fixed ionic groups, are very weak acid exchangers. Sulphonation of the phenol prior to polymerization can be used to increase the acid strength. Phenolsulphonic acid resins are bifunctional with both strong acid $-\text{SO}_3\text{H}$ and weak acid $-\text{OH}$ groups included. The degree of cross-linking is controlled by the amount of formaldehyde.

A resorcinol-formaldehyde polycondensate resin was recently developed, characterized and tested extensively in India for the efficient removal of radiocaesium from alkaline reprocessing waste containing a large concentration of competing sodium ions [27–29]. Under alkaline conditions the phenolic $-\text{OH}$ groups ionize and serve as cation exchange sites with a high selectivity for caesium ions. Incorporation of iminodiacetic acid functional groups in the phenolic polymer gives it the additional property of strontium uptake by chelation; such a resin is presently being used in an industrial scale plant at Tarapur in India for the treatment of alkaline intermediate level reprocessing waste [30]. The development of a similar resin for the removal or recovery of radiocaesium from neutralized high level waste has also been reported in the USA [31].

Other phenolic type resins are produced using resorcinol-formaldehyde, which incorporates phosphoric acid or arsonic acid functional groups.

3.3.2.3. *Acrylic*

A weak acid ion exchange resin with weakly ionized carboxylic acid groups is prepared by the suspension copolymerization of acrylic or methacrylic acid with divinylbenzene. The $-\text{COOH}$ functional groups have very little salt splitting capacity, but under alkaline conditions exhibit a strong affinity for Ca^{2+} and similar ions (such as strontium). The acid strength can be increased by using various phosphoric acid derivative groups, such as $-\text{PO}_3^{2-}$, $-\text{PO}_3^{3-}$ and $-\text{HPO}_2^-$.

3.4. COMPOSITE ION EXCHANGERS

Composite ion exchangers consist of one or more ion exchangers combined with another material, which can be inorganic or organic and may itself be an ion exchanger. The reason for manufacturing a composite material is to produce a granular material, with sufficient strength for column use, from ion exchangers that do not form, or only form weak, granules themselves [32]. Synthetic zeolites are

manufactured in a granular form using inorganic binders such as aluminium oxide, for example. Different organic binders have also been tested at the laboratory scale. A composite ion exchanger has been developed by coating cupric ferric hexacyanoferrate on to polyacrylic fibres. This was done with a view to improving the column characteristics of the hexacyanoferrate. The composite has been used to treat actual radioactive waste arising out of a power reactor.

A granulation process based on the incorporation of various kinds of inorganic ion exchange materials in a polyacrylonitrile gel has been developed in the Czech Republic; these materials have been tested for nuclear waste effluent treatments [33–35]. One of these exchangers, containing a nickel hexacyanoferrate, has been used to treat contaminated fuel pond water at a Slovak nuclear power plant [36]. In this operation 80 L of sorbent was used to remove 8×10^{13} Bq of ^{137}Cs from 550 m³ of pond water.

The absorbers described in Refs [33–35] can be prepared with a greater than 80% ion exchanger content (based on dry weight); the sorption kinetics of the exchanger are not affected by their incorporation into the polyacrylonitrile.

The impregnation of organic resin beads with inorganic exchanger materials is reported in Ref. [37]. The amount of exchanger that can be introduced into the resin is small and the sorption kinetics of the composite material are significantly worse than those of the free exchanger.

A potential application for composite sorbents involves the combination of an inorganic exchanger with magnetite so that the loaded exchanger can be removed from the treated liquid by a magnetic field. This type of exchanger is commercially available from several companies, for example Bio-Separation Ltd in the UK [38]. There has been no reported use of these materials in treating liquid radioactive waste, but they have been used to remove caesium from contaminated milk.

3.5. ION EXCHANGE MEMBRANES

There are two principal types of ion exchange membranes: heterogeneous and homogeneous. Heterogeneous membranes can be prepared using almost any ion exchanger [39–41]. They are prepared by dispersing colloidal or finely ground ion exchange materials throughout an inert thermoplastic binder such as polyethylene, polystyrene or synthetic rubber, followed by rolling, compressing or extruding them into discs, films or ribbons. Ion exchange particles must be in contact with one another in the binder, but not to the complete exclusion of the binder otherwise the membrane will have a poor mechanical strength. Typically, the ion exchange media comprises 50 to 75% by volume of the membrane.

Homogeneous membranes are condensation products of sulphonated phenol and formaldehyde or of nitrogen-containing compounds and formaldehyde. These

strong acid or strong base condensates are laid out in thin sheets on mercury or acid-resistant plates. They can also be prepared by heating a precondensed, viscous reaction mixture between plates. If additional strength is required, membranes can be prepared on a mesh or fibrous backing.

Commercial membranes have also been prepared by interpolymer and graft polymerization techniques. The interpolymer films are obtained by the evaporation of a solution of a linear polyelectrolyte and a linear inert polymer. Although they are not cross-linked, these membranes are insoluble in water. In the graft polymerization method gamma irradiation (^{60}Co) is used to graft styrene, or styrene divinylbenzene mixtures impregnated in a polyethylene film, to a polyethylene base. Sulphonation of the graft copolymer produces a strong acid cation exchange membrane, while chloromethylation and quaternization or amination provide strong base and weak base anion membranes.

The principal disadvantages of ion exchange membranes when used in electro dialysis processes are:

- Their relatively high cost,
- Their limited mechanical stability,
- That chemical precipitation on and in the membrane will affect its useful life,
- Their high electrical resistance at low electrolyte concentrations,
- Their high osmotic and electro-osmotic water transport.

The low mechanical stability of some of the oxide sorbents, such as TiO_2 , has prompted their incorporation in porous stainless steel membranes. It is reported that membranes impregnated with TiO_2 are very efficient for the sorption of radionuclides from aqueous solutions and can be used for the removal of corrosion products from radioactive liquid effluents [42].

4. APPLICATION OF ION EXCHANGE TECHNIQUES FOR THE TREATMENT OF RADIOACTIVE LIQUIDS

4.1. GENERAL CONSIDERATIONS

Ion exchange technology has been applied for many years in nuclear fuel cycle operations and other activities involving the treatment of radioactive liquids [1, 43–45]. In nuclear power plants ion exchange materials have applications in:

- Primary coolant (water) purification,

- The treatment of primary effluents,
- The treatment of fuel storage pond water,
- Steam generator blow-down demineralization,
- Liquid waste and drainage water treatments,
- Boric acid purification for recycling,
- Condensate polishing (for nuclear power plants with boiling water reactors).

Most of the systems and operating methods described will work with many different types of ion exchanger. The selection of an appropriate ion exchange medium is best done using information provided by the media manufacturer together with trials on the actual liquid to be treated.

4.2. FACTORS OF IMPORTANCE IN THE SELECTION OF ION EXCHANGERS AND APPLICATION TECHNIQUES

4.2.1. Waste characteristics

Ion exchange is generally suited only for the treatment of aqueous liquids satisfying the following criteria:

- For use in columns with a downward flow of liquid the concentration of total suspended solids in the waste should be low, normally less than 4 mg/L, to prevent the solids filtered out by the bed of ion exchanger fouling the ion exchange media. Liquids with greater suspended solids loadings should be prefiltered first. Conventional particulate filters or filters pre-coated with powdered ion exchange media can be used to remove particulates and colloids. When columns are used in the upward flow mode the expansion of the bed of the ion exchanger allows fine particulate matter to pass through the bed, and hence a prefiltration of the waste stream may not be necessary.
- The waste should have a low total dissolved salts content, normally less than 1 to 2 g/L, to prevent the rapid exhaustion of the ion exchange capacity of conventional ion exchange resins by inactive ions, but when highly selective ion exchange materials are used the total dissolved salts can be up to several hundreds of grams per litre.
- Radionuclides should be present in a suitable ionic form. Adjustment of the solution pH is often sufficient to convert a radionuclide into a species that can be removed by ion exchange. However, the addition of pH adjustment chemicals will add to the total dissolved salts and may affect the amount of contaminant that can be taken up by the ion exchanger.

- Generally the waste should contain only very small amounts of organic contaminants. Some compounds, such as oils and greases, if present as a separate phase, will result in a severe fouling of the ion exchange media and a loss of ion exchange capacity. Others, such as certain organic solvents, may cause a physical decomposition of organic ion exchange media.
- Strong oxidizing compounds, such as nitrates, can cause a catalytic degradation of organic media when in the presence of some metallic ions. This can create a problem when treating the spent media, for example by drying with warm air, or during some conditioning processes, such as bituminization.

4.2.2. Selection of ion exchanger and treatment process

As described in Section 3, a wide range of ion exchange media is now available, from low cost naturally occurring organic (such as coal and peat) and inorganic (such as clay and natural zeolite) materials to expensive synthetic organics and inorganics engineered to remove specific ions. The chemistry of most ion exchange media has been extensively studied for the nuclear industry and for other applications.

The selection of an appropriate medium depends on the needs of the system. However, if there are large concentrations of chemically similar ions in the waste the process of selection becomes more difficult. If low cost general ion exchange media are used, large volumes may be required, leading to larger volumes of waste to treat and dispose of. Higher cost ion specific exchangers may be a better choice, especially when the extra cost of the media is more than offset by the reduction in the total cost for the treatment and subsequent storage and/or disposal of the spent media.

The ion exchange media must be compatible with the chemical nature of the waste (such as the pH and type of ionic species present), as well as the operating parameters, notably temperature and pressure. The limited operating temperature range of most organic ion exchangers requires some liquid streams, such as reactor coolant circuits, to be depressurized and cooled substantially prior to treatment.

In some applications the chemical form of the ion exchange media is important; for example, in CANDU and other heavy water reactors the ion exchange media must be deuterated prior to being placed into heavy water service. This is done by introducing a controlled flow of heavy water into the media to replace the light water. If the light water was not replaced it would cause an undesirable isotopic downgrading of the reactor heavy water systems. Another example is the use of a Li^+ form of the ion exchange media, instead of the hydrogen ion form, as a pH control mechanism.

The total radioactivity content of the waste should be considered in the selection of the ion exchange process to be used. Concentration of the radioactivity on to the ion exchanger can greatly increase (by many orders of magnitude) the radiation fields surrounding the ion exchange vessels compared with those surrounding the original liquid. Radiation levels can also affect the stability of the ion

exchange media. Media stability is of most concern for long term storage and/or disposal

4.2.3. Cost considerations

Before selecting a particular ion exchange treatment process, a complete economic evaluation should be conducted. The principal cost components to be considered are:

- The capital costs,
- The initial cost of the ion exchange media,
- The operating costs,
- The costs associated with the treatment and disposal of the spent ion exchanger.

In addition, in the event of a new ion exchange system being installed, the reduced costs that result from the use of smaller process systems should be taken into account when highly selective materials are used in small columns.

The total cost of operating a process is the sum of the above costs. The total cost of constructing a plant will depend on the desired treatment rate and decontamination factor, which will govern the size of the equipment and the number of treatment stages. It should be noted that cost alone is not always the most important factor in the selection process, and more expensive options may be selected to meet other technical requirements, such as the availability of materials, compatibility with existing equipment or conformity to national practices.

In some cases the total costs can be reduced by a regeneration of the spent media instead of using a once through process. However, it should be noted that the regeneration process may produce a liquid waste that has higher treatment and disposal costs than the costs saved by a reuse of the media. To be economically viable the volume of such liquids must be substantially smaller than the volume of the original liquid treated by ion exchange. Ideally, the secondary liquids should be treated by existing on-site liquid radioactive waste treatment systems. If new facilities are required, the cost of providing such facilities must be weighed against the cost of not using regeneration (i.e. a higher consumption of ion exchange media). Regeneration options are described in more detail in Section 4.4.

4.3. ION EXCHANGE APPLICATION TECHNIQUES

Ion exchange processes can be implemented in a variety of ways, including in batches, in columns, in continuous loops and, as part of, or in combination with, membrane processes. Each technique has features that make it more or less suitable

for specific applications. The advantages and disadvantages of each method are summarized in Table VII and are described in detail in the following sections.

4.3.1. Batch operation

Batch operation is the simplest method for operating an ion exchange process. It can be used with either organic or inorganic media, does not require sophisticated equipment and can be carried out on any scale at ambient temperatures and pressures. However, it is generally only used for small scale applications for occasional or custom treatments (for up to several hundred litres of liquid).

TABLE VII. SUMMARY OF THE ADVANTAGES AND DISADVANTAGES OF VARIOUS ION EXCHANGE TECHNIQUES

| Technique | Advantages | Disadvantages |
|--------------------|---|---|
| Batch operation | <ul style="list-style-type: none"> Simple to construct and operate Good for small scale applications A wide variety of ion exchange media can be used Easily customized for specific treatment problems Does not need granular materials | <ul style="list-style-type: none"> Manual operation may be cumbersome to operate with large volumes of waste The separation of liquid and ion exchange media is required Can only be operated at atmospheric pressures and ambient temperatures Once through use only |
| Column operation | <ul style="list-style-type: none"> Good throughput Simple to operate A wide variety of media are available Can be operated at elevated temperatures and pressures High decontamination factors are possible | <ul style="list-style-type: none"> Large equipment can be costly The regeneration of media may require extra equipment There are difficulties in transporting some inorganic ion exchangers through pipelines Prefiltration is necessary |
| Membrane operation | <ul style="list-style-type: none"> Can be used either as a waste treatment or fluid concentration technique Prefiltration is not necessary Does not need granular materials High decontamination factors are possible | <ul style="list-style-type: none"> Equipment can be costly to construct and operate on a large scale |

A measured quantity of the ion exchange medium is mixed with the liquid waste in a suitable container. The amount of media required and the rate of exchange can be determined by laboratory tests or by calculation using the following equation:

$$K_d = (DF - 1) \times V/m$$

where

- K_d is the measured distribution coefficient,
- DF is the required decontamination factor,
- V is the volume of liquid to be purified,
- m is the amount of the ion exchange medium needed to reach the required decontamination factor.

The mixture is allowed to equilibrate for a specified time either with or without stirring. At the end of the reaction time the ion exchange medium is removed from the liquid using conventional separation techniques such as decantation, filtration or centrifugation. The treatment can be repeated as required by adding further ion exchange media.

Either powdered or bead type media can be used in batch processing. Bead media are easier to remove by filtration, but powdered media provide a larger surface area for contact between the liquid and the media, resulting in faster sorption kinetics and therefore shorter reaction times.

An example for which the batch operation of inorganic ion exchangers assists in the decontamination of liquid waste is the EARP in the UK, which is used to treat

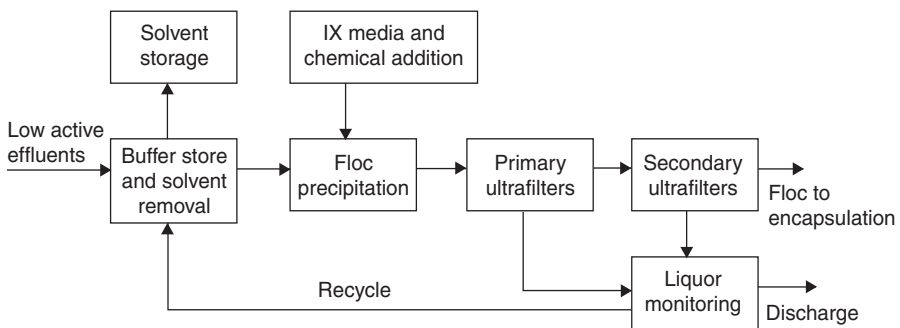


FIG. 2. Low active effluent treatment at the EARP, Sellafield, UK.

both low and intermediate level radioactive waste streams. A schematic diagram of the process is shown in Fig. 2. The EARP is one of the facilities serving the reprocessing of fuel at BNFL's Sellafield site [5].

This system is designed to handle in excess of 60 000 m³/a of liquid effluents containing a total of about 2 TBq of alpha activity. Development work demonstrated that it is possible to improve beta activity removal, particularly in the case of concentrates, by the addition of small amounts of specific inorganic ion exchangers.

4.3.2. Column operation

The most common uses of ion exchange media are as packed beds in vessels or columns. The ion exchange medium is contained inside a steel pressure vessel, with an engineered inlet, outlet and flow distribution system to allow liquid to percolate through the bed of the medium at a specified flow rate. Retention screens on the inlet and outlet prevent the medium from escaping into the process loop. A secondary circuit with unscreened drain and fill lines is used to remove the spent medium and fill the vessel with a new medium. Columns are generally used with bead type ion exchange media and can be constructed in a wide variety of sizes and materials to meet the requirements of the system. The low porosity of beds of powdered media restrict their use to thin layers, usually as a 'pre-coat' on a filter medium.

Typical operating conditions for ion exchange columns are summarized in Table VIII.

TABLE VIII. SUMMARY OF OPERATING CONDITIONS FOR ION EXCHANGE COLUMNS

| | Inorganic media | Organic bead resin | Organic powdered resin |
|------------------------------|--|--------------------|------------------------|
| Particle size | 0.25–3 mm | 0.5–2 mm | 5–150 µm |
| Particle density | 0.5–1.8 kg/L | 0.6–0.8 kg/L | 1.1–1.2 kg/L |
| Water content after draining | 40–80% | 40–60% | 50–80% |
| Type of ion exchange | Anion or cation | Anion or cation | Anion or cation |
| pH | 1–13 | 1–14 | 1–14 |
| Decontamination factor | 100–1000, in special cases up to 1 000 000 | 10–1000 | 10–1000 |

Column operation is most frequently employed in the cleanup of nuclear power plant primary coolants and auxiliary systems (e.g. fuel pond water) and in liquid radioactive waste treatments. Descriptions of typical systems can be found in Refs [1, 43–45].

Column systems can be configured for single bed operation systems (with separate columns for cation and anion exchange) or mixed bed systems, in which cation and anion media are mixed together in a given ratio (usually equal portions). Mixed bed systems are generally favoured as they require less equipment and provide for a simpler operation.

Column operation is usually a semicontinuous process. When the medium in the column becomes spent the column is removed from service and replaced with a fresh medium. In column operation, determination of the medium being spent is usually based on ionic breakthrough, which is the point at which the exit concentration of the ionic species being removed starts to increase sharply to some predetermined level. However, other criteria, such as the radiation field, may also be considered, as described in Section 4.2.2.

If interruptions in the process to replace ion exchange media are not desirable, multiple columns can be connected in parallel. While one set is in operation the other is filled with a fresh medium or, after refilling, is on standby. The frequency of such changeovers is governed by the capacity of the medium relative to the ionic strength and flow rate of the liquid being treated. The capacity of the system is frequently measured in bed volumes, which is the ratio of the volume of liquid treated to the volume of the bed of the exchanger.

An example of the column operation of an ion exchanger is provided by BNFL's Sellafield SIXEP production plant, which reprocesses spent fuel. The SIXEP plant commenced operation in May 1985 and has made a major contribution to the reduction of radioactivity discharged from the site. The plant is described in full in Refs [46–48]. A simplified process flow diagram is shown in Fig. 3.

The main processes in the plant at Sellafield include:

- The removal of suspended solids in the feed by sand filtration;
- pH adjustment from pH11.5 down to pH8.1 using carbon dioxide;
- The absorption of caesium and strontium by ion exchange;
- The interim storage of sludges from filter backwashes, etc., and spent ion exchangers.

In order to minimize the volume of spent ion exchanger arisings, work was done to optimize a system of column reversal such that each charge of material is used first in the trail position followed by use in the lead column. It has been demonstrated that a few per cent of spent ion exchanger remaining in a column after transfer has a marked effect on the decontamination factor obtained from the next charge of ion exchanger in that vessel.

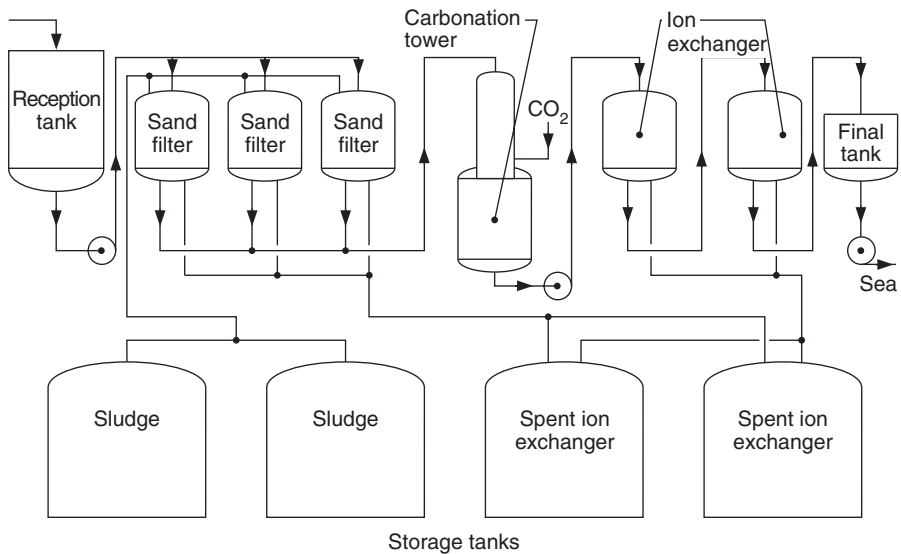


FIG. 3. Simplified process diagram for SIXEP, Sellafield, UK.

The ion exchanger is discharged hydraulically from the columns when it reaches the end of its useful life and is stored in a 1000 m³ tank similar to those used for sludge. Trials with the ion exchange material (naturally occurring clinoptilolite) have shown that it can be satisfactorily encapsulated into a high strength concrete.

An example of a multicolumn ion exchange waste treatment system is shown in Fig. 4. This system, installed at the waste management plant in Kakrapar, India [49], for the treatment of low active liquid waste, has two parallel processing trains rated at 9 to 10 m³/h, each with a particulate filter, followed by a cation exchanger (a synthetic organic strong acid), an anion exchanger (a synthetic organic strong base) and a final mixed bed. The ion exchange vessels are constructed of nitrile rubber lined mild steel, approximately 0.75 m diameter × 1 m high, holding 250 L to 300 L of ion exchange resin.

The plant also incorporates an external regeneration system, with separate vessels for anion and cation regeneration, and a separation vessel for the mixed bed medium. Cation resins are regenerated with 4% HNO_3 and anion resins with 4% NaOH . Spent resins from the system are conditioned in an adjoining polymer fixation facility.

Figure 5 shows an example of a pre-coat filter system. In this type of system a powdered ion exchange medium is applied as a thin coating over the filter elements. The

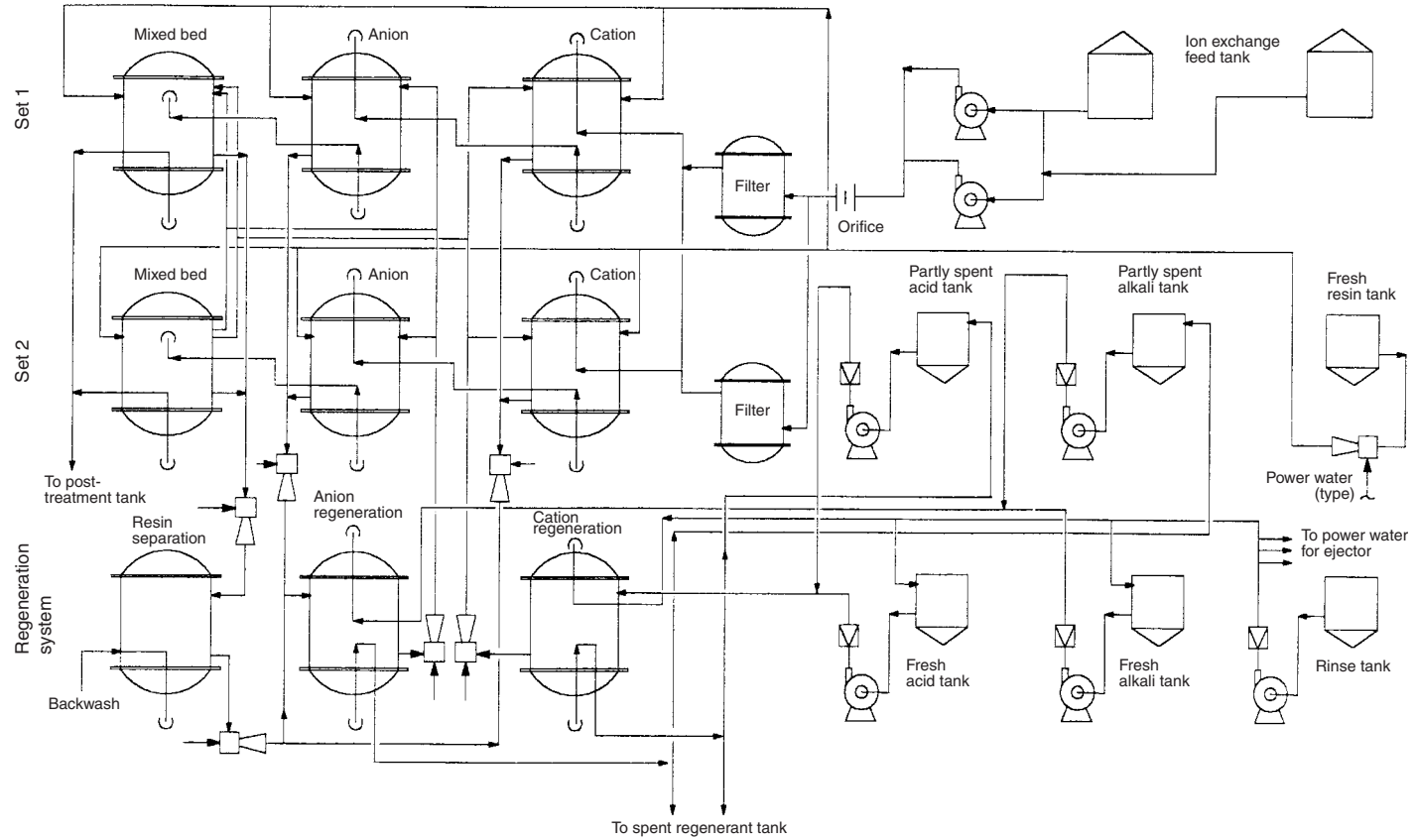


FIG. 4. Multicolumn ion exchange system at the waste management plant, Kakrapar, India.

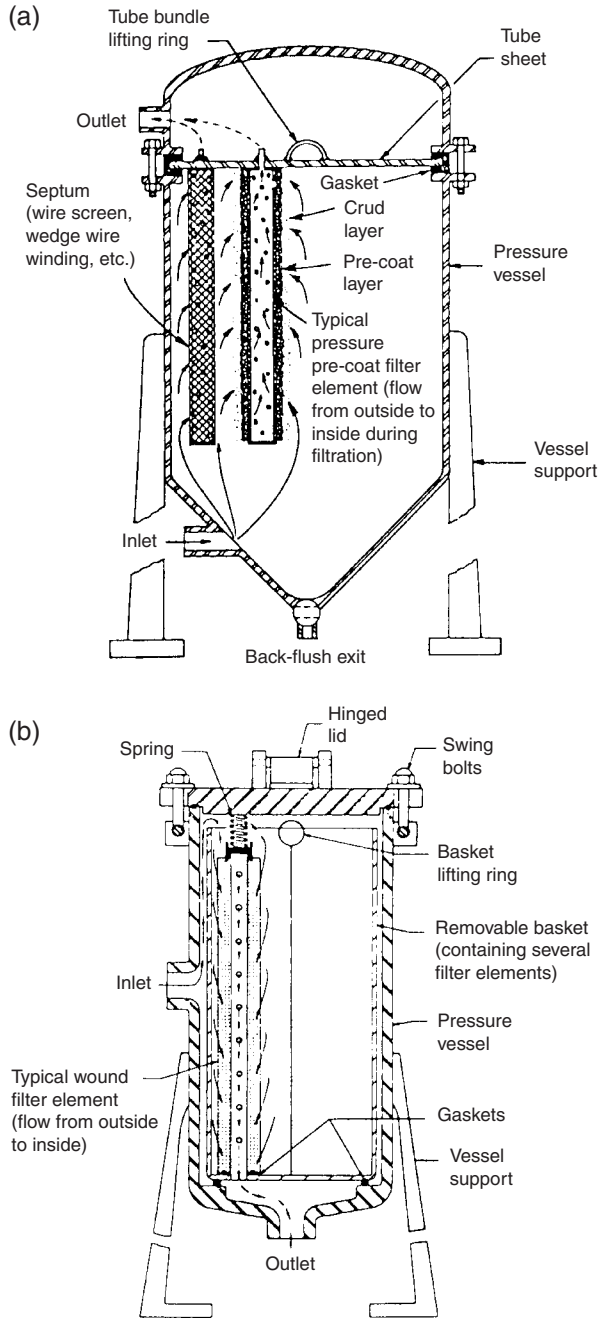


FIG. 5. Typical filters used for liquid waste treatment. (a) Tubular support pressure pre-coat filter; (b) disposable cartridge filter.

coating acts both as a particulate filter and an ion exchanger. When the ion exchange medium is spent the flow in the filter is reversed and the medium is flushed to a storage tank.

An example of the efficient use of selective ion exchange materials in small columns is shown in Fig. 6. This system, installed at the Japan Atomic Energy Research Institute, removes plutonium, caesium and strontium from a waste liquid containing more than 1M of nitric acid. Caesium and strontium are removed by the selective CsTreat and SrTreat media described earlier. Each column contains about 1 L of medium.

The use of ion exchange media in a typical demineralizer system at nuclear power plants in the USA shows that selective inorganic ion exchange media can be used in a normal demineralizer system in combination with conventional organic resins [50].

An alternative to parallel column operation is a continuous loop moving bed or pulsed bed system. These types of system are not currently in common use in the nuclear industry because they are more difficult to control and operate than conventional column designs. However, moving bed and pulsed bed systems can provide a more uniform liquid product and can have a lower media inventory than column systems. Since the media are constantly refreshed, the system does not suffer from breakthrough and the fluctuations in performance that can occur with packed bed systems. Moving bed and pulsed bed systems are also more tolerant to particulates in the liquid.

4.3.3. Membrane systems

Ion exchange membranes are used in a number of treatment processes. The management of waste from these ion exchange membrane processes is mostly concerned with the further treatment of the concentrated salt stream, which can be treated by chemical methods or by evaporation or can be immobilized directly. In some cases the concentrated stream may be the product of primary interest, such as for concentration or the purification of radioactively labelled pharmaceuticals that may be too delicate for conventional concentration techniques (e.g. distillation), or to separate or concentrate certain liquids prior to chemical and/or radiochemical analysis. The ion exchange membranes themselves are thin sheets of polymeric materials. When expired they can be treated as conventional low level solid waste and are suitable for incineration or compaction.

4.3.3.1. Electrodialysis

Electrodialysis is a combination of electrolysis and dialytic diffusion. The ion exchange membranes are used to form barriers between the cells or compartments

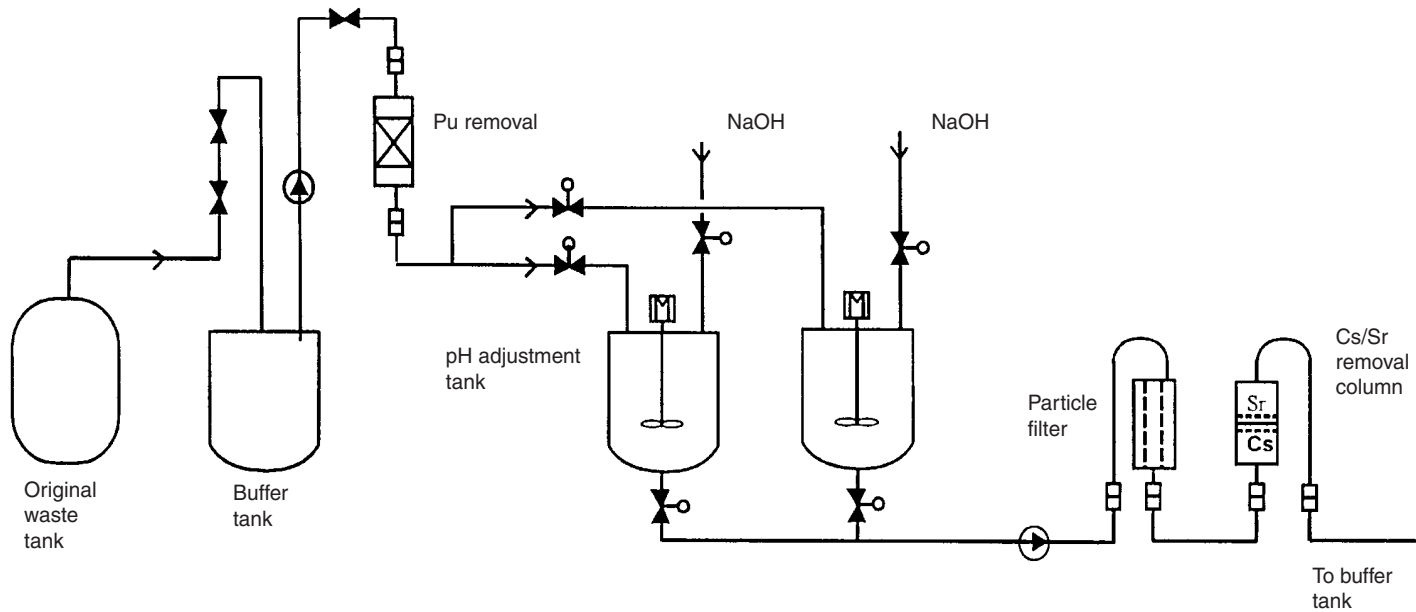


FIG. 6. Flow diagram of the liquid waste treatment system at the Japan Atomic Energy Research Institute utilizing CsTreat and SrTreat ion exchangers.

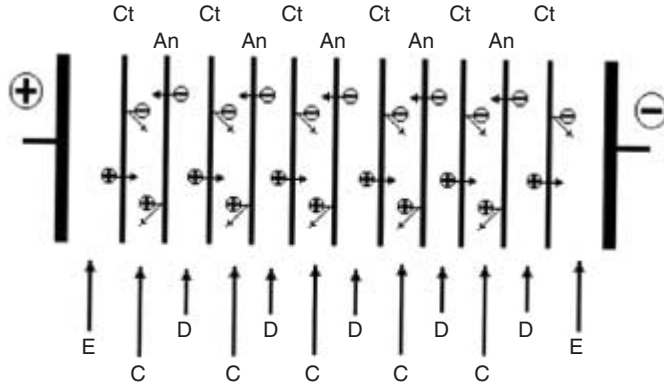


FIG. 7. Scheme of electrodialysis: – anions; + cations; D = dialysate; C = concentrate; E = electrode solution; Ct = cation exchange membrane; An = anion exchange membrane.

containing the electrolyte solutions (Fig. 7). By applying an electric potential across the cells ions can be forced to migrate towards an anode or cathode, depending on the polarity of the ionic charge. The passage towards the anode or cathode is blocked by an anion or cation membrane that allows only ions of the appropriate charge to pass through. A series of cells and membranes will affect the separation of the ionic species, leaving a clean liquid and a concentrated salt stream. Several countries have developed the process in laboratory and industrial scale applications [51–53]. A block diagram of an electrodialysis installation is presented in Fig. 8.

A pilot plant scale study for concentrating low level radioactive waste that employs ion exchange membranes is reported in Ref. [54]. The liquid radioactive waste is first subjected to electrodialysis for radioactive cations, which produces a volume reduction of about 10. The concentrated waste generated during electrodialysis is then used as a feed for an electrochemical ion concentrator to achieve a further volume reduction of 35 to 40, realizing an overall volume reduction factor of 350 to 400. The electrochemical concentrator has three chambers, of which the central chamber is filled with cation exchange resin and is separated from the adjacent cathode and anode chambers by cation exchange membranes.

4.3.3.2. Continuous electrodeionization

Continuous electrodeionization is a process that uses ion exchange resins in combination with membranes. The process is similar to electrodialysis and consists of one or more modules, each consisting of a cell pair, constructed to form a flow-through compartment. Each cell pair consists of a cation permeable membrane on one side and an anion permeable membrane on the other. An electrical charge is applied

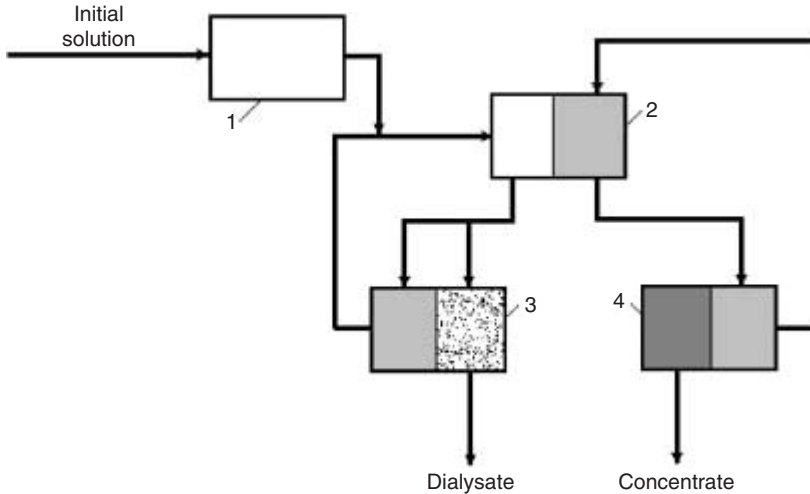


FIG. 8. Block scheme diagram of an electrodialysis installation for the treatment of liquid waste. 1 = preliminary water cleaning; 2 = first stage electrodialyser; 3 = second stage electrodialyser; 4 = electrodialyser concentrator.

across the membranes to drive the flow of ions. The main difference between continuous electrodeionization and electrodialysis is that the space between the membranes is filled with mixed cation and anion resins. The electric field has the added effect of maintaining the resins in a regenerated state, making chemical regeneration unnecessary.

Continuous electrodeionization is used mainly to produce ultra-high purity water and requires reverse osmosis quality feed with a total hardness of less than 1 ppm in order to minimize scaling. It has been tested in nuclear power plant operations to polish the permeate from a reverse osmosis system [55].

4.3.3.3. Electrochemical ion exchange

Electrochemical ion exchange is an advanced ion exchange process that combines the benefits of ion exchange to adsorb ionic species from solution with an electrical driving force that is used to enhance both the adsorption and elution reactions, depending on the direction of the current flow. Electrochemical ion exchange is a separation process that can be considered as a cross between electrodialysis and conventional ion exchange. Unlike the latter, regenerant chemicals are not usually required, which permits a greater waste treatment volume reduction factor. The electrical driving force also allows a high utilization of the ion exchange capacity [56].

In its initial form the electrochemical ion exchange electrode was made by coating a thick layer of ion exchange resin on to a mesh electrode, using a suitable elastomeric binder. The ion exchanger can be organic or inorganic. Both cation and anion exchangers can be used, depending on the ions to be removed. Combined systems, with both cation and anion electrochemical ion exchange electrodes, have also been operated successfully.

This system has been used for the treatment of two waste types as part of a pilot scale European Community co-funded demonstration programme [57]. The first demonstration treated primary coolant from a pressurized water reactor at Doel in Belgium, while the second treated liquid effluent from the United Kingdom Atomic Energy Authority site at Harwell [58].

The overall performance using a three stage process with a pressurized water reactor coolant is as follows:

- The activity is reduced from 52 Bq/mL to <0.7 Bq/mL,
- The chlorine and SO₄ content is reduced from 36 ppm to <0.5 ppm,
- Boron is reduced from 860 to 1800 ppm to <23 ppm,
- The concentration of boric acid is 6500 to 9000 ppm,
- The power consumption for the process is 14 kW·h/m³,
- The liquid waste volume reduction could be >1600.

The Harwell site plant operated for 15 months at 350 L/h and exceeded its objective to reduce caesium/cobalt activity to <0.25 Bq/mL.

More recently, AEA Technology (UK) has developed commercial plants for a range of nuclear and industrial applications based on the same principles and used in combination with high surface ion exchange media constrained between ion exchange membranes. Owing to the higher flow rates and current densities that can be passed in this configuration, reductions in cell sizes and capital costs of a factor of 14 now make this process economically viable.

4.4. ION EXCHANGER REGENERATION OPTIONS

In theory, the ion exchange process is reversible. Most ion exchange media can be regenerated by using an appropriate strong acid (such as HNO₃) for cation media or alkali (such as NaOH) for anion media to replace the bound contaminant ions on the medium and restore it to its original chemical form. Media life can be extended by regeneration, which saves on the costs of the new medium and the disposal of the old. It should be noted that the medium is typically not completely regenerated, with restoration rates of up to 90% being typical. Even with optimal regeneration, therefore, the life of the medium is limited, and it will eventually need to be replaced.

The fact that regeneration is not complete is an important factor for nuclear grade ion exchangers, because nuclear grade quality is maintained only until the first regeneration.

Regeneration is normally done in separate cation and anion vessels. Mixed bed systems usually require a hydraulic separation of the cation and anion beads, as if the acidic and caustic regeneration media were introduced into the combined mixed bed they would neutralize each other before regenerating the ion exchange media. Owing to slight differences in the densities of the cation and anion media, hydraulic separation can be carried out in situ by a gentle backwashing of the bed. The media can then be physically separated into different vessels, or the primary vessel can be designed with the injection point for the regeneration chemicals at the anion to cation media interface, with one regeneration solution flowing upward through the top bed and the second flowing downward through the lower bed. After regeneration, the media are then remixed.

In many countries regeneration is not practised for radioactive systems since the concentrated acid and caustic regeneration solutions are often difficult and costly to treat and produce no benefits over a lower media usage. In addition, the process system itself is complicated and requires additional valving, piping, pumps and tanks to handle the regeneration chemicals. It is therefore generally more cost effective to use the media on a once through basis. However, in situations in which replacing the spent media is more expensive than the treatment and disposal costs, regenerating spent media remains a desirable practice. Regeneration of non-radioactive water treatment systems (such as for secondary side boiler feed water or plant demineralized water), in which much larger volumes of media are typically used to treat high flows of water, is also practised in some nuclear power plants.

4.5. HANDLING SPENT ION EXCHANGE MEDIA

The use of ion exchange media for the treatment of radioactive liquids concentrates the radioactivity on to the ion exchange media. The ion exchange vessels, handling equipment and subsequent treatment equipment will therefore probably require shielding in order to protect the operating personnel from radiation; this is generally done by enclosing the equipment in restricted access rooms and/or behind concrete or lead block shielding walls.

Transferring the spent media from the liquid treatment system ion exchange vessels to the spent media treatment and conditioning system is generally done hydraulically. In order to ease the transfer, the media are preferably kept in a flooded condition to prevent the media clumping, as this can lead to the transfer piping clogging. The transfer piping should be designed with a sufficient diameter (generally greater than 4 cm) to prevent clogging, and with a minimum number of bends and

valves. Where bends are unavoidable, they should have a long radius (the radius of the bend should be at least five times the pipe diameter). Valving should have a full port opening, such as a ball valve, again to minimize clogging. If the spent media are highly radioactive, remote cleanout ports (such as high pressure water injection points) should be provided at the locations where clogging is likely to occur, such as at bends in the piping.

Once the ion exchange media are in the spent media treatment or conditioning system, a further transfer to different parts of the system can be carried out either hydraulically, pneumatically or mechanically, depending on the details of the system. Collection tanks are often provided to allow a sufficient volume of media to collect prior to treatment. These tanks generally are shielded behind concrete walls to shield operators, and include mixing or sparging capabilities to ensure that the spent media do not clump. Several collection tanks may be required in a single facility if different types of media are used. The segregation of similar media from different process systems can also be advantageous in many cases; for example, if certain radionuclides, such as ^{14}C , are present on some waste media but not on others, keeping them separated may result in economic savings during subsequent treatments if the different streams are to be subjected to different levels of attention.

In heavy water systems, such as the CANDU PHWR, residual heavy water is also recovered from the media, prior to going into bulk storage, by a 'de-deuteration' process using a controlled flow of light water to displace the heavy water. This is done for two reasons: (a) economic (to recover the valuable heavy water) and (b) to reduce the tritium inventory (associated with the heavy water) of the spent media.

In some cases, such as with smaller systems, it may be more economical to use a disposable ion exchange vessel rather than providing a hydraulic transfer system. After removal, the disposable vessel is generally dewatered and/or conditioned by encapsulation with a suitable material in a package prior to storage and/or disposal. Remote handling facilities and techniques may be required for the removal and packaging of the disposable vessel if radiation fields are high.

The transportation of spent ion exchange media (e.g. from a reactor site to a waste management facility) requires special shielded transportation packaging, generally designed to IAEA Type A or B specifications, and is subject to national regulations. Remote handling equipment is generally required for loading and unloading the transportation packages. Depending on national practice, various pretreatments, such as dewatering or drying, or the use of special containers, may be required for shipping this type of waste.

If regeneration of the ion exchange media is practised, secondary waste of high acidity or alkalinity may be produced. Regeneration should only be considered if facilities are available, or can be made available, to treat the secondary waste. The volumes of other normal operating and maintenance secondary waste, such as dry active waste, are generally small with ion exchange systems.

Ion exchange media may sometimes be removed from service prior to being chemically spent. This is generally done to limit the radionuclide inventory on the spent media (e.g. to prevent the waste from being classified as a higher category for disposal or to limit the radiation fields). However, this practice will increase the total volume of spent media to be handled.

4.6. INTEGRATION WITH OTHER WASTE TREATMENT SYSTEMS

Ion exchange is frequently employed in combination with other liquid treatment processes, usually as a final or polishing step; for example, conventional filtration can be used to remove particulate crud, and the filtrate then treated by ion exchange. The total dissolved solids may be reduced by chemical precipitation and the clarified liquid can then be polished by ion exchange.

Ion exchange can also be used as a final step in an evaporation process to remove any radioactivity carried over into the distillate. This is especially true for higher temperature processes, such as treating condensates from vitrification or bituminization processes. The permeate from membrane systems such as reverse osmosis can also be polished by ion exchange. Reverse osmosis permeate is generally very low in total dissolved salts, so the ion exchange media will have a long life. Note, however, that none of the above mentioned processes will remove tritium from aqueous streams.

An example of a typical process system using ion exchange in combination with other techniques is shown in Fig. 9. This system, installed at the Bruce A nuclear power plant in Ontario, Canada, incorporates a combination of filtration, ion exchange, bituminization, ultrafiltration and reverse osmosis for the treatment of radioactive liquid waste. The operation of the system is very flexible, since different portions of the system can be used separately, or in series, depending on the needs of the waste being treated.

5. MANAGEMENT OF SPENT ION EXCHANGE MATERIALS

5.1. INTRODUCTION

Spent ion exchange materials represent a special type of radioactive waste and pose unique problems in the selection of their treatment options. Because of the function that they fulfil, spent ion exchange materials often contain high concentrations of radioactivity and pose special handling and treatment problems. In

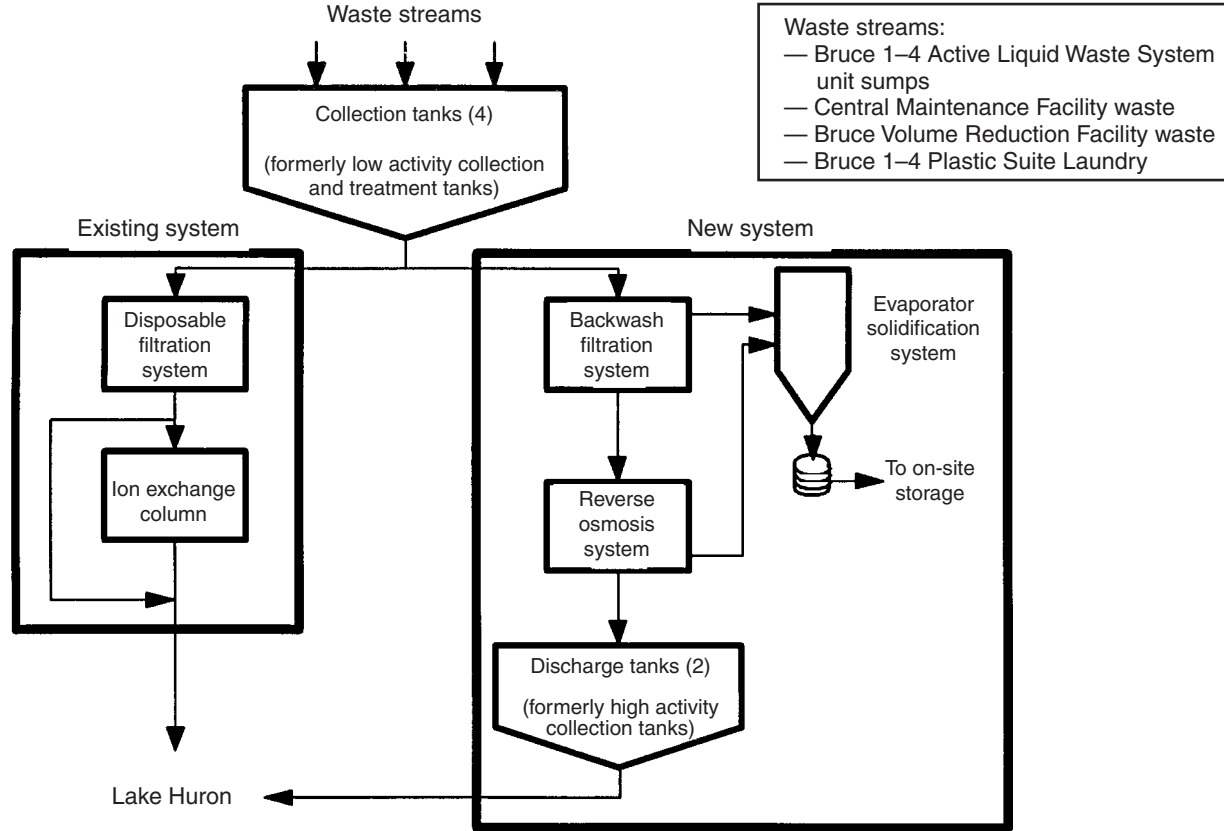


FIG. 9. Liquid waste treatment system at the Bruce A nuclear power plant, Ontario, Canada.

the past these materials were often disposed of in drums or boxes or as disposable ion exchange columns without treatment. In some operations the resins were sluiced from columns and stored in underground tanks as a bed settled in water, pending future treatment, conditioning and disposal.

With the evolution of performance based disposal facility acceptance criteria, it is now required that spent ion exchange materials meet specific quality requirements prior to disposal. Where final disposal facilities exist, waste acceptance criteria define the quality of waste forms for disposal, and therefore will sometimes define appropriate treatment options; for example, disposal facilities normally define acceptable levels of free liquids and requirements for waste form stability as part of their waste acceptance criteria. These waste acceptance criteria will determine if spent ion exchange materials must be dewatered, stabilized or treated in some other manner prior to disposal. In countries in which no final disposal facilities exist, these materials are often stored pending the identification and/or development of an appropriate treatment, while awaiting the development of a disposal capability or until the decay of the short lived radionuclides contained in the ion exchange material is completed.

The selection of treatment options for spent ion exchange materials must consider their physical and chemical characteristics. Basically, there are two main methods for the treatment of spent organic ion exchange materials: (1) the destruction of the organic compounds to produce an inorganic intermediate product that may or may not be further conditioned for storage and/or disposal and (2) direct immobilization, producing a stable end product. Organic resins can be degraded by radiation and by biological action to produce products that are unacceptable to waste repositories. Inorganic ion exchange materials are generally resistant to degradation by radiation or biological actions and are therefore generally treated by the use of direct immobilization or by high temperature processes such as vitrification or plasma incineration. Direct immobilization techniques are discussed in Section 6.

5.2. STORAGE

5.2.1. Storage for decay

Spent ion exchange materials may require interim storage to allow for radioactive decay if the activity levels in the materials exceed the treatment facility acceptance criteria or if the activity levels in the materials will decay sufficiently in a reasonable time to allow the disposal of the materials without further treatment. Storage for decay should only be used on an interim basis when the radionuclides of concern have a short half-life. Most ion exchange materials produced in nuclear power plants contain radionuclides with sufficiently long half-lives (e.g. ^{60}Co) to preclude this option. However, in irradiated fuel reprocessing a number of fission

products have half-lives of a year or less (e.g. ^{106}Ru) and hence storage for a few years can be of benefit.

5.2.2. Storage pending final treatment and/or disposal

Spent ion exchange materials may require storage pending a decision regarding their final treatment, conditioning or disposal. Such storage must consider the role of the materials and container integrity, gas generation (both organic and radiolytic) and material and/or container retrievability.

Spent ion exchange materials are currently considered to be in retrievable storage if their treatment or disposal is deferred. Prior to their placement in storage they can be dewatered or dried to reduce the generation of radiolytic gas, to obtain some volume reduction and to improve long term container performance. If drying is employed before storage, aspects such as swelling by the reabsorption of water must be considered.

In the case of wet storage, provisions are required to facilitate the retrieval of the stored waste at a future date and also to ensure that bed compaction does not take place. This latter concern is generally addressed by hydraulically or pneumatically sparging it or by agitating the resin bed to loosen it on a planned, regularly scheduled basis. Failure to agitate the resin bed regularly may result in a compaction of the resins, which can cause difficulties in removing them at a later date.

5.3. PRETREATMENT

Pretreatment is defined as any processing that precedes the primary treatment or conditioning of the waste for the purposes of:

- The conversion of waste materials into a form required by the subsequent treatment or conditioning step;
- The improvement of the effectiveness or economics of the subsequent treatment or conditioning step; or
- The enhancement of safety, especially in the case of waste placed in extended storage prior to its final treatment.

The selection of a waste pretreatment option is an integral part of the overall waste management system design. The screening and evaluation of pretreatment technologies for application to different treatment methods is described in Ref. [59]. From a technical point of view the same technique may be applied as a treatment or a pretreatment step, depending on the purpose of the process and its sequence in the

overall waste management scheme. Screening and the evaluation of pretreatment technologies for application to different treatment methods is described in Ref. [60].

Available pretreatment processes include but are not necessarily limited to:

- Dewatering (organic and inorganic ion exchangers),
- Drying and heating (organic ion exchangers),
- Crushing and grinding (organic and inorganic ion exchangers),
- Foam preparation (organic ion exchangers),
- Decontamination by activity stripping (organic ion exchangers).

These processes are discussed in the following sections.

5.3.1. Dewatering

In most conditioning processes, such as polymer encapsulation, cementation and bituminization, dewatering the spent ion exchange materials prior to immobilization improves the overall volume reduction while also improving the compatibility of the waste with the immobilization process. Dewatering is generally accomplished by pressure, a vacuum filtration application or centrifugation. The residual water content can be reduced by up to 50%, depending upon the efficiency of the system employed. Centrifugation involves the application of high speed machinery, with significant maintenance requirements. In-drum vacuum dewatering using a vacuum spool pump is now being employed in cases in which small batches of resins are collected in the final conditioning and/or disposal vessels, usually standard drums. Sieving and filtration have also been used for dewatering spent ion exchange materials.

With inorganic ion exchangers, dewatering prior to immobilization is carried out to reduce the water content to that required for encapsulation in the immobilization matrix. At BNFL's EARP a second stage of membrane filtration is used to dewater the concentrate from the primary separation stage to provide a more concentrated sludge that can be directly encapsulated in cement [5].

A technique for the chemical dewatering and surface conditioning of resins using reagents such as methanol has been developed, but owing to the drawbacks of the generation of organic waste it is not widely employed.

5.3.2. Drying and heating

For dry storage or for some conditioning processes a complete dewatering step, or drying, is sometimes required. Steam as an indirect heating medium or air as a direct heating medium are generally used. In the case of air drying, hot air is used as a medium for drying a shallow bed of spent materials. Different types of drying units

in use for drying spent ion exchange materials include fluidized bed dryers, vertical thin film dryers and cone dryers [61, 62].

Spent ion exchange materials may require heating as a pretreatment step in order to prepare them for a final treatment and conditioning. Heating the resins to drive off trimethylamines prior to immobilization significantly reduces the swelling of the resins upon contact with water; for example, in the case of spent organic anionic exchange resins they are first dewatered and then slowly heated in vessels equipped with a mixer to prevent the resin from forming deposits on the heated walls. The resins are dried at low temperatures, about 150°C, and the trimethylamines are separated from the anionic loaded resins. The heated resins can then be stabilized using bitumen or cement. The advantage of the process is especially significant when cementation is the immobilization method selected, because resin loading of the cement matrix can be substantially increased.

In mixed cation–anion resin beds, however, the trimethylamines are not vented to the off-gas treatment system but are usually retained on the cation resins. As a result, the swelling of the resins during cementation is not reduced (at pH values of about 11), but the compressive strength of the hardened cement product is significantly reduced. The reaction rate of the trimethylamines with the cation resins can be reduced by preloading the resins with alkali before heating.

In general, heating resins as a pretreatment step is only economical when there are high material throughput rates.

Composite ion exchangers consisting entirely of inorganic materials or those with a high inorganic content can also be dried prior to immobilization. Some of these dried exchangers are already being stored pending decisions on repository sites.

5.3.3. Crushing and grinding

As pretreatment processes, crushing and grinding techniques are used for size reduction and also to release interstitial water in spent ion exchange materials. They have been applied mainly prior to destruction (e.g. by thermal treatment, wet oxidation, biodegradation) or immobilization (e.g. by bituminization and cementation). The smaller particle size and the destruction of the matrix backbone improves drying, results in a more homogeneous waste for immobilization, allows the easier removal of non-specific materials and facilitates the further destruction of the resins by thermal, chemical or biological methods.

Spent ion exchange resins may also be crushed or ground at low temperatures (–150°C to –190°C), which is known as cryogenic crushing or grinding. Investigations of cryogenic grinding are reported in Ref. [63].

Experience with grinding spent resins has been gained in Sweden at the Barsebäck and Forsmark nuclear power plants and in Studsvik at the radiation waste centre, where grinding is used as a pretreatment step prior to bituminization or

pyrolysis. Additional experience has been gained in Austria (in Seibersdorf) and Germany (in Jülich), where grinding is used in combination with drying prior to the incineration of spent resins.

5.3.4. Foam preparation

Foam preparation as a pretreatment step was developed in France to facilitate the transfer and feeding of spent ion exchange materials to final treatment processes such as pyrolysis, incineration or vitrification. The process provides an alternative to transporting finely divided solids such as spent ion exchange materials by the pneumatic slurry method. In this approach, pulverized solid particles are dispersed within an aqueous foam, thus leading to the formation of a three phase mixture (solid–liquid–gas). The foam is generated by the utilization of conventional foaming agents, and the gas phase is either air or an inert gas. The liquid phase may be water or an emulsion (e.g. oil–water). In this type of mixture the solid particles may have any kind of size distribution (<1500 µm) and the solids content may reach 75 to 80% by weight. The resulting mixture is compressible and can be easily pumped by conventional volumetric pumps.

5.3.5. Decontamination by activity stripping

Activity stripping is similar to the regeneration of ion exchange materials, except that the focus of the process is on preparing the materials for treatment or disposal rather than recycling. Activity stripping is the removal of radionuclides from spent ion exchange materials, usually organic ion exchange resins, for one or more of the following purposes:

- Stripping or eluting activity into an aqueous phase and transferring the activity on to an inorganic sorbent that can be easily immobilized;
- Stripping specific long lived radionuclides that are unacceptable for near surface disposal (e.g. ^{14}C); or
- Stripping volatile long lived radioisotopes as a pretreatment step, prior to thermal treatments (e.g. incineration or catalytic extraction).

5.3.5.1. The PILO process

In the PILO (pilot) process, which was developed in Sweden [64], the activity from organic exchange resins is eluted and passed through columns containing zeolite and titanates. The loaded inorganic sorbents are dried and sintered to form a ceramic material. The chemical durability of the product is comparable with that obtained by direct immobilization in bitumen. The process offers the advantage of a volume

reduction combined with a conditioned end product. The process, however, has not been applied at full scale.

5.3.5.2. *Stripping for ^{14}C removal*

Spent ion exchange resins may be loaded with ^{14}C , especially when used to treat waste from heavy water reactors. The ^{14}C is formed by the activation of ^{17}O in heavy water, and also by the activation of ^{14}N and ^{13}C , which are components of steel. The presence of this long lived radioisotope influences the strategy for the disposal of spent resins because most near surface disposal facilities have strict concentration limits for long lived radioisotopes. The removal of ^{14}C and its separate fixation therefore becomes a desirable feature. Two methods for ^{14}C removal from spent resins are under development: acid stripping and thermal stripping.

5.3.5.3. *Acid stripping*

Acid stripping is based on the removal of all exchanged ions on resins by treatment with acids. Research carried out so far has shown good efficiency for the removal of ^{14}C with HCl (more than 99.9% in bench scale tests), but the removal of other radionuclides from the resins is inevitable [65, 66]. The separation of ^{14}C from other radionuclides stripped by the acid must be investigated prior to the operational use of this methodology. If successful, the spent resins treated by acid stripping are almost completely depleted of radioactivity and can therefore easily be incinerated.

Acid stripping with HNO_3 and the recycling of the acid after the sorption of the radionuclides on glass frit is an alternative treatment that warrants consideration. A similar technology is applied for the treatment of high level radioactive waste and has the advantages of stripping ^{14}C and other radionuclides in one process, recovering the HNO_3 for recycling, and the sorption and immobilization of the radionuclides on the glass frit [65, 66].

5.3.5.4. *Thermal stripping*

Thermal stripping is based on the removal of carbon dioxide from resins by heating, and has the advantage of the preferential removal of ^{14}C while leaving other radionuclides on the resins. Carbon-14 stripped from the resins is immobilized as a carbonate of a much smaller volume for disposal, most likely in a deep geological repository. The remaining spent ion exchange resins that contain the bulk of the radionuclides require treatment (e.g. incineration or immobilization) prior to disposal. Immobilized ash or immobilized resins are suitable for shallow land disposal. If the efficiency of thermal stripping can be proved to be above 99.9%, further phases of this potential technology should be investigated.

Other processes for thermal stripping are described in Refs [67–69].

5.4. DESTRUCTIVE METHODS FOR SPENT RESIN TREATMENTS

Destructive methods for the treatment of spent ion exchange materials are intended to alter the chemical, radiological and/or physical characteristics of the spent ion exchange materials in preparation for their final disposal. These processes include thermal and non-thermal treatments, which are described in the following sections.

5.4.1. Thermal processes

5.4.1.1. Pyrolysis

Pyrolysis is a low temperature thermal process that operates over a temperature range of 500°C to 700°C. During pyrolysis the resins are degraded in an inert atmosphere and the long chain polymer resin material is disassociated into a solid residue (one third of the resin weight) and a gas–vapour fraction (two thirds of the resin weight). The advantages of pyrolysis are that there is:

- A significant volume reduction of the waste (e.g. a volume reduction factor of ten),
- A biologically and geochemically stable end product (a solid compacted pyrolysis residue),
- An almost total retention of non-volatile radioactivity in the pyrolysis residue (i.e. a retention factor of 10^6).

Pyrolysis experiments in Canada [70] and in Japan [71, 72] have demonstrated the potential of this process. In Germany a new conceptual approach has been developed and has been used by Studsvik in Sweden [62]. Based on this technology, the thermal organic reduction (THOR) process has been developed and patented by Studsvik, which utilizes pyrolysis–steam reforming technology [73]. The THOR process utilizes two fluid bed contactors to process a wide variety of solid and liquid waste. Figure 10 provides an overview flow diagram of the THOR process. Solid, dry, granular waste such as charcoal, graphite, etc., is metered into a pyrolyser by a solid feeder. Liquid and slurry waste such as ion exchange resins, sludges, oils, etc., is metered into a pyrolyser by a pump.

The pyrolysis–reforming THOR system comprises a pyrolysis contactor–pyrolyser (stage one), a reformer–contactor (stage two) and associated filters. The pyrolyser is designed to operate at up to 800°C. Organic components are destroyed at this stage; the resulting synthesis gas exits the pyrolyser and the residual

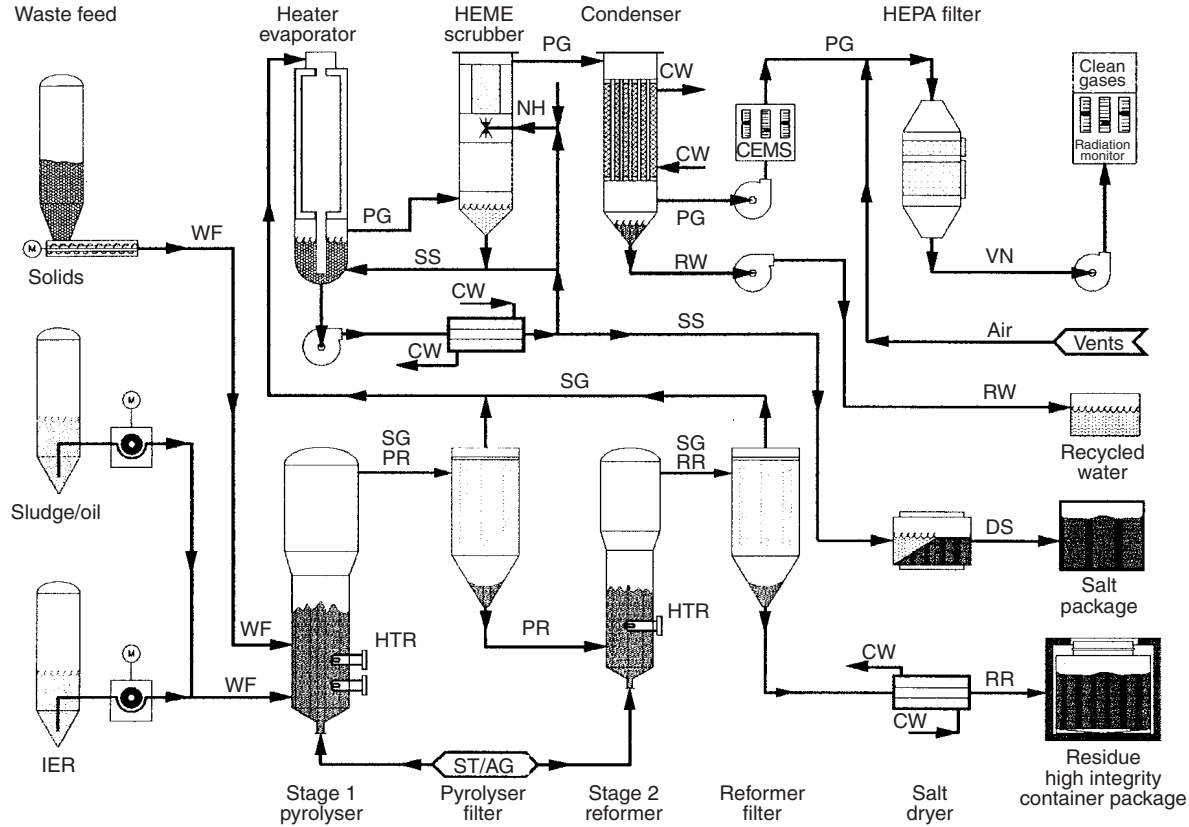


FIG. 10. THOR process flow diagram. DS = dry salts; WF = waste feed; RR = reformed residue; CW = cooling water; SS = salt solution; ST = steam; NH = sodium hydroxide; PG = process gas; AG = autothermal gas; SG = synthesis gas; VN = ventilation; PR = pyrolysed residue; RW = recycled water; IER = ion exchange resin.

solids, with most of the incoming radionuclides, are removed from the pyrolyser and collected in a ceramic filter vessel. These residues are transferred to the electrically heated, fluidized bed reformer, which is operated at 800°C. The reformed low carbon final residues are collected in the stage two ceramic filter and transferred into high integrity containers.

5.4.1.2. Incineration

Spent organic ion exchange materials may be incinerated in combination with other combustible waste or in an incinerator solely dedicated to that purpose [74]. The incineration of spent resins in an oxygen rich atmosphere results in the oxidation of the initial feed material and produces a volume reduction factor ranging from 30 to 100. The final volume reduction factor depends on the further treatment methods selected for conditioning the incineration residues.

Several commercial systems have been developed that are capable of incinerating resins in addition to shredded dry solid waste. These systems include rotary kiln and fluidized bed incinerators and an air suspension burning device. Incineration of radioactive waste in a two stage fluidized bed has been performed with success at the US DOE's Rocky Flats plant [75, 76]. In addition, solid low level waste has been incinerated at the US DOE's Waste Experimental Reduction Facility incinerator at the Idaho National Engineering and Environmental Laboratory (Fig. 11), USA, and the Consolidated Incinerator Facility at the Savannah River Site, USA (Fig. 12).

The Waste Experimental Reduction Facility incinerator and the Toxic Substances Control Act Incinerator in Oak Ridge, USA, have also been used to treat mixed low level radioactive and hazardous waste. The Consolidated Incinerator Facility and Toxic Substances Control Act Incinerator are both rotary kiln incinerators with secondary combustion chambers [77].

The incineration of resins in a single stage fluidized bed pilot plant has been performed at the Technical Research Centre in Finland [78]. In Japan a system with a controlled oxygen consumption has been used to incinerate ion exchange resins [79]. The incineration of 800 t of pretreated resins was carried out from 1991 to 1996 in the incineration facility of the Austrian Research Centers Seibersdorf [80]. A bench scale facility specially developed for resin incineration has been used at the German Research Centre in Jülich [81]. The treatment of ion exchange resins by catalytic incineration has also been studied in Japan [82]. The specific heat content of the spent ion exchange resins is in the range of 2 to 6 MJ/kg, depending on the water content. Because this range of specific heat is insufficient to allow the resins to self-burn, they are usually mixed with liquid fuel or other combustible waste in order to increase the efficiency of combustion.

Incinerators dedicated to the treatment of spent ion exchange resins tend to be more complicated than incinerators used for conventional waste because of the problems

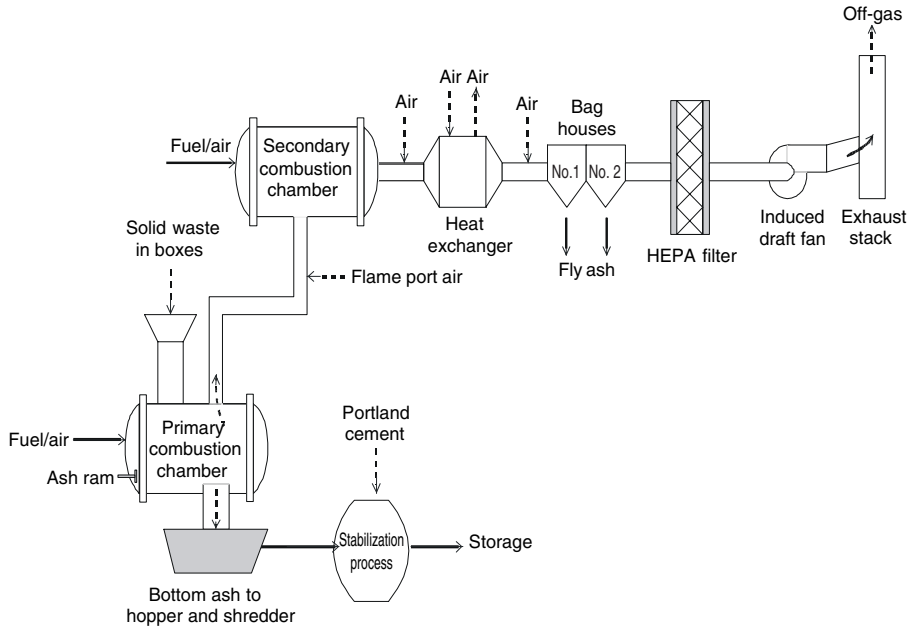


FIG. 11. Process flow diagram of the Waste Experimental Reduction Facility at the Idaho National Engineering and Environmental Laboratory, USA.

associated with resin combustion and off-gas treatments. When fed into an incinerator, resins have the tendency to form large clusters by melting before burning, thus causing problems with the incinerator refractory as well as problems related to incomplete combustion. Also, since ion exchange resins contain significant amounts of sulphur and nitrogen, incinerator off-gases are highly loaded with SO_2 and SO_3 and slightly with NO_x , thus requiring an efficient off-gas scrubbing system. Additionally, radionuclides such as caesium and ruthenium are volatile at temperatures above 800°C , further complicating off-gas treatments. Tritium and ^{14}C may also be present in the off-gas.

In most designs the resins, often mixed with combustible waste, are fed into the incinerator in a slurry form. In recent developments special pretreatment techniques have been applied prior to the incineration of the resins.

As an example, Fig. 13 gives a simplified process scheme of the incinerator at Seibersdorf. The incinerator is a shaft type unit originally constructed for feeding in batches from the top (at 40 kg/h). A modification for continuous powder feeding was later installed in the lower part of the unit. Depending on the effective calorific value (17 650–18 830 J/kg), about 70 kg/h of dried powdery resins (equivalent to about 140 kg of wet resins) can be blown into the combustion chamber. Without a secondary burner the incineration temperature ranges between 900°C and 1000°C .

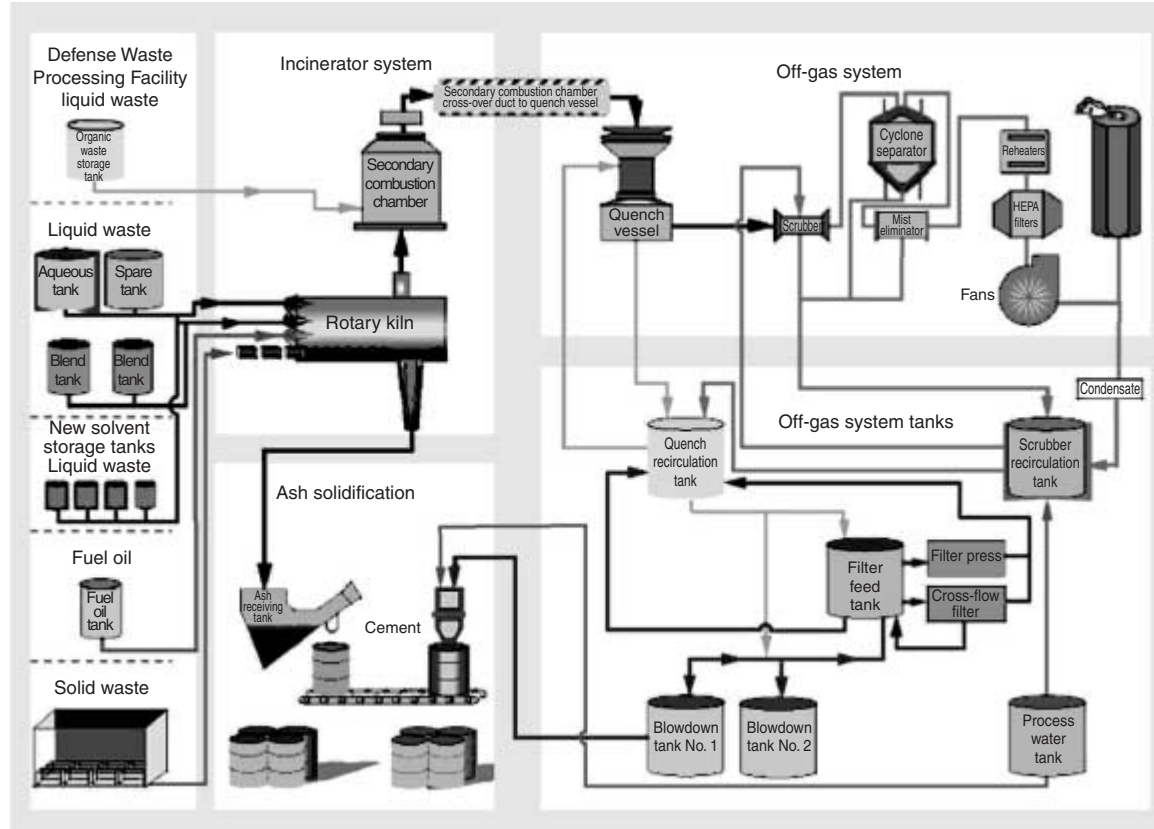


FIG. 12. Process flow diagram of the Consolidated Incinerator Facility at the Savannah River Site, USA.

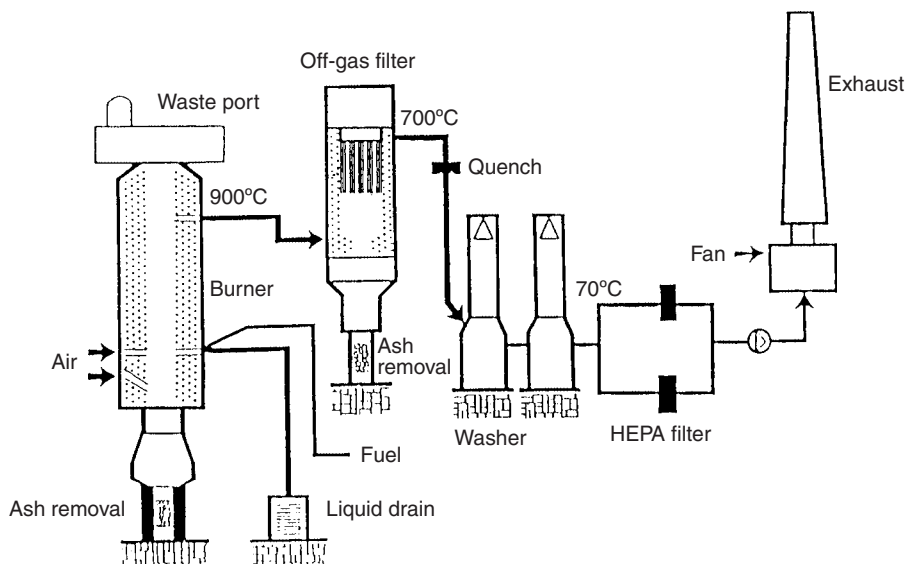


FIG. 13. A simplified process scheme of the incinerator at the Austrian Research Centers Seibersdorf.

Incinerating mixed bed ion exchange resins produces a large volume of acidic off-gases. Mixed bed resins contain about 19 g of sulphur and more than 8 g of nitrogen per litre of resins processed. The sulphur dioxide released by the burning waste is chemically captured by a sodium hydroxide solution. Experience indicates that at the second stage of the scrubber the use of H_2O_2 at pH8.2 results in the best reduction of SO_2 in the off-gas. NO_x emissions are effectively suppressed by maintaining combustion temperatures between 900°C and 1000°C at low gas flows; that is, maintaining low excess air at combustion. The residual ash from the incinerator is a free-flowing powder that is partially soluble in water and acids and must therefore be immobilized or packed in high integrity containers prior to disposal or long term storage. The amount and nature of the ash will strongly depend on the type and characteristics of the resins and other waste incinerated. In particular, fully loaded cation resins will form a large fraction of the ash. When the acidic off-gases are neutralized and the salts produced are added to the ash, an overall volume reduction of 30% and a weight reduction of 20% can be obtained.

Low active resins from the secondary reactor water circuits of Belgian nuclear power plants have been routinely incinerated in Belgoprocess's Evence Coppee Incinerator. Spent ion exchange resins are incinerated separately or in combination with other combustible waste. Before 1994 the resins were only drip dried and contained about 53 wt% of water, which considerably hindered combustion. Since 1994, however, resins are dried at the power stations as a pretreatment step, reducing the water content

to about 25 to 35 wt%. External firing and long residence times in the furnace are thus required to achieve weight losses of greater than 90%. The ash after cooling is discharged into 200 L collection drums that stand in a water bath. The ash drums are supercompacted, loaded into 400 L drums and encapsulated with a cement mortar for conditioning. The average volume reduction factor achieved with the supercompaction of ash drums is 1.77. The overall volume reduction factor obtained by the incineration of ion exchange resins followed by supercompaction and conditioning is at least 62. Between 1993 and 1996 a total of 167 500 kg of resins was incinerated.

Experience has shown that the incineration of spent ion exchange resins mixed with other waste is not ideal because combustion air is preferentially consumed by the other waste, and also because the resin beads become coated with large amounts of ash from the other waste. Much better results are obtained when the resins are incinerated separately. However, external firing is then required to maintain the temperature in the combustion chamber at 750°C. This is achieved by injecting a spray of contaminated oil or fuel oil into the combustion chamber.

5.4.1.3. Multicomponent particle combustion

The use of foams as carriers for transportation and incineration is particularly well suited for the treatment of separated solids, which are difficult to incinerate. In multicomponent incineration spent ion exchange materials or other waste are fed into the incinerator as a three phase foam, as a solid, gas and liquid mixture [83]. The process is based on dispersing the waste in an aqueous solution containing a surfactant, and if necessary a carbonizing agent, to modify it into a low pressurized foam, and then injecting it into a furnace running on oxygen for destruction. The combustion intensity is controlled by an adjustment of the composition and feed rate of the foam. Liquid and solid feeds must be atomized or pulverized into smaller droplets or particles in order to increase the surface area exposed to the hot gas and to facilitate rapid gasification and mixing with the oxygen-rich atmosphere [84].

The self-propelling nature of the mixture allows it to be fed into the incinerator under its own pressure, avoiding the need for injection pumps. The pressure of the foam causes it to enter the incinerator as a fine spray, improving its kinetic properties for combustion. The fineness of the structure of the cellular network enables this fine spray to be obtained without using small diameter nozzles. This property is advantageous for the treatment of solids.

The homogeneity of the foam, together with the use of oxygen as the combustion agent, allows higher throughput rates, steady combustion and a reduction in off-gas production. Importantly from an operating standpoint, the process makes use of standard equipment (e.g. tanks, mixers, mixing–swelling apparatus, furnaces) and does not require special technological research and development support. At Belgoprocess this multicomponent particle combustion process will be implemented

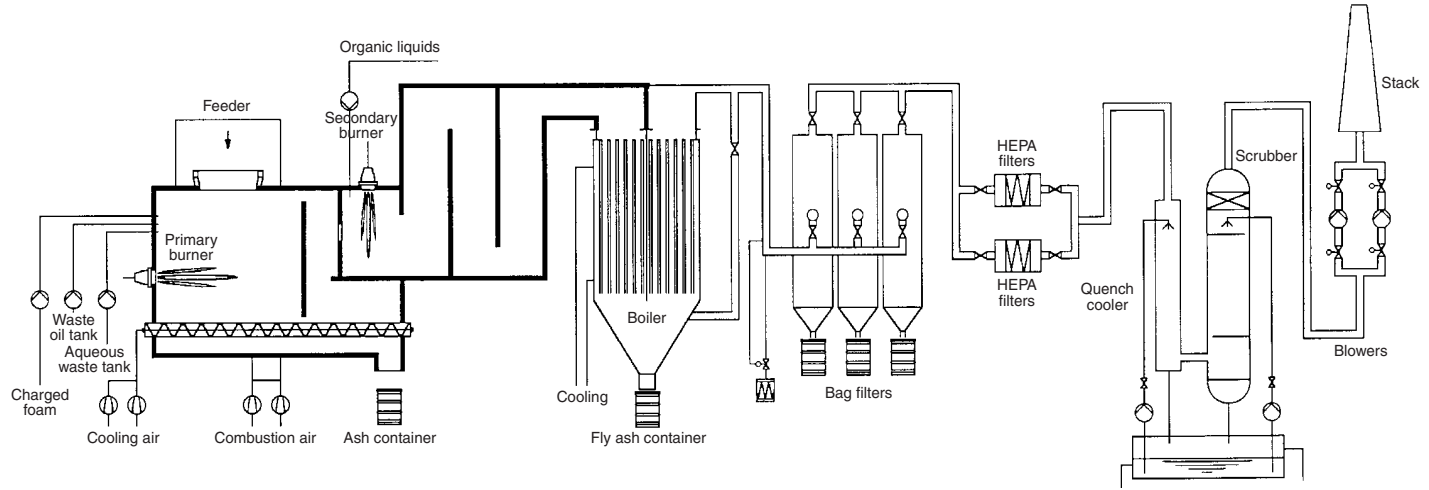


FIG. 14. The CILVA low level waste incineration facility, Belgium.

in the new incinerator at its CILVA plant [85]. Figure 14 shows the layout of the CILVA installation.

In this incinerator spent ion exchange resins are burnt together with other combustible waste. By burning a mixture of resins and other waste there is an upper limit for the content of the resins (25%). Above that limit combustion is not complete. When no other combustible waste is available, resins in a three phase mixture in the form of a combustible loaded foam are injected into the incinerator. The incinerator unit consists of the following components:

- A primary combustion chamber, in which the radioactive waste undergoes a combined process of combustion and pyrolysis at a temperature range of 900°C to 950°C;
- A secondary combustion chamber, in which the unburned gases and soot particles are mixed with excess air to complete oxidation to the primary components;
- A boiler to cool the off-gases;
- Off-gas purification, consisting of a bag house with bag filters and high efficiency particulate air (HEPA) filters;
- A wet off-gas scrubbing system, consisting of a quench tower and a counter current scrubbing tower using caustic liquid to remove HCl and SO₂.

Two treatment techniques are employed for immobilizing the incinerator residues: incorporation into cement or supercompaction into pellets.

5.4.1.4. Catalytic extraction

The molten metal catalytic extraction process, currently being developed in the USA, is essentially an adaptation of steel making technology for the waste treatment industry [86]. Dried ion exchange resins are ground to about 100 µm in size and then injected with a sub-stoichiometric quantity of oxygen and methanol into the bottom of a molten iron bath. The operating temperature of the molten metal iron bath is about 1540°C at 1000 kPa. Under these conditions most of the transition and heavy metals contained in the resins (e.g. cobalt, manganese, chromium, nickel and iron) are reduced to the metallic state and dissolve in the molten iron matrix. The carbon content of the resins is reduced to iron carbides and carbon monoxide. The sulphonate content of the resins is mostly reduced to H₂S, although some metal sulphides remain dissolved in the iron melt; 20–40 wt% of the sulphur is retained in the metallic phase, while a maximum of 2 wt% remains in the slag phase.

Gases (i.e. H₂, CO, H₂S and N₂) are generated that, along with volatile metals such as zinc and caesium and some particulate matter, are carried over into the off-gas train. The presence of normal glass forming or ceramic forming contaminants in

the spent resins results in a ceramic-like slag phase on the top of the iron melt. Uranium, transuranics and halogens (e.g. radioiodine) are soluble in this ceramic phase and are effectively trapped. Ceramic forming materials may be deliberately added to the melt to ensure the effective removal of these species.

The catalytic extraction process is operated as a semibatch procedure, with a fixed charge of iron loaded into a ceramic crucible that is inductively heated. Resins are added to the melt continuously over a number of days. The duration of the run is limited by the free volume remaining in the crucible, with the crucible level rising through the introduction of both metallic and ceramic materials. When the maximum crucible level is reached, the crucible is cooled and then emptied into a high integrity stainless steel container that is then remotely seal-welded.

5.4.1.5. Hot pressing

Hot isostatic pressing has been used to make dense synthetic mineral blocks from a wide range of particulate waste. The hot pressing of spent resins was recently applied as a treatment method at the nuclear power plant in Philippsburg, Germany [87].

In this process spent resins are first dewatered or dried to a residual water content of between 12 and 50%. The drying takes place in a drying vessel that holds the contents of two 200 L drums (Fig. 15). This vessel can also be used for mixing bead and powder resins. Spent ion exchange resins may also be mixed with other radioactive waste, such as sludges and evaporator bottoms, with high water contents.

In the oil heated drying and mixing unit the resins are heated to the necessary process temperature for the hot pressing step and then placed into special metal cartridges, which are automatically lidded and immediately transferred to a high force compactor.

After high force compaction the pellets are transferred to a measuring unit, where the dose rate, height and weight are automatically measured and recorded. The final disposal containers are loaded in the container loading area and delivered to the storage facility pending disposal.

A volume reduction factor of approximately six is achievable using hot pressing techniques. The compacted pellets must, however, be packed into watertight packages in order to avoid the resins swelling owing to contact with water.

5.4.1.6. Vitrification

Vitrification has been widely evaluated for the immobilization of highly active waste, such as waste from the reprocessing of spent nuclear fuel, and has recently been evaluated for the treatment of ion exchange resins [88, 89]. The excellent leach resistance property of the resulting glass waste form is the principal advantage of

- 1 Lid removal
- 2 Lift-tilt facility
- 3 Thermal resin treatment
- 4 Lid machine
- 5 High pressure compactor
- 6 Pellet measurement

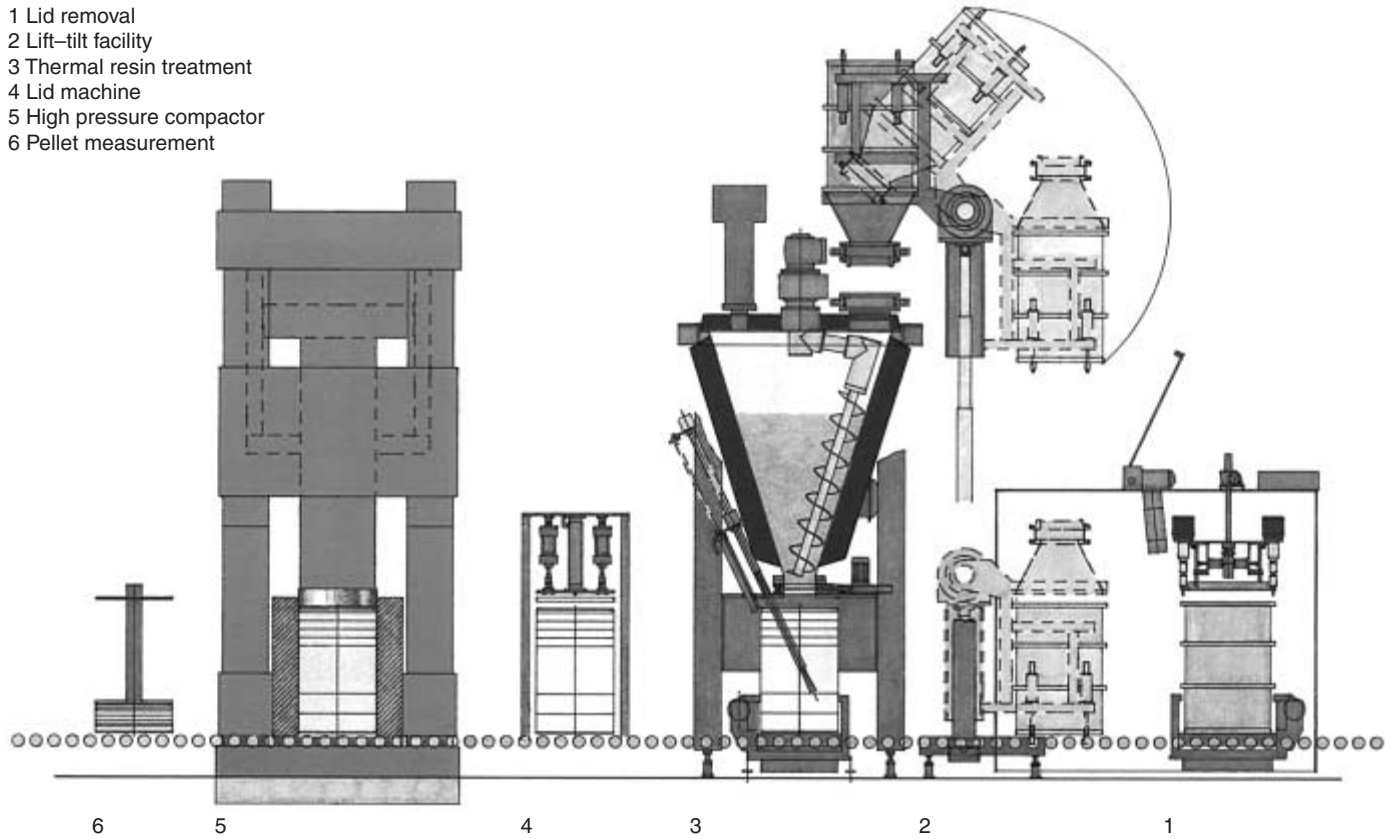


FIG. 15. Simplified flow diagram for the hot pressing of resins.

vitrification. Vitrification processes are capital intensive and the melters have a relatively short operational life (c. five years). Vitrification processes operate at temperatures ranging from 1100°C to 3000°C, depending on the waste composition and glass forming additives used. A very wide range of vitrification technologies has been tested.

Vitrification is similar to the incineration of ion exchange resins, in which the organic content is oxidized to carbon dioxide and water, with the sulphur and nitrogen from the functional groups evolved as SO_x and NO_x. The active and inactive metals inventory of the resins largely dissolves in the glass melt. Some volatile radionuclides, such as ruthenium and iodine, will be carried over in the off-gases, which therefore require scrubbing. Depending on the glass forming additives used, vitrification can be conducted at similar or lower temperatures than incineration. As a secondary treatment the residual ash from incineration or pyrolysis may be immobilized by vitrification.

In addition to government sponsored vitrification systems, several commercial ion exchange resin vitrification suppliers have emerged in the USA [60, 89].

Framatome of France has evaluated resin vitrification at its pilot plant at Bollene. This facility, which has a processing rate of 25 kg of organics per hour, has operated for about seven years. The process operates at 1000°C to 1100°C, and at this temperature Framatome reports a 90% retention of caesium in the melt. Inactive resins have been successfully treated at the maximum throughput rate of 25 kg/h.

The incorporation of inorganic ion exchange materials into glass has been studied in the USA. The vitrification of a composite absorber consisting of nickel hexacyanoferrate and polyacrylonitrile has also been reported [90]. Melts containing up to 5% (w/w) of the absorber were transparent and homogeneous and the leach resistance met the requirements for long term storage as high level waste.

5.4.1.7. Plasma techniques

Plasma technology has become a valuable technique for the thermal treatment of a variety of chemical and mixed radioactive and hazardous waste. The method can also be applied for the treatment of spent resins. The method is described in Ref. [91], and a schematic diagram of a plasma plant is shown in Fig. 16.

In this technique radioactive waste, including spent ion exchange resins, is fed into a plasma furnace; waste packages filled with resins are fed directly into the furnace. The melting capacities depend on the design of the specific facility; for example, a plasma torch melter in Switzerland has a melting capacity of about 50 kg/h. The hearth of the plasma furnace rotates with a speed that prevents melt from dripping through the orifice. For pouring, the rotational speed is lowered, which allows the melt to be dripped into a mould. Additives can be used to control the quality of the residues produced. The plasma process gives a glassy, solid waste

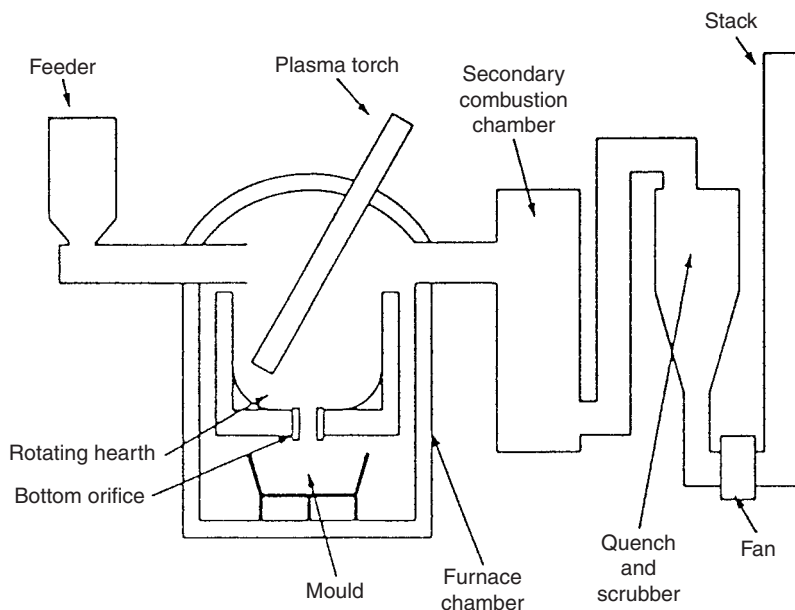


FIG. 16. Schematic diagram of a plasma plant.

product, which is placed into 200 L drums. A full scale facility is currently under start-up testing at the Zwilag plant in Switzerland [92].

The volume reduction for spent resins is in the range of 15 to 30, depending on the amount of additives used. The treatment process is rather costly and is economical only when operated at high throughput rates and not operated solely as a facility dedicated to the treatment of ion exchange resins.

The use of non-thermal inductively coupled plasma for the treatment of ion exchange resins has been investigated in Japan [93]. Initial cold bench scale tests have been promising, and experiments using actual power plant waste resins are planned.

5.4.2. Other treatment methods

There are a number of chemical treatment methods developed and operational for the processing of hazardous chemical waste. These methods may also be considered for the treatment of radioactive waste, including spent ion exchange resins. In some cases they will need additional study and testing before they can be used for the treatment of radioactive waste, in particular for spent ion exchangers. These methods are briefly discussed below.

5.4.2.1. Acid digestion

The acid digestion process involves the conversion of combustible waste to carbon dioxide and water by the action of sulphuric and nitric acids at about 250°C. This process has been considered a promising method for the treatment of spent ion exchange resins, but the use of concentrated acids at high temperatures requires the use of expensive, corrosion resistant materials and increases the complexity of the off-gas scrubbing system owing to the presence of oxides of nitrogen and sulphur. Developmental work that has been done in this field is described in Refs [56, 94, 95].

5.4.2.2. Wet oxidation

The wet oxidation process involves the reaction of waste with an oxidant in excess water in the presence of a catalyst [96]. The thermal oxidation processes discussed earlier in this report use elevated temperatures while employing air as an oxidant. Wet oxidation is a more recent development and uses hydrogen peroxide as the oxidant. The oxidation can be carried out at 100°C and at atmospheric pressure.

A research programme in the UK demonstrated the application of peroxide wet oxidation at low temperatures for the treatment of ion exchange resins [97]. This research programme was performed as part of the European Atomic Energy Community's programme.

The resins are delivered to a mixing station and mixed with other drummed waste. After the catalyst is added, the slurried mixed waste is loaded into the plant in batches of between 15 and 30 kg. The mixing station is designed to accept partially full drums of bead ion exchange resins. The mixed waste is heated to boiling point (slightly above 100°C) and the addition of an antifoaming agent is started. Hydrogen peroxide (50% by weight) is then added. No heating is necessary during the following stages of the reaction, as the heat generated by the exothermic reaction is sufficient to maintain the mixture at boiling point. Treatment is continued until the off-gas contains less than 5% carbon dioxide and the carbon dioxide evolution rate is less than 5 L/min.

The off-gas produced during the reaction is mainly a mixture of carbon dioxide and oxygen; a small amount of carbon monoxide is also produced. During processing the water that is produced by peroxide decomposition is removed by evaporation.

The product of the process, after neutralization with lime, is approximately 120 L of sludge that has a density of 1.28 g/cm³. The total solids present, determined by evaporation and weighing, is about 38%. The sludge settles readily.

Wet oxidation for the treatment of ion exchange resins has also been demonstrated in the USA [98]. A pilot scale facility has been developed for evaluation purposes. The results of tests indicate that more than 99% of the organic matter was destroyed, with a minimal carry-over. Operational problems related to foam generation and carry-over were believed to be correctable.

In India the process has been developed and demonstrated on a bench scale, using catalysts such as copper sulphate and iron sulphate. The JGC Corporation of Japan has investigated the process on a full scale and has put it into regular operation at a nuclear power station site.

5.4.2.3. *Molten salt oxidation*

In the molten salt oxidation process spent ion exchange materials and air are continuously introduced into a bed of molten sodium carbonate for oxidation. The molten salt medium permits lower reaction temperatures and the bed acts as a scrubbing medium for acid gases as well as for other elements of concern such as phosphorus, sulphur, arsenic and the halogens. In time, the inorganic constituents build up and must be removed from the molten salt if its ability to absorb acidic gases is to be retained. The ash residue content must be kept below about 20 wt% to maintain melt fluidity.

This process is being considered as an alternative to incineration and has been evaluated for application to the treatment of ion exchange resins in the USA [99]. Advantages include the lower oxidation temperature, with no NO_x emissions, and the retention of halogens and other pollutants in the bed. Disadvantages are the corrosivity of molten salt, limitations on process feed rates to produce low ash waste with a low water content and that the material separation steps associated with salt recycling can be troublesome.

5.4.2.4. *Electrochemical oxidation*

This process offers an alternative oxidation method to incineration and has some parallels with the wet oxidation process. Both processes operate at much lower temperatures than incineration and do not have the problems of off-gas cleanup that are associated with incineration.

Both wet oxidation and electrochemical oxidation processes feature the use of strong oxidizing agents. Whereas the wet oxidation process features the use of hydrogen peroxide, the electrochemical oxidation process uses Ag(II) in a solution of silver nitrate and nitric acid, and involves placing the solution in the anode compartment of an electrochemical cell and passing through a current.

The anode and cathode cells are separated by a semipermeable membrane that allows the passage of the ions carrying the current through the cell but prevents gross mixing of the contents of the compartments. Aqueous Ag(I) is oxidized to Ag(II) electrochemically. In the anolyte the Ag(II) reacts with water to form oxidizing and reactive species such as $\text{OH}\cdot$ radicals. These reactive species react with the organics fed to the anolyte, ultimately oxidizing them to carbon dioxide, some carbon monoxide, water and other inorganic products. There is no volatilization of the low

molecular weight species formed as intermediates during the destruction process, and the process can be readily started and stopped by switching the current on or off [100, 101].

5.4.2.5. *Barix process*

The Barix process is a thermal destruction method under inert conditions for resins. The process leads to the formation of three phases: an aqueous phase, an organic phase and a solid phase. Both the liquid and organic phases are non-radioactive and the activity is concentrated in a dry residue that can be disposed of as it is or after further treatment.

The process breaks the polymer chemical bonds, releasing the original components. Barium is added prior to the heating process in the form of a liquid hydroxide. The barium acts as a catalyst in the depolymerization process and also reacts with the sulphur in the cationic functional groups to form barium sulphate, which has been shown to act as a binder for the metallic species in the waste, including radionuclides. The reaction occurs in an inert atmosphere at moderate temperatures to prevent the oxidation of the organic species. During the heating process bound water is first driven off and collected by condensation; this drying process occurs at up to 135°C. The temperature is then gradually increased to about 400°C, at which point all of the organic material is volatilized and is recovered by condensation using water cooled and air cooled condensers. An inert gas sweep is used to ensure a complete recovery of the vapours. Resin destruction occurs in a reactor that is kept under a slight negative pressure to prevent out leakage.

The high pH provided by the barium hydroxide ensures that the metal species attached to the resins form hydroxides during the drying and destruction steps and hence stay in the dry residue. Anion resins with ^{14}C attached in the form of a carbonate or bicarbonate will release ^{14}C to form barium carbonate, which is insoluble in water and will stay with the dry residue. The tritium inventory is recovered with the water phase.

For most resins (non-tritiated) the water phase is recovered, which is non-radioactive. This water can be recycled for reuse or discharge.

5.4.2.6. *Thermochemical treatment*

In the Russian Federation the Moscow Scientific and Industrial Association has developed a process in which wet spent ion exchange resins are mixed with a metal powder, a combustion activator and some additives. On ignition, the mixture burns without any extra energy being supplied and generates enough heat to evaporate the water present and decompose the resins. Pilot plant studies have shown that the

radionuclides contained in the resins are chemically bound in the ash residue. The ash consists of metal oxides, spinels, silicates, etc. More than 90% of the ^{137}Cs and up to 95% of the ^{90}Sr and ^{60}Co are fixed in the ash. The residue volume is several times smaller than the initial volume of wet resins [102].

5.4.3. Processes under development

Other processes at various stages of development include:

- Microwave drying for plasma arc incineration,
- Biological degradation [103],
- Cold crucible melting [104].

The biological degradation of organic radioactive waste, including ion exchange resins, has been extensively studied in Finland [103]. The anaerobic digestion of resins can reportedly give volume reduction factors of 10 to 20, but the processing time is long, ranging from days to weeks. Although the process has been developed and commercialized, the microbial degradation of spent resins does not appear to have yet been adopted at Finland's nuclear plants.

5.5. CONSIDERATIONS FOR SECONDARY WASTE RESULTING FROM DESTRUCTION PROCESSES

Secondary waste is often of a nature similar to primary waste and can therefore be treated and conditioned by the same or similar methods used for the primary waste. In some instances, however, the secondary waste may be different (e.g. incineration ash) and may require a specific treatment and conditioning. An evaluation of the secondary waste quantities and characteristics, as well as the choice of their treatment and conditioning methods, is an essential step that should not be omitted or underestimated. The results of this evaluation could significantly affect the overall volume reduction factor, the economics of operation or even the selection of the primary treatment process itself.

The dry or wet residues resulting from the secondary treatment of ion exchange materials generally require immobilization prior to their final disposal. The matrices commonly used for these residues are cement, bitumen, polymer, composite matrices such as a cement-polymer and, in certain cases, glass and ceramics. The composition, activity level and disposal option of the final product govern the choice of matrix to be used.

5.5.1. Incinerator ash

The main conditioning processes employed for ash are compaction, pelletization, immobilization in a cement matrix, placement into high integrity containers, sintering and melting. The choice of the process is governed by the activity level, the chemical characteristics of the ash and the storage and/or disposal options contemplated for the conditioned product. In some cases ash may be subjected to grinding or a recovery of radionuclides before conditioning. The immobilization options discussed in Section 6 are generally suitable for ash.

5.5.2. Wet residues

In some treatment processes, such as wet oxidation, the bulk of the activity is retained in the bottoms as a wet residue. This can be treated further by dewatering. A treatment of the wet residues by specific ion exchange materials can also be considered in special cases. The final wet residue will require immobilization in a suitable matrix.

The selection of matrix materials and the evaluation of the waste forms is carried out in a similar way to that for the direct immobilization technique described in Section 6.

6. DIRECT IMMOBILIZATION AND ENCAPSULATION OF SPENT ION EXCHANGERS

Immobilization is the process of incorporating waste (in this case either organic or inorganic ion exchange materials) into a matrix material for solidification or directly into a storage and/or final disposal container. Before immobilization, organic ion exchange materials may require one or more of the pretreatment and/or treatment methods described in Section 5. However, in some cases this can be done without pretreatments other than the removal of excess water.

The immobilization matrices currently used for spent ion exchangers are cement, bitumen and some polymers. In some countries high integrity containers are used for the storage and/or disposal of spent ion exchange media, without incorporation into a solidification matrix. Vitrification and other 'one step' treatment and conditioning methods have already been discussed in Section 5. Most of the processes using the above matrices are performed on an industrial scale and are described in detail in many publications [105–110]. Table IX summarizes the general advantages and limitations of these immobilization matrices.

TABLE IX. SUMMARY COMPARISON OF IMMOBILIZATION PROCESSES

| Matrix | Advantages | Disadvantages |
|--------------------------|---|---|
| Cement | <p>Material is readily available and not expensive</p> <p>Compatible with a wide range of materials</p> <p>Excellent radiation stability</p> <p>Non-flammable product</p> <p>High pH results in a good chemical retention of most radionuclides</p> | <p>Swelling of organic bead resins may cause cracking of the matrix</p> <p>Waste loading can be low, the volume of the final waste form is greater than the original waste volume</p> <p>Moderate leach resistance for many radionuclides, for example caesium</p> |
| Bitumen | <p>Good leach resistance</p> <p>All the water in the waste is removed by the process, resulting in good waste loadings</p> | <p>The waste form will soften at moderate temperatures</p> <p>Requires a container to maintain structural stability</p> <p>Organic bead resins may swell and compromise the waste form if there is a prolonged contact with water</p> <p>The organic waste form may be flammable and subject to biodegradation</p> <p>Has a lower radiation stability than cement</p> |
| Polymer | <p>Wide variety of polymers are available</p> <p>Good leach resistance for many polymers</p> | <p>Generally more expensive than bitumen or cement</p> <p>Polymerization reactions can be affected by trace materials in the waste</p> <p>Has a lower radiation stability than cement</p> |
| High integrity container | <p>Simple and inexpensive to operate and handle</p> <p>Steel containers have excellent radiation stability</p> | <p>Relies entirely on the container integrity</p> <p>Not accepted in all jurisdictions</p> <p>Polymer containers can have a low radiation stability</p> |
| Vitrification | <p>The glass waste form has an excellent radiation stability and leach resistance</p> <p>Substantially reduces the volume of waste</p> | <p>Is a high temperature process</p> <p>Is expensive to operate</p> |

It should be noted that the specific application of a matrix for a given waste must be evaluated on an individual basis. Pilot level studies may be required to determine the optimum waste loading and matrix composition. This is especially true for cements and some polymers, for which trace amounts of certain materials within the waste may adversely affect the properties of the product (by, for example, preventing the cement or polymer from solidifying, or producing a product of poor quality).

In addition to the technical factors outlined above, other factors, such as national standards and waste acceptance criteria for storage and/or disposal facilities, must also be considered.

6.1. CEMENT IMMOBILIZATION

The technique of immobilizing radioactive waste in cement has been used in the nuclear industry and at nuclear research centres for more than 40 years. Detailed descriptions of the process can be found in references such as Refs [105, 109]. Cement has many characteristics in its favour: it is readily available and widely used in civil engineering, the raw material is inexpensive and the processing equipment can be based on conventional technology. The resulting waste forms are strong, non-combustible and radiation resistant, have a high density (providing radiation shielding), have a reasonable chemical stability and have a moderate resistance to the release of radionuclides. The high pH conditions typical for cement results in a low solubility for many radionuclides by the formation of hydrolysed species, carbonates, etc., which provides a good resistance to leaching.

The main disadvantage of the cementation of spent ion exchange materials is that the final waste volume is high compared with the initial volume, owing to the low waste loadings that are achievable. The loadings can be increased by a pretreatment, such as grinding, of the spent ion exchange materials before cementation, which improves the quality of the final cemented products.

Another disadvantage of cementation for organic ion exchange materials is that a swelling of resin beads after contact with water may occur in some disposal repositories. The swelling can result in micro cracks in the cement or even in the overall cracking of the cement structure. Experience has shown that, owing to their size being less than 0.1 mm, an overall cracking of the cement structure does not occur with powder resins. The cementation of spent bead resins without a pretreatment such as grinding should therefore be avoided.

Inorganic absorbers have been immobilized in cement, as discussed in Ref. [111]. The study examined the encapsulation of the oxides of titanium and manganese, the phosphates of titanium and zirconium, polyantimonic acid and copper hexacyanoferrate. It was found that, with each of these absorbers, a 33 wt% loading in the waste could be reached, which provides a good quality solidified product.

TABLE X. APPLICATIONS OF TYPICAL CEMENT TYPES

| Cement type | Application |
|---------------------------|--|
| Ordinary Portland cement | The general immobilization of most aqueous liquids, organic ion exchange materials, inorganic ion exchange materials and secondary process waste (dry and wet) |
| Blast furnace slag cement | Slower setting time (longer working time), lower permeability, increased sulphate resistance and lower curing temperatures |
| Pozzolanic cement | Lower permeability, increased strength and an increased resistance to cracking and seawater attack |
| High alumina cement | Increased resistance to sulphate and acid attack, rapid curing and a high early strength |

The immobilization of a composite absorber in cement has also been examined [90]. Loadings of 5 to 9 wt% of absorber produced acceptable waste forms.

6.1.1. Cement types used for immobilization

The word cement is applied to a broad range of products. The cements referred to in this section are hydraulic cements, which are essentially made of calcium silicates and calcium aluminates. The main types of cement and their typical applications are listed in Table X. Typical chemical compositions can be found in, for example, Refs [105, 111].

Because of their high mechanical strength, the most commonly used cements are the ordinary Portland cements. High alumina as well as pozzolanic cements are more and more used or under investigation for many applications. Blast furnace slag cements are applicable in the event that a fluid grout with a long working time is required.

National standards usually define the composition of and mechanical, chemical and physical requirements for the different types of cement. Although these requirements are not identical in all countries, a basic international standard classification has been adopted [112]. These standards and formulations were generally developed for the civil engineering industry, although many of the cements are also applicable to waste management needs, since the standard cements form the basis of most immobilization formulations. In addition, specifications for the specialty cements that are often used for immobilization, such as sulphate resistant cement, are also defined in these standards.

TABLE XI. SUMMARY OF CEMENT ADDITIVES

| Additive | Function |
|---|---|
| Sodium silicate | Improves the setting of cements incorporating ion exchange resins containing boric acid; also lowers the volume increase factor and improves fluidity |
| Zeolites, vermiculite, clays | Improves the retention of cations such as caesium |
| Vermiculite, silica, diatoms and other absorbents | Absorbs excess water |
| Organic derivatives | Improves fluidity characteristics and watertightness |
| Formaldehyde | Prevents bacterial growth, which can cause an internal buildup of gas pressure |

Appropriate additives can be used to improve specific properties of the waste form (e.g. its chemical durability or mechanical strength). The additives most frequently used are summarized in Table XI.

To improve one or more of the characteristics of cement waste forms, new matrix materials based on cement have been studied in several countries; for example, the polymer impregnation of concrete after a conditioning of the waste has been examined at Casaccia in Italy [113], in which methylmethacrylate or styrene is used as a pore filler after drying the cement waste form at 165°C. The compressive strength of the impregnated material is better than that of the concrete alone and the leach resistance is significantly enhanced. Applications of cement-polymer matrices in the USA have also been reported [114, 115]. At the Commissariat à l'énergie atomique at Cadarache, France, an improvement of the weathering and aging resistance of cemented ion exchange resins has been obtained by using a matrix material containing a mixture of 56 wt% sand (0.5–2 mm size), 29 wt% Portland cement and 15 wt% of a commercially available bitumen emulsion (HR-Everfast) used in civil engineering [116].

Recent developments for immobilizing spent ion exchange resins in cement can be found in many publications, such as Ref. [109].

6.1.2. Preparation for immobilization in cement

A considerable amount of research has been carried out to determine the limits for the composition of an acceptable resin-cement mixture. The process for immobilizing waste consists of mixing the cement with the waste and allowing the mixture to harden. The basic criterion is to obtain a monolithic product in which there is no free-standing water.

The composition of a cemented waste form is often described by its waste content and water/cement ratio. The waste content is the amount of waste in the final waste form, which is one of the most important properties; the water/cement ratio governs the strength of the cement matrix.

In selecting the composition of a mixture, workability is a decisive factor. Good workability is required in order to provide a homogeneous mixture within a reasonable time. The waste content, water/cement ratio and consistency of a waste–cement mixture are interdependent. If the waste content is increased while the water/cement ratio is kept constant, the mixture becomes more viscous and is thus more difficult to mix. The same phenomenon occurs if the water/cement ratio is decreased while the waste amount remains constant. If too high a water/cement ratio is used the different components tend to separate in the waste mixture and there can also be free water present after the setting of the product, which is not desirable. Compositions for products that pass certain tests have been published in the literature. This information is generally given in the form of ternary composition phase diagrams, an example of which is shown in Fig. 17. They present the limits of the composition for free-standing water, for mixability and for the composition of the

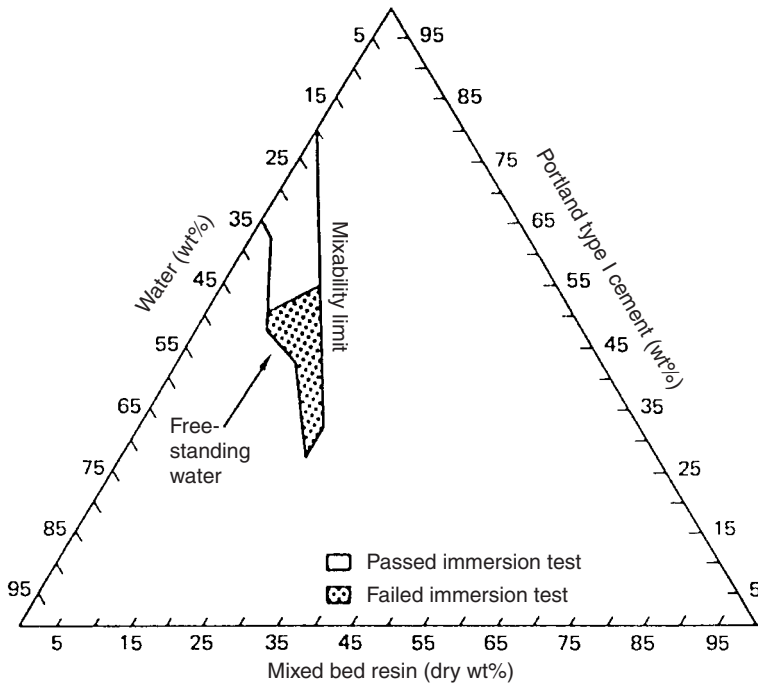


FIG. 17. A typical waste–cement composition diagram.

forms capable of passing a water immersion test. The weight percentages of water, cement and dry ion exchange resins are used to express the compositions.

The loading of spent organic ion exchange resins in cemented products is about 20 wt% (calculated on the basis of the dry resin product), which achieves a compressive strength of about 20 MPa. With higher loadings the compressive strength of the cement product could be decreased to the extent that the acceptance criteria of storage and/or disposal are not fulfilled. The influence of resin content and water/cement ratios on compressive strength is presented in detail in references such as Refs [114, 115].

Other examples of the effects of waste loading on waste form performance are given in the literature, such as Ref. [117], in which Portland type III cement was used with a water/cement ratio of 1:2. The samples, containing 10 wt% dry resin, fractured upon immersion in water. To obtain higher resin loadings and more durable waste forms, the resins were coated with water extendible polyester (without an initiator). It was thus possible to obtain loadings as high as 23 wt% of dry resin. These waste forms did not crack during curing and did not deteriorate during wet and dry cycling.

Special attention has to be paid to the solidification of spent resins that contain boric acid, since the boric acid affects the setting of the cement. In practice, for pressurized water reactors the boric acid content is 50 to 70 g per kg of resin, which leads to lower waste loadings in the product, as well as the need for additives such as sodium silicate.

6.1.3. Cementation process

Usually the cementation process is performed in batches directly in the final storage container, which could be a drum or fibre reinforced concrete container. Other containers of various materials and sizes are also used. The same basic process applies to both organic and inorganic media, although the relative proportions of some of the components may vary. Typically, some or all of the water used to transfer the spent media (slurry) is used as the water for the cement mixture. A measured amount of the resin slurry can be added to the container first, followed by the cement mixture. Alternatively, the cement mixture can be added first, followed by the resin slurry. In either case the ratio of resin–water to cement must be carefully controlled to achieve a satisfactory quality of solidified product. Mixing can be provided by a powered paddle, by tumbling the container or by a fixed paddle and a rotating drum. Cementation usually takes place in a hot cell facility or behind appropriate shielding, owing to the high levels of radiation. More details of the different cementation processes can be found in Ref. [105]. Figure 18 shows, in outline, the cementation process of the spent ion exchange process in operation at the waste management plant in Narora, India.

If a spent ion exchange medium is contained in a small column, the entire column can be encapsulated with cement in its storage and/or disposal container,

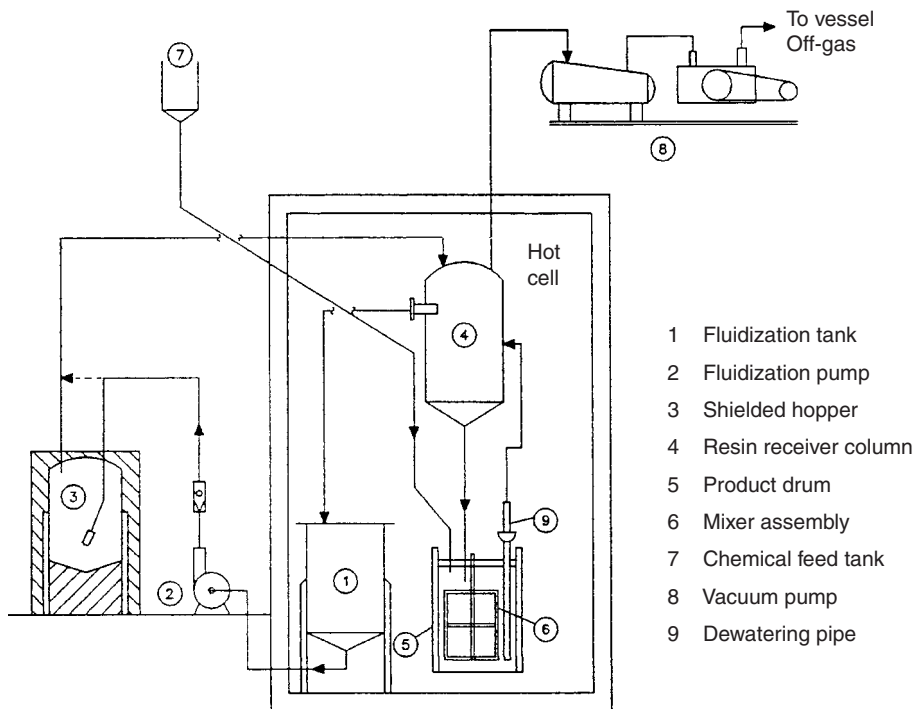


FIG. 18. Operational flowsheet of the spent ion exchange resin cementation system used at the waste management plant, Narora, India.

although additional care should be taken to ensure that as much of the water as possible has been removed from the column and that a sufficient thickness of cement exists around the column so that if any residual water does leak out in the long term it is contained by the cement. The quality of the final waste product should correspond to the waste acceptance criteria approved by the national regulatory body for storage and/or disposal.

6.2. BITUMEN IMMOBILIZATION

Like cement, bitumen has been used for many years as an immobilization matrix for radioactive material. The processes and methods of bituminization are described in detail in the literature. General descriptions of the process are given in references such as Refs [107, 115, 118].

6.2.1. Bitumen types used for immobilization

Bitumen is a generic term used to cover a wide range of high molecular weight hydrocarbons. Several bitumen varieties are commercially available for the immobilization of radioactive waste, including spent ion exchange resins. They include:

- Direct distilled bitumens, which are the residues from petroleum distillation;
- Oxidized bitumens created by blowing air through petroleum residues;
- Cracked bitumen generated from the thermal breakdown of heavy oil fractions;
- Bitumen emulsions, which are prepared by emulsifying directly distilled bitumens with water.

The main characteristics of bitumen that make it suitable as a matrix material for spent resins are:

- Its insolubility in water;
- Its high resistance to the diffusion of water;
- Its chemical inertness;
- Its plasticity and good rheological properties;
- Its good ageing characteristics;
- Its high incorporation capacity, which leads to high volume reduction factors;
- It is readily available at a reasonable cost.

However, since it is an organic material, bitumen has the following disadvantages:

- It decreases in viscosity as a function of temperature, leading to a softening of the matrix, which melts at temperatures of about 70°C;
- It is combustible, although not easily flammable (the flash point and flammability temperatures are higher than 290°C to 350°C, depending on the type of bitumen);
- It has a lower stability against radiation than cement, especially under the higher radiation fields often associated with spent ion exchange media;
- It reacts with oxidizing materials such as sodium nitrate.

It should be noted that the low melting temperature and the possibility of combustion in the case of an accidental fire has led in some countries to restrictions on the use of bitumen as a solidification matrix. Several fires have happened in different countries during the filling of bitumen into the final storage drums at temperatures of about 120°C. However, it should be emphasized that all these fires happened with bitumen containing nitrates from the evaporator concentrates of reprocessing plants.

Since spent resins from nuclear power plants contain no nitrates or only small amounts from laboratories, the autocombustion that can be caused by nitrates is not likely to occur with bituminized resins from nuclear power plants. Nevertheless, if a combustion of the bitumen–resin matrix happens during a bituminization operation, the fire can be easily extinguished, for example by spraying carbon dioxide or water into the hot cell in which the operation usually takes place. Bituminization facilities must therefore include a fire suppression and/or extinguishing system.

6.2.2. Preparation for immobilization in bitumen

Pretreatment steps are necessary prior to bituminization. Bead resins are generally ground to a finer mesh size in a wet grinder. Subsequent dewatering and drying usually takes place before the resins are fed into the bituminization unit. Drying and immobilization can take place simultaneously when heat is applied to melt the bitumen (e.g. in extrusion or evaporator processes).

6.2.3. Bitumenization processes

Details of bituminization processes and the experience gained from operating industrial scale processes can be found in Refs [107, 110]. These processes are either batch or continuous operations. The applications of different techniques for different type of bitumen is summarized in Table XII. Batch processes usually involve drying the resin followed by mixing the dried material in molten bitumen. Continuous processes require the introduction of the resins, as a slurry, to equipment capable of simultaneously mixing the bitumen (if an emulsion is used). The bitumen mixture, which flows from the process equipment to a suitable storage container, solidifies upon cooling.

TABLE XII. APPLICATIONS OF TYPICAL BITUMEN TYPES

| Bitumen type | Application |
|------------------|--|
| Direct distilled | Batch melter, thin film evaporator |
| Oxidized | Batch melter, extruder, thin film evaporator |
| Cracked | Extruder |
| Emulsion | Thin film evaporator |

6.2.3.1. *Batch bituminization process*

In this process predried resins are continuously introduced into a metered volume of molten bitumen at about 200°C. The mixing vessel is externally heated. Any water present evaporates and the solid resin particles are mixed with the bitumen. When the required composition of the waste form is reached, the addition of the resins is stopped. The mix is heated and stirred for some time to evaporate the residual water and is then discharged into drums or other containers to cool and solidify.

6.2.3.2. *Continuous bituminization processes*

Continuously operating bituminization processes are generally based on either extrusion or film evaporation systems. With extrusion systems the predried resins are fed into a multiple screw extruder together with bitumen at 200°C. During passage through the heated extruder, an intensive mixing of waste and bitumen occurs, with the simultaneous evaporation of any water. The temperature of the bitumen–resin matrix is kept reasonably low (140°C) to minimize the separation of trimethylamines from some types of anion resins; at lower temperatures the viscosity would be too high to maintain the extrusion process. The final product is extremely uniform, with individual resin particles coated with a layer of bitumen. The bituminized product is discharged into drums and allowed to cool and solidify.

In a film evaporator system the resins and bitumen are separately fed to where the two streams mix and flow down the heated wall, at the top of the evaporator unit. The water content of the mixture is progressively evaporated and the bituminized waste material is drained near the bottom into steel containers. The vapours generated are condensed, first in the built-in condenser in the evaporator and subsequently in an external condenser. Figure 19 shows a simplified flow diagram of a film evaporation process for the bituminization of spent ion exchange resins at Barsebäck nuclear power plant in Sweden [2]. In this process ion exchange resins are immobilized in bitumen together with evaporator concentrates.

6.3. POLYMER IMMOBILIZATION

The immobilization of spent ion exchange resins in polymers is practised at many installations worldwide. Different types of polymers are used and further studies to improve cost effectiveness, process simplicity and product quality are being carried out in many countries. Among the many polymers used are epoxy resins, polyesters, polyethylene, polystyrene and copolymers, urea formaldehyde, polyurethane, phenol-formaldehyde and polystyrene [106].

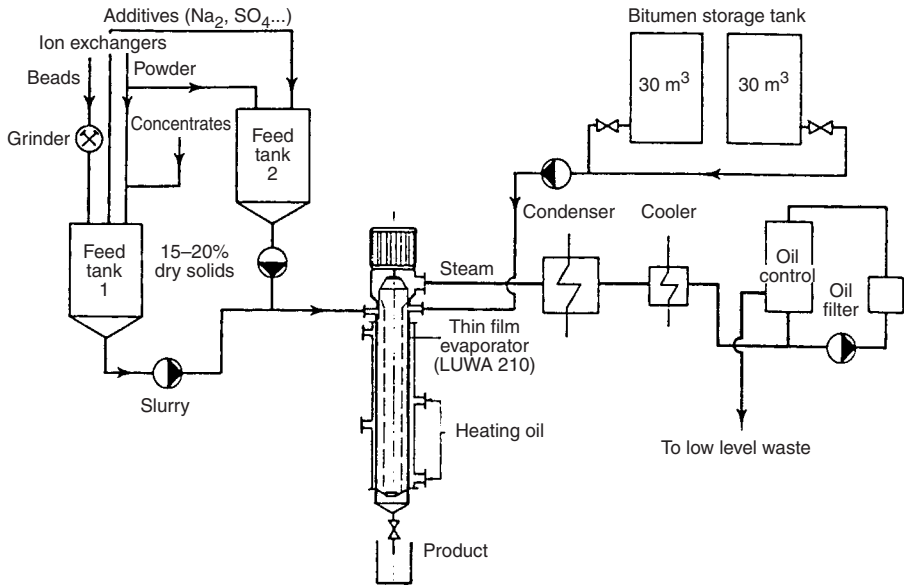


FIG. 19. Bituminization of spent ion exchange resins at Barsebäck nuclear power plant, Sweden.

Polymers fall into two main categories: thermoplastic polymers and thermosetting polymers. Thermoplastic polymers become soft (or melt) with the application of heat. They are generally supplied in a solid form and heated when combined with waste. Thermoset polymers are handled in a liquid form and are then polymerized to a solid form using a catalyst and/or heat after waste has been added. The use of the thermoset variety has become more popular owing to its ambient temperature processing capability. In a majority of cases a batch immobilization process in a disposable container (usually a standard drum) is used. Spent resins are generally compatible with the polymer matrix material. Inorganic ion exchange materials and secondary process residues such as ash and liquids are generally not immobilized using polymers because they are more acceptable to other immobilization matrices such as cement. Each particle of resin is coated with the matrix material. In most cases there is no chemical bonding between the polymer and the resin.

6.3.1. Preparation for immobilization in polymers

The moisture associated with resins does not pose a compatibility problem as long as it remains as intrinsic or bound water or as a thin film of surface moisture.

Free water present in the resin bed or bound water released during the course of processing is known to lead to problems such as separation without fixation and inhomogeneities in the product. It is therefore important that the moisture content of spent resins is controlled by employing pretreatment processes such as dewatering or drying.

Another preparatory step that sometimes becomes necessary is the rendering of constituents on the resins ineffective if they have a tendency to interfere with the chemistry of polymerization. This is normally achieved through a chemical treatment given to the resins to render such constituents insoluble. A specific example is resins containing boric acid, since boric acid delays the curing process. In India, during an active commissioning trial of a plant at Narora, it was found that the pretreatment of resins with alkali, leading to the insolubilization of borates, helped achieve solidification in a reasonable time and provided a product with better homogeneity.

6.3.2. Polymer immobilization processes

Not all polymers are suitable for immobilizing ion exchange resins. The various types used are summarized in Table XIII and described below in further detail.

Among the various polymer fixation processes developed, the most widely used are the polyester and epoxy processes. Both of these are ambient temperature processes and are comparatively simple considering the equipment and operations involved. The processes are in use in Japan, France, India, Switzerland and Germany. A detailed study has been carried out for unsaturated polyesters used as immobilizing agents, specifically with respect to controlling the reaction time and

TABLE XIII. APPLICATION OF TYPICAL POLYMER TYPES

| Polymer type | Application |
|-------------------------|---------------------------------|
| Epoxy resin | Batch mixing and semicontinuous |
| Polyester | Batch mixing and semicontinuous |
| Polyethylene | Extrusion process |
| Polystyrene | Batch mixing |
| Polymethyl methacrylate | Batch mixing |
| Phenol-formaldehyde | Batch mixing |
| Polyvinyl chloride | Batch mixing |
| Urea formaldehyde | Batch mixing |
| Polyurethane | Batch mixing |

reducing the reaction temperature. The effect of the choice of the catalyst–accelerator system and its concentration has been noted [119]; this has helped to reduce the maximum temperature achieved during the process and also to improve the product’s quality.

A polymer fixation facility employing a polyester embedding agent is in operational at the Narora nuclear power plant in India for the immobilization of spent resins (Fig. 20). The system uses a DMA/BPO (dimethyl aniline/benzoyl peroxide) catalyst–accelerator system.

Spent ion exchange resins from reactor purification systems are received in about 100 L quantities. The resins are hydraulically fluidized by a closed loop water circulator and transferred into a receiver located in a hot cell. The resin slurry from the receiver, which also acts as a batching tank, is drained into a specially designed drum and then subjected to vacuum dewatering. Thereafter the chemicals, namely two equal parts of the polyester formulation premixed separately with optimized concentrations of the catalyst and accelerator, are added to the drum in a predetermined sequence, and the drum contents are stirred. The contents are well mixed and allowed to gel and cure before the drum is taken out for disposal.

All operations in the cell are carried out remotely. Product characterization is performed using core drilled samples taken from full scale blocks during inactive trials. Leaching studies are also undertaken using blocks made during hot commissioning.

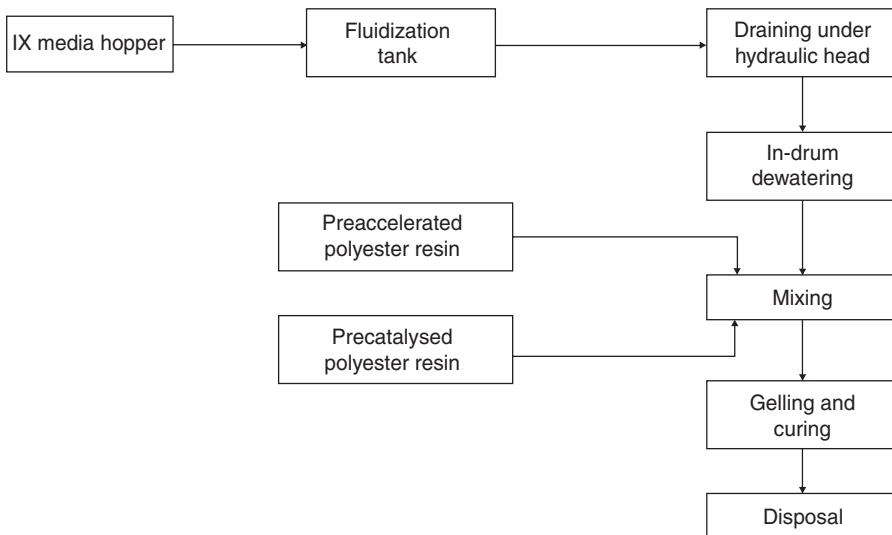


FIG. 20. Schematic diagram of the polymer fixation facility for spent ion exchange resins at the Narora nuclear power plant, India.

Similar systems are operated in France, Sweden and Japan, which have both fixed and mobile plant designs. All these systems, which operate at ambient temperatures, can also use epoxy formulations for immobilization. Some particular examples of applications of polymers for the immobilization of spent ion exchangers are briefly discussed below.

6.3.2.1. *Epoxy resins*

An epoxy matrix (such as Araldite) has been used for the incorporation of dry ion exchange resins, based on the experience of the General Electric Company's Inert Carrier Radwaste Process [120] and of the French Commissariat à l'énergie atomique [2]. Dewatered resins are mixed with an epoxy material that coats each individual dry particle of ion exchange resin. A hardener is added to the coated waste in a static mixer. The final waste form cures in about three hours.

6.3.2.2. *Polyester*

Waste forms can be prepared with polyester-styrene, vinylester styrene and water extendible polyesters.

Polyester-styrene. Processes for immobilizing spent resins in this matrix have been studied at several centres [121]. The solidified waste form has the advantage of a high mechanical integrity. The simplicity of the process, which involves solidification at ambient temperatures, makes it suitable for adoption on an industrial scale. The reaction temperatures reached in the process are low, so it is convenient and quite safe for the operating personnel and does not require elaborate equipment for heating large volumes of the active resins. These aspects give such a process substantial advantages over those requiring high temperatures.

Vinylester styrene. In this system, the Dow binder process of the Dow Chemical Company [122, 123], the vinylester styrene is a commercially modified vinylester product. Polymerization is achieved by an additional mechanism using a promoter-catalyst system that permits curing without external heat. No chemical reaction takes place between the resin and binder material. Solidification is complete in 5 to 20 minutes, depending on the volume and the amount of catalyst and promoter used.

The system uses in-container mixing techniques with a disposable mixing blade. Pretreated dewatered resins are added to the container, followed by the binder and then the promoter-catalyst, and mixing is accomplished with a high torque mechanical agitator.

Water extendible polyester. Water extendible polyester resin (e.g. Aropol WEP 661-P [124, 125]) is mixed with water in the weight ratio of 1:2 to prevent the product from cracking. Spent resin is added and mixed into the emulsion. An initiator, methyl

ethyl ketone peroxide, is added during the stirring stage and the mixture is poured into suitable containers for curing.

6.3.2.3. *Polyethylene*

Polyethylene is a thermoplastic and can be used to immobilize waste in a manner similar to a bitumen extrusion process. Hot polyethylene is mixed with the damp or dried resin and extruded into a waste container. The polyethylene is usually supplied as small beads and is heated to its melting point just prior to injection into the extruder. Any residual water on the resin is driven off by the hot polyethylene.

6.3.2.4. *Polystyrene and copolymers*

Many forms of this category of polymers have been investigated. A polymerization process using a mixture of styrene and divinylbenzene as the binder and isobutylnitrile as a catalyst has been developed in Germany [126]. Substitute products such as acrylic acid, types of acrylates and heterocyclic compounds such as pyridine derivatives can be used for the styrene. Many divinyl compounds can be substituted for the divinylbenzene. The process is exothermic and the temperature is controlled by precisely metering the catalyst. Reaction times are intentionally lengthened, with solidification occurring within about two days. Complete hardening is obtained after 6 to 12 days. The styrene divinylbenzene matrix is chemically identical to the material used in most organic ion exchange resins.

6.3.2.5. *Urea formaldehyde*

A urea formaldehyde prepolymer is mixed with wet waste and resin slurry and then an inorganic acidic catalyst is added to this mixture [127, 128]. The catalyst is either a weak acid such as NaHSO_4 or Na_2HPO_4 or a dilute solution of strong acids such as HNO_3 or H_2SO_4 . The pH range required is from 1 to 2. Under the right conditions polymerization starts when the catalyst is added, and is completed within about 30 minutes. The cross-linked polymeric structure entraps the resin particles and any free water.

The process is very sensitive to waste chemistry and, even under ideal conditions, the reaction between the mono and dimethyl urea results in the release of free water, which is acidic. The low pH (1 to 2) required for the polymerization reaction prevents the use of ordinary carbon steel containers. The final form has very poor mechanical properties. The use of urea formaldehyde cannot be considered to be competitive, since the leachability characteristics are also relatively poor. Some

recent studies have indicated the possibility of working in a pH range of 4 to 5, the avoidance of the release of water and improvements in the product quality. Process details and product characteristics are covered in, for example, Ref. [129].

6.3.2.6. *Polyurethane*

A polyurethane process has been developed in Sweden and proposed for the solidification of all waste from nuclear power plants as well as for spent ion exchange resins [130]. The resin slurry is fed to an evaporator, where the water is distilled off. The dried residue is mixed with polyalcohols, one of the constituents of the polyurethanes, and brought in batches to the final storage drums. Isocyanate and a catalyst are then added and, during a few minutes of stirring, the mixture solidifies. In this process a disposable mixing blade is used. Phosphorus compounds can be added to obtain a better fire resistance. A wet process is described in Ref. [131] in which the evaporator step is avoided.

6.4. IMMOBILIZATION IN HIGH INTEGRITY CONTAINERS

Dried spent ion exchange resins can be encapsulated in high integrity containers for storage and/or disposal without immobilization in an additional matrix in a process in which dewatered or dried resins are transferred directly into the final storage casks. The water is removed from the resins by evaporation with a vacuum drying system in conjunction with a jacket heating system for the cask. The waste casks can be made of ductile cast iron, high density polyethylene, fibre reinforced concrete or steel. A nodular cast iron container is shown in Fig. 21 [132].

In a process developed in the UK [133] resins are dried in a vessel using hot air at about 100°C. The dried resins are measured into a compactor, where they are pressed into pellets, put into the final storage container and the free space around and above the pellets filled with cement grout. The final product of dried resins itself has no function as a barrier; the main barrier for safety considerations in storage and/or disposal is the thick wall of the container (which could be sealed by welding, for example). Thick walls have the additional advantage of providing radiation shielding.

The advantages of this process are the low production costs and low equipment requirements. High integrity containers are, however, expensive; the process is therefore mainly used for low outputs of resins or when direct immobilization in cement or other matrices creates a costly increase in the disposal volume. A primary condition for taking this process into consideration is to fulfil the storage's acceptance criteria.

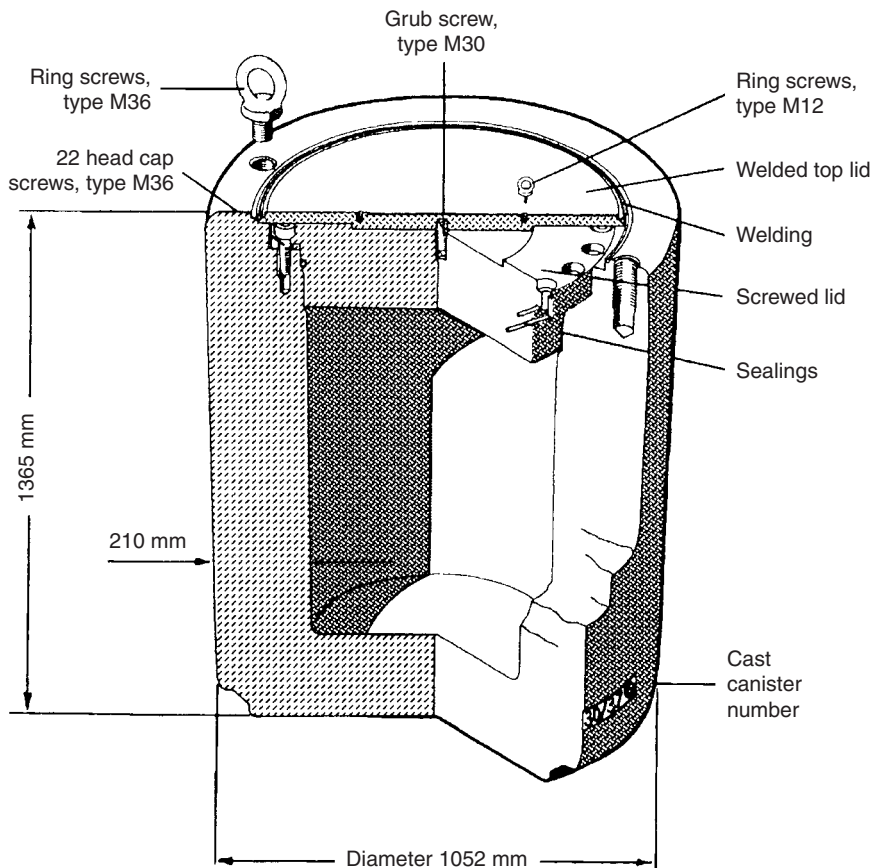


FIG. 21. German nodular cast iron container.

6.5. PROPERTIES OF IMMOBILIZED WASTE FORMS

There are a number of immobilized waste form properties, including their mechanical, chemical and thermal characteristics, that are important for long term storage and/or disposal. Typical acceptance criteria for the properties are given in, for example, Ref. [133]. A summary of the important properties for waste forms incorporating ion exchange media is given in Table XIV. A detailed description of waste form properties is available in Refs [105, 134]. Descriptions of testing methods and requirements can be found in, for example, Refs [135, 136].

Properly formulated cement waste forms generally have good mechanical strength; waste forms created from improper formulations, however, can have poor mechanical properties, such as low strength and a tendency to crumble.

TABLE XIV. SUMMARY OF TYPICAL WASTE FORM PROPERTIES

| Property | Cement | Bitumen | Polymers |
|---------------------------|---|--|--|
| Compressive strength | Excellent if properly formulated | Poor to moderate (material is plastic) | Moderate to good |
| Waste loading | 10–25% dry weight for organic IX resins, can be higher for inorganic exchangers | 25–50% dry weight for organic IX resins Not considered for inorganic exchangers | 25–50% dry weight for organic IX resins Not considered for inorganic exchangers |
| Biodegradation resistance | Stable | Moderate | Moderate to stable |
| Thermal stability | Good | Poor: will melt and ignite | Moderate: some types will melt and/or char when heated |
| Leach resistance | Poor to excellent, depending on the formulation and radionuclide | Excellent for most radionuclides | Good to excellent for most radionuclides |
| Radiation resistance | Excellent | Moderate | Moderate |
| Gas generation | Low | Moderate to high | Moderate |
| Chemical compatibility | Good for most materials (can be affected by some, for example boric acid or chelating agents) | Good for most materials (can be softened by solvents and oils) | Good for most materials (some polymers are affected by excess water in the waste, some are attacked by organic solvents) |

Bitumen waste forms rely on their container for their mechanical strength. Under heat and/or pressure the waste form will tend to soften and to some extent will flow. Because of their waterproof nature, bitumen waste forms tend to show good water resistance, but their prolonged submersion in water may lead to the progressive rehydration of organic ion exchange media and a subsequent failure of the waste form through the expansion of the ion exchange resins.

The effects of various degradation processes are cumulative and may interact in various combinations; for example, irradiation of a waste form and radiolytic gas generation may lead to a reduction in mechanical strength and a subsequent formation

of cracks, which could allow water to contact the interior of the waste form and increase the leach rate. If this infiltrated water were to freeze it could cause a further cracking of the waste form.

6.5.1. Mechanical properties

In many cases the mechanical properties of a waste form are an important part of the waste acceptance criteria for storage and/or disposal of the waste. The waste form may undergo a series of tests, such as a determination of its compressive strength, to demonstrate that it will maintain its integrity over the required period of time. Tests are often performed on newly created waste as well as aged waste that has been subjected to various conditions, such as irradiation and thermal cycling.

Polyester waste forms are reported to have a good mechanical strength and are not affected by thermal cycling, finite irradiation, water immersion or biodegradation. The presence of water or higher waste loadings (above 50%) are known to decrease their compressive strength [119]. Compressive strength also decreases at high (5×10^6 Gy) absorbed dose and with an increasing mesh size of the material.

Polyethylene forms (both high and low density) have shown compressive strengths of up to 300 kg/cm². These, however, show a tendency to soften when subjected to water immersion tests.

6.5.2. Resistance to biodegradation

Biodegradation is important from a long term storage and/or disposal perspective. If the waste form is attacked by microbial organisms it can lose its physical integrity over a period of time and release its radionuclide contents into the environment. It can also lead to the formation of gases, such as hydrogen, that may be of concern for the design of a repository.

Cement materials are inorganic and generally considered to be resistant to biological attack. However, any organic materials contained within the matrix, such as organic ion exchange materials, can be biodegraded under certain conditions. This process is reduced somewhat by the highly alkaline conditions that exist within cemented waste forms. If required, additional biocidal additives can be used in the cement matrix.

Although they are organic, polymers generally cannot be degraded easily by microbes and hence are usually regarded as non-biodegradable. However, many polymers can be degraded by prolonged exposure to ultraviolet radiation. Studies are therefore continuing to evaluate their biodegradability by subjecting test blocks to direct sunlight to observe any photodegradation. Studies of the growth of different strains of microbes in the presence of polyester waste forms have shown that they have an insignificant effect on the polyester. Lysimetric studies using the polymerized

waste products of ion exchange resins under particular disposal conditions could provide more information on biodegradation.

6.5.3. Thermal stability

There are two main considerations for thermal stability: the production of heat during the solidification process and the effect of exposure to heat (or cold) after the solidification of the waste form.

Cement curing and the polymerization of thermosetting materials are both exothermic reactions. In some cases the amount of heat released can be sufficient to affect the mechanical properties of the waste; for example, if peak temperatures reach more than 100°C any water present will boil off and the steam generated can produce cavities and cracks in the final product.

Once solidified, cement, hard bitumen and thermoset polymer waste forms may be degraded by freeze–thaw cycles. Soft bitumen and thermoplastic polymers tend to be more resistant to freeze–thaw cycles because the materials are more elastic and can stretch or shrink as required to accommodate the differential temperatures.

Cement waste forms are not flammable. Thermoplastic waste forms (such as polyethylene and bitumen) tend to be less resistant to thermal damage than thermoset waste forms. Bitumen and polyethylene will both melt. The resulting liquid is flammable, so combustion may still continue if the source of the flame is removed. Thermoset polymers will char when contacted with a burning flame but will tend to self-extinguish once the flame is removed. Flame retardancy can be improved by the addition of inorganic additives such as antimony chloride. Epoxy, polymethyl methacrylate matrices and polyester are adequately stable up to about 280°C, as established by thermal testing [137].

6.5.4. Leaching behaviour

A key property of any waste form is its leach resistance, which determines how well the radionuclides of concern are retained within the waste form when it is subjected to wet conditions. There are two mechanisms that influence leaching behaviour. One is the creation of a physical barrier between the radionuclide and the environment, which is how most polymer and bitumen systems work. The other mechanism involves an actual chemical reaction between the radionuclide and the matrix, which occurs most often in cement based systems. It should be noted that this behaviour is very waste form and radionuclide specific. It can be altered by the chemistry of the waste material, the formulation of the immobilization matrix and the chemistry of the leaching water. Some radionuclides, such as ^{14}C and most transuranics, are retained very well by common cement owing to the high pH

conditions and the chemical reactions that occur in the matrix. Other radionuclides, such as tritium, are not retained very well, if at all, within such a matrix.

A number of studies have been carried out, and others are in progress, for the evaluation of polymer waste forms with respect to their leaching behaviour. Most of these are laboratory scale studies with inactive blocks or test blocks made with simulated or real active waste. Some studies have been made using samples drawn from full scale active polymer block forms made in an operating plant [138].

In the USA field lysimetric studies are currently in progress on cement and vinylester resin products to generate data on the effect of aging and self-irradiation over a 20 year period. Data on compressive strength and radionuclide migration have been compiled for 10 to 12 years. The objective of the project is to study the following aspects:

- The degradation effects of radiation on ion exchange resins,
- The adequacy of recommended test procedures,
- Obtaining information on solidified ion exchange resins in the disposal environment,
- The conditions of liners and engineered barriers used in disposal.

The leach resistance of various cemented, bitumen and polymeric ion exchanger media waste forms has also been studied in Canada [124], Republic of Korea [119], Brazil [139], India [129, 138] and numerous other countries. Leaching studies with polymer matrices such as polyvinyl chloride and urea formaldehyde are reported in Refs [129] and [140], respectively, the former covering the effect of irradiation on the chemical durability of the product.

The leach resistance of a caesium loaded hexacyanoferrate immobilized in cement has been measured [111]. It was found that the presence of the hexacyanoferrate reduced the cumulative fraction leached but not the overall leach rate. The leach resistance of a hexacyanoferrate composite absorber immobilized in cement has also been determined [141].

6.5.5. Radiation stability and gas generation

It is well known that subjecting organic materials to radiation fields can alter their physical properties. Increasing cumulative exposures to gamma radiation will generally cause organic materials to become more brittle or otherwise lose mechanical strength. The degradation process will also result in the generation of gases such as hydrogen and methane that may readily escape through cracks in the waste form. The buildup of internal pressure in a waste container through gas generation may be sufficient to crack or rupture the waste form or its container. In addition, the gases may be radioactive if the original waste contained, for example, tritium or ^{14}C .

Inorganic materials such as cement are generally more resistant than organic materials to the effects of radiation. However, under the intense radiation fields often associated with spent ion exchange media localized degradation through the radiolysis of pore water in the cement matrix can occur. This can lead to gas generation and a subsequent spalling or cracking of the cement form.

7. CONSIDERATIONS FOR THE STORAGE AND/OR DISPOSAL OF IMMOBILIZED ION EXCHANGE WASTE

As discussed previously, the selection of the treatment methods and packaging for spent ion exchange materials must take account of their ultimate disposal. The final waste form must meet all applicable regulatory and facility waste acceptance requirements. In addition to the general waste form concerns, there are some related specifically to ion exchange waste forms, owing to the higher concentration of radionuclides generally found on this type of waste, their associated radiation fields and the nature of the ion exchange materials themselves.

7.1. WASTE ACCEPTANCE CRITERIA

Waste acceptance criteria can be defined as a set of rules reflecting the legal and regulatory principles mentioned above, plus the technical and economic considerations of the operator of the waste storage and/or disposal facility. It should be emphasized that a proper quality assurance system, fulfilling internationally accepted standards, is of a crucial importance in all the components of radioactive waste management systems. Waste acceptance criteria and quality assurance requirements for waste storage and/or disposal are described in detail in Refs [134, 135, 142, 143].

Acceptance criteria can be developed based on all the stages of handling spent ion exchange materials. Each processing step may have different requirements, and the requirements may be set by different agencies or facility operators. The main steps of the waste management cycle are described below.

7.1.1. Acceptance criteria for waste packages

National or facility standards could dictate requirements and standards such as the:

- Construction, geometry and dimension of the waste packages;
- Maximum weight of the waste packages;

- Durable labelling of the waste packages;
- Content of gamma emitting radionuclides;
- Maximum surface dose rate of the waste packages;
- Maximum surface contamination of the waste packages;
- Corrosion resistance of the waste packages;
- Physical strength, durability and resistance to impact of the waste packages;
- Maximum radiation induced degradation of the waste packages or their contents;
- Homogeneity of the waste;
- Chemical composition of the waste;
- Restrictions on free-flowing liquids in the waste packages;
- Restrictions on gas production in the waste packages;
- Resistance against fire of the waste packages;
- Restrictions on chemical reactivity of the waste packages;
- Resistance against leaching by water of the waste packages.

7.1.2. Acceptance criteria for waste transportation

These and other requirements are usually defined by the waste transportation options to interim or long term storage and the available or expected conditions for final waste disposal. These requirements may impose restrictions on the radiation dose rate and radionuclide concentration. The transportation of waste between two locations by road, rail or sea is described in Ref. [144].

7.1.3. Acceptance criteria for interim storage

In addition to the requirements formulated for the disposal of waste packages, the operating conditions for an interim storage facility should consider some additional requirements, for example the surface dose rate of the waste packages and the maximum storage time. Water intrusion into the storage facility is a particular problem, because it can lead to ion exchange resins swelling, with a subsequent disintegration of the waste form. Record keeping and the retrievability of the waste may also be of importance.

7.1.4. Acceptance criteria for final disposal

The acceptance criteria for waste forms and packages are based on the final safety report of the repository and may influence and/or be defined by the type of the repository, its location in the host geological environment, the specific design features and the engineered barriers provided. It may include restrictions on the total inventory of the radionuclides, restrictions for specific long lived radionuclides and special

requirements for accepted waste forms and packages. If there is an existing disposal option and the acceptance criteria are known, these will define the selection of particular treatment, conditioning and packaging options for achieving the final waste form to satisfy these requirements. Restrictions on the radionuclide inventory and on releases to the biosphere, for example, are conditions that should be consistent with the final safety report for a planned repository. Restrictions on releases to the biosphere may be brought about by a multiple barrier system that prevents radionuclides from migrating to the biosphere in unacceptable concentrations.

7.2. INFLUENCE OF STORAGE AND/OR DISPOSAL REQUIREMENTS ON THE CHOICE OF CONDITIONING PROCESS

Conditioning processes applicable to ion exchange media have been described in Section 6. The requirements for a given storage or disposal facility in a country can influence the choice of conditioning process in a number of ways, as outlined below.

7.2.1. Life cycle plan

Some countries require ion exchange media to be immobilized in a matrix such as cement, bitumen or a polymer, while others will accept media that have been dewatered and enclosed in a high integrity container. In Sweden and the UK cement is preferred as the immobilization matrix for low and intermediate level waste, in part due to its ability to retard the mobility of the transuranium elements (such as plutonium) as well as ^{14}C .

At present, in many countries, owing to the fact that no final repository is available at present, the long term interim storage of unconditioned spent ion exchangers is preferred. A planned interim storage time in excess of 50 years is an option in some countries. An advantage of long term interim storage is an improvement in radiation protection, owing to the decay of short lived radionuclides such as ^{60}Co . The disadvantage with this procedure may be the degradation of organic ion exchangers owing to radiolysis, oxidation and other reactions, resulting in the potential release of some radionuclides, and the loss of information over time, especially if different waste batches are mixed together.

Another option that is used in countries that have a final repository, such as Sweden, is the short term interim storage of ion exchangers, either in an unconditioned or conditioned form. After the decay of short lived radionuclides and conditioning the waste is placed in the final repository. All information regarding the waste packages is stored in a durable form at the final repository. It is possible to check the radionuclide specific total nuclear inventory at any time. The main

advantages are the minimization of the risk of the loss of information and the absence of stockpiled waste at unsuitable facilities. The latter is important in connection with the decommissioning of a nuclear power plant, as accumulated large amounts of radioactive waste could significantly delay the decommissioning process.

7.2.2. Economics

The costs of storage and/or disposal will influence whether any volume reduction is performed prior to immobilization. If the cost of disposal is high compared with the volume reduction costs, processing for volume reduction is easily justified on an economic basis. If, however, the storage and/or disposal costs are lower, volume reduction may not be economical. Methods such as incineration, vitrification or plasma arc melting could, apart from reducing volume, also be used to destroy the organic complexing agents that may otherwise facilitate the migration of transuranic elements towards the biosphere.

7.2.3. Waste volume

The volume of waste to be treated, and its radionuclide specific properties, including its dose rate, will have an influence on the choice of conditioning process. If the country or facility concerned produces only a small amount of ion exchange media waste, then a simple process such as in-drum cementation is preferred over more complicated processes, such as incineration, which are too expensive to operate on a small scale. The availability of facilities for the treatment of other waste types will influence the choice; for example, if a cementation plant is being used for the immobilization of liquid waste then the same plant can often be adapted for use with ion exchange media at little or no additional cost.

Treating spent inorganic sorbents, which have a high selectivity and ion exchange capacity, may allow other options for final disposal to be considered. Owing to their high exchange capacity, these materials can often be used in small columns. After use, the columns can be dewatered and disposed of in a shielded container. The container acts as a final waste package and the waste remains in a stable form in the column. If water enters the waste after a loss of integrity of both the concrete container and steel column, only very high concentrations of competing ions will cause a leaching of the absorbed radionuclides from the ion exchange material into the water [145].

The size of the columns and of the final disposal container may differ, depending on the circumstances. Several small ion exchange columns can be encapsulated in one container. Empty space inside the container can be filled with radiation shielding or a buffer material, such as cement grout. Enclosure could also

be done prior to its use by placing a column, for example, in a cement lined drum, which has the advantage of providing shielding during its operation and during the column's removal.

7.2.4. Long term stability

Long term stability of the waste form is generally required for storage and/or disposal. However, it can be affected by radiolytic, biological and chemical degradation processes, which can further influence the radiological, chemical and physical properties of the waste form [146, 147].

7.2.4.1. Chemical and radiological stability

Since ion exchange media tend to concentrate radioactivity, the associated radiation fields can be high. When integrated over long time periods, this may result in radiolytic damage to organic ion exchange media, to organic immobilization matrices (such as polymers and bitumen) and to organic container materials (such as polyethylene high integrity containers). Damage to the ion exchange medium may reduce its capability to retain radioactive ions, while damage to the immobilization matrix will reduce the mechanical integrity and physical durability of the waste form. This could, for example, increase susceptibility to leaching by water. The radiolysis process may also produce combustible or explosive gas mixtures (e.g. hydrogen, methane and oxygen), as well as corrosive liquids (e.g. sulphuric acid and nitric acid).

The chemical and biological degradation of organic ion exchange media has been known to occur. The results of such degradations are generally similar to those of the radiolytic effects. In addition, chemical attack can be initiated by localized high concentrations of strong oxidizing agents, such as nitrates, in combination with the transition metals, acting as catalysts, that may be present on some media. Once initiated, such chemical reactions can be highly exothermic, resulting in a rapid oxidation of the material and a subsequent release of radionuclides.

The degradation of organic materials by any of the above processes can also lead to the formation of water soluble degradation products, which are able to chelate the absorbed radionuclides and thereby increase the mobility of these radionuclides in the repository.

Another problem specific to many organic ion exchange media is that of dehydration and rehydration. An ion exchange resin bead may contain 50% or more water by weight. As discussed previously, an obvious means to reduce the volume and weight of the material to be disposed of is drying it. However, if the dried media subsequently come into contact with water, as may happen over time in a disposal repository or storage facility, they will rehydrate. The rehydration process will cause the resin beads to expand to their original volume, exerting enormous forces on the

surrounding matrix or container. The pressure created by such expansion has been sufficient to cause immobilization matrices to crumble and containers of all types to split open.

With inorganic ion exchangers and composite absorbers with a high inorganic content, reswelling after drying does not normally occur.

Dehydration occurs during heat based immobilization processes such as bituminization and polymer extrusion. Dehydration–rehydration may also take place to some extent in immobilization processes such as cementation. This effect can limit the amount of organic ion exchange media that can be incorporated into the cement. If the proportion of ion exchange media in the cement mixture is too high, the media may undergo dehydration and rehydration during curing, causing the cement to crack.

When a waste form containing a dehydrated organic resin is subjected to a water immersion test, the ion exchange medium on the outer edge of the matrix begins to swell, causing cracking. These cracks promote further water penetration into the matrix, causing progressively more and deeper cracking until the matrix ultimately fails. Although such failure mechanisms can be very slow, the long time periods associated with the requirements for radioactive waste storage and/or disposal allow ample time for the actions to occur.

Since the bond between the radioactive ion and the ion exchange medium is fairly weak, specifically in organic ion exchange resins, the spent medium must be kept away from materials that could break the bond, such as the calcium or sodium ions contained in many groundwaters or cement materials. Therefore, when a complete isolation of waste forms from the disposal environment is required, a multiple barrier concept is employed, which considers an immobilized waste form itself as a sealed container. It is crucial for long term stability that complexing agents that could increase the mobility of radiotoxic long lived radionuclides are excluded from waste packages that may come into contact with water; such a situation could occur, for example, in an underground bedrock repository.

7.2.4.2. *Structural integrity*

Some countries, such as the USA, require immobilized waste forms to retain their structural integrity over long periods. This is generally to control the subsidence of near surface waste disposal facilities and applies directly to ion exchange media waste forms. Structural integrity can be provided by a solidified matrix or a container. In the event that a container is relied upon for structural strength, a supplemental container, generally a concrete shell, is sometimes placed around the primary container. This concrete shell serves both to support the load of backfill material placed over the container and also to provide supplemental radiation shielding during the loading phase of a facility.

7.2.5. Waste handling

Since the radioactivity levels of spent ion exchange media are typically much higher than those of dry active waste, shielding the waste during storage, transit and disposal is often an important concern. Supplemental shielding is usually provided by the use of shielding overpacks or specially designed shielded containers; for example, some countries use a concrete cubical container or concrete lined drum for the immobilization of ion exchange media [148]. In addition, additional self-shielding is provided if a concrete immobilization matrix is used.

At a storage or disposal facility, supplemental shielding can be provided by other waste packages or in special shielded structures; for example, in Canada 3 m³ cylindrical steel containers of spent ion exchange media are stacked for storage in steel and concrete in-ground structures. Most of the shielding is provided by the ground surrounding the structure and by a thick concrete shield plug that is placed on top.

Waste packages placed in interim storage will require eventual retrieval for disposal. Storage facilities therefore require a means to retrieve the waste packages. Because of the radiation levels often encountered, special remote handling tools and procedures may be required for this purpose.

8. FUTURE TRENDS AND DEVELOPMENTS IN THE USE AND MANAGEMENT OF ION EXCHANGERS

8.1. CONSIDERATIONS OF MINIMUM LIFETIME (OR LIFE CYCLE) COST

Future trends in the design of operating systems employing radioactive material will probably focus on reducing waste volumes and toxicity (both chemical and radiological) by selecting processes that minimize waste generation and maximize the recycling of effluents. Efforts will focus on developing and utilizing the ion exchange processes and materials that result in the most manageable secondary waste products in the event that the transfer of contaminants to aqueous systems is inevitable. This consideration is likely to favour the use of stable inorganic ion exchangers in preference to organic materials.

The generators liable for the disposal of spent ion exchange materials will also require the development of cost effective solutions. Treatment methods that are fully integrated into the production and operating process and that minimize environmental risks are therefore likely to provide the best overall life cycle costs.

As more synthetic organic and inorganic ion exchange materials are developed, it is expected that they will be used in concert with existing ion exchangers to provide

an improved wastewater treatment train. These new ion exchangers may be used as pretreatment steps, prior to the main treatment process, or as polishing steps. Currently few, if any, inorganic ion exchangers can replace the organic bead resins that are used to control the chemistry in important reactor process systems. In some applications inorganic ion exchangers may be used up-stream of the more conventional organic resins to remove radioisotopes selectively. This approach would produce a smaller volume of waste material with a higher specific activity. This has some advantage, since shielding a smaller vessel is simpler and the majority of the radioactivity is contained in a more stable inorganic structure. The trend will be to seek out materials and process arrangements that are successful in controlling the risks and providing a minimum lifetime cost solution.

In the area of spent ion exchange treatment and immobilization, future trends will probably be away from incineration and towards treatment technologies with less complex off-gas systems and emissions. At the same time, immobilization approaches will probably favour technologies that offer long term chemical, radiological and physical stability, such as vitrification, in order to ensure that the disposal site performance requirements are met.

8.2. DEVELOPMENTS IN THE SELECTION OF ION EXCHANGE PROCESSES

8.2.1. Materials

The current trend in the selection of ion exchange media is towards high capacity, high selectivity media that can remove target ions with a good efficiency in the presence of other ions or under harsh operating conditions. A number of such media are currently available to remove caesium or strontium from liquids with a high concentration of salts, for example. Although currently more costly than natural or conventional materials, the advantages of applying these materials is a reduction in the volume of secondary waste (i.e. the spent ion exchange media produced) and an improvement in the quality of the final conditioned waste product. In many cases this results in overall monetary savings for the waste management programme, especially for those cases for which waste disposal costs are high.

The screening and comparative evaluation of potential new ion exchanger materials is carried out in the UK by the Novel Absorber Evaluation Club. Standardized batch and column tests are used to assess the selectivity of candidate materials for the removal of a range of elements, including manganese, cobalt, chromium, zinc, silver, ruthenium, caesium, strontium, cadmium, mercury, plutonium, americium, neptunium, iron, technetium and uranium. Descriptions of these standardized tests are provided in the Annex.

Several new polymers have been developed for organic ion exchange media that have improved thermal and radiation resistances, although their acceptability for storage and/or final disposal remains to be determined.

Ion exchange and sorption processes are also being developed for the removal of radioactive contaminants from non-aqueous liquids such as oils and solvents.

8.2.2. Process arrangements

The consideration of the minimum lifetime cost may require an arrangement of the ion exchange columns containing the selective exchangers that initially appears more expensive in terms of the capital costs. The ease of removal of the ion exchanger may also be a factor taken into account in seeking the optimum arrangements of plant consistent with an acceptable waste product disposal strategy. Concentrations of radioactivity on the ion exchanger will result in high dose rates and a consideration of the 'as low as reasonably achievable' principles to protect the workforce. Remote methods for removing spent ion exchangers are likely to be preferred (i.e. hydraulic transfer or remote manipulation).

8.2.3. Plant design philosophy

It is important to consider some of the main underlying requirements that need to be addressed when selecting an ion exchange process, as these will influence system design trends. To be considered are that:

- A full account should be taken of the whole cycle, from the source and characterization of the waste to be treated by ion exchange through to the final disposal of the immobilized waste, including maintenance and secondary waste.
- When selecting a particular ion exchange technique, a full account should be taken of the social and economic aspects of waste management, and compliance should be demonstrated with the national regulations at costs that can be justified.
- The benefits derived in terms of reducing discharges to the environment, with a consequential reduction in doses to the public, should not be achieved at the expense of an increased dose uptake to the operating and maintenance personnel.

For example, one objective considered by BNFL when designing new plants has been that the average radiation exposure to plant personnel should not exceed 5 mSv/a, which can be compared with the statutory UK limit of 50 mSv/a or the International Commission on Radiological Protection recommendation of 20 mSv/a. The trend will continue to be downwards.

Such considerations are likely to lead to the use of remote operations and remotely maintainable plant.

8.3. DEVELOPMENT OF SPENT ION EXCHANGE MEDIA TREATMENT TECHNOLOGIES

The current trend in treatment technologies for spent ion exchange media must be viewed in a wider perspective encompassing the treatment of all waste. General waste management will therefore tend towards:

- Providing an acceptable product quality for safe final disposal;
- Producing more stable product waste forms;
- Minimizing waste volumes;
- Maximizing waste loadings in stabilized matrices;
- The transfer and concentration of radioactivity from organic to other, more stable, media.

Although there is a trend towards minimizing waste volumes, this must be offset by the need to meet the acceptance criteria of interim storage or final disposal. Power plants have a need to consider the disposal cost per unit volume, and hence have a reason to reduce waste volumes. National disposal regulators may argue that the fixed costs of providing a final repository may be 90%, whereas the variable costs are only 10%. Under these national cost considerations, the drive to reduce waste volumes is less important compared with providing a stable, safe product form for disposal for many hundreds or thousands of years.

Most high volume reduction processes are based on the thermal destruction of the medium's matrix. This is specially suited to organic media. Inorganic media can also be volume reduced by some thermal techniques, such as sintering, plasma arc melting or vitrification.

Cement encapsulation is viewed as low cost and will form a major part of low level waste and intermediate level waste immobilization technologies. Very stable waste forms with moderate to high loadings have been developed specifically for ion exchange media. The quality of immobilized waste forms is continually being improved.

Some waste treatment methods, such as plasma arc melting, vitrification or molten metal techniques, result in both a high volume reduction and very stable waste forms.

The reversible nature of the ion exchange reaction has resulted in the development of several activity stripping processes, which can result in the concentration of the radioactivity into a smaller volume of a more stable compound. The stripped ion

exchange medium is much lower in radioactivity and can often be treated by less rigorous methods. A good example of this is the ^{14}C stripping process for CANDU (PHWR) ion exchange resins. If the ^{14}C was left on the ion exchange resins it would probably require disposal in a deep geological repository. Once the ^{14}C has been removed, however, the residual resins can be disposed of as conventional low level waste, with only the much concentrated, reduced volume of the ^{14}C -containing matrix disposed of in a geological repository.

9. CONCLUSIONS

A wide range of materials is available for the ion exchange treatment of liquid radioactive waste. These materials are available in a variety of forms and have widely differing chemical and physical properties. Ion exchange is used for processing liquid effluents in nearly all phases of the nuclear fuel cycle, including the early stages of uranium ore treatments, the chemical control of primary circuit coolants during nuclear power plant operations and polishing water effluents at spent fuel reprocessing plants. This method is one of the most widely used both in the nuclear industry and the conventional chemical industry for the purification, separation and partitioning of particular non-radioactive and radioactive species with different chemical properties. Organic and inorganic, naturally occurring and synthetic ion exchangers have found their specific fields of application in different purification and liquid waste treatment processes.

In many cases ion exchange is the most appropriate and the most efficient method for the treatment of a variety of low and intermediate level liquid waste streams. With respect to economy and efficacy, ion exchange stands between the other two major liquid waste treatment processes of evaporation and chemical precipitation. While evaporation may yield higher decontamination factors, it is also more costly than ion exchange. The development of new ion exchangers is narrowing the gap in decontamination factors between evaporation and ion exchange. Chemical precipitation, however, is often less expensive but is not always effective in removing radionuclides from solution.

A large number of natural and synthetic inorganic and organic ion exchangers has been developed and is in use today. In spite of their advanced stage of development, various aspects and components of ion exchange technologies have been continuously studied to improve the efficiency and economy of their application in radioactive waste management. Efforts to develop new ion exchangers for specific applications are continuing. Novel composites using combinations of existing and new ion exchangers are also being investigated.

In order to develop an ion exchange process for a specific application, it is necessary to evaluate fully the aqueous stream to be treated and the options for conditioning the spent ion exchange materials, while always considering the method of final disposal. It should be kept in mind that a modern trend among authorities and industry is to avoid using organic based materials with a limited radiation stability. Subjecting organic materials to radiation fields and high cumulative exposures can alter their physical properties, including producing a loss of their mechanical strength. Special concern should be paid to the possible radiation induced generation of gases, especially hydrogen, in long term storage and/or final disposal. Inorganic materials are generally more resistant to the effects of radiation.

A variety of pretreatment, treatment and immobilization options exist for spent ion exchange materials. While a number of systems are in place and operating today, other processes utilizing new, innovative technologies are in varying stages of development. These technologies will probably be required in the future as more stringent operating requirements at disposal facilities are translated into more restrictive waste acceptance criteria.

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Annex

DETAILS OF THE TEST PROCEDURE OF THE NOVEL ABSORBER EVALUATION CLUB

The objective of the Novel Absorber Evaluation Club is to remain aware of new sorbent developments and produce decontamination data on these products for direct comparison with standard benchmark materials. The decontamination data are obtained by batch contact experiments using one or more reference waste streams, depending on the type of absorber being tested. By using these reference waste streams in all tests it is possible to compare directly the performance of one ion exchanger with another

A-1. REFERENCE WASTE STREAMS

Five reference waste streams are generally used in the test programme known as NAEC (Novel Absorber Evaluation Club) — S1, S2, S3, S4 and S5. Other streams that have been used during this period are S6 and S-Cs, which is used as a screening basis for caesium absorbers. All waste streams are prepared from standard Amersham sources in 0.05M sodium nitrate and are adjusted to the test pH immediately before use. The standard test pH is 9, but other values may be used according to requirements and the specified absorber operational range.

The standard isotopic compositions and methods of analysis are as follows:

- NAEC S1 contains ^{137}Cs , ^{60}Co , ^{65}Zn , ^{51}Cr , ^{59}Fe , ^{54}Mn , ^{106}Ru , ^{203}Hg , ^{109}Cd and $^{110}\text{Ag}^{\text{m}}$ at a nominal level of 100 Bq/mL and is analysed by gamma spectrometry.
- NAEC S2 contains ^{99}Tc as the pertechnetate (TcO_4^-) at a nominal level of 40 Bq/mL and is analysed by beta scintillation counting.
- NAEC S3 contains $^{239}\text{Pu}(\text{IV})$ at 2 Bq/mL, ^{241}Am at 1 Bq/mL and ^{90}Sr at 5 Bq/mL. Analysis is by both alpha and beta scintillation counting.
- NAEC S4 is NAEC S1 plus 0.25 g/L ethylenediamine tetra-acetic acid (EDTA) added as the sodium salt and 0.15 g/L citric acid. Analysis is by gamma spectrometry.
- NAEC S5 contains $^{239}\text{Pu}(\text{IV})$, ^{241}Am and $^{237}\text{Np}(\text{V})$ at 1 Bq/mL plus 1 g/L NaHCO_3 (to produce anionic carbonate species in an alkaline solution). Analysis is by alpha scintillation counting.
- NAEC S6a contains 0.1 mg/L uranium (as uranyl nitrate) with 1 g/L NaHCO_3 prepared in demineralized water and is analysed for total uranium by inductively coupled plasma mass spectrometry (ICP-MS).

- NAEC S6b is the same as S6a but prepared in tap water (to introduce competition from calcium, in particular) and is analysed for total uranium by ICP-MS.
- NAEC S-Cs contains 100 Bq/mL ¹³⁷Cs and may be analysed by either gamma spectrometry or beta counting.

The waste streams used in the test will depend on the type of sorbent being examined. NAEC S1, S3 and S4 will be generally used for cation absorbers and S2, S4 and S5 for anion absorbers.

A-2. SORBENT CONDITIONING

Prior to their use, sorbents are conditioned by washing with water adjusted to the experiment pH value using a sodium hydroxide solution or dilute nitric acid. The washings are continued until the pH of the wash remains at its original value for two to three hours, or preferably overnight.

The absorber is used in a wet condition after decanting the wash liquor and removing the excess moisture with a cellulose tissue.

A-3. BATCH CONTACT EXPERIMENTS

One millilitre portions of the conditioned absorber are measured into 100 mL borosilicate conical flasks using a hypodermic syringe that has had the conical end removed to provide a full-bore syringe. Fifty millilitres of the reference waste stream is added and the flask sealed with a polythene stopper before being agitated gently at room temperature. Portions of the liquid (1.5 mL) are removed after 1, 2, 4, 6 and 24 h, centrifuged and then 1 mL removed for counting.

When magnetic absorbers are being tested, the conical flask is allowed to stand for two minutes on a disk permanent magnet (rare earth) to settle the absorber prior to sampling.

The analytical results are presented as Bq/mL and also as a calculated decontamination factor with reference to the original waste stream activity level:

$$\text{Decontamination factor} = \frac{\text{Activity per mL in the feed}}{\text{Activity per mL in the sample}}$$

No correction is made for the volume changes resulting from sampling.

A-4. COLUMN EXPERIMENTS

Glass columns of 1 cm bore are packed with 5 mL of absorber; 500 mL of water adjusted to the test pH is washed through each column to condition the absorber. The columns are operated at a throughput of ten bed volumes per hour (approximately 400 mL/d) using reference streams NAEC S1, S2 and S3, as appropriate. The pooled effluent is sampled daily for analysis. Results of testing and comparisons of some sorbent materials can be found in Ref. [A-1].

REFERENCE TO THE ANNEX

[A-1] HOOPER, E.W., KAVANAGH, P.R., WELLS, A.F., "The Novel Absorber Evaluation Club — a review of recent studies", *Advances in Ion Exchange for Industry and Research* (WILLIAMS, P.A., DYER, A., Eds), Royal Society of Chemistry, Cambridge (1999).

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Technical Committee Meeting

Vienna, Austria: 16–20 February 1998

Consultants Meetings

Vienna, Austria: 9–13 June 1997, 22–26 March 1999