## 3. LIQUID AND WET WASTE

### Basic principles of management (Berlin 1989)

Liquid waste is generally subjected to processing to reduce the volume of waste requiring disposal, to change the waste form, and to separate the radioactive components from the nonradioactive component in the waste stream. LLW processing generally takes place when it is necessary to satisfy regulatory requirements or if processing improves the overall cost effectiveness of disposal. Waste processing takes the form of treatment and/or conditioning. Treatment involves processing of the wastes to produce a waste stream that has a smaller volume and higher concentration of radioactivity than the original waste, and a second stream of sufficiently lower radionuclide concentrations than the original waste to permit release or reuse. Conditioning includes those operations that transform the LLW, with or without prior treatment, into forms acceptable for transportation and disposal.

Treatment can be further subdivided into transfer, concentration, and transformation technologies. Transfer technologies are employed to remove the radioactivity from the waste stream and transfer it to another medium, permitting reuse or discharge of the original waste stream or use of other treatment technologies that are more cost effective. These techniques are usually applied to liquid wastes, but may also be applied to regeneration of ion-exchange resins. Concentration technologies achieve a smaller waste volume by concentrating the radioactivity in the original waste form matrix. Transformation technologies also result in concentration of the radioactivity in the waste, but require changing the physical form of the waste. They are used for processing liquids, and both wet and dry solids. The effectiveness of each of these technologies is generally enhanced by a pretreatment step involving the removal of excess water in liquids and semisolids or such activities as sorting and/or shredding for dry solids.

The management of liquid radioactive waste (LW) encompasses each step in the system from the generation of the waste source to final disposal. The action taken at each step in the waste management process influences the type and volume of waste material shipped to the disposal site; in turn the design and operating constraints at the disposal site influence the other steps in the waste management process. Thus, it is necessary to consider the entire waste management system and the interactions between the various steps. With the increasing pressures to reduce the volume of waste shipped to disposal sites, the ability to minimize waste generation and to optimize subsequent processing to achieve a high degree of cost-effective volume reduction becomes a more significant aspect of LW management. Volume reduction pressures derive primarily from the increasing costs of transporting and disposing LLW, which in turn are driven by evolving federal and state regulations for parameters such as waste form and classification. These pressures will continue to intensify as the individual LLW compacts impose further constraints on LLW received at their disposal facilities. The determination as to what path these generated and collected wastes take to the disposal facility is a function of the following factors, which are considered sequentially : whether the as-generated LLW form can be packaged and shipped to a disposal facility, the acceptability of the packaged waste for disposal. The assessment of these factors leads either to the selection of treatment and/or conditioning steps prior to handling and ultimate disposal, or to the direct shipment of the as-generated and packaged waste to the disposal facility.

Waste forms and sources (Berlin 1989)

The physical form of the LLW is the primary consideration in the selection of the treatment alternative for the material, and in the choice of packaging approach. Liquid LLW streams are fluids with relatively low concentration of solids, generally less than 1% suspended solids. The "liquid" designation, however, may be applied to fluids containing up to 10% suspended solids, which would then be categorized as slurries. The predominant liquid LLW form are:

- Decontamination solutions generated from decontamination of building and equipment surfaces. These solutions are either water based, containing suspended solids and small quantities of chemicals and detergents, or chemical based, containing strong detergent agents that are usually also chelating agents.
- Chemical regenerative solutions produced from the regeneration of organic ion-exchange media such as demineralizer beds and resin beds.
- Contaminated oils arise from the oil/water separators used to treat floor and equipment drains, from hydraulic scrubbers used in system piping, and from used oil from reactor coolant pumps.
- Liquid scintillation fluids generated as organic solvents (e.g., toluene, xylene) in liquid scintillation counting operations.
- Miscellaneous liquid wastes produced from varying sources such as laundry waste, discharges from equipment and floor drains, process and steam condensate, steam-condensate cooling water discharge, and rinse water from cleaning and purging operations. Semisolids often are produced from the treatment of liquid waste, or as thick (high solids content) slurries (e.g., tailings) from a materials processing operating. This waste form covers evaporator bottoms, expended filter cartridges, biological waste (i.e., animal carcasses, animal bedding, excreta, vegetation, culture media), and miscellaneous slurries. Liquid radwaste is generated by nuclear fuel cycle operators and by institutions, hospitals, universities and government research centers.

Reactors (NPWT 1978)

Nuclear reactors are the major source of liquid radwastes. These can be classified as :

1. High-purity waste (BWR) is liquid of low electrical conductivity but potentially containing some suspended

(particulate) solids and dissolved oils. Major sources of high-purity waste are equipment drains from the dry well, the reactor, turbine, radwaste, auxiliary, and fuel-pool buildings; ultrasonic resin cleaner overheads; resin backwash and transfer water; filter backwash; phase separator decant liquid; and radwaste evaporator condensate.

2. Low-purity waste (BWR) is liquid of moderate to high conductivity and potentially has high suspended and/or dissolved solids content. Sources of low-purity waste include floor drains from the dry well, reactor, turbine, radwaste, and fuel-pool buildings; uncollected valve and pump seal leakoffs; and water resulting from dewatering of slurry wastes.

3. Chemical waste is liquid of high conductivity and high total (suspended plus dissolved) solids content. The primary source of this waste is the regenerant solution from ion exchange columns (condensate polishers). Other sources include laboratory drains and non detergent chemical decontamination wastes.

4. Detergent waste is liquid with a high suspended solids and organic chemicals (detergents, soaps, etc.) content. On the average, it contains very little radioactivity. Major sources of detergent waste are on-site laundry, personnel shower and detergent type decontamination wastes as well as laboratory wash water.

5. Miscellaneous waste (PWR) is composed of liquid having various qualities from a variety of sources, as the name implies, which may not be readily amenable to processing and reuse as reactor coolant make-up water. The main sources of miscellaneous waste are floor drains; outdoor controlled-area wastes; sampling station radioactive wastes; aerated systems and equipment drains; and primary system ion-exchange and filter wastes.

6. Secondary system waste (PWR) is liquid of low electrical conductivity from the secondary system (excluding condensate polishing regenerant solution, if any). Sources of such waste are mostly steam generator blowdown and turbine building drains.

Table 19 Expected average daily inputs to the liquid waste processing system of a 1000 MW BWR from normal operation (gallons/day).

Equipment drains : Drywell : 3400, Containment, auxiliary building and fuel pool : 3720, Radwaste building : 1060, Turbine building : 2960, Ultrasonic resin cleaner : 15000, Total : 26140;

Floor drains : Drywell : 700, Containment, auxiliary building and fuel pool : 2000, Radwaste building : 1000, Turbine building : 2000, Total : 5700;

Laundry drains : 1000, Lab drains : 500, Chemical lab waste : 100, Grand total : 33440;

## Reprocessing

In reprocessing operations about 5 $m^3$ of highly-active liquid waste is produced per tonne of fuel reprocessed. In the case of high burn-up oxide fuel this can be concentrated to about 0.25 $m^3$/t by evaporation for storage in the liquid form. At present it is the general practice in all countries to store this concentrate in high-integrity tanks. These tanks are housed, in thick-walled concrete cells, and cooling arrangements are provided to remove fission product decay heat. The following basic principles relating to the management of highly-active liquid waste are now widely accepted. Present techniques for conditioning and storage of this waste are entirely satisfactory for the protection of the human environment in the time-scale of several decades. In the longer term, additional study is required to provide the most effective system for the isolation of this waste from the human environment for the very long periods of time that are necessary. Large-scale transportation of liquid high-level waste is to be avoided. High-level liquid wastes should be solidified at the earliest practicable time for safe extended storage. A large engineering development and scientific effort is now directed to the development of solidification processes, e.g. the PIVER and ROTARY CALCINER processes in France, the VERA project in Germany, the SPRAY CALCINER process in the United States and the FINGAL/HARVEST process in the United Kingdom. It is anticipated that the amount of vitrified waste produced by these techniques will be about 0.075 $m^3$/t of fuel reprocessed.

With present reprocessing techniques, about 60 $m^3$ of medium-active liquid waste (containing about 10 Ci/$m^3$) may be expected to be produced for each tonne of fuel reprocessed. These wastes comprise: aqueous raffinates from the second and subsequent solvent extraction cycles, liquids used for purifying solvent for recycle within the solvent extraction system, liquids used for scrubbing some active gas streams, condensate from steam-stripping of highly active liquid waste, distillate from the highly-active liquid waste evaporation process. It is anticipated that there will be significant improvements in reprocessing techniques which will reduce significantly the problems of dealing with this type of waste. The main improvements expected are: improved activity removal in the first cycle solvent extraction which will reduce the amount passing into the medium-active waste streams, and the reduction in the use of salts in the main processes (solvent washing and partitioning) which will allow some medium-active waste streams to be routed with the highly-active liquid waste with higher waste concentration factors achieved, and smaller volumes of solidified waste.

## Institutions (Berlin 1989)

Volumes of liquid scintillation waste requiring disposal have decreased significantly in the last few years. The scintillation fluids are generally used to detect beta-emitting nuclides and many are primarily composed of flammable organic solvents such as toluene. Such fluids are therefore a mixed (radioactive and hazardous chemical) waste. Liquid scintillation vials containing specified small amounts of 14-C and 3-H have been exempted by the NRC from having to be disposed as LLW and may be disposed as a chemical waste instead, frequently by incineration. Use of aqueous-based scintillation fluids rather than organic materials enables the fluid to be discharged to the sanitary sewer in accordance with 10 CFR Part 20 rather than as LLW. Lack of coordinated regulations (between NRC and EPA) results in mixed wastes being ineligible for disposal by land burial solely in accordance with 10 CFR Part 61. Such wastes are currently being stored at the point of generation pending resolution of regulatory requirements. Similar storage is being used for radium sources that are not subject to 10 CFR Part 61 regulation. Such wastes are currently being accepted at one disposal site if special pre approved packaging is used. Other liquids produced at institutions from preparation and analysis of samples such as elution of Tc generators, radioimmunoassay procedures, and radioactive tracer studies are generally shipped in packages containing absorbent material equal to twice the volume of liquid to comply with transport regulations (10 CFR Part 71) designed to limit the release of radioactive material in transit.

## Management of wet waste (NPWT 1978)

Many nuclear power plants are moving toward a concept of "maximum recycle" or near "zero release" for radioactive liquids. Either of these modes of operation necessarily results in an increased volume of solid radwaste to be shipped off-site for disposal. Although many of the early nuclear plants still ship solid wastes in the form of dewatered sludges and resins (powdered or bead) or evaporator concentrates immobilized by entrapment on sorbent materials, some of these older plants are now being, or have been, serviced by mobile solidification units. All new plants now being licensed are required to have solidification systems. The boundary between liquid and solid radwaste systems is not easily defined. Most utilities and architect-engineer firms define the start of the solid radwaste system as the tanks or receiving vessels which collect the scurries from the demineralizers, filters, evaporators, and reverse osmosis equipment. Treatment of these wet wastes can be broken down into four basic subsystems, consisting of waste collection, waste pretreatment and volume reduction, solidification agents and mixing, and packaging, container handling, and storage. The waste collection subsystem is usually provided by the utility itself or through its architect-engineer. The subsystems required for solidification and packaging are frequently purchased from a single supplier and are chosen on the basis of compatibility with the solids pretreatment subsystem which may be supplied by a different vendor. The interface between the solids pretreatment and solidification subsystems is a critical area in radwaste treatment because the amount of residual water associated with the treated solids can be a factor in determining what solidification method would be most economical. Likewise, the suitability of a pretreatment subsystem could also depend upon the prior choice of a particular solidification process. Some general considerations apply to all solidification systems, among them such things as location of solidification agent handling equipment in low-radiation areas to minimize exposures to operating personnel; compatibility of the equipment with the chemical and physical properties of the solidification agent employed (e.g., corrosion resistance of catalyst tanks and piping in liquid systems, and dust containment in systems using cement); and environmental restrictions on solidification agent storage (e.g., relatively low temperature for urea formaldehyde, and low humidity for cement).

## Waste collection

Adequate tankage for waste collection is essential to smooth power plant operation. Under normal circumstances, provision for at least 60 days of radioactive decay for primary system wastes such as reactor water clean-up or chemical and volume control system resins or sludges prior to solidification is desirable for eliminating the bulk of short-lived isotopes. For other wastes which ordinarily have much lower radioactivity levels (e.g., radwaste filter sludges and evaporator concentrates), 30 days decay is usually sufficient. In addition to providing time for radioactive decay, the waste collection tanks can also provide surge capacity to accommodate periods of abnormally high waste generation or outages in the solid waste processing system. The tanks should be designed with capability to receive all liquid inputs to the waste solidification facility including auxiliary streams under all anticipated conditions.

## Waste pretreatment

Pretreatment equipment for solids and liquids must be designed to reliably process the expected range of physical and chemical stream compositions. Special design considerations may be necessary to ensure that dewatered or concentrated radioactive solids can be handled remotely with minimum equipment contact by operating and maintenance personnel. Where manual access to solids pretreatment equipment is necessary, the capability for completely flushing all radioactive materials from the affected parts must be designed into the system. If compressed gases are used for the drying or transport of radioactive materials, appropriate air filtration devices are needed to remove particulates that may be entrained in the exhaust gas stream. Waste pretreatment is basically a volume reduction process serving to minimize the quantity of waste to be solidified and shipped off site.

## Dewatering

The wet wastes generated at a nuclear plant contain large volumes of water. Removal of this water from spent bead or powdered resins and filter sludges can be accomplished by any of several methods, among them: decantation (either in the collection tank or in a separate decant tank), centrifugation or filtration. Decantation or in-tank filtration can reduce the water content of the solids to the range of 70 to 80 % by weight. The centrifuge is more efficient at water extraction and is capable of producing solids containing only 50 % water on a weight basis. Travelling-belt and centrifugal-discharge filters give solid products containing 50 to 70 % water. Most evaporator concentrates at BWRs are 10 to 25 % sodium sulfate, where as at PWRs they are 10 to 20 % boric acid. In the past, usual practice has been to solidify these slurries without further pretreatment. The amount of residual water is intimately related to the solidification procedure selected. A waste containing 25 % solids is about the right content for incorporation in cement. If the water content of the pretreated slurry is 50 % or less, some water or liquid waste would probably have to be reintroduced to maintain the consistency required for cementing. Some BWRs that have centrifuges have added evaporator concentrates to dewatered filter sludge for the purpose of providing the additional water needed to make a cement product.

Wet waste treatment technologies (Berlin 1989)

Semisolids (wet solids) require treatment and/or conditioning to reduce the free water content to less than 1% and thus make them acceptable for disposal. The selection of the appropriate technology for processing semisolids is dependent upon a number of characteristics of the waste, the most important of which are waste generation rate, free-water content, chemical characteristics, and concentration and specific activities of the radionuclides in the waste. Most of the liquid HLW treatment techniques are also applicable to wet solids. Conditioning technologies (solidification and/or sorption) may also be more cost effective than treatment technologies in achieving the stipulated low free-water content in the as-shipped waste packages. Filtration could be used to treat semisolids if the liquid content of the waste is greater than 90%. Chemical regeneration is another transfer technology that can be used for the removal of radionuclides from loaded ion-exchange resins. The resultant liquid waste stream will require further treatment. Among the available concentration technologies, centrifugation is a technique that can be applied to semisolids as well as liquids, with the primary application being dewatering of resins and filter sludges. Sedimentation is used to treat high water-content wet solids (slurries, floor drains) to remove solids as a step before use of ion-exchange techniques. Liquid removal techniques using concentration technologies that are particularly applicable to treatment of semisolids are dewatering and drying. In dewatering, either pumping and/or gravitational drainage is used to remove the water from a semisolid. A commonly employed approach for treating ion exchange resins, called "in-container dewatering," involves the use of multiple filter elements placed in a disposable container and connected to a pump. Drying uses heat to drive off the water to produce a dry solid. Drying has been used at DOE facilities and will undoubtedly be more frequently applied at commercial facilities in the future to meet the 1% free water requirement at competitive costs.

The conditioning technologies of solidification and absorption are applied to the treatment of semisolids. In applying solidification technology, the choice of the binder material based on relative economics to yield a monolith that meets regulatory criteria is generally the governing factor. This choice is dependent on factors such as the extent the semisolid must be dewatered prior to solidification, the chemical compatibility of the waste and binder, the degree of mixing needed to yield an acceptable product, the packaging efficiency of the solidified material (i.e., the bulk volume of the dewatered wet solids relative to the volume of the solidified product), and the relative cost of binder materials. As a rule, all other factors being equal, the technology that produces the highest packaging efficiency is usually the most cost effective. The primary application of absorption technology is also to reduce free water levels in packages to within established limits.

### Absorption (Berlin 1989)

Absorption is a conditioning technique, used primarily for institutional liquid LLW, in which the liquid is stored within a porous material such as vermiculite and diatomaceous earth. The liquid, which substantially increases the total volume when absorbed, can be subsequently extracted. Generally, these sorbants can be used by themselves because they do not immobilize the free liquid and thus prevent the waste package from meeting NRC and DOT regulations. However, they may also be used as additions to the solidification agents previously discussed to produce the necessary monoliths. Vermiculite, silica, and selected clays are inorganic materials that have low leachability and long-term stability, but have a number of disadvantages including being usually limited to alkaline wastes and not providing volume-reducing capability. Organic sorbents, which generally have larger surface areas and significant absorptive and ion-exchanging properties, are also being developed. These materials can be used to absorb residual free water, oils, and solvents. One class of organic polymers, referred to as "Superslurpers," has been demonstrated to be useful in cleaning up radioactive spills because of its high absorption capacity with cement to solidify tritium waste.

### Sludge handling (Collins 1960)

The chemical sludges produced in the treatment of radioactive liquid wastes are often colloidal in nature, do not settle well and are difficult to filter. Normal pressure or vacuum filtration, though possible, produces a cake which is bulky and may contain up to 84 % water. Centrifuging gives no better results and the centrifuged effluent often contains additional colloidal matter formed during the process. At Harwell, the majority of the sludges produced undergo a freezing treatment. In this process the sludge is frozen, thawed and the resultant liquor filtered. The freezing treatment concentrates the electrolytes present around the colloidal particles thus giving rise to coagulation. The final solid matter is granular and settles and filters extremely well. The solids content of the sludge cake, after filtering, is often twice that obtained by straight filtration of the untreated sludge and the final sludge volume is approximately 50 % of that normally obtained. The freezing must be complete and, for maximum benefit, the sludge must be frozen slowly. After thawing violent agitation should be avoided. The sludges discharged to the graveyard in Russia, referred to above, also undergo freezing during the winter months. Very similar results are obtained, the volume after thawing and filtering being approximately 30 % of the original. Both British and Russian experience shows that no radioactivity is released from the sludges during the freezing process.

## Management of liquid radwastes in NPPs (NPWT 1978)

A problem that arises in the production of electricity by using nuclear power is the generation of wastes that contain or are contaminated with radioactive nuclides. The liquid radwastes generated by operation and maintenance activities at light water reactor (LWR) plants depend upon several factors. Foremost among these are whether the plant has a boiling water reactor (BWR) or a pressurized water reactor (PWR). Other factors include type and arrangement of equipment as well as operating philosophy.

The development of facilities and equipment to collect and process liquid radwastes has given the nuclear industry the capability to hold releases of radioactive material in liquid effluents within applicable regulatory limits. These limits are most readily met by reducing the volume of liquids discharged or by decontaminating the liquids to a high degree before discharging them to the environment. A liquid radwaste processing system should be designed to allow the maximum reuse of waste water in the plant consistent with the overall plant water balance. There are a number of Nuclear Regulatory Commission (NRC) Regulatory Guides, Standard Review Plans, and Effluent Treatment Systems Branch Positions which together provide a detailed picture of the present requirements that must be met in the design and operation of liquid radwaste processing facilities. The main here is consideration of methods or unit operations (viz., evaporation, ion exchange, filtration, reverse osmosis, and centrifugation) used to treat or decontaminate liquid radwaste.

## Reactor radwaste processing systems

A liquid radwaste treatment representative of that used in many current BWR and PWR plants is:

High-purity waste - Since it has low electrical conductivity and potentially contains some suspended solids, high-purity waste is usually processed by filtration and ion exchange. After analysis, the processed waste is generally recycled to the condensate storage tank.

Low-purity waste - If the electrical conductivity is low (generally less than 100 mcmho/cm at 25 C), low-purity waste is normally processed by filtration and ion exchange; but, if the conductivity is higher, evaporation is used. Whether or not a filter precedes the evaporator depends upon the design (susceptibility to fouling) of the evaporator and the properties (extraneous undissolved substances) of the feed. If required, condensate from the evaporator can be treated further by the high-purity waste ion exchange unit or by a separate ion-exchange polishing unit.

Chemical waste - Because it has a high concentration of dissolved and undissolved solids, chemical waste is processed by evaporation in most cases. Polishing of the condensate by ion exchange may be needed to meet recycle or discharge requirements.

Detergent waste - Since it contains very little radioactivity, but does contain appreciable amounts of suspended solids and organic chemicals which can adversely affect the operation of conventional evaporators or ion-exchange units, detergent waste is normally processed by filtration only.

Miscellaneous waste - This waste is usually processed by evaporation followed by condensate polishing in an ion exchange unit. Evaporation is used since it can efficiently separate water from both soluble and insoluble impurities. Feed to the evaporator may be filtered to reduce the deposition of material on sensory elements and heat transfer surfaces. Condensate that meets specifications can bypass the polishing ion exchange unit.

Secondary system waste - Steam generator blowdown is commonly processed by filtration and ion exchange (sometimes utilizing the condensate polishing ion exchange unit). While liquid from the turbine building drains is not expected to require treatment because of its low radioactivity content, provisions to process it through the miscellaneous waste treatment system should be available.

## Volume reduction

In recent years volume reduction has become an increasingly important factor in nuclear plant waste management since operating data have shown that actual waste volumes are much larger than originally expected while disposal costs have continued to increase dramatically. The prime advantage of a large volume reduction is the substantial savings in transportation and handling costs between the plant and burial sites due to the fewer shipments required. Another less obvious advantage is lower plant construction costs owing to smaller on site space requirements for storing filled shipping containers.

Several types of volume reduction equipment are available that can produce solids from wet wastes (e.g., evaporator concentrates) that have final water content between almost nothing and 50 to 60 %. The fluid-bed dryer, the fluid-bed incinerator calciner, the thin-film evaporator, and the crystallizer are such examples. Interfacing these units with a cement solidification process can present the same problem (sufficient water to make a workable paste) as described above for combining centrifugation with cementation. Similarly, other factors, which may or may not depend upon residual water content, must be taken into account when one of these volume reduction methods is tied to a solidification system using organic polymers such as urea-formaldehyde resin or water-extended polyesters. The asphalt extruder/evaporator can unite volume reduction and solidification in a single operation, but in some cases it may be advantageous to precede the extruder with a fluid-bed dryer or a thin-film evaporator. Descriptions of some of the equipment commonly used in volume reduction are given below.

The requisite cleanup of liquid streams contaminated with radionuclides is obtained by the selection and combination of a number of physical and chemical separations processes or unit operations. Presently, the unit operations used most frequently for treating liquid radwaste are evaporation, ion exchange, and filtration. Used to a lesser extent are centrifugation and reverse osmosis.

### Drying (NPWT 1978)

A fluid-bed dryer with an optional incinerator was developed to produce anhydrous, free-flowing, granular solids from nuclear power plant liquid radwastes. For example, the initial concentration of evaporator concentrates typically ranges from 5 to 25 % salts ($Na_2SO_4$, $Na3PO_4$, $Na_2B4O_8$, or $NaBO_2$). Such wastes can be processed by the fluid-bed dryer at rates of up to about 190 litres (50 gallons) per hour. In the electrically heated (650-950 F) fluidized bed, the air-atomized liquid waste is vaporized upon injection, leaving behind as residue the anhydrous solid product. These granular waste solids are removed from the dryer by the product conveyor and transported to a storage hopper. The water vapor and fluidizing air containing some entrained fine solid particles are passed through a gas/solids separator where the bulk of the fines is removed and discharged to the product conveyor. The off-gas from the gas/solids separator is directed to a venturi scrubber where virtually all particulates remaining in the gas are removed. The water vapor originally produced in the fluid bed is then condensed in a packed scrubber condenser unit and sent back to the radwaste evaporator. Most of the effluent air is routed through an exhaust gas heater prior to recompression and recycle to the fluid-bed dryer. A small portion of the exhaust air is continuously bled from the system via an absolute filter and a charcoal absorber, monitored for radiation, and discharged to the atmosphere. The granular solids from the dryer may be rendered less mobile by incorporation in asphalt.

### Drying and incineration

A volume reduction system that is both a fluid-bed dryer (calciner) and incinerator has been developed. The unit operates at a higher temperature than the Aerojet system and can burn spent ion exchange resins as well as produce anhydrous granular solids from evaporator concentrates. Also, solid combustible wastes such as paper, rags, and contaminated clothing can be shredded and then injected into the incinerator/calciner by a jet air pump or conveyor. A silver zeolite bed, for removal of iodine from the off-gas, is located between the final high efficiency particulate air (HEPA) filter and the discharge blower. This off-gas cleanup is especially important when ion exchange resins are burned. The dry solid product from the system is removed by gravity and can be incorporated into one of the immobilization agents. A thin-film evaporator consists typically of a vertical or horizontal tube partially heated with a steam jacket. A coaxially mounted rotor hurls the liquid feed against the heated wall by centrifugal force. The rotor is equipped with blades that either maintain a close clearance with or actually ride on the film of liquid adhering to the wall. Heat is transferred from the outside to the inside of the cylindrical tube causing vaporization of liquid in the thin film. The vapor is exhausted through the vapor outlet after passing through the space between the rotor blades and the internal entrainment separator. The product (slurry or solid) can be incorporated into one of the immobilization agents to be described in a later section.

## Crystallization

Crystallization (F 6) is another method used for reducing the volume of evaporator concentrates at both PWRs and BWRS. The radwaste crystallizer is essentially a specially designed forced-circulation evaporator consisting of a vapor body, recirculation pipe, large recirculation pump, and a two-pass vertical heater. Steam applied to the shell side of the heater condenses outside the tubes and imparts heat to the liquid circulating inside the tubes. Processing rates up to 120 lpm (30 gpm) are expected to be readily achievable. Supersaturation, nucleation, and crystal growth within the circulating magma are the mechanisms involved in producing scurries containing up to 50 % salt by weight, depending upon the solute solubility.

## Evaporation

Evaporation is the process by which the volatile and nonvolatile (dissolved and undissolved) components of a solution or slurry are separated via boiling away the volatile component. It is a unit operation that has wide application in the nuclear industry for reducing waste volumes and the amount of radioactive nuclides in liquid effluents. Evaporation can be used on solutions or scurries having vastly different compositions and concentrations; however, it is most effectively used on liquid radwastes having high concentrations of impurities. Speaking broadly, when compared to ion exchange, the lowest electrical conductivity that a radwaste can have and be economically processed by evaporation is approximately 100 mcmho/cm (at 25 C).

An evaporator is a device designed for transfer heat to a liquid which boils and to separate the vapour thus formed from the liquid. The unit or building block in which heat transfer takes place is called a heating element or calandria. The unit in which vapour-liquid separation takes place is called a body, vapour head, or flash chamber. The term body is also used to denote the minimum building block of an evaporator, i.e., one heating element and one flash chamber. A radwaste evaporator system consists basically of the following building blocks: a heating element; a flash chamber; one or more deentrainment devices to separate or disengage liquid droplets from the vapour; a condenser to cool and convert the vapour back to liquid; and pumps as required to feed the system, to circulate the contents where forced circulation is employed, and to discharge the concentrated liquid (bottoms).

The principal engineering considerations involved in the design of a radwaste evaporator are heat transfer and vapour-liquid separation. Reliable and maintenance-free operation are important factors which must also be seriously taken into account with a radwaste evaporator system. The selection of corrosion-resistant materials of construction and a design that minimizes the loss of heat-transfer surface (capacity), due to films or solids of low thermal conductivity being deposited on the surface, are vital to avoiding operational and maintenance problems. Other factors influencing the design include the amount by which the feed is to be reduced in volume and total operating costs.

## Types of evaporators

Circulation of liquid past the heating surface of an evaporator may be induced by the density variations brought on by boiling (natural circulation) or by mechanical means such as a pump (forced circulation). The heating element may be built into the evaporator body (internal heater) or separated from the body (external heater). Heaters may be vertical or horizontal, long- or short-tube.

### Natural circulation

The natural-circulation short-tube vertical evaporator, also called calandria or standard evaporator, is one of the earliest types still in widespread commercial use. Circulation of liquid past the heating surface is induced by boiling in the tubes, which are usually 2 to 3 in. (5-8 cm) diameter by 4 to 6 ft (1.2-1.8 m) long. The body vessel is a vertical cylinder and the tubes are expanded into horizontal tube sheets that span the body diameter. The tube bundle is located in the centre of the body diameter and the bottom tube sheet is supported above the vessel bottom. The circulation rate through the tubes is many times the feed rate; so, there must be passage from above the top tube sheet to below the bottom tube sheet. An annular downtake between the tube bundle and the vertical vessel walls is commonly used. So that frictional losses through the downtake do not appreciable impede circulation up through the tubes, the area of the downtake should be of the same order of magnitude as the combined cross-sectional area of the tubes. Circulation and heat transfer in this type of evaporator are strongly affected by the liquid level. Highest heat-transfer coefficients are achieved when the level, as indicated by an external gage glass, is only about halfway up the tubes. Slight reductions in level below the optimum result in incomplete wetting of the tube walls with a consequent increased tendency toward the deposition of solids on the tubes and a rapid reduction in capacity. When this type of evaporator is used with a liquid that has properties which contribute to salting or scaling, it is customary to operate with the liquid level appreciably higher than the optimum and usually appreciably above the top tube sheet. In evaporator terminology, salting is the growth on body and heating-surface walls of a material having a solubility that increases with increase in temperature; scaling is the deposition and growth on body walls, and especially on heating surfaces, of a material undergoing an irreversible chemical reaction in the evaporator or having a solubility that decreases with an increase in temperature; fouling is the formation of deposits other than salt or scale and may be due to corrosion, solid matter entering with the feed, or deposits formed by the condensing vapour. Circulation in the standard short-tube vertical evaporator is dependent entirely on boiling; thus, suspended solids will settle out when boiling stops. The use of natural-circulation evaporators at LWR plants is being phased out. The main reason for this appears to be the high degree of salting, scaling, and fouling experienced with LWR plant waste when this type evaporator is used. These phenomena can be exaggerated by the low liquid velocities and boiling in the heater-exchanger tubes inherent in natural circulation evaporators. The deposition of material with low thermal conductivity on the tube walls leads to reduced heat transfer and concomitant reduced capacity. Continued deposition can lead to blocked or plugged tubes which require cleaning by chemical and/or mechanical means. Frequent cleaning results in greater downtime and exposure of personnel to radiation.

### Forced-circulation

The forced-circulation evaporator is generally conceded to be suitable for the widest variety of evaporator applications. The use of a pump to ensure circulation past the heating surface makes possible separation of the heat transfer, vapour-liquid separation, and crystallization functions. The pump withdraws liquid from the flash chamber and forces it through the heating element back to the flash chamber. Circulation is maintained regardless of the evaporation rate so this type of evaporator is well suited to crystallizing operation where solids must be maintained in suspension at all times. The liquid velocity past the heating surface is limited only by the pumping power needed or available and by accelerated corrosion and erosion at the higher velocities. Tube velocities normally range from a minimum of about 1.2 m/s (4 ft/s) in evaporators containing five % or more solids, up to about 3 m/s (10 ft/s) in evaporators having liquid containing only a small amount of solids. Even higher velocities can be used when corrosion is not accelerated by erosion. Forced-circulation evaporators are frequently of the submerged-tube type, where the heating element is placed far enough below the liquid level or return fine to the flash chamber to prevent boiling in the tubes. The hydrostatic head must be sufficient to prevent boiling since this prevents salting of the entire tube. A restriction orifice or piping pressure drop in the return fine to the flash chamber can also prevent boiling in the tubes. This allows more flexibility in building arrangement. Evaporators of this type have horizontal or vertical heating elements (usually two-pass), but the vertical single-pass heating element is used wherever sufficient headroom is available. The vertical element takes up less floor space and is less prone to sedimentation than a horizontal heater. Forced-circulation evaporators of the submerged-tube and/or restriction-orifice type are relatively immune to salting in the tubes since no supersaturation is generated by evaporation in the tubes. The tendency toward scaling is also reduced since supersaturation in the heating element is generated only by a controlled amount of heating and not by both heating and evaporation. In these evaporators, all heat is imparted accessible heat, resulting in a temperature rise of the circulating liquid that reduces the overall temperature difference available for heat transfer. Temperature rise, tube proportions, liquid velocity in the tubes and head requirements on the circulating pump all influence the selection of circulation rate. A typical evaporator design of the forced-circulation units, which have gained favour in the nuclear power industry, features a large flash chamber with a sloped or conical bottom, a vertical external reboiler, and a mechanical deentrainment device followed by a distillation tower (plate or tray column). When forced circulation is combined with a conical bottom, the undissolved solids in the evaporator can be kept in suspension by the high circulation rate. During concentrate pumpout, the reboiler pump is kept in operation. The result is a reduction in the buildup of radioactive solids in the evaporator vessel bottom. Among the difficulties reported to be frequently encountered with forced-circulation evaporators are plugging of tube inlets by salt deposits detached from the walls of equipment, poor circulation caused by higher than expected head losses, salting due to boiling in tubes and corrosion or erosion.

### Operating characteristics

There are several modes in which evaporators can be operated: batch, semibatch, and continuous. In batch operation, the evaporator initially contains the entire quantity of liquid to be processed. In semibatch operation, which is most commonly used in radwaste service, the feed is continually added to maintain a constant level in the evaporator until the entire charge reaches a final density for drumming in the solid radwaste system. In continuous operation, feed and product (bottoms and distillate) flows are kept constant; the operation is at steady state.

## Decontamination factors

The decontamination factor (DF) for radwaste evaporators is normally expressed as the feed to distillate concentration ratio. Evaporators are designed to produce a specific separation from the bottoms to the distillate at the maximum bottoms concentration. Hence, it is only initially when the liquid in the evaporator body is at the same composition and concentration as the feed (for those evaporators in which the feed mixes with the concentrated liquid) that the DF and the SF are the same. Reductions in the SF (and DF) may result from foaming, splashing, entrainment, or volatilization of solute.

Table 20 Decontamination factors used by NRC for evaporators.

| Type of waste | All* | Iodine |
|---|---|---|
| No Detergent Waste | 10000 | 100 |
| Detergent Waste Included | 100 | 100 |
| Boric Acid | 1000 | 100 |

* except iodine

## Separation factors

The separation factor (SF) is defined as the bottoms to distillate concentration ratio. Separation factors in the range of 100000 - 1000000 for nonvolatiles can be obtained for a simple evaporator with a cyclone separator. The addition of a reflux column to the evaporator plus an entrainment separator, if properly designed, can add several orders of magnitude to the SF. Volatilization of solute (e.g., iodine and boron) is an important concern in the design and operation of radwaste evaporators. Use of sieve trays or packed columns with reflux, the adjustment and control of the pH, and tile addition of completing agents, are the most common ways of reducing this effect.

## Materials of construction

The heating tubes, evaporator body-portion containing concentrated liquid, and associated piping should be constructed of materials that can withstand the boiling concentrate. In this deliberation, attention must be given to the impurities that will be present. For example, chloride stress corrosion has been a problem in several evaporators used at LWR plants. Chlorides will normally be present in floor drains, miscellaneous waste streams, and the condensate polishing regenerant streams.

## Design considerations

Foaming losses usually result from the presence in the evaporating liquid of colloids or of surface-tension depressants and finely divided solids. Foam tends to increase the entrainment by raising the effective liquid level, decreasing the amount of disengagement space, and by supplying bubbles that can be carried by the vapour. Antifoam agents, such as silicone preparations, are very effective in reducing foam. Serious foaming can force an evaporator to be operated at reduced rates to maintain the desired SF.

Splashing occurs when the boiling is violent and erratic. Splashing losses are usually insignificant if a reasonable height between the surface of the boiling liquid and the exit of the evaporator body has been provided. Entrainment losses result from the presence of droplets in the vapour that cannot settle against the upward vapour current. The extent of losses will be dependent on the size distribution of droplets and the vapour velocity. Larger droplets are the major source of entrainment losses unless they settle back into the liquid or are removed by entrainment separators.

Entrainment increases at higher vapour velocities; thus the SF generally decreases with increased vapour flow rates. At very low vapour flow rates, small droplets are produced by the gentle boiling and are also carried up by the vapour. For an evaporator without deentrainment devices, an optimal vapour flow rate exists for minimum entrainment at a mass vapour velocity of approximately 10 to 20 $g/cm^2/h$. Cyclone separators and knitted wire mesh are often used to the carryover of liquid as entrainment. Reflux sieve trays and packed columns are also used to reduce entrainment; however, these devices are primarily used for obtaining a better separation factor for volatile components such as iodine or boric acid in a PWR. Decontamination factors for deentrainment devices generally increase with mass vapour velocity; therefore, the desired operational point is where the product of the SF of the evaporator and the DF of the entrainment device is at a maximum. This point does not necessarily occur at the vapour flow rate at which the evaporator SF is a maximum.

The design of the heat exchanger should minimize the deposition of scale or crud during operation so that filtration of the feed is not required. The use of high liquid velocities and the suppression of boiling in the tubes tends to reduce fouling of the tube bundle. The control system should be such that after the initial concentration in the normal mode, the feed can be terminated and the final concentrating accomplished by reducing the volume in the evaporator body. This decreases the time the heating surfaces are in contact with the concentrated liquid and lessens the potential for fouling.

The evaporator should be designed so that chemicals for cleaning may be added easily. Attention must be given to designing the evaporator for easy and quick maintenance so that exposure of personnel to ionizing radiation may be kept at a minimum. This means that the evaporator components should be separated to the maximum extent possible. Individual components may be in separate cubicles (cells) or separated by shielding walls.

### Ion exchange (NPWT 1978)

Ion exchange is generally used for purifying liquid radwastes having an electrical conductivity less than about 1E-2 mhos/m at 25 C. In this range, it is usually more economical than evaporation. Ion-exchange resins are insoluble high molecular weight polyelectrolytes which can reversibly exchange their mobile ions with those of equal charge from the surrounding solution. Exchangers in which the anionic portions are able to react, or are mobile, are anion exchangers; those in which the cationic portion is mobile, are cation exchangers. Although the nature of the exchangeable ions associated with a given ion-exchange resin is determined, in general, by the user, resins used in radioactive liquid waste applications are usually either in the hydrogen or in the hydroxyl form. However, other forms such as lithium, potassium, ammonium, and borate are also used. The exchange involves no permanent alteration in the structure of the resin. The very nature of the ion-exchange process demands that radionuclides in various liquid streams at power reactor plants be in ionic form for this decontamination process to be effective. Non-ionic forms [insoluble particulates, colloids, as well as neutral molecules, and neutral complexes] which are incapable of undergoing ion exchange can be responsible for poor solution decontamination. Varying fractions of some particulates and colloids may pass through the resin bed, and the part which is trapped may coat the resin particles and reduce their efficiency.

Table 21 Characteristics of typical ion-exchange resins.

| Type | FG | R | RL - % | C-eq/l | pH | MOT-F |
|---|---|---|---|---|---|---|
| SA | S | $H_2SO_4$ | 95 | 1.5-2 | 1-14 | 250 |
| SB | QA1 | NaOH | 80 | 0.5-1 | 1-14 | 140 |
| SB | QA2 | NaOH | 80 | 0.5-1 | 1-14 | 100 |
| WB | amines | NH4OH | 95 | 1.5-2.5 | 1-7 | 200 |

SA = Strong acid, SB = Strong base, WB = Weak base, FG = Functional Groups (S = Sulfonic, QA = Quaternary ammonium (types 1 or 2)), R = Regenerant, RL = Regeneration level, C = Capacity, MOT = Maximum operating temperature.

### Type of ion-exchange resins used in NPP

Styrene-divinylbenzene copolymers are the network materials used in the preparation of synthetic ion-exchange resins widely employed in nuclear power plants. Ionic forms other than H+ and OH- are also available for specific applications, as mentioned above.

Strong-acid cation resins (H+ form) are characterized by their ability to readily interact with a weakly ionized or neutral salt, dissociating the salt into its acid in solution and converting the resin to the salt form. Likewise, a strong-base anion resin (OH- form) will dissociate a weakly ionized or neutral salt into its base in solution, simultaneously converting the resin to the salt. A disadvantage common to these resins is low regeneration efficiency, i.e., they require a large excess of regenerants in relatively high concentrations. In contrast, a complete regeneration of both weak-acid cation and weak-base anion resins is achievable with nearly stoichiometric amounts of regenerants. However, they have disadvantages in that they are slow and less effective in dissociating weakly ionized and neutral salts. In addition, the ion-exchange efficiency of weak resins is considerably more sensitive to the solution pH than that of strong resins. Further, the weak resins are generally more expensive and have a shorter life expectancy than the strong resins. Nevertheless, the smaller amounts of regenerants required for weak resins may be an important advantage in view of possible problems associated with disposal of regenerants. The quality of water being used in LWR nuclear power plants must be very high in order to minimize corrosion problems, and to reduce formation of neutron activation products and radiochemically produced compounds. To satisfy this requirement, nuclear grade ion-exchange resins were introduced commercially. They are basically the same as the regular grade with regard to structure, but have much smaller amounts of leachable impurities (organics in particular); more uniform particle sizes (cation resins: -0.45 mm; anion resins; -0.6 mm, < 1% fines); and a higher degree of conversion to the desired ionic form (>95% for cation resins, >80% for anion resins).

## Factors affecting performance

The performance of an ion exchange system is governed by the physical and chemical properties of the exchange resin as well as by the operating conditions. Important properties of the ion exchange resin include exchange capacity, swelling equilibrium, degree of cross-linking, resin particle sizes, ionic selectivity, ion-exchange kinetics and chemical and physical stability. Important operating conditions include chemical and physical forms of species in feed solution (ionized or non ionized species, ionic sizes, and valences), temperature, pH, and flow rate of feed solution, design and dimension of ion exchange beds (method of packing, whether a multistage system with separate cation and anion exchanger units or a mixed-bed system is used, height-to-diameter ratio), and level, or degree of completeness, of regeneration.

## Selectivity

Numerous theories have been developed to explain factors influencing ionic selectivity. However, no satisfactory quantitative prediction of this property can be made for a system involving a multicomponent ionic mixture. Current practice in the use of ion-exchange systems is to estimate the selectivity based on empirical rules usually applicable to dilute aqueous solutions at ordinary temperatures. The selectivity tends to diminish with increasing concentration and temperature, but exceptions to the rules are found.

## Particle size

Particle sizes of regular-grade strong-acid cation and strong-base anion resins commonly used in nuclear applications generally range from approximately 0.4 to 0.7 mm. The use of small particle size resin will increase the number of theoretical plates in a given column; however, the pressure drop across the ion exchange column will be greater for the same flow rate. Consideration of the advantage of small particle sizes led to the development of a fine powdered mixture of cation and anion exchange resins (> 90% -325 mesh) which is known under the trade name "Powdex". One use of such powdered resins involves coating the outside surfaces of filter cartridge elements [nylon; 2.5 in. (6.4 cm) diam by 10 in. (25 cm) high; -0.5 $ft^2$ (0.046 $m^2$) surface area] with thin layers [1/8 to 1/2 in. (1/3 to 1-1/3 cm)] of resin. In these arrangements, the resin functions both as a filter and as an ion exchanger. Four or more cartridges are stacked in tiers, one above the other, and the entire assembly is placed in a pressure vessel. A large pressure vessel unit may be 6 ft (1.8 m) in diameter and 6.5 ft (2 m) in height and contain as many as 300 filter cartridges with a total surface area of about 800 $ft^2$ (74 $m^2$). With a feed flow of about 4 gpm/$ft^2$ (160 l/min/$m^2$), the pressure drop may range from approximately 2 to 5 psi (0.14 to 0.35 kg/$cm^2$) for fresh resins and from 20 to 30 psi (1.4 to 2.1 kg/$cm^2$) for resins near exhaustion. Exhausted powdered resins are not regenerated. Thus, the time and cost associated with regeneration are eliminated. However, the precoating step usually requires 1 to 1.5 h. Powdered ion-exchange resins are used in other industries for the efficient removal of colloidal silica, iron, copper, and nickel. The equipment is simple and the pressure drop across the bed is relatively low when the resin is fresh. Some of the disadvantages are relatively high initial cost and relatively high replacement costs of filter cartridges.

## Mixed vs separate bed

The ion-exchange system most frequently employed in water and liquid waste treatment is the mixed-bed system which consists of a stationary bed containing mixed anion and cation resins. The liquid stream is fed from the top of the bed, and percolates downward through the bed during operation of the process. When ionic contaminants begin to appear in the effluent in significant quantities (breakthrough), the bed is considered exhausted or loaded and the feed is discontinued. The bed is then regenerated (followed by rinsing with deionized water) or the bed is discarded and replaced with fresh resins. These beds containing resins with a particle size range of 0.4 to 0.7 mm may have dimensions varying from 2 to 8 ft (0.6 to 2.4 m) in diameter and from 3 to 6 ft (0.9 to 1.8 m) in depth and contain from 30 to 180 $ft^3$ (0.85 to 5.1 $m^3$) of resin. The flow rates through these units range from 1 to 50 $gpm/ft^2$ (40 to 2000 $l/min/m^2$) of resin bed cross-sectional area, and the pressure drop may reach 25 psi (1.8 $kg/cm^2$). Pressure drops as well as volumes of feed processed per volume of resin are fairly similar to those for the powdered-resin system. A disadvantage with the mixed-bed system is the time required for regeneration, which entails separation of the two types of resin by flotation making use of the difference in density, followed by transfer to individual regeneration vessels. After regeneration, the resins are again thoroughly mixed and returned to the column. Some mixed-bed systems are designed to permit regeneration in a single vessel. An advantage of the mixed-bed system is that the cation and anion exchange reactions take place simultaneously and ions removed from the resin (e.g., H+ and OH-) react with each other, thereby reducing the electrolyte concentration. The favourable ionic equilibria thus achieved in the column result in a high column efficiency. For removal of both cation and anion contaminants from liquid waste, two separate ion-exchange beds in series, a cation bed ahead of an anion bed, are sometimes used instead of a mixed bed system. The separate bed arrangement may be preferred for the purpose of removing specific radionuclides. Regeneration is much simpler with a separate bed than with a mixed-bed unit.

### Operating experience

The results of the survey on the application of ion-exchange technology to the treatment of radioactive liquid streams at LWR nuclear power plants show that the resin types used most frequently by nuclear power plants are strong-acid cation and strong-base anion exchange resins of polystyrene matrix. These resins are routinely used in many large-scale water treatment operations, and the results of much practical experience are available. Mixed-bed units are the most widely employed ion exchange systems, although separate cation and anion units are in common use. Conventional systems use resins with a particle size range of 0.4 to 0.7 mm. In a number of BWR plants, a powdered form of resin (over 90% of the particles are smaller than 0.03 mm) is used in very shallow beds with large surface area. They function as a filter as well as a demineralizer and are used to treat primary coolant and steam condensate. Separate-bed units are used to treat steam generator blowdown, primary coolant, and feed and condensate in the boron recycle system at PWR plants.

### Flow rate

Flow rate of feed to various ion exchange systems ranges from approximately 1 to 50 $gpm/ft^2$ (40 to 2000 $l/min/m^2$ ) of resin bed cross-sectional area for BWR plants, the highest rate being applicable to steam condensate. In PWR plants, the variation is not as wide and generally fails in the range 5 to 20 $gpm/ft^2$ (200 to 800 $l/min/m^2$); the higher rates are frequently used for the letdown stream from the primary coolant system. The flow rate in the powdered-resin systems is about 4 $gpm/ft^2$ (160 $l/min/m^2$) of resin bed surface area. Temperatures of the feed streams are usually below 140 F (60 C). Higher temperatures can cause increased deterioration of resins and shorten their service life. The pH values of the feed streams in BWR plants are near neutral under normal conditions, but in PWR plants the pH values may range from 4 to 10.5. Performance data on ion exchange systems with respect to specific radionuclides are not readily available in spite of the important role played by these systems in nuclear power plants and other types of nuclear installations. Most data are based on gross radioactivity measurements which do not distinguish between the various chemical and physical species in the feed and effluent. Electrical conductivity of the effluent and pressure drop across the resin bed are other properties frequently monitored at BWR plants. Many plants do measure radioiodine. The determination of other individual radionuclides is strongly recommended.

### Decontamination factors

Decontamination factor, defined as the ratio of the feed to effluent concentration, is used by designers and operators to express the performance of an ion-exchange system. However, it is not generally the determining factor for resin replacement or regeneration. Such replacements or regenerations are often scheduled for convenience in plant operation (during refuelling), are determined by radiation levels around the ion-exchange equipment or are dictated by excessive pressure drop across the bed. Radionuclides exist in different forms which have different removal characteristics. Some exist primarily as ionic species which behave in accord with ion-exchange principles. Some exist as insoluble particles of various sizes, and their behaviour is related to particle properties in regard to filtration and adsorption on surfaces. Some tracer level ions adsorb on (or exchange with ions in) these solid particles, and subsequently behave like the solids. As a result, some nuclides do not behave as their chemical properties might indicate. Their behaviour may be different for different streams within a plant and from plant to plant. Thus, removal of particulates may be as important as removal of ionic constituents. Modes of operation of ion-exchange systems often differ from that in water treatment experience. In particular, extremely large specific volumes of water may be processed before resin regeneration or replacement. Superior performance could be achieved by more frequent resin replacement or more complete and frequent resin regeneration.

Table 22 Decontamination factors that can be attained with various ion exchange systems.

| System | Cations | Anions | Cs,Rb |
|---|---|---|---|
| Mixed Bed ($Li3BO_3$) | 10 | 10 | 2 |
| Mixed Bed (H+OH-) | | | |
| Powdex (Any System) | 10(10)* | 10(10) | 2(10) |
| Radwaste | 100(10) | 100(10) | 2(10) |
| Cation Bed | 100(10) | 1(1) | 10(10) |
| Anion Bed | 1(1) | 100(10) | 1(1) |

* For two demineralizers in series, the DF for the second unit is given in parentheses. For a polishing demineralizer after an evaporator use DF for second unit in series.

These DFs represent time-average (or volume-average) values over the operating life of the column. They are derived from water treatment experience, ion-exchange fundamentals, laboratory data, and plant operating experience. They take into consideration anticipated operational occurrences. They are not intended as upper limits or as values typical of unusually careful operation and should be reexamined as new data are obtained for specific nuclides in operating systems. The DFs are considered to be attainable in the treatment of aqueous solutions having concentrations of radioactivity that are less than 0.1 mCi/l, provided that a sufficient amount of ion-exchange resin (e.g., strong acid and strong base, polystyrene matrix) is employed, that concentrations of both suspended and dissolved solids are normally less than 1 000 ppm, and that good engineering practice is used in the design and operation of these systems. These values are justified by plant operating experience supported by laboratory data.

The DFs listed in the Table above represent average values expected over extended operation rather than maximum values indicating the DFs attainable under optimum conditions. For a given ion-exchange system, the DFs will be higher if less waste is processed before the ion-exchange bed is replaced or regenerated (and will be lower if more waste is processed). However, each ion-exchange system can attain a predicted or desired DF, if the feed and effluent are measured frequently, and if the feed is terminated and the resin replaced or regenerated when the maximum permissible concentration in the effluent is reached.

## Effluent handling

Recycling of effluent from an ion-exchange system through the same system to improve the quality of the effluent will do no good if the resin is loaded or partially loaded, if the distribution coefficient is low for the species being removed, or if the species is in a nonexchangeable form. Resin replacement (or regeneration) or a different resin (or process) is needed for improved performance in such cases. The results of laboratory experiments at Oak Ridge National Laboratory (ORNL) using feed solutions containing trace amounts of 137-Cs, 131-I and Sr-90 and large amounts either of NaCl (1 000 and 2500 ppm) or of a mixture of

$Na_2HPO_4$ (1 000 ppm), $H_3BO_3$ (1 700 ppm), and LiOH (7 ppm) bring out that breakthrough of trace radionuclides as well as nonradioactive nuclides takes place earlier when the feed flow rate or the concentrations of the nonradioactive nuclides are increased.

### Filtration (NPWT 1978)

Filtration is defined as the separation of suspended, undissolved, particulate solids from a fluid mixture by passage of most of the fluid through a septum or membrane that retains the solids on or within itself. The mixture to be separated is called tile feed slurry, the fluid that passes through the septum is called the filtrate, and the septum is called the filter medium. When the separated solids accumulate in amounts that visibly cover the medium, they are called the filter cake. Filters selected for radwaste service should be capable of producing an effluent concentration of less than 1 ppm insolubles.

### Types of filters

Traditionally, BWRs have for the most part used pressure precoat filters, while PWRs have largely used disposable cartridge filters. These and other types of filters currently in service, or to be installed, at LWR plants are described in the following sections. Disposable filters are designed with replaceable elements which are thrown away when contaminated. These elements are usually constructed of pressed paper, matted fibres, or porcelain materials. Cotton fabrics are, by far, the most common type, primarily because of their low first coat and wide availability. Disposable filters are available in pore sizes ranging from ten millimicrons (membrane type) up to several hundred microns. In general, these types of elements are best suited for the removal of gross contamination from low pressure, low temperature systems.

### Metallic filters

These elements are partially cleanable and are constructed of woven wire or sintered metal. As in the case of disposable elements, several variations are available. Wire mesh elements are available in pore sizes down to approximately eight microns absolute. Sintered elements are available in pore sizes down to approximately five microns absolute. Backflushing does not completely clean these filters, and they are best suited for the removal of medium sized contaminants.

### Precoat filters

In precoat filters, filtration elements support and retain a filter medium created by passing a slurry of a precoat material through the filter. The precoat deposits on the element forming a layer which becomes the filter medium. Usually, with all precoat filters, additional precoat material, called body feed, is added to the process feed stream as it is fed to the filter. This creates a continually thicker, porous filter medium which tends to prevent the feed particles from clogging the initial precoat. The addition of body feed significantly extends the run life of the filter while maintaining filter efficiency. Upon high pressure differential or upon attaining a design total coating thickness, the filter is taken off stream and backflushed. The clean filter is then again precoated and the filtration cycle resumed. Diatomaceous earth (DE) is commonly used as the precoat and body feed material. It is also useful in removing suspended or dissolved oil in the feed stream. This type of filter can provide high levels of filtration efficiency, but is limited by temperature and pressure extremes. In addition, the large quantities of precoat and body feed material which must be disposed of can present significant problems in terms of waste handling. Several types of precoat filters are in use in radioactive waste treatment systems. The principal types are septum, flatbed, and centrifugal. The septum precoat filter utilizes a number of vertical woven-wire or sintered-metal cylinders which form the support for the precoat in a closed pressure vessel. The size, number, and spacing of the septum elements determine the flow rate and total solid capacity of the filter.

### Flatbed filters

The flatbed filters are horizontal travelling permanent screen (belt) type filters which are precoated with diatomaceous earth. They operate as closed pressure filters during the precoat, filtration, and air-drying phases of the filter cycle. After a flatbed filter has been precoated, radioactive liquid waste is pumped through the filter until a high differential pressure condition or maximum solids deposit occurs, at which time the operation is stopped. At completion of the filtration cycle, the flatbed filter cake is discharged by moving the belt over an end roller and spilling the cake into a chute. Flatbed filters have a suspended solids removal capability of greater than 95 % for a particle size of 1 micron or larger. When precoated with diatomaceous earth, the flatbed filters can remove a limited amount of dissolved solids and suspended oil. Experience with the flatbed filters for treatment of liquid radwaste has shown that they are relatively effective in producing water acceptable for recycle (approximately 5 % of clean waste processed must be reprocessed) at reasonable maintenance cost. The prime disadvantage of the flatbed filter system is the large amount of filter medium required for effective operation. Other disadvantages are silica carry-over to the radwaste ion exchange column and condensate system, short run lengths with high crud loading, and occasional particulate "fines" breakthrough.

### Centrifugal filters

The centrifugal filter is a vertically mounted, closed pressure vessel inside of which are horizontal filter discs fitted with woven wire screens and stacked on an axially located hollow shaft. The centrifugal filter is precoated with diatomaceous earth via a precoat tank and pump. After precoating, radioactive liquid waste is pumped through the filter until a preset condition, such as high differential pressure [4.2 kg/cm$^2$ (60 psi)] across the unit, high effluent turbidity, or maximum solids occurs, at which time feed is terminated. Filter cleaning is accomplished by the operation of an externally mounted electric motor which spins the vertical filter shaft, thus removing the spent filter sludge from the horizontal discs by centrifugal force. The filter sludge is discharged and routed to the solid radwaste treatment system. For a particle size of one micron and larger, the removal efficiency of the centrifugal filter is greater than 95 %. Centrifugal precoat filters are suitable for application in radwaste service and have been used extensively for this purpose in Europe. Several future installations are now planned for domestic U. S. nuclear power plants. The main advantage of the centrifuge precoat over the flatbed filter system could be a slight decrease in waste volume due to the ability to operate at a higher differential pressure. Water quality, however, is the same as for both these types of filters.

Etched disc filters

The etched disc filter is a vertically mounted closed pressure vessel containing filter elements made up of stacks of chemically etched, mechanically compressed stainless steel discs. Radioactive liquid waste is pumped through the filter until a preset high differential pressure [5.3 kg/cm$^2$ (75 psi)] across the unit or high turbidity is reached. The feed is then terminated and the etched disc filter is backflushed with an impulse of high pressure air [~0.2 m$^3$ (6 ft$^3$) at a gage pressure of ~25 kg/cm$^2$ (350 psi)] provided from an air accumulator system. The backwash water and air discharged from the filter is directed to a backwash hold tank where air is vented to the radioactive off-gas system. The backwash slurry is sent to an evaporator or waste solidification system. The suspended solids removal efficiency for an etched disc filter is 100 % for a particle size of 5 micron and larger. Precoating is not required but may be used for specific applications. Advantages of an etched disc filter over the flatbed include smaller waste volumes since precoat is not required and reduction in off-line time for backwash (2 vs 40 min.). A 5-micron absolute filter rating with automatic backflushing equipment is recommended to provide adequate run lengths for clean waste processing. This design is comparable to the flatbed filter for suspended solids removal. Etched disc filters have been tested in radioactive service at domestic nuclear power plants. A recent installation for fuel pool cleanup has given excellent results during the first year of operation. Color and oil are not removed unless precoat is used. If a high crud holding capacity is required, it must be specified since the standard design, for economic reasons, only provides relatively low crud holding capacity.

### Other filter types

There are a number of other filter types which are being installed or tested but which are not presently in widespread use for radwaste service. These include the walnut shell deep bed filter, the clam shell, which is a type of precoat filter, and the magnetic filter. The magnetic filter uses an electromagnetic field to attract magnetized crud to the filter medium. It is cleaned by turning off the magnetic field and flushing the bed. A sand filter has been tried in one nuclear plant, but operation was not satisfactory. Both the sand filter and the walnut shell deep bed filter require the continuous addition of polyelectrolyte to the feed stream,for efficient performance.

### Reverse osmosis

The phenomenon of osmosis may be defined as the spontaneous passage of liquid from a dilute to a more concentrated solution across a semipermeable membrane which allows the passage of the solvent but not the dissolved solids. This transfer continues until the pressure, defined as the osmotic pressure, is large enough to prevent any net transfer of the solvent to the more concentrated solution. If pressure is applied on the concentrated side at higher than the osmotic pressure, the phenomenon of reverse osmosis (RO) takes place, wherein the solvent flows from the concentrated side to the more dilute side. The semipermeable membrane normally used today is a modified cellulose acetate film. Factors which affect the performance of RO systems include compaction, hydrolysis and fouling of the membrane. Compaction of the membrane is the densification of the membrane reduces water flux rates (amount of product recovered per unit of time from a unit area of membrane) with increasing time of operation under pressure. Hydrolysis of the membrane is a reaction which lessens the salt rejection capability of the membrane. The rate of hydrolysis is decreased by lowering the temperature [usually, well below 55 C (130 F) and by controlling the pH (normally, between 4 and 6). Fouling of the membrane is a deposition of foreign material on the membrane which reduces water flux rates. Remote chemical cleaning of the membrane (either during operation or while the unit is out of service) or replacement of the membrane is required to return the RO unit to its expected capability.

### Types of units available

Various types of reverse osmosis units with varying degrees of prefiltration requirements for acceptable operation are on the market today. There are spiral-wound, hollow-fibre, and internal- or external-tubular designs with feed pretreatment for suspended solids ranging from prestraining to filtering out five-micron particles to prevent fouling.

### Spiral-wound

The spiral-wound type RO unit consists of a spirally wrapped sandwich of two sheets of cellulose acetate membrane glued along their common edge and separated by a porous backing material. The pressurized feedwater passes longitudinally through the spiral package along a mesh spacer that separates the sandwich layers and also promotes turbulent flow. The permeate travels spirally through the material into a central, perforated tube. A significant advantage of the spiral design is that it has a high membrane surface area per unit volume compared with other tubular configurations. However, it appears that the spiral-wound units are easily plugged and fairly hard to clean (flush).

### Hollow-fibre

The hollow-fibre type RO unit represents a newer development in membrane configuration. Rather than being cast into a sheet, the membrane material (aromatic polyimide) is spun into fine, hollow fibres. The ends of a large bundle of looped fibres are then potted into a header and installed in a pressure housing. The feed [pressurized up to 42 $kg/cm^2$ (600 psi)] permeates the fibre wall and is carried through its hollow centre to the header. The rejected water passes through the housing. Although the flux is substantially less than for sheet membranes, the hollow-fibre configuration permits the economical packaging of vast membrane surface into an exceptionally compact volume. The fibres may be as thin as human hair (100 to 200 microns) but are hollow (with walls about 25-microns thick) and are in strength like thick-walled cylinders. Thus, they are able to withstand the large pressures required in RO without collapsing, while eliminating the need for space-consuming porous support media which is essential to other designs. One advantage of hollow fibre is its ability to handle streams with pH ranging from 2 to 14. The high density packaging and the small inside diameter of the fibres seriously limits the acceptable suspended particle size in feed streams. Even though high pretreatment is normally necessary, it may not completely eliminate the high fouling tendency attributable to both the very fine fibre diameters and the low tolerance of the fibres for chlorides.

### Tubular

The internal-tubular type RO unit has the membrane (cellulose acetate) either cast as a tube or rolled together creating a spiral tube which is inserted into a porous tubular support. A number of individual tubes are attached to headers and encased in a housing. This type of RO unit has less tendency toward fouling than either the spiral-or hollow-fibre wound; but the small opening limits the turbulence necessary for an optimum performance and cleaning. Excessive velocities of feed streams sometimes cause membranes to collapse from the support tube. Further, with this design it is difficult to determine the location of membrane failure making full unit replacement necessary, even when only one tube has failed. In addition, since the membrane is in tension, internal tubular systems are limited to operating pressures in the neighbourhood of 42 to 56 $kg/cm^2$ (600 to 800 psi). The external-tubular type RO unit has a cellulose-acetate-membrane coat on the outside of a porous core. This configuration allows for higher working pressures up to around 105 $kg/cm^2$ (1 500 psi). As a consequence, a larger variety of feeds with high osmotic pressures can be processed. Like the internal-tubular configuration, a number of cores (tubes) make up a unit with the external tubular and, as with the spiral-wound configuration, turbulence promoters are used.

## Ultrafiltration (NPWT 1978)

The process of ultrafiltration is related to reverse osmosis. Contaminated water is forced trough a membrane which is considerably more porous than the RO membrane. As a result, all soluble species (except those of molecular weight of about 100 or higher) pass through the membrane with water. Colloids, suspended solids and high molecular weight organic molecules (HMWO) do not pass. Because of porous nature of the membrane, the process can operated with high fluxes at relatively low pressures in contrast to the high pressures required by RO. This advantage stems from the fact that the osmotic pressure of colloids and HMWO is low. To date, ultrafiltration has not found use in radioactive liquid systems other than as a prefilter for an RO unit.

## Centrifugation (NPWT 1978)

This is another unit operation used to remove suspended solids from solutions. Centrifuges are mechanically driven rotating devices which employ centrifugal forces to separate solids from liquids. Three types commonly found are tube, disk and basket. The tube and disk types use rotational force to cause solids to migrate to a wall where they can be collected. Basket centrifuges force liquid trough a rotating screen which collects the solids on a filter aid which is supported by the screen. Units were installed in early BWR plants to dewater resins and filter sludge but there were some plugging problems with them.

## System design and component arrangement

Results from presently operating nuclear power plants demonstrate that by use of the proper unit operations, all liquid wastes can be adequately decontaminated for recycle or discharge, meeting all effluent requirements. The keys to successful operations lie in providing adequate tankage, sufficient processing capacity, and flexibility in routing feed and process streams.

Equipment redundancy and consideration of the requirements for sampling, operations, and maintenance while minimizing operator exposure must be an integral part of the design philosophy. In addition to consideration of the capabilities and requirements of the individual items of equipment, the designer must consider factors relating to the operation of the entire integrated system.

## Storage tanks

Requirements and recommendations for storage tanks in a radioactive liquid treatment system include : conical, rounded, or sloping tank bottoms should be used as sludge accumulates on the bottom of flat bottom tanks; a minimum manway opening of 60 cm (24 in.) should be provided. Access with protective clothing and masks requires adequate space; provide mixing capability for tank contents by pump recirculation, mixers, or eductors; if more than one tank or unit of equipment containing significant activity is installed in a cubicle, provide shield walls in between; provide a flanged connection on the normal tank effluent line exterior to the cubicle for temporary pumping system access; allow adequate room over the top and around the sides of the tank for access; install permanent ladders where required; use proper materials of construction. Experience has shown that the use of carbon steel with and without interior coatings has frequently not been satisfactory. Stainless steel or fibreglass are preferred; provide adequate sampling points installed in locations where radiation exposure is low.

## Evaporators

Requirements and recommendations for evaporators used to treat radioactive liquids include: install components in segregated, shielded areas so that maintenance can be performed on individual items without undue exposure; provide access to the reboiler for tube inspection and cleaning; provide for sampling of the concentrate while preventing freeze-up, clogging, or operator exposure; consider maintenance requirements in selecting the type and location of instrumentation sensors. Evaporator corrosion has been a major problem in older plants. Provide materials of construction which are compatible with the most demanding conditions anticipated. For radwaste service, incoloy 825 and alloy 20 are recommended.

## Resin handling systems

Requirements and recommendations for the sludge and resin handling systems include: for resin and sludge transport, consider minimum velocity requirements; avoid excessive vertical lift and possible crud traps in piping runs; provide adequate flushing capability; provide access at critical points for line cleanout in case of plugging; select valves which provide full port opening, and do not have unflushable areas allowing crud or resin accumulation; in designing storage, decanter, vent, and drain systems, prevent carry-over of resin or sludge into overflows and vents; use conical bottom tanks.

### Operation of system

The importance of the radwaste system to the overall operation of the nuclear power plant must be recognized by management and the recognition transmitted to the operators. Proper design features and automatic controls will assist, but cannot replace, adequate planning and intelligent operation. Factors that must be considered in the operation of a liquid radwaste system are several. The system designer must include operating procedures in designing the liquid radwaste system. For example, if the chemistry laboratory is to operate normally only on one shift per day, adequate holdup of processed liquid while awaiting analysis must be provided. The radwaste system should not be a bottleneck with a potential for causing plant shutdown. Processing capacity must be provided for handling peak loads. Redundancy and cross-connections should allow utilization of alternate equipment are desirable. A thoroughly trained operating force is mandatory to obtain successful operation. Written operating procedures for both normal and emergency conditions are necessary. A trained and adequately staffed operating force, recognizing the importance of their contribution, is the keystone of a well run system.

### Solidification of high-level waste (Grover 1978, Murray 1989)

Since the earliest days of nuclear energy, the management of radioactive wastes has been a major concern, both for the public and those engaged in the industry, particularly with regard to the release of radioactive materials to the environment and possible risks of contamination. The largest quantity of radioactivity is contained in irradiated nuclear fuel. Reprocessing involves the dissolution of the irradiated nuclear fuel, usually in nitric acid solution, and the removal by solvent extraction of the plutonium and unburned uranium. The remaining solution, containing more than 99.9% of the non-volatile fission products, together with some additional constituents from cladding materials, traces of unseparated plutonium and uranium, and most of the transuranic elements, constitutes the high-level waste. This liquid waste is usually concentrated by evaporation and stored as an aqueous nitric acid solution in high-integrity stainless steel tanks. Experience with tank storage has been good, but persisting with this practice would involve continuing technical supervision and periodic replacement of tanks over the centuries. While liquid storage can be considered acceptable for some decades, with the expansion of nuclear power, it is generally agreed that in the longer term it is better to replace liquid storage by an alternative system based on solidification of the waste.

### Basic features of solidification processes

The primary aim of any solidification process is to convert the high-level waste solution to a product that is less mobile, requires less surveillance and is more suitable for final disposal. This product should satisfy certain criteria: e.g., it should maintain its mechanical integrity; have a good resistance to irradiation; adequate thermal conductivity and, ideally, a very low leach rate. Under the present state of knowledge, glasses and ceramics are considered suitable for final disposal. The basic solidification processes consist of evaporation, followed by denitration (or "calcination") of the waste solution to form a calcined product which can either be in granular or solid form and solidification. Calcines are considered only as interim products as they do not sufficiently fulfil all the above criteria. However, the granular calcines can be mixed with additives and melted to form a glass or ceramic product. An alternative route is to mix the additives with the waste solution and evaporate, denitrate and melt, to form a glass or ceramic product in one step. Another variant is the use of an adsorption process followed by a high temperature treatment to produce a ceramic product. Attempts have been made to improve the properties of the products by further treatment, such as the incorporation of the calcine or glass into a coated particle or metal matrix to improve the leach resistance and thermal conductivity. Glass has been studied extensively and is the material selected for most defense wastes. Glass has several favourable features. It mixes well with wastes of various compositions, casts easily into proper form, conducts heat well, and resists attack at low temperatures. Some other properties are its non crystalline (amorphous) form, in contrast with substances such salt. It is in a vitreous condition (a supercooled liquid) that is strong but brittle. Under excessive heat, stress, or radiation, glass could devitrify and break into pieces. The smaller the fragments, the more easily the glass is leached (dissolved) by water. The glass-waste mixture used by the French has a composition that is more like Pyrex, the glassware used for cooking made by Corning. It is a borosilicate type, in which boron oxide replaces lime. When fission products are included, the glass is black rather than transparent.

## Vitrification in France (Bonniaud 1976)

The first radioactive glasses were produced in 1958. These were compared with synthetic materials such as mica which had already been investigated, but similar leaching rates, an easier process for making the glass and greater flexibility in handling the product lead to a definitive choice of vitrification.
In 1963 glass blocks from 5 to 15 kg in weight with specific activities of about 1000 Ci/l were made by a gelling technique in a graphite crucible.

### Pot technique

Simultaneously, other processes of industrial interest were under development. The pot technique was the first in operation. A pot made of inconel, heated by induction, was fed with the fission product solution and a slurry containing glass-making chemicals. Drying and calcination were continued until the pot was 80 % full. The material was then melted by increasing the temperature to 1180 C and the glass was poured, after refining, through a drain tube heated by induction. The empty pot was used again for another run. In 1969, the PIVER pilot plant, using this process, was operated under fully-active conditions at Marcoule. Its operation was continued until 1973, processing waste solutions from natural uranium spent fuels. 12 t of glass with a maximum activity of 3000 Ci/l were produced in this plant. During each run, using a 250 mm diameter pot, 200 litres of solution were vitrified, producing 90 kg of glass. Decontamination factors of 1E+6 for liquid wastes and 1E+10 to 1E+11 for off-gases were achieved. An experimental disposal area built to store the PIVER glasses comprising 32 pits, 10 metres deep, enclosed in a concrete structure equipped with forced-circulation at cooling now has 164 containers and 8 used pots in storage.

## Continuous process

After the successful operation of PIVER, it was decided in 1972 to build an industrial vitrification plant at Marcoule. Economic studies were carried out to compare the pot process with a more advanced continuous vitrification process technique which had been developed in the meantime. The continuous process was chosen for the Marcoule vitrification plant (AVM) as it was found to be more flexible, cheaper from the standpoint of investment and operating cost and easier to scale-up for higher throughputs. Fission product solutions at present stored in France have derived mainly from the processing of natural uranium fuels from gas graphite reactors. When highly-concentrated waste solutions from these are vitrified, 8 l to 30 l of glass per tonne of spent fuel processed are produced. Vitrification of similar wastes from the reprocessing of enriched oxide fuels of high burn-up from LWRS and FBRs produces 67 to 300 l of glass per tonne of fuel processed. These types of waste will not arise in significant amounts in France until after 1978. The Marcoule vitrification plant will process mainly the first type of solution. The vitrification plant at the La Hague reprocessing plant (AVH) is used particularly to vitrify the wastes from high burn-up fuels. Vitrified waste is stored for an interim period on these sites in engineered storage facilities which will ensure cooling and control and allow retrieval if desired The type of storage to be employed depends upon the heat content of the glass. Up to 80 W/l, forced-air cooling with optional subsequent natural convection, is a cheap method and was chosen for the AVM. For higher specific power, air cooling is appropriate after a period of cooling in a water pool. This is the system adopted for the AVH.

The continuous vitrification process comprises a rotary calciner coupled to a melting furnace. The calciner, which receives a feed of 40 l/h, comprises a tube of wrought Uranus-65 which was machine-finished. The ends of the tube are fitted with graphite ring air seals. These end-fittings lie on 'fore and aft' movable trolleys. The tube lies on easily removable roller bearings, has a slight slope, rotates at 30 rpm and is heated by 4 separate heaters arranged in zones. The solution is fed through the upper end-fitting and dried in the first half of the tube. The dry product, which is calcined in the second half of the tube at a temperature of 300-400 C, leaves by gravity through the lower end-fitting and passes to the melting furnace which is fed, through another connection with small batches of glass frit.

The connection from the calciner to the furnace is fitted with a glass gasket which may be easily removed by heating the glass with induction. The furnace, which was scaled up from the PIVER equipment, comprises a 350 mm diameter pot of inconel 601 and is fitted with a draining system. It is heated with an assembly of separate coils. Its maximum through-put is 20 kg/h and glass pouring is carried out at 6 to 8 hour intervals. All parts of the calciner are removable by means of a bridge crane and special tools. The presence of a free rod inside the tube and the use of a chemical additive produces a more consistent calcined product and prevents material sticking to the inside surface of the tube. Off-gases are exhausted through the upper end-fitting. Entrained dust is removed by a wet scrubber and recycled to the calciner. Less than 0.1 % of the calcine escapes the scrubber and reaches the condensate.

The Marcoule vitrification plant is contained in a building 20 m wide and 36 m long. The overall height is 30 m, 18 m of which is superstructure. The plant contains facilities for the storage of glass as well as the vitrification equipment. The capital cost of this plant is about 60 M francs. The vitrification part of the plant mainly comprises a 12.5 m x 3.5 m x 10.5 m central cell containing the calciner, the melting furnace, the feeding device, part of the off-gas treatment equipment, handling facilities for containers, and equipment for welding container lids and cutting solid wastes, a maintenance cell for the maintenance of the bridge crane, which is also used for the transfer of containers into and out of the plant, a cell for container transfer and decontamination, a liquid storage cell containing 2 stirred and cooled 15 $m^3$ tanks, a cell for the transfer of radioactive wastes, a cell containing the remainder of the off-gas treatment equipment which will operate at a lower radiation level, an airlock chamber for the entry of containers to the plant. Other facilities comprise a control room, additive feeding equipment, a medium-frequency generator room and facilities for the generation and supply of general utilities. All the equipment in the high activity cell is removable using a bridge crane (2 t), 8 shielded windows and master slave manipulators fitted in the cell. The equipment in the low activity cells is not remotely removable. In this case, direct maintenance is employed if required, after decontamination.

## Operation of the AVM plant

The calciner is fed with radioactive solution using an air-lift and a metering device at a flow rate of 30 l/h. A slurry of chemical additive and 5 l/h of liquid (to recycle dust which would otherwise leave the calciner) are also fed to the calciner. Calcined materials fall into the melting furnace at the rate of 9 kg/h together with a glassy frit at the rate of 9-10 kg/h. Every 8 hours, 200-140 kg of glass containing 40 W/l of fission product decay heat) are poured into a container with a diameter of 50 cm and an effective height of 1 m. The off-gas passes through a counter-current water scrubber which continuously returns the waste liquid to the calciner.

The remainder of the off-gas treatment equipment is composed of a condenser, an absorption column and a washing column. Low-level liquid wastes are returned to the reprocessing plant for concentration. The storage containers (made of high temperature stainless steel) are fitted with lids automatically welded with a plasma torch and transferred to the decontamination cell where they are washed with high-pressure water jets. They are then checked and transferred in a shielded cask to the storage area. Contaminated solid wastes are partially cleaned by acidic washing and are then put into containers similar to those used for glass. Welded lids are fitted and decontamination is carried out prior to transfer to the solid waste disposal area.

The glass storage facility is underground and is equipped with a forced air cooling system. The first section built has 220 pits, each 60 cm in diameter with an effective depth of 10 m. The air flows from bottom to top at a velocity of 10 m/s and is exhausted at a temperature of 100 C. The walls of the vault are insulated and air-cooled. In the case of a fan failure, safety is maintained by changing to natural convection, the air then leaving at 150 C. The external temperature of the upper storage slab, which is composed of metallic containers filled with concrete, does not reach 45 C under steady-state. The air is filtered before passing to atmosphere.

The La Hague vitrification plant will differ from the AVM in the following respects: the plant should be capable of processing 800 $m^3$/y of waste solutions arising mainly from the processing of spent oxide fuels, the glass will have a fission product decay heat content of 100 W/l, two lines, each equipped with a 50 l/h calciner and a 25 kg/h melting furnace is needed. A third line is planned as a stand-by, the solutions is continuously concentrated by a factor of 1.44 prior to their introduction into the calciner, partial or complete denitration of the waste solutions before calcination could be effected if desired and the containers of solidified waste is stored in a water pool for about 4 years and then transferred to air-cooled storage.

## Vitrification in the US (Murray 1989)

The vitrification process that has been developed for HLW by the Pacific Northwest Laboratory starts with liquid waste. It is mixed with glass-forming chemicals, and the combination is introduced into a melter, as shown in the sketch. The mixture dries and the resultant solid melts. The equipment is operated remotely, behind a concrete wall 4 ft thick. At the temperature of 1150 C, organics are destroyed and inorganics dissolve in the glass. Heat is generated in the molten glass by a large electric current. A turntable allows a canister to be filled with glass, then moved around to cool, bringing up an empty canister. Gas from the process is treated to remove water, heat, and radioactivity such as C-14, Ru and I-129. The canisters are welded shut, decontaminated, and stored in racks or air-cooled vaults, awaiting disposal in a repository. Much research has been done on glass as a waste form. The influences of mechanical stress, radiation, and corrosion have been examined. Of special interest is the effect of water, saltwater brine, and bitterns, which are brackish residues after salt has crystallized out of saltwater. The amount of leaching depends on the element. For example, the amount removed per day in micrograms/$cm^2$ is 1 for cesium, 0.1 for strontium, 0.01 for cerium, and 0.001 for ruthenium.

A novel spinoff of the above solidification process that may be useful in stabilizing certain types of radioactive waste is "in situ" (in place) vitrification. Developed at the Pacific Northwest Laboratory, it consists of converting contaminated soil into a glasslike solid by electric heating. Four electrodes are sunk 20 ft deep in the ground in the form of a square. A starter path composed of graphite plus glass is laid down between the electrodes. An electric power of 3.5 MW (approximately that used by a good-sized hotel) is applied to raise the temperature of the soil to 1500 C, well above the melting point. A cover is provided to catch gases. The vitrified zone grows until it includes the whole block between the electrodes. A substance like volcanic obsidian is formed after a cooling that takes months. The leach rates are comparable to those of vitrified HLW, and it is estimated that the glass will hold wastes for over one million years. The method appears to be very promising for several situations besides contaminated soil. One possibility is hazardous chemical waste deposits. The cost is small and competitive with other options.

## Solidification of medium-level waste (Berlin 1989)

Solidification is a conditioning technique in which small volumes of liquid wastes are immobilized within an inert matrix or binder. Solidification of large volumes of liquids is generally not cost effective compared to treatment methods to remove the radionuclides from the waste stream and produce a smaller volume of waste. As a result of current LLW regulations that restrict free water content in a waste package and then require that the LLW be mixed with a material that can form a monolithic solid, the use of solidification has become widespread at nuclear facilities. Solidification is also used to immobilize semisolids and dry solids at these facilities. The optimal solid incorporating radioactive waste should not fracture under load and have high mechanical strength, be resistant to radiation damage for a long time period, have good thermal resistance, resist leaching from water infiltrating the package, and demonstrate chemical compatibility between the binder and the incorporated waste. Since this combination of characteristics is difficult to achieve in a binder, cement, asphalt (bitumen), and plastic-based materials have evolved as the most suitable materials. Even though urea-formaldehyde was one of the earliest materials used to solidify liquid-bearing LLW, and has been generally displaced because of its inability to immobilize water, other plastic-based organic polymers are growing in popularity for use as solidification agents. Among this class of polymers, polyester-type resins, which form a hard permanent solid that can immobilize free water in the cell structure of the matrix, are particularly attractive.

## Desirable properties (NPWT 1978)

The properties that are usually considered of primary importance to the safety and economics of solidified waste management are low leachability, high thermal conductivity, chemical stability, radiation resistance, mechanical ruggedness, non corrosiveness to container, minimum volume and cost. Low leachability is important in case of an untoward event. It will improve safety by reducing the consequences of a major accident. Stated another way, the magnitude of an accident that can occur and not release unacceptable amounts of activity is increased by low leachability. High thermal conductivity increases the amount of activity that can be stored in a container (i.e., increases the permissible volumetric heat generation rate). In the main, it is not a major consideration with the wastes generated at LWRS. Good chemical stability and radiation resistance are necessary if waste forms are to retain their original properties and pressurization of the container by radiolytic gases is to be minimal. Mechanical ruggedness is desirable to reduce the probability of waste products breaking into smaller pieces since such pieces would be more readily dispersed under accident or normal circumstances. Non corrosiveness to the container is necessary since, in part, it determines the life of the primary container. In most cases, corrosion from the outside should outweigh corrosion from the inside with solidified products. Minimum volume is desirable primarily for economic reasons. Minimum cost which does not affect product quality is an obvious advantage. As the above list of desired properties brings out, solidified waste should be in the form of a non dispersible, free-standing monolith inside the shipping container and no residual or free water should be present.

## Free liquid detection

Liquid radwastes sometimes have wide variations in chemical species which prevent or retard solidification thus making control of the process difficult. There is, therefore, a potential for free liquids to remain in the container following the solidification step. Also in view of this, the NRC considered it necessary that designers and operators of solidification systems implement some procedures to assure the absence of free liquids. Measures currently acceptable to the NRC are either a Process Control Program or a Free Liquid Detection System, which are:

- In the Process Control Program, boundary conditions (in the form of process parameters for the solidification system) will be established such that operation within these limits will give reasonable assurance that solidification is complete. The boundary conditions for each solidification system is determined by tests with chemical wastes that could be found in the liquid wastes from the nuclear power plant. These boundary conditions will be established as measurable physical parameters important to the solidification process such as: chemical content of the liquid waste being solidified (e.g., pH, oil content, etc.), chemical quality of solidification agents (e.g., catalyst pH, type cement, etc.), and liquid waste to solidification agent ratios. Once the boundary conditions are fixed the operator is expected to stay within these limits since they will be part of the solidification system operating procedures.
- The Free Liquid Detection System requires a checkoff each container to verify that free liquids are absent. Visual inspection of the upper surface of the waste product is not alone sufficient to ensure that no free liquid remains in the container. Methods used to verify the absence of free liquids should take into consideration that some solidification procedures may create a thin dry layer or crust of solidified material on top while the waste underneath remains only partially solidified.

Cement (NPWT 1978)

Portland cement is often used in radwaste solidification processes. The major constituents of portland cement are tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$), and tetracalcium alumina ferrite ($4CaO.Al_2O_3.Fe_2O_3$). Portland cement is classified as Type I, II, III, IV, or V, depending on the proportions of these compounds in the mixture. Minor constituents such as lime (CaO), magnesia (MgO), or gypsum ($CaSO_4$) can have a significant effect on the swelling and setting properties of the cement. Gypsum is added to prevent flash setting. The American Society for Testing and Materials has defined the restrictions on the chemical composition of portland cements as imposed in all national standard specifications. Studies on the fundamental chemistry of the hardening and setting of portland cement show that upon addition of pure water, both the dicalcium and tricalcium silicates react to form an amorphous, high-strength "rigid gel" or "mineral glue" composed of colloidal tricalcium disilicate hydrate ($3CaO.2SiO_2.3H_2O$) in a nearly homogeneous mass. The tricalcium aluminate and tetracalcium alumina ferrite apparently form the crystalline hexahydrates ($3CaO.Al_2O_3.6H_2O$ and

$3CaO.Fe_2O_3.6H_2O$) indicating a capacity for holding water that is nearly double that of the silicate components. The total amount of water chemically tied in hardened portland cement paste corresponds to approximately 25 % by weight. In the initial setting process, a coagulation structure is formed by individual crystallises in the amorphous gel; subsequent hardening proceeds as a fine crystalline network builds within the coagulated framework. In actual power plant practice, where radwaste solutions and scurries (instead of pure water) are combined with the portland cement, the chemistry of solidification becomes far more complicated and undefinable. Practical experience, however, has shown that although Type I portland cement is the one most commonly available, Type II is preferable in most radwaste applications because it is more resistant to sulfate deterioration. Boric acid wastes are known to retard the setting of portland cement and some investigation of this effect is being done. In general, cement-radwaste products with satisfactorily high mechanical strength and low leach rate contain about 5 to 10 % waste solids with a rapid decrease in strength reported, when the waste solids exceed 10 to 15 wt %. Marked decreases in mechanical strength may also occur when dewatered resins and/or filter sludges are incorporated in cement. Using cement as the solidification agent for liquid radwaste always results in a net volume increase. The final solidified waste volume for radwaste-cement products can be as much as a factor of 2 or more greater than the volume of the incorporated liquid. The use of additives such as clays, shales, fly ash, or sodium silicate can either enhance or mitigate certain chemical or physical properties of the cementing process. The addition of sodium silicate to portland cement-sodium sulfate mixtures is reported to increase shipping efficiency (i.e., volume of waste per unit volume shipped) by up to 75 % over that of cement only. Also the addition of sodium silicate to mixtures of portland cement and concentrated borate solutions is said to yield a good solid. The liquid tolerance of portland cement is increased by sodium silicate addition, thus permitting greater shipping efficiencies when dewatered sludges are mixed with waste evaporator concentrates.

Advantages of cement solidification : Material and technology is well known and available; is compatible with many wastes; most aqueous wastes chemically bound to the matrix; low cost of cement; good self-shielding; no vapour problems; long shelf life of cement powder; good impact and compressive strengths; low leachability for some elements; no free water if properly formulated; rapid controllable setting; in-container and on-line processes available.

Disadvantages of cement solidification : some wastes affect settling or otherwise produce poor waste forms; pH sensitive - pretreatment may be necessary; swelling and cracking occurs with some products under exposure to water; volume increase and high density in shipping and disposal; excessive setting exotherms may develop with certain cement and waste combinations; dust problems; equipment for powder feeding is difficult to maintain; potential problems resulting from premature cement setting, especially in-line mixers; may require heating or pressing equipment for some processes.

Polymer-concrete (Berlin 1989)

The polymer-concrete process, used to solidify dry waste, also offers promise for future growth as a solidification agent.
Polymer-concrete solidification advantages : high waste loading and low volume increase; no-free standing water; low leachability; high compressive and impact strength; relatively insensitive to chemical nature of waste; simple process for combining waste and binder.
Disadvantages : limited binder shelf-life; hazards associated with monomer handling; some wastes may interact chemically and affect or prevent polymerization; relatively expensive materials; not commercialized to full-scale use.

Urea-formaldehyde (NPWT 1978)

Many companies now offer solidification systems using urea-formaldehyde (UF) resin as the solidification agent. The UF resin used in radwaste solidification systems is a viscous, syrupy, milky coloured material which is commercially available from a number of suppliers. The resin is formed by reacting urea, $(NH_2)2CO$, with formaldehyde (HCHO) under alkaline or neutral conditions which produces a water soluble mixture of monomethylol urea ($NH_2CONHCH_2OH$) and dimethylol urea ($CH_2OHNHCONHCH_2OH$). The final composition of the mixture depends upon the initial ratio of urea to formaldehyde reacting and the conditions of the reaction. The monomethylol and dimethylol ureas are then partially polymerized by a condensation mechanism under slightly acidic conditions followed by neutralization to pH 7-8 to terminate the reaction. The resulting white, highly viscous product is the UF resin which typically contains 60-65 % solids. The product has a limited stability or shelf life which ranges from about six months to one year depending upon the temperature.

Upon prolonged exposure to air or with addition of an acid catalyst, cross-linking polymerization occurs and a solid is obtained. When used as a solidification agent for radwaste, the mixture of UF resin and radwaste is adjusted to pH 1-2 by addition of a weak acid or acid salt catalyst such as phosphoric acid ($H_3PO_4$) or sodium bisulfate ($NaHSO_4$). To minimize the amount of catalyst needed to adjust the pH for highly buffered solutions (e.g., partially neutralized boric acid wastes), dilute solutions of strong acids may be used. Upon addition of the catalyst, a condensation polymerization reaction occurs which is similar to the reaction that took place during the partial polymerization that was used in preparation of the resin. The reaction is slightly exothermic and is both temperature and pH dependent. The amount of catalyst added controls the setting time. All of the several possible mechanisms for forming the cross-linked UF polymer produce water as an end product of the reaction. The UF polymer formed varies according to reaction conditions, but typically has a low molecular weight and an average degree of polymerization of 6-7. The time required for the polymer to reach full strength is shortened by increasing the temperature or increasing the catalyst concentration. In actual nuclear power plant practice, the volume ratio of evaporator concentrates to UF resin is in the range of 1 to 3. The amount of catalyst required to reach the desired pH must be determined for each waste and normally comprises about 2 to 3 volume %. A suitable mixture begins to gel within a minute or two and should be well solidified after half an hour. Curing to a reasonably hard solid takes place over several hours and sometimes free, slightly acidic water, which can be mildly corrosive to the container, is released in the process. Portland cement or sorbent materials have been added to the waste containers to eliminate such residual water after the mixture has gelled. Urea-formaldehyde resin is also used to encapsulate radwastes such as dewatered filter sludges and spent demineralizer resins slurried with small quantities of liquid waste. Certain wastes (e.g., soap solutions and concentrated $Na_2SO_4$) are difficult to incorporate into UF. Acceptable sodium sulfate products can be obtained with fresh UF by diluting the $Na_2SO_4$ to less than 10 % by weight prior to UF addition, or by precipitating the excess sulfate with calcium chloride. Paper pulp or wood flour impart strength when added to UF formulations. Also, many of the same substances that are added to cement can also be added to UF to make it less leachable. It should be kept in mind however that in general, product strength decreases and leachability increases as the ratio of liquid to UF increases. On the other hand, UF products exposed to air lose water by evaporation and may become friable if completely dehydrated.

### Other organic polymers

Several other organic polymers have been examined as media for immobilizing radwastes. Among the thermoplastics, polyethylene has been investigated as a substitute for asphalt. Among the polymerized resins, water-extended polyesters have been developed. At present, only the Dow Chemical Company Nuclear Services Division is offering a commercial radwaste solidification system that on superficial observation exhibits properties similar to those of water-extended polyesters. The Dow system, like the UF system, encapsulates the waste which is combined with the matrix material prior to addition of a catalyst solution that promotes solidification. It is claimed that water is not produced as an end product of the polymerization step in the Dow process as it is in UF polymerization. However, the fundamental chemistry of the Dow product has not been made available to date since the company considers this proprietary information. In pilot plant development studies, mixing has been done in an open top 210 l (55 gal) drum using a motor driven paddle-type mixer.

Vinyl ester styrene solidification (Berlin 1989)

Advantages : adaptable to both liquid and solid wastes; no-free standing water; low leachability; high compressive and impact

strength; good radiation stability; ease of working with liquid components; in-container mixing available;
Disadvantages : limited binder shelf-life; hazards associated with monomer, catalyst and promoter handling;some wastes may interact chemically or prevent polymerization; relatively expensive materials; mixing method important.

Asphalt (NPWT 1978)

The term asphalt covers mixtures of high molecular weight organics related in their nature to the aliphatic and aromatic hydrocarbons. Asphalt can be separated by suitable solvents into two fractions or phases: the asphaltenes, which precipitate out as a black tar, and the malthenes, which remain in the solution in the form of a dark viscous oil. The properties of the fractions obtained depend only on the solvent (usually normal heptane). There is no sharp boundary between the two phases. The malthenes have the properties of a viscous liquid. The asphaltenes impart colloidal properties to the asphalt. Asphaltenes show a tendency, in combination with the aromatic fraction of the malthenes, to form complex micelles suspended in the malthene phase. If there are sufficient aromatic substances to saturate the absorption capacities of the asphaltenes, the micelles are mobile in the malthene phase and the colloidal solution is in the sol state. If there are insufficient aromatic substances, the micelles are attracted to each other and form a network. The solution is then in the gel state, giving the asphalt elastic properties. Mechanically, asphalts can behave either as elastic solids or as viscous liquids with intermediate states of behaviour also possible. Asphalts that are used or considered for use in radwaste solidification include straight-run distillation asphalts (DA), which are the residues obtained from refining of heavy petroleums, oxidized (or air-blown) asphalts (OA), which are highly colloidal products formed by blowing air through certain petroleums, cracked asphalts (CA), which are products obtained by pyrogenic breakdown of heavy petroleum molecules and emulsified asphalts (EA), which are emulsions of asphalt and water formed using surface active agents.

Temperature fluctuations usually have little effect on OA but they have a considerable effect on CA. CA are used mainly in cases where good flow at high temperatures and subsequent rapid hardening on cooling are required. Alkaline soaps and amine salts are the agents primarily used for anionic and cationic EAs, respectively. On contact with a prepared surface, the emulsion spreads over it, the water evaporates, and an asphalt coating is left on the surface. Being petroleum derivatives, all of these asphalts are capable of supporting combustion. The properties of asphalts considered most strongly in radwaste applications are penetration, viscosity, and flash point.

Table 23 Properties of some asphalts.

| Asphalt | SP - C | P - mm | D | LW - % | FP - C | E - mm |
|---|---|---|---|---|---|---|
| DA | 34-65 | 2-22 | 1.-1.1 | <2 | >230 | >25 |
| OA | 70-140 | 0.7-4.5 | 1.02 | | 250-90 | |
| CA | 77-85 | <0.5 | | | | |

SP = softening point, P = penetration at 25 C, D = density at 25 in g/cm$^3$, LW = loss of weight on heating, FP = flash point, E = elasticity at 25 C.

Asphalt (or bitumen, Berlin 1989) is principally used in Europe as an immobilization agent, where it has been popular for several decades. The material is a mixture of asphaltene and malthene hydrocarbons obtained generally from the "bottoms" from petroleum refineries and/or coking plants. Although there are a number of forms of asphalt used as an immobilizing agent, the straight run distillation and oxidized asphalts are most commonly employed. Additives may also be employed to aid in fixing specific constituents in the matrix. The use of an asphalt solidification system requires that the asphalt be heated to over 150 C to soften the material, and vaporize and drive off the water in wet wastes. This heating process may result in a fire hazard during processing, requiring use of special equipment and protection of workers, and has been the primary reason that the use of asphalt solidification has not grown rapidly in the United States.

Advantages of bitumen solidification (Berlin 1989): Material and technology is well known and available; compatible with many wastes; volume reduction of aqueous wastes; low cost of bitumen; no free-standing water; individual waste particles are coated; long shelf life of bitumen; low leachability; no difficulty with improper setting because it is not a chemical process.

Disadvantages : bitumen is flammable and burns spontaneously at temperatures as low as 390 C; limited loading of salts because of hardening effects; may swell in water leading to increased leachability and product degradation; potential for radiolytic gas formation; exposure to heat may cause melting or phase separation; process requires elevated temperatures; heating must be well controlled and spread evenly; storage of asphalt before use requires elevated temperatures to maintain fluidity of material; capital equipment costs are high; generation of off-gas during processing oil evaporate may clog filters.

Several techniques have been developed and used for incorporating radwaste into asphalt. These include thin-film evaporator and extruder/evaporator processes. The earliest processes for incorporating radwaste in asphalt used stirred-batch electrically-heated evaporators. The long residence times and high surface temperatures in these processes caused hardening of the asphalt and distillation of light oils and tars which make off-gas purification difficult. The processes or systems which have gained favour are those which use a fluid heat transfer medium (steam) and devices with low holdup volume (extruder evaporator or thin-film evaporator).

Comparisons of solidification agents (NPWT 1978)

Immobilization of radwastes by incorporation in cement has been practised for several decades. Despite these years of experience, solidification with cement is not completely understood. Because of the complex chemistry (interactions or lack of interactions between the waste constituents and cement), it is generally conceded that each new application must be considered and tested individually. Solidification with cement does not require the application of heat as does solidification with asphalt. There is an inherent risk in working organic materials at elevated temperatures. However, the incorporation of inert material into asphalt does not increase the risk of fire. Obviously, no material that is unstable at the working temperature should be added to asphalt. Asphalt can accommodate a wide range of wastes and waste proportions while, as mentioned above, cement solidification requires a rather rigid formulation. Since incorporation of radwaste in urea-formaldehyde resins was originally developed by private industry as a proprietary process, detailed information on product characteristics is limited when compared with cement and asphalt products which were, for the most part, developed with public funds. A greater accumulation and publication of data on UF products is needed by the nuclear industry for proper appraisal of this system. Free standing water is frequently cited as a problem with UF products. This liquid is acidic and can lead to corrosion of the container. If UF is used after its shelf life has been exceeded, or at low temperatures, or low viscosity, the "cottage cheese" effect (i.e., incomplete solidification and a settling of materials of different density within the container) is reported to occur.

Table 24 Comparison of cement, urea formaldehyde resin and asphalt solidification agents used with radwastes.

| Comparison Factor | Cement | Resin | Asphalt |
|---|---|---|---|
| Shelf life of immobilizing agent | Long | Short | Long |
| Mix fluidity | P | G | F |
| Mixer cleanability | P | G | F |
| Chemical tolerances for: | | | |
| Boric acid solution | P | G | G |
| $Na_2SO_4$ solution | F | RE | G |
| Alkaline solution | G | RE | G |
| Detergent waste solution | P | P | F |
| Organic liquids | P | P | F |
| Ion exchange resins | F | G | F |
| Sludges | G | G* | G |
| Volumetric efficiency$ | 0.5 | 0.6-1 | >2 |
| Product form | ML | ML | ML |
| Product density, g/cm$^3$ | 1.5-2 | 1-1.3 | 1-1.5 |
| Water binding strength | G | F | WE |
| Residual free water | Seldom | O | Never |
| Mechanical strength | G | F | G |
| Product stability | G | LW | G |
| Combustibility | No | Yes | Yes |
| Freeze/thaw resistance | F | P | G |
| Leach resistance | M | M | High |

RE = Reduced efficiency, * = may require pH adjustment, $ = Defined as the ratio of the volume of radwaste treated to the volume of final product. G = Good, P = Poor, F = Fair, M = Moderate, WE = Water evaporation during preparations, LW = loses water, ML = Monolith, O = Occasionally

Management of high-level liquid defense wastes in the US (Murray 1989)

For nearly a half century, radioactive defense wastes have been generated, first in the World War II atom bomb project, and ever since in producing materials for nuclear weapons and in reprocessing fuel from nuclear-powered naval vessels. Given the national policy to maintain a nuclear defense apparatus, the production of wastes is inevitable. The defense products have always had the highest priority, and wastes have been handled in ways that seemed appropriate at the time. Thus decisions were made to store waste in temporary single-walled underground tanks, as at Hanford, or to bury them in ways regarded as inadequate by modern environmental standards, as at Idaho Falls. Waste management plans must include remedial action as well as current needs. We can appreciate the complexity of the defense waste problem by the mere listing of its many dimensions. First are the sources: from treatment of fuel from several types of reactor-those for production of plutonium and tritium, naval reactors, and test reactors-and from weapons production and research programs. Second are the geographic locations of the laboratories that produce waste; the major ones are Hanford, Savannah River, Idaho Falls, Oak Ridge, and Los Alamos. Third are the types of waste-high-level (HLW), low-level (LLW), and transuranic (TRU). Fourth are the forms in which the wastes are currently stored. Fifth are the various forms into which the waste can be put-capsules, cement-waste mixtures, and glass-waste mixtures. Sixth is the status-buried, stored, or freshly produced. Seventh are the possible ways to dispose of the waste-stored for future decision, immobilized in its present location, shipped to a special repository, or prepared for disposal in the planned commercial repository. The stated purpose of the defense waste program of the Department of Energy is to provide safe and economic management.

## Storage tanks

The wastes from reprocessing to remove plutonium and uranium are composed of a great variety of chemicals, including the fission products and the residual chemicals used in the treatment. They are in the form of liquids or sludges, which traditionally have been stored in underground tanks, especially at Hanford and at Savannah River. The early tanks at Hanford were single-walled, and in the 1960 leaks developed in some of them, with an estimated 500,000 gallons of liquid escaping. Fortunately, most of the wastes had been stored in tanks about 250 ft above the water table, and the soil in that dry area of Washington State could retain the contaminants. Later, double walled tanks were installed. On detecting a leak in the inner wall, there is ample time to transfer contents to another tank. Tank storage, however, is not regarded as disposal, and it is necessary to immobilize the wastes.

## Management of low-level medical waste (Burns 1988)

Low-level radioactive waste generated at university medical centers arises from activities in both the clinical practice of medicine and biomedical research. The clinical practice area includes nuclear medicine, in vitro radioassays, and radiation therapy. Biomedical research involves many types of in vitro studies and animal studies performed with small amounts of radioactivity, predominantly C-14 and tritium. The bulk of the waste related to clinical activities is generated by the manufacturers of the isotopes. At Washington University, 88% of the total volume of low-level radioactive wastes (containing 99% of total activity) was disposed of by burial at one of the three low-level radioactive waste sites open at that time, while 12% of the volume (containing 1% of the activity) was disposed of by incineration. The primary approach to reduction of the amount of material sent for burial and incineration is segregation of the various types of waste.

Table 25 Low-Level Radioactive Waste Disposal Methods and Costs at Washington University, 1984.

| Category | Method (B=Burial,I=Incineration + Unit Cost) | Annual Cost |
|---|---|---|
| Dry Solids | B : 1$/lb, I: 0.8$/lb | 60,000$ |
| Absorbed Liquids | B : $40/gal | 228,000$ |
| Scintillation Vials | B : 10.5 c/vial I: 3.5 C/vial | 79 000$ |
| Animal Carcasses | B : $2.25/lb | 14,000$ |
| + Labour Cost | | 28,000$ |
| Total Annual Cost | | 409,000$ |

Waste disposal practices

A significant proportion (80%) of the waste being produced contains radionuclides with half-lives greater than 90 days or relatively small amounts of radioactivity in scintillation vials also containing organic solvents. The bulk liquid, which has radioactive material with half-lives of less than 90 days, can be stored to allow for decay and, after decay, can be disposed by discharge into the sanitary sewage system. Small amounts of deregulated material containing tritium or C-14 in scintillation vials can be shipped for incineration at approved sites. Other short-lived organic material also can be shipped for incineration. Therefore, the only material that needs to be shipped for burial is material with half-lives greater than 90 days, including solid, aqueous, or organic material, with high levels of radioactivity. Segregation of the radioactive waste into these classes reduces the total amount of material shipped for burial from major medical centers, and could have significantly reduced the amount that was shipped over the past few years. This will ultimately increase the useful life of the burial disposal sites for low-level radioactive waste.

Table 26 Current (1985) Low-Level Radioactive Waste Disposal Practices at Washington University.

| Waste Type | Category | Disposal Method |
|---|---|---|
| Liquid | Aqueous < 90 d : | Hold for decay and local drain release |
| | Aqueous > 90 d : | Ship absorbed for burial |
| Liquid* | Organic containing# : | Ship in bulk for incineration |
| Liquid* | Organic not listed above : | No convenient disposal route |
| Dry | : | Hold for decay and compact and ship for burial |
| Animal Carcasses | (3-H and/or 14-C< 50 nCi/g) : | Ship for burial |
| | < 90 d : | Hold for decay and local incineration |
| | > 90 d : | Ship for burial |

* Including scintillation vials, # 125-I, 51-Cr, 59-Fe, 35-S, 32-P, 45-Ca, 22-Na, 57-Co, 86-Rb, 67-Ga, 65-Zn, 111-In, 36-Cl, 203-Hg, 33-P, 131-I, 75-Se, 68-Ge, 109-Cd, 141-Ce, 46-Sc, 64-Cu, 195-Au, 99-Tc, 153-Gd, 113-Sn, 119-Sn and 3-H and/or 14-C.

The total storage capacity will accommodate 2000 drums (55 gallons), of which 1000 are for the decay of short-lived radioisotopes and 1000 are held in reserve for emergency storage of long-lived radioactive waste. At present a maximum of 100 drums of long-lived radioactive waste are being generated per year; thus the medical center has an emergency storage capacity sufficient to store waste for ten years. An alternative to long-term storage is onsite incineration, and this is certainly a consideration at many large research institutions. Major medical centers will continue to produce low-level radioactive waste as a by-product of essential activities in four areas: diagnosis, radioassay, therapy, and research. The amount of such waste is likely to grow in volume, and the costs of its disposal will likely increase in the current regulatory environment. Extensive planning for the separation and proper disposal of radioactive waste can yield an appropriate compromise for immediate and safe handling of low-level radioactive waste produced by these essential clinical and biomedical research activities.

## Disposal of low level liquid waste

Radioactive material released into the environment through liquid effluents from nuclear generating stations can potentially result in radiation doses to members of the public as a result of direct irradiation, ingestion of contaminated food or water. The doses to which members of the public may be exposed as a result of routine emissions from nuclear generating stations are too low to measure in order to determine compliance with these regulations. To ensure that the public dose limit is not exceeded, the amount of radioactive materials released in effluents from nuclear facilities is limited. These effluent limits are derived from the public dose limit and are referred to as Derived Emission Limits (DELs). Further, operating targets for effluent releases are set based on the ALARA principle (i.e. that doses be kept As Low As Reasonably Achievable, taking social and economic factors into account), and are typically a small fraction of the DELs.

## Ground disposal (Collins 1960)

One method of disposal of liquid wastes which has received considerable attention, particularly in the United States, is termed ground disposal. In certain locations, pits are dug in the earth and the radioactive effluents transferred to these excavations. The original concept was that these might act as storage basins or ion exchange columns, but the former idea has been largely abandoned as few, if any, earth materials are sufficiently impermeable. However, these pits do provide some decree of security, as the contents cannot be released suddenly as would be the case from a ruptured tank. The cost is very much less than for tank storage, but the difficulty of determining the ultimate fate of the liquid which seeps out calls for extreme caution before the practice becomes widespread.

Three establishments practise this form of disposal in the United States, namely the Hanford Works, the Oak Ridge National Laboratory and the Savannah River Plant. Approximately 1.3E+11 litres containing over 2.5E+6 curies have been discharged to the ground from these three sites. The procedure was only decided upon after the most careful study of the local conditions including stratigraphy, texture, porosity and other properties related to the possible movement of the wastes through the soil. The total amount of waste that can be discharged in any one area depends, very largely, on how good an ion exchange column is provided by the surrounding earth. This is a difficult question to answer as it depends on a detailed knowledge of the hydraulic and chemical properties of an underground mass of rock which, in most cases, is far from homogeneous.

However, over twelve years experience has been gained in this method of disposal and it is claimed that no hazard has arisen as a result. The disposal areas are surrounded by monitoring wells from which samples can be taken or down which monitors can be lowered. At Hanford there are up to nine wells within 8 to 10 metres of each crib centre and additional wells at greater distances in the indicated direction of movement. At Oak Ridge there are some fifty observation wells surrounding the disposal area. Laboratory tests had indicated that the radionuclide most likely to travel through the soil without absorption would be radioruthenium and this has been confirmed in the field. Ru-106 has been the only radionuclide definitely identified in the water at significant distances from the pits. Nitrate ions, however, travel relatively quickly and provide a useful indication of the direction of flow. At Hanford, it was found that this ion could be detected at 520 metres after 8 years, whilst Ru-106 could only be identified at 370 metres in the same time.

Further lines of investigation in the US are the possible use of abandoned salt mines and the disposal of liquid wastes into deep, porous and permeable formations. The solution cavities formed in the mining of salt appear particularly suitable. These are formed by dissolving the salt in situ and bringing the brine back to the surface. At the present time, laboratory studies are being made with various waste solutions. It has been shown that rock salt is almost as soluble in the waste solutions as in water. It would appear, therefore, that saturation of the waste with brine before disposal might be essential. Gas formation by the interaction of the liquids and the salt is also being studied, but results to date indicate that this would not be a serious problem.

The possibility of deep well disposal is based on the present practice in the petroleum industry of discharging millions of gallons of waste brines annually into underground formations. It is known that many deep porous sandstones contain connate water trapped in them when they were deposited hundreds of tons of years ago. If injections into these are made, it seems reasonable to suppose that retention could be expected. Before any such discharge could be contemplated, a most careful survey of the proposed area would have to be carried out. Consideration would also be given to the possible interaction of the waste with the minerals with which it would come in contact and the temperature increases that would result due to the radioactivity of the liquids discharged.

## Discharge into the sea (Collins 1960)

It is always desirable to disperse polluting matter in the largest possible volume of water. The sea, therefore, is most attractive as a receiving body for any effluent. In particular is it so for an effluent which can cause radioactive pollution because, since the sea is not usually a source of drinking water supply. The contamination of drinking water, which is the most limiting of all the public health considerations in the disposal of radioactive wastes, is thereby eliminated. However, it should never be assumed that once the wastes have been discharged into the sea, they are out of sight and may be forgotten. The exact point at which the effluents are to be discharged needs very careful selection, in order to obtain the maximum benefit from the tidal currents and winds which effect the dilution and carry the wastes away from the land. Indeed, in certain circumstances as will be seen, it could be possible for the wastes to be concentrated and carried back to the shore. On being discharged into the sea, liquid effluent becomes subjected to three processes. Immediately after leaving the pipeline and while still retaining the kinetic energy of discharge, it is subject to 'initial dilution'. In a study of the dispersion of sewage off tile coast of California,it was shown that the initial dilution was approximately proportional to the square of the path length from the discharge orifice of the pipeline to the surface. Assuming that the density of the effluent is less than that of sea water, a better dilution is obtained by directing the jet horizontally along the sea bed than by pointing it directly upwards to the surface. In the latter case the path length would be the depth of the pipe outlet, whereas in the former, the path length is the parabola described by the jet on its way to the surface. If multiple jets are used, then the effective path length and the cross-sectional area in which the effluent may be dispersed are increased. The initial dilution of the effluent can be assisted considerably, therefore, by careful design of an arrangement of multiple diffusers in the pipeline end.

The discharge velocity of the waste stream is reduced quickly by the surrounding water mass and when the waste has taken up the movements of the sea the second process, 'eddy diffusion', comes into play. Eddy diffusion is responsible for the ultimate dispersion of the effluent throughout the sea and is caused by the turbulent conditions set up by wind and tide. Theoretically, eddy diffusion continues indefinitely, since diffusion processes are continuously at work transporting material both horizontally and vertically in the oceans. However, the application of Fick's Law of Molecular Diffusion to the case of eddy diffusion would imply that the rate of eddy diffusion is directly proportional to the concentration gradients between the elements in solution in the effluent and those naturally in solution in the sea water. The coefficient of eddy diffusion is usually so considerably in excess of the coefficient of molecular diffusion that the latter is negligible except under extraordinarily calm conditions. In order to take advantage of the wind and tide effects in any particular situation, a thorough knowledge of local conditions is necessary. Full benefit may be obtained from the wind by siting the pipeline end as far from the shore as is economically possible, so that there is a minimum of shelter on the surface. In such a position there is also a maximum volume of surrounding water for eddy diffusion by currents. Moreover, being sited further from the shore, the pipe outlet is in deeper water, a factor which will assist the initial dilution. A study of the local tidal streams should be made, therefore, to obtain information enabling the outlet to be sited in the most favourable position and an estimate to be made of the rate of eddy diffusion to be expected in the area. As far as possible, the experiments should be carried out in a variety of weather conditions. Experiments with floats are successful in plotting the tidal streams and discharges of dye may be made to determine the probable rate of eddy dilution of the effluent.

### Reconcentration

While eddy diffusion is taking place, the third process of reconcentration may come into operation. This is the accumulation of the waste material by adsorption on to surfaces or by absorption into marine life. The facility with which chemical elements are concentrated selectively by natural processes in the marine environment necessitates the utmost caution in disposing of radioactive material into the sea. The concentration occurs as a result of natural physical, biological and chemical action. It is a process which is continuously at work in the marine environment causing the concentration of naturally occurring elements and it can act on the waste products, therefore, at any time after discharge. However, since the radioactivity of the isotopes decays in accordance with their respective half-lives, concentration of isotopes with short half-lives becomes progressively less of a problem with increasing time. It is important to realise that these concentrating processes occur as well with stable as with unstable isotopes and that it is not the radioactivity of the latter which is responsible for their concentration. In the oceans, sediments and micro-organisms are found in suspension at all depths and their fine structure presents a maximum surface area for physical adsorption of radioactive particles in the effluent. When conditions are calm enough for settlement of the heavier particles, much of the finer material is brought down at the same time. As a result, the silt on the sea bed may contain concentrations of the radioactive material present in the sea above.

Concentration may occur biologically when organisms take up the radioactive isotopes from the sea water and use them in their metabolism. Micro-organisms in the sea may adsorb or absorb activity present in the sea water. It is probable that they first adsorb on to the cell-water layer and then absorb in solution. The micro-organisms are eaten by fish which, in their turn, concentrate the activity by adsorption on to the gills or by metabolism into one of their organs. Later, the fish may become food for man and in this way food chains develop in which the concentrations of both stable and unstable elements in edible materials may be higher than in the surrounding water. Chemical concentration may occur as a result of interaction between the constituents of the waste and the sea water. The latter is naturally alkaline with a pH of about 8.2 and this may cause the precipitation of some of the isotopes in the effluent. The precipitates will settle to the sea bed where the activity will again tend to be accumulated. The reconcentration of the isotopes may be the result, therefore, of a combination of physical, biological and chemical processes. Assuming a maximum intake for each seafood, the permissible concentration for each RI can be calculated on the basis of ICRP value. Coupled with the concentration factor determined and dilution rate (100 $m^3/s$), the corresponding safe release rates can be calculated.

Table 27 Concentration factors (CF), Derived Working Limits (D) for seawater, ICRP Permissible Daily Intakes (PDI) and safe release rates (RR) for fish (F) and white mussel (WM) .

| RI | Fe-59 | Zn-65 | Cs-137 | Sr-90 | H-3 | Pu-239 |
|---|---|---|---|---|---|---|
| CF-F | 5300 | 5200 | 74 | 1 | 1 | 5 |
| CF-WM | 27000 | 13000 | 14 | 1 | 1 | 290 |
| D-nCi/l | 48 | 140 | 2400 | 880 | 26E+6 | 380 |
| RR-Ci/y | 150 | 450 | 7500 | 2800 | 8E+7 | 1200 |
| PDI-nCi | 130 | 220 | 44 | 0.22 | 6600 | 11 |

## Environmental surveys

When it is desired to discharge radioactive liquid wastes into the sea, the first step, therefore, is to select a discharge point which will give the most favourable opportunities for dilution and dispersion of the effluent. The choice of this point will depend to some extent on the routing of the pipeline into the sea, the length of the pipeline and the associated costs of construction. Economic factors such as these must always be taken into account. The next step is to carry out a survey aimed at giving a complete picture of all the ways in which members of the public might be subject to either external or internal radiation, through their contact with the marine environment, or its products, if these were to become contaminated. Having obtained the overall picture, each individual possibility whereby man may be irradiated is studied in detail. Data are collected from which maximum permissible concentrations can be calculated for any isotope on each of the marine materials involved. It is important to distinguish between the external and the internal radiation problems.

External radiation is caused by ionizing radiations originating outside the human body. In this case, the time which the individual spends in the path of the radiation, his proximity to the source and the strength of the source determine the external dose which he will receive. External problems arise from the radioactivity dispersed in the sea becoming transferred by settlement or adsorption on to some surface with which man comes into contact. The time spent by people on the beach, for example, must be studied to determine the dose which could be received if the beach were to become contaminated. Fishing gear which has been in contact with contaminated sea bed could itself become contaminated by picking up radioactive silt or mud. The external dose received by the men handling this fishing gear will depend on the time of contact of their hands with the contaminated nets and lined and the amount of activity picked up from the sea bed.

Internal radiation occurs after the individual has been breathing contaminated air or has consumed contaminated food or drink. In these cases, the quantities taken into the body, their behaviour in the body and their activity concentrations determine the internal dose. A survey of the internal problems necessitates a study of the uses of marine materials as food. The quantities of fish, shell-fish or edible seaweed taken from the vicinity of the pipeline must be known, effects of each isotope are additive and the total dose must not exceed the maximum permissible for that organ. However, because of the short range of beta particles in tissue, external and internal beta radiation effects are treated separately.

## Preliminary discharge

When the maximum permissible concentrations of all the radioactive isotopes involved have been established, the next step when a major discharge is intended ultimately, is to discharge these isotopes at low concentrations. Concurrently, an environmental sampling programme is undertaken, in which samples of the marine materials by which the activity might return to man are collected from the sea or the sea shore at regular intervals. The samples are analysed in the laboratory for the amount of each radioisotope which has been taken up. The preliminary discharge may take a considerable period of time to complete in order to obtain a true picture of the uptake of the isotopes in the environment. It should be continued for sufficiently long to allow any uptake to occur and for an adequate number of samples of each material to be collected. If possible, the preliminary discharge should be carried out under all weather conditions and it is usually necessary to continue it for a minimum of three months.

On the assumption that the uptake of an isotope in the environment is proportional to the amount discharged in the effluent, the discharge of each is calculated which will result in the maximum permissible concentration being reached in each type of sample. The sample material which permits the lowest rate of discharge of a particular isotope is then the critical material for that isotope and limits its maximum permissible discharge.

Let us assume that during a preliminary discharge lasting, three months, Ru-106 was put into the sea at a rate of 10 curies/week and that analysis of the environmental samples showed an average ruthenium concentration on beach sand of 4 nCi/g and in fish flesh of 0.2 nCi/g. The maximum permissible concentrations of Ru-106 for these materials were calculated above as 24000 nCi/g on sand and 100 nCi/g in fish flesh. Therefore, by considering the sand, the maximum permissible discharge of ruthenium-106 is 24000 X 10/4 = 60000 curies/week, and by considering the fish it is 100 X 10/0.2 = 5000 curies/week. In our example, therefore, the uptake, in the fish is the limiting factor and the maximum permissible discharge of Ru-106 is 5000 curies/week.

## Operational discharge

The maximum permissible discharge of ruthenium-106 just calculated is considerably above the levels of activity put into the sea during the preliminary discharge. The rate of discharge of the active isotope may now be increased, therefore, to a figure somewhere between the preliminary rate and the maximum permissible rate. At the same time, a further sampling programme is conducted to provide results for a recalculation of the permissible discharge on the basis of the new levels of radioactivity in the environment. In this way the permissible levels of activity in the samples are approached gradually and full information is obtained on the ultimate fate of the radioisotopes. As the discharge rates are increased to the operational level, the sampling programme is maintained, so that a continuous record is available of the uptake of the isotopes in the environment and periodic cheeks are possible of the maximum permissible levels of discharge.

## Disposal in rivers

The problems associated with the disposal of radioactive effluents in rivers are similar to those of disposal in the sea. The initial dilution obtainable in a river is very much better than in the sea, since there is continual and relatively fast flow of river water past tile discharge point. By regulating the rate of effluent discharge in accordance with the flow-rate of the river, it is possible to control the initial concentration of the radioactive material in the river water. However, in designing such a discharge system, particular attention must be paid to the dry-weather flow of the river. Conditions for eddy diffusion in rivers are less favourable than in the sea. The physical bounds of the river restrict the volume of water in which diffusion may take place and at the same time shelter the surface from wind effects. In a river, radioactive isotopes are taken up and concentrated by algae, fish and sediments as they are in the sea. However, since most rivers are a source of drinking water supply, this consideration usually overrides all others in the assessment of the public health problems. The maximum permissible concentrations recommended by the ICRP are used as standards for the level of radioactivity in river water.