PREDISPOSAL MANAGEMENT OF CARBON-14 BEARING ORGANIC-RESIN WASTES

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ABSTRACT

Spent organic-based ion exchange resins containing carbon-14 (5730 years half-life) are generated at nuclear power plants and irradiated-fuel processing facilities. Resin waste containing more than 3.0×10^{11} Bq/m^3 (8 Ci/m^3) of carbon-14 is generally classified as intermediate-level waste and is not suitable for near-surface disposal. In the absence of suitable disposal facilities for carbon-14 bearing resin wastes, such wastes are stored on an interim basis in different configurations. These storage configurations include resin-water slurry storage tanks, storage in containers after removal of freestanding water, and storage in containers after stabilization in various binders such as cement, bitumen and polymers. There is an expectation that additional treatment and packaging will be needed for the resin waste prior to preparing the waste for long-term storage and final disposal.

Resin-waste management comprises different operations such as pretreatment (waste segregation), treatment (waste volume reduction and radionuclides removal), and conditioning (stabilization and containerization) to produce a waste package suitable for handling, transport, storage and disposal. A spectrum of resin-waste treatment methods is available. Some methods have been applied to specific situations while others are being developed for future applications to meet the need to reduce worker dose, environmental releases, and waste-management costs.

This paper describes the results of an assessment of several predisposal management options for resin wastes containing relatively high carbon-14 inventories. The analysis shows that removal of the majority of the freestanding water and pore water from the resin waste appears to be a necessary step for interim storage. This approach would meet environmental and safety targets for storage of the waste, while providing sufficient flexibility to select future treatment options to meet applicable waste acceptance criteria for the eventual disposal of the waste.

INTRODUCTION

Organic-based ion-exchange resins are commonly used in the purification circuits and contaminated water treatment systems at nuclear power plants (NPPs) and irradiated-fuel processing facilities 1. The spent resins (or resin wastes) are a class of radioactive solid wastes generated by light water nuclear reactors e.g., pressurized water reactor (PWR), boiling water reactor, (BWR) and pressurized heavy water nuclear reactor (CANada Deuterium Uranium reactor, CANDU reactor). The quantities of the resin wastes and their contaminants-inventories vary widely among different nuclear power plants. Depending on the regulatory philosophy in the particular jurisdiction where the power plant is located, the types and amounts of radionuclides, metals and other chemical contaminants in the resin waste will determine the disposal options and also the extent of treatment and packaging required for storage or final disposal of the waste. For example, resin wastes that contain significant amounts of long half-life radionuclides, such as carbon-14 (C-14) may not be suitable for near-surface disposal.

In the absence of suitable disposal facilities for carbon-14 bearing resin wastes, such wastes are stored on an interim basis, awaiting long-term storage and final disposal. Resin wastes degrade gradually with time in storage because of biological, chemical, physical and radiolytic effects. Releases of contaminants that occur as a result of resin degradation during storage could cause adverse environmental issues, requiring frequent monitoring and repackaging of the waste, as necessary. It is anticipated that the C-14 bearing resin waste will have a relatively long period of storage before emplacement in a disposal facility. Therefore, there is a need for safe long-term storage of the waste through appropriate treatment and packaging.

Resin-waste treatment and conditioning comprises different operations such as waste volume reduction, radionuclides removal, stabilization and containerization that produce a waste package suitable for handling, transport, storage and disposal. Several aspects of the contaminants that have significant impact on waste treatment and the overall management cost are the concentrations of short half-life (arbitrarily less than approximately 30 years) radionuclides with high gamma decay energies, long half-life radionuclides such as carbon-14, and toxic metals present in the waste. A spectrum of resin-waste treatment methods is available. Some methods have been applied to specific situations while others are being developed for future applications to meet the need to reduce worker dose, environmental releases, and waste-storage and disposal costs.

This paper describes the results of an assessment of several predisposal management options for resin wastes containing relatively high C-14 inventories with the objective to prepare the waste for long-term storage and eventual final disposal.

RESIN-WASTE CHARACTERISTICS FROM NUCLEAR POWER PLANTS

Most organic-based ion-exchange resins are made by the co-polymerization of styrene with divinylbenzene (DVB) to form a cross-linked resin matrix. The functional group is then attached to this matrix by sulphonation (e.g., sulfonic acid functional group) for cation resins, and by chloromethylation and amination (e.g., quaternary ammonium functional group) for anion resins. Generally, mixed-bed (anion plus cation exchangers) resin columns consisting of resin beads are used in the majority of PWRs and CANDU reactors. Powdered resins are used in BWRs for purification.

The quantity of resin-waste generation varies widely depending on the operational goals of the individual power plant. The Light Water Reactors (LWRs) generate resin wastes in the range of 3 to 150 m^3/a (PWRs: 3 to 10 m^3/a/reactor; BWRs: 75 to 150 m^3/a/reactor). The CANDU plants generate radioactive resins in the range of 5 to 10 m^3/a/reactor 2.

Resin wastes generated from nuclear power plants contain a variety of contaminants including radionuclides, toxic metals and chemicals. The principal radionuclides in spent resins include H-

3, C-14, Cr-51, Fe-55, Co-58/60, Zn-65, Sr-89/90, Zr-95, Ru-106, Sb-124/125, I-131, Cs-134/137 and Ce-144. The total radioactivity generally ranges from 10^{11} to 10^{13} Bq/m^3 2. Non-radioactive cations and anions are also present in the resin wastes. The commonly found species are Al, B, Ca, Cr, Cu, Fe, Gd, Li, Mn, Ni, U, W, Zn, carbonate, chloride, nitrate and sulphate. The concentrations of these species vary from tens of mg/kg to hundreds of mg/kg, depending on the source of the feed treated by the resin. Bulk chemicals used in the plant operations may also pass through ion-exchange resin purification systems; examples include hydrogen peroxide, hydrazine, morpholine (tetrahydro-1, 4 oxazine) and ammonium hydroxide. Resin wastes arising from decontamination activities are expected to have varying amounts of complexing agents such as oxalic acid, citric acid, and EDTA 2.

Carbon-14 in Resin Wastes

The resin wastes generated from moderator and coolant purification systems in nuclear reactors contain C-14 at different concentrations. The dominant reactions leading to C-14 production in nuclear reactors are: the (n,p) reaction with N-14; the (n,α) reaction on O-17; and (n,γ) reactions with C-13. The main C-14 production in the CANDU reactor comes from: 1) moderator system, 2) primary heat transport system, 3) annulus gas system and 4) fuel elements. Among the four systems, the moderator system has been recognized to be the largest contributor to C-14 production because a large volume of heavy water is exposed to high thermal-neutron fluxes 3. An estimate of C-14 in LWRs 4 suggests O-17 activation and to a lesser extent N-14 as the main sources. On the basis of O-17 as the source isotope for C-14 production, the BWRs produce approximately 3.4×10^{11} C-14 Bq/GWe-a (9.2 Ci/GWe-a), whereas PWRs produce only approximately 1.2×10^{11} C-14 Bq/GWe-a (3.3 Ci/GWe-a). CANDU reactors produce approximately 2.8×10^{13} C-14 Bq/GWe-a (770 Ci/GWe-a) by O-17 activation.

Resin sampling studies have revealed varying levels of C-14 in the resin wastes generated from US LWRs 5 and Canadian CANDU plants operated by Ontario Power Generation (OPG) 6. The C-14 inventories in spent resins generated from PWRs, BWRs and CANDU plants operating in Canada are summarized in Table I. The wide range of C-14 inventory can be attributed to differences in power plant design, and methods of resin sampling and analysis. The C-14 inventory in the combined moderator and primary heat transport resin-waste in CANDU plants operated by OPG is estimated 7 to be approximately 1.2×10^{12} Bq/m^3 (~32 Ci/m^3). This value is about four times greater than the maximum C-14 inventory of 3.0×10^{11} Bq/m^3 (8 Ci/m^3) that the U.S. Nuclear Regulatory Commission (US NRC) uses as a cutoff value for 'Class C' low-level waste classification. As a result, this resin waste is not suitable for near-surface disposal, and may have to be considered as Intermediate-Level Waste (ILW) for long-term storage and final disposal considerations.

ISSUES RELATED TO RESIN-WASTE TREATMENT AND STORAGE

Because of the relatively long half-life of C-14 (5730 years), the magnitude of its inventory in the waste and its stability in the waste are key factors that impact on the management of the waste. Carbon-14 has the potential for high mobility in the geosphere and biosphere as carbonate ion or carbon dioxide gas, and it has the ability to be incorporated easily into organisms through biological carbon cycles. Safety and environmental impact assessments for various disposal concepts indicate that C-14 is one of the radionuclides that often contribute significantly to radiological risk 1.

Table I. Carbon-14 Inventories in Spent Resins Generated from Various Reactor Types

Reactor Type	**Purification System**	**C-14 Inventory (Bq/m^3)^a**
PWR	Coolant Purification	7.4×10^6 to 1.5×10^{10}
BWR	Coolant Purification	1.0×10^6 to 1.1×10^9
CANDU	Moderator Purification	3.7×10^{10} to 5.9×10^{14}
CANDU	Primary Heat Transport Purification	3.7×10^{10} to 3.7×10^{11}

[a]: The bulk density of spent resin is assumed to be 1000 kg/m^3.

Resin wastes degrade gradually with time because of biological, chemical, physical and radiolytic effects. Storage of resin wastes should consider several factors including the stability of resins with respect to gas generation, in particular for gases such as H_2, O_2, CH_4, container integrity, monitoring and capturing of emissions, and resin and/or container retrievability to repackage or to further treat for long-term storage or final disposal requirements.

Biological activity has been implicated as a contributor to gas generation in organic resins 8. A number of US utilities have reported gas generation in low-level radioactive waste containers, resulting in several cases of container pressurization. It was determined that biogenic, rather than radiolytic mechanism was the main source of gas production in these wastes, which were comprised mostly of filtration media and spent resins.

Elevated temperatures during resin treatment and storage can also result in appreciable resin degradation. Resin manufacturers and numerous articles in the literature suggest that the anion resin is more susceptible to losing its functional groups than the cation resin at elevated temperatures. For commonly used resins in nuclear power plant applications, elevated temperatures could decompose anion-resin functional groups relatively easily to produce methanol and trimethylamine. Depending on the system temperature, if weakly exchanged volatile radionuclides such as C-14 and I-129 exist on the resin, some of these radionuclides could also be released.

The continuous degradation of the ion-exchanger resins and their environment due to radiation effects can result in: 1) change in pH, 2) significant gas evolution, 3) agglomeration of the resin matrix, and 4) increased corrosion. It is generally recognized that the radiation effects on ion exchange resins, as well as radiolysis of water within the resin matrix, produce a variety of products that could significant change the pH of the overall matrix. Generally, the prior exposure of the resin to radiation fields is not expected to result in significant decomposition of resin in storage. However, some radiolytic hydrogen generation can occur, which can be a problem for confined or contained storage of resin waste. Relatively high hydrogen gas contents have been found in the dewatered resin-waste storage containers.

Water appears to be the primary contributing source for gas generation, corrosion of the container, and biological activities. Thus, complete removal of water (freestanding and pore water) from the resin waste should minimize gas generation and corrosion of the container.

RESIN-WASTE MANAGEMENT PRACTICES

The practices for the management of radioactive resin wastes in selected countries are summarized in Table II.

In general, the resin-waste management practices can be classified as:

- Interim storage as resin-water slurry in spent resin storage tanks (e.g., Canada)
- Storage/disposal of in containers after dewatering to remove the bulk of freestanding water (e.g., Canada, Sweden and United States)
- Storage/disposal of in containers after physical treatment such as dewatering, drying, compaction, etc. and stabilization in various binders such as cement, bitumen and polymers (e.g., Finland, Japan and Sweden).
- Storage/disposal of the residue in containers after thermal treatment such as incineration (e.g., Belgium and France)

Some of these approaches produce waste packages that are suitable for long-term storage or disposal depending on the Waste Acceptance Criteria (WAC) of the facilities. However, the others are only suitable for interim storage. Additional treatment and packaging of the resin wastes will be required prior to preparing the wastes for long-term storage or disposal.

Resin wastes that are generated from moderator purification systems at CANDU reactors, contain higher carbon-14 activities (at least an order-of-magnitude) than the resins generated from LWRs. Therefore, some waste management approaches used for the LWR spent resins may not be suitable for the CANDU resin waste that is classified as ILW. One approach by OPG for the C-14 bearing resin waste has considered stabilization and packaging the waste, and disposing it by co-locating with high-level spent-fuel waste in a geological disposal facility.

Currently, there are two disposal facilities that have silos designed for ILW. One is the VLJ repository in Finland and the other is the Swedish Final Repository (SFR) in Sweden 9. The VLJ repository is an underground disposal facility for operational Low and Intermediate-Level Waste (LILW) generated by the Olkiluoto nuclear power plant and is located 700 m away from the reactor site. The repository consists of two silos excavated at a depth of 60-100 meters in the bedrock. The silo for LLW is a rock silo. For ILW a reinforced concrete silo has been constructed inside the rock silo. The upper activity limits for the important nuclides allowed in the VLJ repository are summarized in Table III.

Table II. Resin-Waste Management Practices in Selected Countries 1

Country	Practice
Belgium	Resin wastes are dried at the power plants and then sent for incineration by the Belgoprocess. The ashes from incineration are super-compacted into pellets, and the pellets are placed in 0.4 m^3 drums and embedded into cement.
Canada	Most CANDU plants store resin wastes (low and high C-14 content resins) as resin-water mixture in on-site storage tanks. OPG plants in Ontario have been dewatering the resin waste in 3 m^3 containers and storing the waste in centralized facilities in Bruce, Ontario.
Finland	Resin wastes are stabilized in bitumen in 0.2 m^3 steel drums at Teollisuuden Voima Oy NPP and in cement in concrete containers at Imatran Voima Oy NPP. The stabilized waste packages are shipped to the VLJ repository for disposal.
France	The low-level radioactive resin wastes, which meet the waste acceptance criteria for near-surface burial, have been stabilized in cement and disposed (e.g., Centre de L'Aube disposal facility). Recently, the resin wastes have been volume reduced by incineration and the residue is containerized and disposed in a near-surface disposal repository.
Germany	Resin wastes have been super-compacted, stabilized in cement in containers and placed in underground caverns, to which pumpable grout is injected to provide an additional barrier.
Japan	Some of the resin wastes from LWRs have been dried and compacted for volume reduction, and the compacted resin waste is then stabilized using the high-performance cement and disposed of as LLW.
Republic of Korea	The resin wastes from Korean LWRs are currently stabilized in cement or polymer matrices. A vitrification plant, based on the cold crucible melter technology, is being developed by Commissariat a 'Energie Atomique (CEA) and Societe Generale pour les Techniques Nouvelles (SGN) in France and Nuclear Environment Technology Institute (NETEC) in Korea for the resin waste, plastic and cellulose waste, borated concentrate and sludge.
Spain	Some resin wastes have been encapsulated in urea formaldehyde previously. Because of the poor quality of the resulting waste form, a new resin conditioning process (involving drying, compaction and cementation) has been introduced.
Sweden	Resin wastes are stored on-site as resin-water slurry in storage tanks prior to conditioning. Some low-level radioactive powder resins (e.g., at Oskarshamn NPP) are dewatered in transportable concrete tanks prior to disposal. Most of the spent resins are stabilized using either cement or bitumen in concrete or steel containers. In general, all the wastes treated at power plants are stored in interim storage facilities on site. The stabilized resin wastes are then shipped to the Swedish Final Repository (SFR) for disposal.
United States	The majority of ion-exchange resin wastes are not stabilized prior to disposal. These wastes are typically dewatered and disposed of in large carbon steel containers or in High Integrity Containers (HIC) as LLW. Also in the United States, certain spent resins (e.g., resin wastes from coolant system decontamination) have been stabilized in cement or polymer matrix. The majority of the resin wastes generated from LWRs is designated as Class A or Class B low-level wastes and are suitable for near-surface disposal.

The SFR has been in operation since 1988 and receives short-lived LILW from operating and maintenance of the Swedish nuclear power plants. The repository is built in the bedrock under the Baltic Sea close to the Forsmark nuclear power plant. A 50-meter layer of rock covers the repository caverns under the seabed. There are different caverns for different ILW and LLW packages in the SFR. The ILW packages (drums and boxes) are disposed of in a concrete silo.

The LLW packages are disposed of in 160 m long caverns 10. The nuclide-specific activity limits of SFR are listed in Table IV.

The upper allowable C-14 limit in the stabilized resin for the VLJ repository is 3.0×10^{8} Bq/package (e.g., 200-L drum). The SFR can receive up to 6.8×10^{12} Bq of C-14 in its ILW-silo in 2010 10. The total limit of C-14 in the silo is 2.1×10^{13} Bq 11. The allowable C-14 inventories in these ILW facilities limit the amounts of C-14 bearing resin waste disposed in the facilities. For example, only 17.5 m^3 of combined resin-waste (with 1.2×10^{12} Bq C-14/m^3) from a CANDU plant can be housed in the ILW silo at SFR. However, the steps employed by these facilities to perform environmental assessment of the C-14 waste could be expanded to assess the suitability of disposal of the carbon-14 bearing resin-waste.

Table III. Upper Activity Limits for the Most Important Nuclides in Various Waste Packages for the ILW-Silo in the VLJ Final Disposal Facility (The limits refer to the moment when the waste is transport to the facility) 9

Nuclide	**Stabilized Resin**	**Filter Rods and Metal Scrap**		
	Steel Drum (Bq)	**Steel Drum (Bq)**	**Steel Box (Bq)**	**Concrete Box (Bq)**
C-14	3.0×10^{8}	3.0×10^{7}	2.0×10^{8}	3.0×10^{8}
Ni-59	2.0×10^{8}	2.0×10^{7}	1.0×10^{8}	2.0×10^{8}
Co-60	3.0×10^{11}	3.0×10^{10}	2.0×10^{11}	3.0×10^{11}
Ni-63	3.0×10^{10}	3.0×10^{9}	2.0×10^{10}	3.0×10^{10}
Sr-90	3.0×10^{10}	3.0×10^{9}	2.0×10^{10}	3.0×10^{10}
Tc-99	2.0×10^{7}	2.0×10^{6}	1.0×10^{7}	2.0×10^{7}
I-129	9.0×10^{4}	9.0×10^{3}	6.0×10^{4}	9.0×10^{4}
Cs-135	9.0×10^{5}	9.0×10^{4}	6.0×10^{5}	9.0×10^{5}
Cs-137	3.0×10^{11}	3.0×10^{10}	2.0×10^{11}	3.0×10^{11}
Pu-238	3.0×10^{7}	3.0×10^{6}	2.0×10^{7}	3.0×10^{7}
Pu-239/240	3.0×10^{7}	3.0×10^{6}	2.0×10^{7}	3.0×10^{7}
Am-241	3.0×10^{7}	3.0×10^{6}	2.0×10^{7}	3.0×10^{7}
Cm-243/244	3.0×10^{7}	3.0×10^{6}	2.0×10^{7}	3.0×10^{7}

Table IV Nuclide Specific Activity Limits for ILW Silo of the SFR (The limits refer to the year 2010) 9

Nuclide	**ILW Silo (Bq)**
H-3	1.3×10^{14}
C-14	6.8×10^{12}
Fe-55	7.1×10^{14}
Ni-59	6.8×10^{12}
Co-60	1.8×10^{15}
Ni-63	6.3×10^{14}
Sr-90	2.5×10^{14}
Nb-94	6.8×10^{9}
Tc-99	3.3×10^{11}
Ru-106	6.1×10^{12}
I-129	1.9×10^{9}
Cs-134	8.1×10^{14}
Cs-135	1.9×10^{10}
Cs-137	4.9×10^{15}
Pu-238	1.2×10^{12}
Pu-239	3.8×10^{11}
Pu-240	7.8×10^{11}
Pu-241	4.2×10^{13}
Am-241	1.0×10^{12}
Cm-244	1.2×10^{11}
Total Activity	9.2×10^{15}

PREDISPOSAL MANAGEMENT OF CARBON-14 BEARING RESIN WASTE

Decisions on steps to manage radioactive wastes prior to disposal are often made at a time when a disposal facility is not available and the waste acceptance criteria for the facility are still unknown 1. Recognizing this situation, the management steps should focus on stabilizing the waste for long-term storage, and the interim waste package can be further treated and packaged at a later time to meet the WAC for final disposal. The steps involved in a predisposal management plan are summarized in Fig. 1. The main steps are pre-treatment (e.g., waste minimization and segregation), treatment (waste volume reduction and radionuclides removal), conditioning (e.g., stabilization and containerization) and interim storage. To select appropriate treatment and packaging technologies for the waste when no disposal facility is available, assumptions have to be made about the likely disposal option. Consideration has to be given to the potential conflict between the need to contain and store the waste in a passive, safe condition and the desirability to retain flexibility in a waste form to avoid prejudicing the choice of disposal options. In the absence of a disposal facility, a viable approach for C-14 bearing resin waste is to adapt a "staged" process that involves long-term storage and provides the option to proceed towards disposal. At each stage, time is available to build sufficient confidence before moving to the next stage, while retaining the ability to retrieve waste and pursue an alternative option if they are available and preferred. A flow diagram for decision making for the resin-waste management is shown in Fig. 2.

Waste Pretreatment (Waste Minimization and Segregation)

Waste minimization is an essential objective for radioactive waste management. Considerations should be given to facility design and operational features that can significantly reduce the generation of ion-exchange waste. The criteria for ion-exchange column change are usually well defined, so that further reduction of the resin waste volume during normal operations may be a challenge. However, the use of ion-exchange processes for some secondary systems, such as irradiated fuel bay purification and active liquid waste treatment should be re-examined. Preliminary analysis indicates that some commercially available advanced water treatment technologies (e.g., membrane technology) are cost effective. These alternative treatment processes produce good quality treated water with smaller volumes of secondary waste.

Radioactive wastes should be collected and segregated properly, taking into account their biological, chemical, physical and radiological characteristics. For example, waste containing predominantly short-lived radionuclides should not be mixed with long-lived waste. The main factors in planning the segregation of waste are: 1) physical and chemical characteristics of the waste; 2) types and half-life of the radionuclides in the waste; 3) concentrations of the radionuclides in the waste; and 4) specifications or requirements to be fulfilled for further waste treatment.

Some CANDU plants in Canada (e.g., Hydro Quebec's Gentilly-2) store the fuel-contact resin (e.g., primary heat transport related and irradiated fuel storage bay resins) and the non-fuel contact resin (e.g., moderator related, liquid zone control and end-shield cooling resins) separately in the spent-resin storage tanks. Some plants (e.g., OPG's Darlington NPP) store the moderator resin separately because of it contains high carbon-14 concentrations.

For disposal purposes, only the long-lived isotopes are generally important. Thus, the C-14 resin waste should be segregated from other resin wastes and stored. Benefits of segregation are improved safety, lower occupational exposure to radiation and costs for subsequent waste management. However, these benefits must be weighed against the costs of pre-treatment steps to achieve segregation.

Waste Treatment (Waste Volume Reduction and Radionuclides Removal)

Waste treatment includes processes that improve the safety and costs involved in the management of the waste. The primary goal for treatment is to achieve desired waste characteristics to allow direct disposal or to permit additional treatment involving waste stabilization and containerization that makes the waste suitable for storage and final disposal. The basic waste treatment steps are volume reduction (defined by a volume reduction factor, VRF, the ratio of original waste volume to final waste volume after treatment) and radionuclide removal to achieve target inventories for radionuclides. The actual treatment needed would rely on the specific waste and its characteristics, and the overall strategy for waste management.

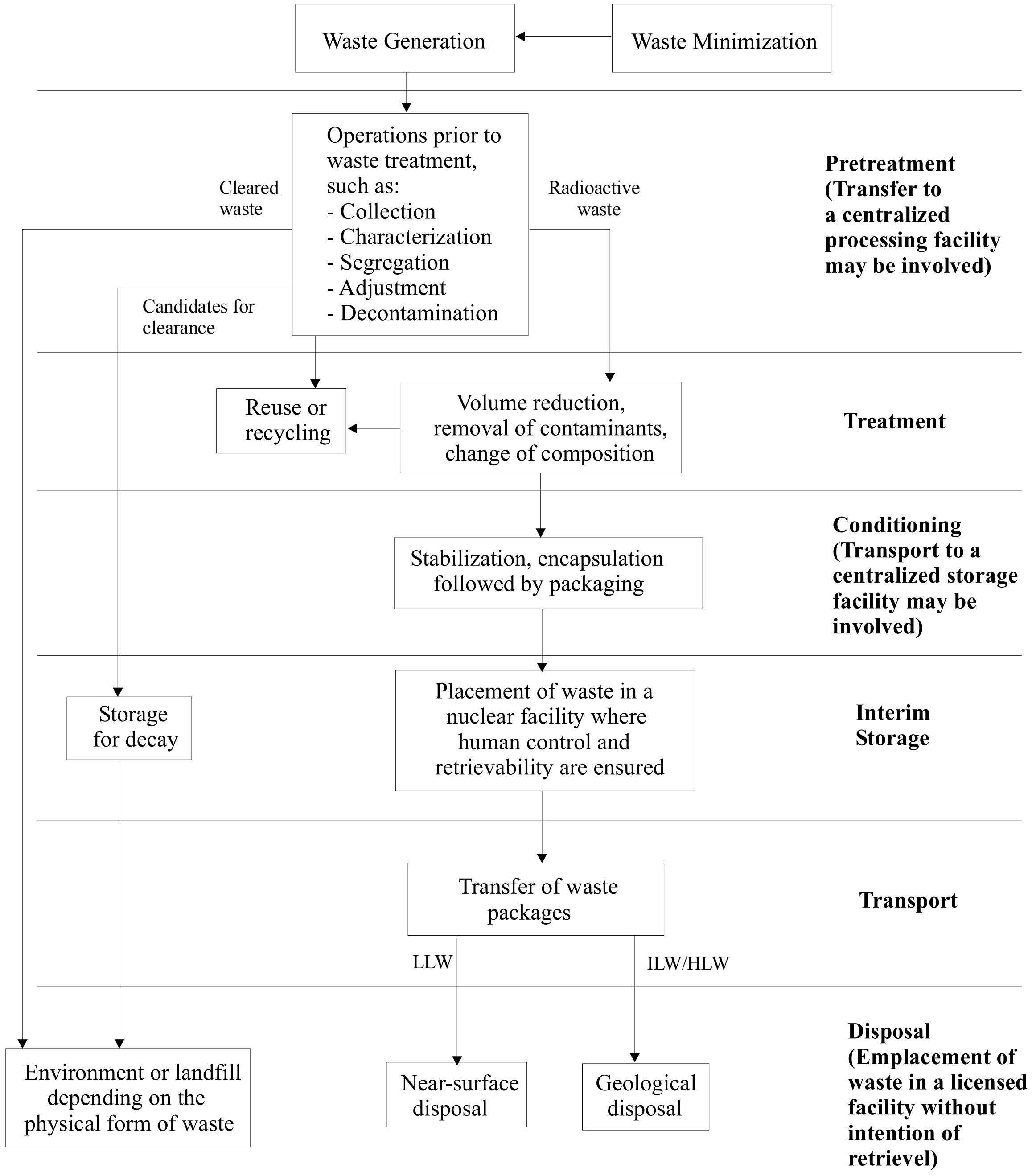

Fig. 1 Radioactive waste-management steps

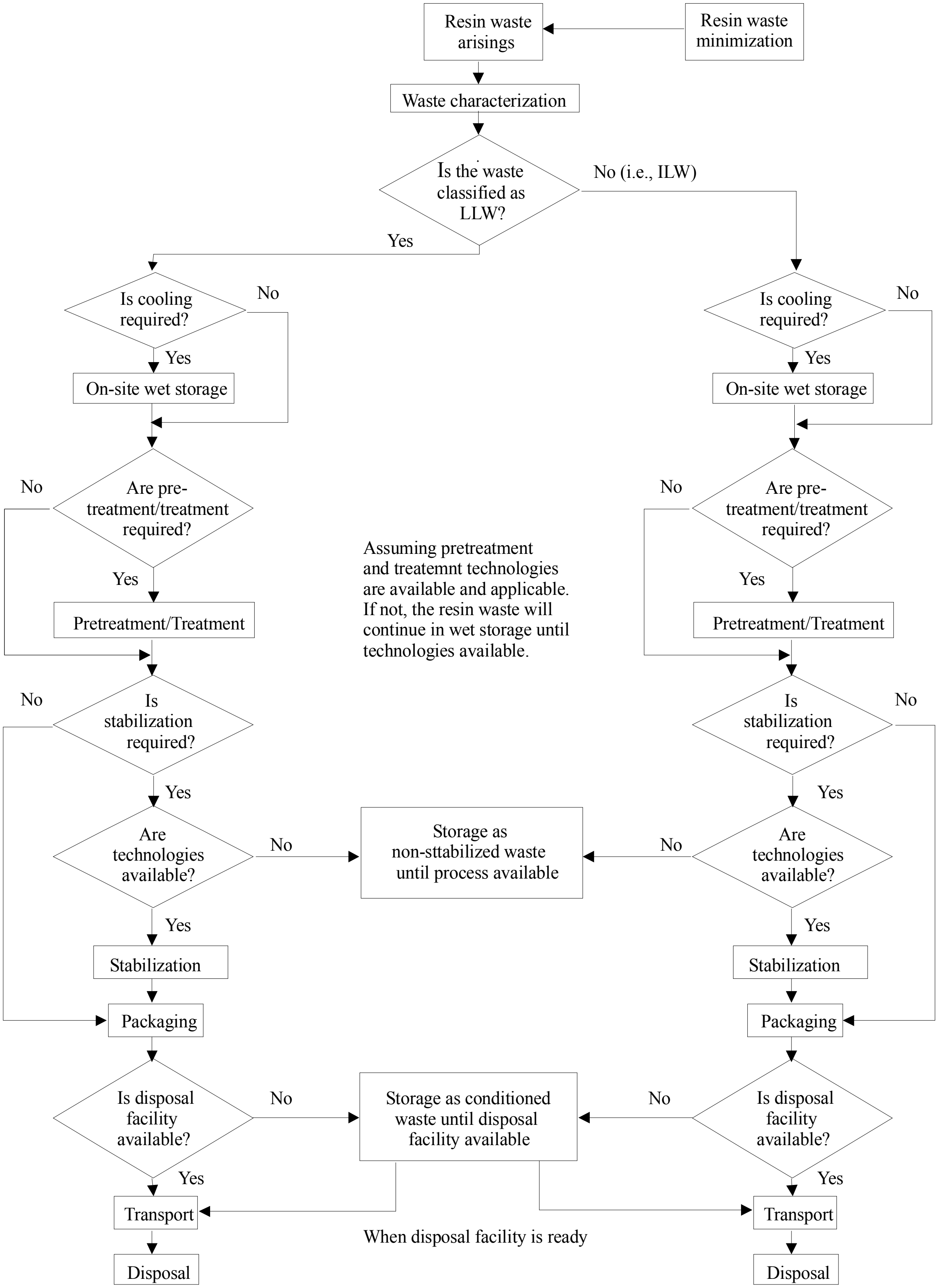

Fig. 2 Flow diagram for decision making in the management of C-14 resin waste

Depending on the treatment method employed, significant reductions in the resin-waste volume can be obtained. Some methods, such as waste vitrification and pyrolysis produce a waste form directly. The need for radioactive waste-volume reduction appears to be driven by savings in the cost and facility space required to store or dispose the waste. However, it is not always correct to assume that the reduction in storage and disposal costs is proportional to the waste VRF because: 1) waste disposal charges are generally calculated from volume and the inventory of radionuclides (if the waste volume is reduced, there will be an increase in radionuclide concentration to offset some of the volume reduction gains); and 2) volume-reduction incurs higher waste processing costs.

The available treatment methods for spent resins include: 1) drying and compaction; 2) activity stripping including acid stripping and thermal stripping; 3) acid digestion; 4) pyrolysis; 5) wet oxidation; 6) incineration; and 7) vitrification. Details of these methods are described in the literature 1. A microbial process 12 for dry organic wastes including resin waste was tested in a pilot-plant at Loviisa NPP in Finland. The process was capable of decomposing radioactive resin waste completely within seven days. The process produced gases and small residual solid volumes. The gases consisted mainly of CO_2 and CH_4, and minor amounts of H_2 and H_2S. There was no release of radionuclides observed in the tests. An assessment by OPG 13 suggested that: 1) the majority of the resin treatment techniques involves some degree of resin degradation, which results in some contaminant (e.g., C-14) releases; and 2) drying and compaction at low pressures appears to be the most economic among the available methods.

Each of these treatment methods has its advantages and limitations while achieving high waste-volume reductions. However, a portion or all of the carbon-14 on the spent resins will be released as $^{14}CO_2$ during treatment and, therefore, the capture and stabilization of $^{14}CO_2$ in the off-gas will be essential. This will result in an increased secondary waste volume that requires additional treatment and packaging suitable for long-term management.

Waste Conditioning (Waste Stabilization and Containerization)

Waste conditioning involves operations that transform radioactive wastes into a solid waste form suitable for handling, storage, transportation, and/or disposal. The operations may include stabilization of the radioactive waste, placing the waste into containers, and providing additional packaging.

Stabilization means that the resin waste is incorporated into a matrix material such as cement, bitumen, polymers, etc. This approach offers the advantage of a quick and simple operation. In general, the chemical and physical properties of the spent resin remain the same, and the inert encapsulation materials (e.g., bitumen, polymers, etc.) provide a barrier for water and movement of the radionuclides. The direct stabilization by itself does not result in a volume reduction of the waste, but in fact will result in an overall volume increase 1.

The choice of waste-form matrices for the waste will be dictated by the requirements of storage and final disposal. As there are no disposal facilities currently available for C-14 bearing resin waste, there are no pressing needs to stabilize such wastes after a short period of interim storage.

Waste packages are designed to provide primary containment during handling, interim storage, transportation, the operational phase of the disposal facility, and in some cases to retard release and migration of radionuclides and hazardous constituents in the long term (e.g., post-closure phase of the facility). It is anticipated that the C-14 bearing resin waste will have a relatively long period of storage before emplacement at a disposal facility. Thus, the main requirements that a container for such resin waste should meet are: 1) to be sufficiently durable to remain intact during future retrieval and transport from interim storage to long-term storage or disposal facilities; 2) to have the mechanical strength to permit stacking; 3) to be sufficiently corrosion-resistant to guarantee waste containment during the storage period. Loss of contaminants due to corrosion would require repackaging of wastes and additional occupational radiation exposure, which could also result in increased waste volume; and 4) to satisfy regulations for off-site transport of radioactive materials.

Waste Storage

Storage is the placement of waste in a facility where isolation, environmental protection, and monitoring are provided. It is an interim waste management option with the goal that the waste will be retrieved at a later time for release from regulatory control or further processing prior to long-term storage and final disposal. However, in many instances disposal facilities are not available and storage may be necessary for extended periods of time. Thus long-term storage becomes a critical option that has to be considered in any waste management strategy. Since no disposal facility is currently available for the C-14 bearing resin waste, the waste must be packaged suitably for long-term storage with the provisions for future retrievability, reprocessing and disposal.

Predisposal Management Options for C-14 Bearing Resin Waste

Based on the resin-waste management practices pertaining to LWR and CANDU plants in different countries combined with ongoing developments in resin-waste treatment and conditioning, the following options have been identified for the predisposal management of C-14 bearing resin wastes:

1) Store in spent resin storage tanks with light water;
2) Remove the majority of the freestanding water in resin-waste containers (with built-in dewatering components) and store in solid-waste storage facilities;
3) Remove essentially all freestanding and pore waters from the resin waste (e.g., by thermal drying) and transfer the water-free resin in containers for storage;
4) Dry resin waste to completely remove freestanding and pore waters, pressure compact the dried resin for additional volume reduction, and transfer the compacted resin in containers for storage; and
5) Remove C-14 from the resin (e.g., thermal stripping) to classify and manage the processed resin as low-level waste (e.g., less than 3.0×10^{11} Bq/m^3); capture released C-14 in a suitable medium as small-volume waste for long-term storage.

Similar to LWR plants, CANDU reactor sites have been practicing wet storage of resin wastes in storage tanks (Option 1). Experience thus far suggests that this option may be sufficient for interim storage on the basis that adequate tank capacity is available. This option also provides the required conditions for decay of short half-life isotopes. During resin transfer and storage, however, some amounts of radionuclides, primarily C-14 could be released to the environment. Carbon-14 spikes have been observed when nitrate-loaded resin-waste is transferred into the storage tanks. The releases are attributed to pH changes that resulted when the different resins were added. Some CANDU plants have also observed caking of resins with impurities in resin-waste storage tanks (e.g., Hydro Quebec's Gentilly-2) after several years of operation. Such problems may impair pumping and transfer abilities of the resin slurry. Presently, the stability of resin over long periods with respect to chemical, radiation and biological effects have not been fully understood. Furthermore, the potentially corrosive characteristics of the resin slurry would require at a minimum stainless steel tanks instead of the carbon-steel tanks lined with epoxy. The difficulties with a wet-storage option suggest wet storage is not the preferred option for long-term storage.

The practice to storedewatered resin waste (with less than 1 vol.% of freestanding water of the total waste volume) in suitable containers in belowground or aboveground storage structures (Option 2) has been applied in specific facilities (e.g., in the US and Canada). The rationale for the acceptance criterion of less than one volume percent for freestanding water in resin package for interim storage is not evident. As long the freestanding water does not freely flow within and outside of the waste package, the waste should be acceptable for storage in a solid-waste storage facility. For chemical reactions that could occur in the presence of water with time in storage, the majority water contained in the pores would be more significant than the freestanding water since the resin usually contains approximately 50 wt.% of pore water. As for the container integrity, it appears that the amount of pore water in the resin waste may not be an issue because it is strongly held up by the capillary forces, unless excessive thermal cycling takes place in storage. Furthermore, there are no simple techniques available presently to ensure that the residual freestanding water in the resin container after dewatering is less than a target value. Option 2 appears to be an improvement to the Option 1 for interim storage. However, the impact of long-term storage on resin stability and radioactivity containment is not clear.

Options 3, 4 and 5 involve the removal of freestanding and pore waters by drying the resin wastes at a pre-determined temperature (usually higher than 110^{o}C). Option 3 is the first key step in the Hitachi process for the LWR resin-waste treatment 2. Our laboratory-scale tests with mixed-bed resin (Purolite NRW-37LC) samples at 170^{o}C have further confirmed that approximately 50% volume reduction (VRF ~2) can be achieved by drying.

Since the dried resin can re-absorb water from the surrounding air during storage in Option 3, the container should be specially designed with appropriate seals and/or adequate humidity control to minimize water re-absorption. As a result, containerization of the dried resin is more complex for long-term storage.

Option 4 uses the Hitachi approach 2 in which the dried resin is compacted under pressure to produce pellets or crushed within the drum to produce a compacted resin product. Drying and compaction, depending on the temperature used, can physically destroy the resin structure, which in turn can minimize re-absorption of water by the resin-waste. The dried and compacted resin waste is placed in suitable containers for storage. Thus, Option 4 may be an improved approach with slightly higher waste volume reductions (VRF ~3-4) than Option 3 for longer-term storage.

Studies were performed by AECL on drying of high C-14 content resins at temperatures up to 170°C. The results suggest that up to 10% of the C-14 inventory in the resin could be released while achieving a residual water content of approximately 5% (w/w) in the resin. The use of a shallow bed of a CO_2-water absorbent over the resin-bed during drying is sufficient to capture the C-14 released. However, the VRF of the combined process reduces to 1.6 (compared with the VRF of 2 based on only drying) because of the generation of additional spent absorbent waste.

Recent studies related to Option 5 by AECL have shown that the majority of the C-14 can be removed during the drying almost selectively by appropriately controlling the temperature and water removal to achieve residual C-14 inventory of less than 3.0×10^{11} Bq/m^3 (8 Ci/m^3) in the resin. This would allow the reclassification and management of the treated resin waste as low-level radioactive waste. The expectation is that the volume of C-14 captured secondary-waste would be significantly lower than the original resin waste-volume and appropriately containerized for long-term storage as intermediate-level waste. Demonstration of this option is in progress at Chalk River Laboratories using simulated and actual high C-14 content resin wastes.

CONCLUSIONS

An evaluation of the predisposal management options for the high carbon-14 content resin waste has suggested that:

- In the absence of a disposal facility, a staged approach involving partial treatment and packaging of the C-14 bearing resin waste for dry storage would provide the flexibility for final disposal. The flexibility allows retrievability for further processing and packaging as appropriate in the future to meet the waste acceptance criteria for the final disposal facility, when such a facility becomes available.
- Among the various predisposal management options for resin waste, drying and compaction with appropriate containerization appears to be a suitable option for long-term storage.
- The potential to remove and capture of C-14 from the resin waste into a small-volume waste for long-term storage during drying allows the treated resin waste to be reclassified and managed as low-level waste is a favorable option to consider.

REFERENCES

1 International Atomic Energy Agency (IAEA), "Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers", Technical Report Series No. 408, Vienna (2002).

2 S. VIJAYAN, M. KIKUCHI, and A. KOMATSU, "Technology Perspectives on the Management of Spent-Resin Wastes Generated from Nuclear Power Reactor Operations",

Proc. 10th International Conference on Nuclear Engineering, Arlington, VA, USA, April 14-18, 2002, The American Society of Mechanical Engineers (2002).

3 C.R. BOSS, and P.J. ALLSOP, "Radioactive Effluents from CANDU 6 Reactors During Normal Operation", AECL-11506, Atomic Energy of Canada Ltd., Canada, December (1995).

4 G.R. BRAY, C.L. MILLER, T.D. NGUYEN, and J.W. RIEKE, "Assessment of Carbon-14 Control Technology and Costs for LWR Fuel Cycle", PB-291- 244, US EPA, Office of Radiation Programs, Washington DC, September (1997).

5 J.E. CLINE, J.R. NOYCE, L.J. COE, and K.W. WRIGHT, "Assay of Long-Lived Radionuclides in Low-Level Wastes from Power Reactors", NUREG/CR-4101, T185 901372, U.S. Nuclear Regulatory Commission, Washington, D.C. (1990)

6 R.E. MILLER, I. ERDEBIL, M. SOLAIMANI, D.W. EVANS, and M. CARNEY, "Life-Cycle Management of Spent Ion-Exchange Resins from CANDU Reactors", Waste Management '97, Proc. of the Symposium on Waste Management, Tucson, Arizona, USA, March 2-6, 1997, 13-34 (1997).

7 H. LEUNG, Ontario Power Generation, Ontario, Canada, private communication (2002).

8 B.S. BOWERMAN, and P.L. PICIULO, "Technical Considerations Affecting Preparation of Ion-Exchange Resins for Disposal", BNL-NUREG-51987, NUREG//CR-4601, Brookhaven National Laboratory (1986).

9 T. KEKI, and A. TIITTA, "Evaluation of the Radioactive Waste Characterization at the Olkiluoto Nuclear Power Plant", STUK-YTO-TR162, STUK, March (2000).

10 SKB, "SFR – Final Repository for Radioactive Operational Waste", Svensk Karnbranslehantering AB Web site (www.skb.se), (2003).

11 M. SKOGSBERG, Swedish Nuclear Fuel and Waste Management Co., private communication (2003).

12 E.H. TUSA, "Microbial Treatment of Radioactive Waste at the Loviisa NPP, Finland", Waste Management '89, Proc. of the Symposium on Waste Management, Tucson, Arizona, February 26-March 2, 1989 pp. 485-488 (1989).

13 S.C. BIEBER, and K.S. BAGLI, "Spent Radioactive Resin Processing in Ontario Hydro – A Review of the Present Status and Available Options", Report No. 81229, Ontario Hydro, Nuclear Materials Management Department, June (1981).