

PROCESS CONCEPT FOR THE STORED LIQUID WASTE REMEDIATION PROGRAM, PHASE 1, AT CHALK RIVER LABORATORIES

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ABSTRACT

AECL, the Federal Crown Corporation charged with leading the development of peaceful applications of nuclear technology in Canada, has generated and stored approximately 300 m³ of intermediate- and high-level legacy wastes, arising from a diverse nuclear research and development program, operation of associated facilities and radioisotope production. The Liquid Waste Transfer and Storage (LWTS) Project, the initial phase of a two-phased approach to remediate the wastes, will provide the infrastructure to retrieve, transfer, chemically condition and consolidate legacy and isotope production wastes into an integrated liquid Waste Storage System. The consolidated and conditioned wastes will reduce health, safety and environmental risks, reduce operating costs and position the wastes for future waste solidification.

This paper describes the design objectives and design concept decisions, which form the basis of the process design of the liquid Waste Storage System.

INTRODUCTION

In 2000, AECL launched the Stored Liquid Waste Remediation program, with the intention of developing the infrastructure required to retrieve 300 m³ of high- and intermediate-level wastes, solidify these wastes into a waste form suitable for ultimate disposal and provide long-term storage of solidified waste, until such time as a waste repository is available. These wastes, accumulated over 50 years of nuclear operations at the Chalk River Laboratories, are not conducive to treatment in existing low-level waste management facilities. A waste characterization program, and the development of a waste treatment strategy, concluded that the stored liquid wastes were amenable to vitrification and that vitrification would produce a waste form suitable for permanent disposal. Formulation of Canadian federal disposal guidelines and waste repository acceptance criteria remains in the development stage. Therefore, interim objectives were developed for the first phase of the Stored Liquid Waste Remediation Program. The Liquid Waste Transfer and Storage project was launched to address the continued storage of liquids in aging infrastructure and position the wastes for future processing. The interim objectives, with a focus on risk reduction [1], are:

- Consolidate the liquid wastes that are currently in the 20 older tanks into a new storage system that meets current standards for design and construction and that has improved systems for waste sampling and retrieval; and

- Condition the high-level liquid medical isotope production wastes to reduce criticality safety constraints and monitoring requirements during storage and subsequent solidification.

To meet these objectives, the project refined the waste treatment strategy to meet the interim objectives, conducted a number of design concept development studies, and developed the conceptual design of an interim liquid Waste Storage System. The balance of this paper describes the basis for design concept decisions for the processing scheme developed for the Liquid Waste Transfer and Storage Project, including the impact on future waste solidification.

Waste Characterization

Legacy radioactive liquid wastes stored at the Chalk River Laboratories include the following high-level wastes (HLW), in order of highest to lowest total radioactive content:

- Isotope Processing Waste (IPW);
- Historic Fuel Reprocessing Wastes (HFRW);

and the following intermediate-level wastes (ILW):

- Ion Exchange Regenerant Wastes (IXRW);
- ⁶⁰Co Production waste (CPW);
- Reactor Loop Decontamination Wastes (LDW).

A summary of waste characteristics is provided in Table I.

Table I. Stored Liquid Waste Streams: Estimated Volumes and Waste Characteristics.

Waste Stream	Number of Storage Tanks	Total Waste Volume (m ³)	Waste Volume: Sludge (m ³)	Acidity/Alkalinity (pH)	Radioactive Content (Bq)	Percent Total Radioactive Content	Percent Total Waste Volume
High-level Medical Isotope Waste	2	45	0.1	<0.1 - 2	5.2E+15	73%	16%
Cobalt-60 Production ¹	2	60	1.0	14	1.98E+12	0.03%	20%
Historical Fuel Reprocessing	3	17	0	<0.1	1.7E+15	24%	6%
Ion Exchange Regeneration	6	153	1.2	0.5 - 12	1.94E+14	3%	54%
Loop Decontamination	8	12	2.6	9.0 - 14	5.97E+11	0.01%	4%
Total	21	287	5		7.1E+15		

¹ Current Volume and Content. Cobalt-60 Production continues to generate approximately 3 m³ of liquid waste per year.

The high-level medical Isotope Processing Waste, with 73% of the total activity, originates from the nitric acid dissolution of metallic targets and the processing of this solution. Historic Fuel Reprocessing Wastes, which are raffinates from a solvent extraction process, have similar radioactive and chemical composition to the medical isotopes wastes. Both have significant nitric acid and salt nitrate content, and minimal undissolved solid content.

The slightly acidic, and near neutral ion exchange regenerant wastes result from the regeneration of ion exchange resins used for wastewater cleanup operations. CPW is highly caustic liquor resulting from the sodium hydroxide chemical de-cladding of aluminum-encapsulated cobalt targets for ^{60}Co production. Loop Decontamination Wastes are fluids from reactor test loop decontamination operations.

Most of the wastes are of low solids content (less than 5%), with the exception of reactor loop decontamination wastes, which have been decanted, leaving behind high solids content sludges. Overall, the solids content of the wastes, prior to waste conditioning, averages less than 5%.

An extensive sampling and waste analysis campaign was conducted to characterize the wastes. Bubbler tube volume measurement, validated by camera inspections presented in a poster session at WM'04^(a), was used to determine liquid waste inventory, sludge volume and sludge characteristics. Other measured waste characteristics include pH, radionuclide content by gamma spectrometry and alpha counting. Elemental analysis was conducted by Inductively Coupled Plasma techniques, nuclear magnetic resonance, high performance liquid chromatography and other techniques. A variety of analyses were carried out to determine organic content, and ion chromatography was used to determine anion concentrations.

Disposition of Fissile Material

High-level Medical Isotope Wastes are stored in a fissile solution storage tank commissioned in 1986, which is nearing full capacity. The fissile solution is stored in a safe by concentration configuration, which invokes restrictive operating limits and conditions and monitoring requirements, including frequent sampling, with associated operating costs and radiation doses. The safe by concentration configuration is suitable for the in-process storage of fissile solution while there is remaining capacity in the tank, to collect the fissile solution and enable radioactive decay. The needs to limit operational radiation doses and reduce operating cost have driven AECL to find a less restrictive configuration for longer-term interim storage.

Isotopic dilution (downblending with depleted uranium) and separation of fissile material from the medical isotope fissile waste solution were compared as candidate processes to reduce the criticality safety constraints associated with extended storage of liquid medical isotope fissile wastes. The dissolved fissile material stored in the fissile solution was determined to be a financial liability as opposed to an asset. The cost of fissile material recovery, including all capital costs (process equipment, modification of an AECL shielded facility, interim fissile material product waste storage), and operating costs, including separation and purification, were assessed to exceed the market value of the fissile material by a factor of four.

Downblending will involve the bulk transfer of the fissile solution from its present storage tank into a heel of chemically compatible depleted uranyl nitrate in nitric acid solution in a new storage tank. Once the two solutions are mixed, the final enrichment will be reduced to a Slightly Enriched Uranium (SEU) enrichment of 1.4 wt%. The added uranium will increase the combined uranium content of all of the legacy wastes from 3 Mg to 18 Mg, and the stored liquid volume by 50 m³. Downblending costs include the installed cost of a marginally larger storage tank, and the purchased cost of depleted uranium solution. These costs are small compared to the cost of fissile material recovery. The impact of downblending on down-stream waste solidification was also assessed as will be described later in this paper (under 'Impact of Downblending on Criticality Safety Constraints' and 'Impact of Downblending on Waste Vitrification – Criticality Safety').

Impact of Downblending on Criticality Safety Constraints

Downblending is expected to reduce the frequency of sampling and destructive assay of the solution mandated by nuclear material safeguards requirements by a factor of four, from quarterly to annually, or less. The AECL-imposed sampling requirements to ensure operating limits and conditions are met will be substantially reduced as well. This reduction in sampling requirements will result in significant reductions in operating cost and worker radiation exposure.

Downblending will also eliminate the need for temperature control, which is one of the measures used in the fissile solution storage tank to reduce the probability of crystallization of nitrate salts from solution. Avoidance of precipitation underpins the criticality safety case for existing fissile solution storage. As discussed in the following section, uranyl nitrate at 1.3-1.4 wt% ²³⁵U is critically safe, even in crystalline solid form, regardless of geometry.

Criticality Safety of Downblending in the Waste Storage System

Initial assessments of downblending recommended that the fissile solution be downblended to 80% of the single parameter limit for enrichment of ²³⁵U for uranyl nitrate, or 1.37 wt%. Below the single parameter limit enrichment (<1.96 wt% ²³⁵U), [2] uranyl nitrate solution, up to saturation (> 2 M uranyl nitrate) is sub-critical, which means that the SEU solution is *safe by enrichment* regardless of mass. AECL KENO [3,4] analyses supported by a review of published criticality safety data [5], which form part of the basis of the single parameter limits of ANS 8.1, have further shown that crystalline uranyl nitrate, which could precipitate from solution following extensive volume reduction by evaporation or by freezing the solution, is also safe by enrichment, at 1.37 wt%. This means that an infinite quantity of *homogeneously* distributed uranyl nitrate at the target ²³⁵U concentration, in liquid form or crystallized to a credible solid form, is sub-critical ($k_{\text{eff}} = 0.82$, with no credit for poisons present, such as mercuric nitrate).

Recent KENO calculations indicate that even a *heterogeneous* array of SEU uranyl nitrate solid, moderated by water, is sub-critical at 1.37 wt% ²³⁵U. A heterogeneous arrangement does not increase k_{eff} (no upward trend, regardless of SEU nitrate solid pin geometry or spacing).

Uranyl nitrate solid is a chemically stable compound. The melting point of the solid is 60°C. Dehydration starts at 120°C (the boiling point of uranyl nitrate hexahydrate liquid). Denitration (the start of calcination to an oxide) starts at about 180°C. There is no source of heat in the solution. Total decay heat in the solution is less than 1 kW, which is readily dissipated by the storage vessel to its confinement structure. Therefore, there is no credible way for the uranium to change chemical form, e.g., from a nitrate to an oxide, which could form a critical mass at the target ^{235}U enrichment. Evaporation and freezing of the SEU solution are extreme conditions that could lead to SEU crystal formation in the SEU solution. Even if sufficient evaporation were to lead to the crystallization of SEU solids from solution, the uranyl nitrate hexahydrate crystals - $\text{UO}_2(\text{NO}_3)_2 \bullet 6 \text{H}_2\text{O}$ – are chemically stable (further concentration of the crystalline material is not possible without additional heating). The tanks will be located in underground vaults, where the ground temperature below the frost line will prevent freezing if building heat is lost for extended periods of time in peak winter. Even if freezing were to occur, the uranyl nitrate crystals that would be formed in the resulting nitrate salt slush would remain sub-critical.

Because precipitation of material from an acidic nitrate solution does not result in critical conditions, temperature control of the solution is not required as a criticality safety measure. Nevertheless, the facility will be designed such that significant evaporative loss and the potential for freezing are improbable conditions. Routine liquid volume and temperature monitoring will be provided for the duration of the liquid storage period.

The simplest sequence of events that could possibly lead to criticality would be initiated by a chemical excursion that converts sufficient uranyl nitrate to a compound with a greater uranium density in solution or as a precipitate. At 1.37 wt% enrichment, the maximum safe quantity or Sub-Critical Limit (SCL) of U as UO_2 , is 14.9 kg ^{235}U in a homogeneous slurry, or 6.6 kg ^{235}U in a heterogeneous array [5]. SCLs are greater for other uranium compounds (hydroxide, carbonate, sodium diuranate, and other oxides). The sequence of events must include separation of neutron poisons (mercury) from the precipitate for criticality to be possible. This would be physically difficult.

A scenario has been examined in which there is an addition of untreated, unconditioned caustic CPW into the SEU tank. The worst-case scenario would occur when the SEU tank contained only downblended fissile solution. The effect of blending the chemically similar but more acidic historic high-level wastes with the downblended fissile material was assessed as well.

It was concluded that:

- The safe volume (volume that could not, under any conditions, result in precipitation of a critical mass of uranium oxide) of CPW solution that could be inadvertently added to the SEU tank containing only downblended fissile solution is 2.7 m³.
- The safe volume of CPW solution that could be inadvertently added to the SEU tank containing the historic high-level wastes and acid rinses is about 6.6 m³. The historic wastes and acidic rinses add to the acid content of the SEU tank, making the SEU blend more resistant to neutralization than the downblended fissile solution alone.
- Other caustic wastes would have larger 'safe volumes' since they have lower equivalent alkalinity.

A limit of 6 m³ on the receipt of caustic solution could be considered as a limiting condition. These safe volumes were calculated assuming that the inadvertently added caustic would cause the local precipitation of uranyl hydroxide, and that the precipitate accumulated into a critical volume. This is extremely unlikely, since the addition rate of liquids to the storage tanks is limited by the pumping rate, and re-dissolution of the hydroxide in the bulk acid solution (about 2 N nitric acid) is far more likely, since the addition of wastes to the storage tanks in the waste storage system will be accompanied by mixing in the storage tanks. Complete neutralisation of the free acid in the SEU tank would require most of the inventory of a 40-m³ caustic waste tank to be added in four consecutive transfers, with no detection of the waste routing error. This is considered to be incredible.

Downblending to greater than 1.37 wt% could overly constrain the volumes of unconditioned caustic waste that could be handled in the facility in the proximity of stored SEU solution. At 1.5 wt% enrichment, the maximum safe quantity or Sub-Critical Limit (SCL) of U as UO₂, is 10.8 kg ²³⁵U in a homogeneous slurry, compared to 14.9 kg ²³⁵U at 1.37 wt% enrichment [5]. The 'safe volumes' of caustic solutions at 1.5 wt% enrichment would be proportionately smaller than at 1.37 wt%.

The co-storage of caustic wastes and acidic SEU solution in the waste storage system would require measures to segregate the wastes, process piping and secondary confinement structures. As will be described in this paper (under 'Waste Blending and Conditioning'), criticality safety has influenced the waste conditioning and storage approach for the caustic intermediate-level wastes.

Impact of Downblending on Waste Vitrification – Glass Volumes

AECL's long-term waste treatment strategy for the stored liquid wastes is predicated on keeping to a practical minimum the cost of facilities required for waste treatment, while producing a durable waste form that would ultimately be accepted in a waste repository. Glass is presently the preferred waste form, since it has leach characteristics that are similar to spent UO₂ reactor fuel, the primary waste form in a Canadian waste repository, and results in a small stored waste volume. The impact of downblending on a vitrification process was therefore assessed from both technical feasibility and life cycle cost perspectives.

Reducing the number of glass waste forms to a minimum number was considered to benefit the licensing process for waste forms, and reduce the processing and glass formulation costs. A single glass formulation based on vitrification of a blend of all the stored wastes, including the downblended material, was therefore assessed. Combining all the wastes into a 'maxblend' prior to vitrification, and taking credit for the sodium in the combined waste as flux in the sodium borosilicate glass formulation, would produce about 60 m³ of glass. It was determined that the sodium content of the wastes and the uranium content were both limiting. If the sodium bearing intermediate-level wastes and the high uranium content high-level wastes were vitrified separately, a total of 120 m³ of glass would be produced. These calculations confirm that considerable economies would be gained with a single glass formulation, and one waste immobilization process.

Downblending to 1.4 wt% has no net effect on the volume of glass required to immobilize all of the legacy and isotope production wastes, assuming a target uranium concentration in the glass waste form of 14 wt%. Downblending of the fissile solution below 1.4 wt% would add to glass volume unnecessarily, which would be regarded as contrary to Canadian waste management principles^(b) and an international convention that Canada has ratified [6].

Article 11 of the international convention [6] requires taking appropriate steps to:

- i. ensure that criticality and removal of residual heat generated during radioactive waste management are adequately addressed;
- ii. ensure that the generation of radioactive waste is kept to the minimum practicable;
- iii. take into account interdependencies among the different steps in radioactive waste management.

The conceptual criticality safety assessment described above meets the intent of step i. Downblending to 1.4 wt% meets the requirements of step ii, while providing a large margin for criticality safety. The analysis of criticality safety for a conceptual vitrification process (below) meets the requirements of step iii.

Impact of Downblending on Waste Vitrification – Criticality Safety

Downblending fissile solution to 1.37 wt% and further blending with historic wastes results in an isotopic concentration of 1.3 wt% (+/- 0.05 wt%) in the SEU tank. The nitrate chemical form is stable, and is sub-critical as uranyl nitrate in solution, or as uranyl nitrate solid. Vitrification and pre-vitrification process steps would result in conversion of the uranyl nitrate solution to solid oxides of uranium. Chemical denitration starts in feed preparation steps, followed by thermal denitration in the melter cold cap to sodium metauranate or diuranate (sodium/uranium oxide compounds). Uranium oxides then dissolve into the bulk glass solution from the cold cap, and the sodium borosilicate glass, with dissolved uranium oxide, is then poured into glass canisters and allowed to solidify.

The Stored Liquid Waste Remediation program developed a conceptual flowsheet for vitrification of the downblended fissile solution, and conducted a conceptual criticality safety assessment of the process, with support from consultants with expertise in vitrification chemistry and vitrification plant design. These consultants advised AECL that the stored liquid wastes in the Waste Storage System could be processed over a five-year period in three-week batches, using a proven joule-heated melter design. The three-week batch size is consistent with international experience for vitrification plants.

Figure 1 is a simplified flow diagram of the proposed vitrification process, prepared for a conceptual criticality safety assessment. The core of the process consists of a melter feed system, a joule-heated melter, glass canisters which receive the melted glass periodically, an off-gas quencher, a mist elimination package and condensate collection tank(s). Preliminary sizing of the melter, melter feed tanks and the first steps in the off-gas system, which comprise the equipment that could contain oxides of uranium in aqueous slurries, was conducted.

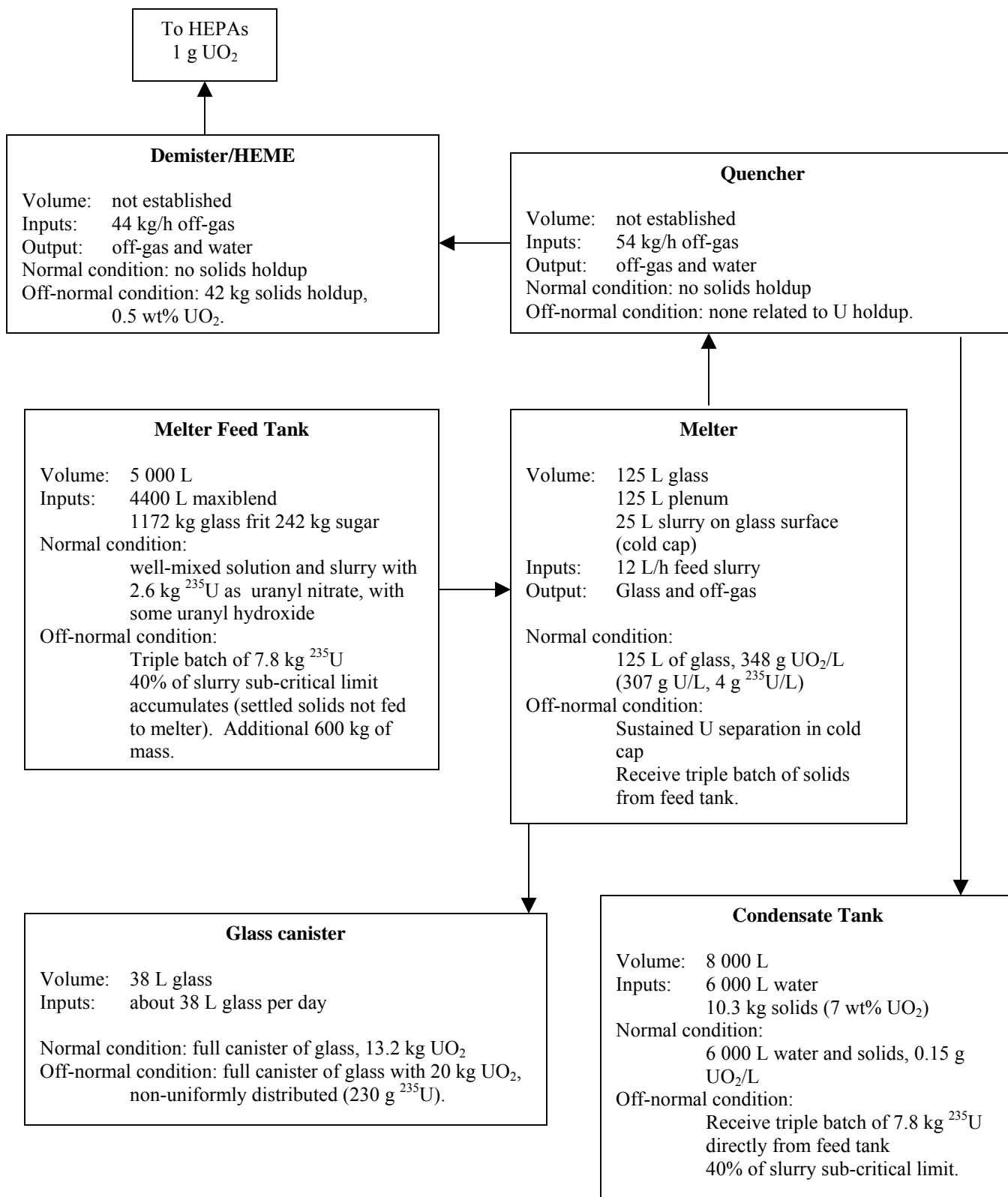


Fig. 1. Vitrification process material flow diagram for criticality safety assessment

The process feed system consists of two parallel tanks, one feeding the melter, with the other in reserve for the preparation of the following batch. A slurry feed system was assumed, with glass frit added to the stirred tank, and fed as a slurry to the melter. Each feed tank was sized to hold sufficient volume to feed the melter continuously for three consecutive weeks.

Excess nitric acid and nitrate ions in the maxblend are reacted with sugar added to the feed tanks. The chemical reaction will start slowly in the feed tanks, and go to completion in the melter cold cap, where thermal conditions favour rapid denitration. The reaction will result in the formation of a slurry containing hydroxides of major solutes, including uranium, to a small extent in the melter feed tank, but largely in the melter cold cap. The mass of fissile material in the feed tank ($2.6 \text{ kg } ^{235}\text{U}$) is about 34% of the sub-critical limit of ^{235}U for an optimized lattice of UO_2 fuel pins in water ($7.65 \text{ kg } ^{235}\text{U}$), and 13% of the sub-critical limit for a homogeneous slurry of UO_2 in water ($19.8 \text{ kg } ^{235}\text{U}$ [5]), with no credit for the presence of neutron poisons in the batch tanks. A triple batch of uranium mass in the feed batch tank would be sub-critical even under optimized conditions for neutron multiplication. An optimized configuration of a lattice of UO_2 pins is not a credible configuration of nuclear material in a process feed tank.

Batch size control, determined by tank size constraints, inspection for residual material between batches, uranium inventory control supported by chemical analysis and tank mass measurements (load cells), and, if appropriate, credit for poisons already present in the system, will meet the double-contingency principle. Similar arguments apply to the quencher tank, and condensate collection tanks which follow downstream of the melter, as shown in material balance calculations summarized in Figure 1.

The melter was analysed under normal and abnormal operating conditions. The uranium and other hydroxides dehydrate at the interface between the melter cold cap and the waste glass melt to form metal oxides, which dissolve in the melt. It was demonstrated that the double-contingency principle could be met, without imposing geometric constraints on the melter. One abnormal condition assumed the accumulation of up to three consecutive three-week batches (less than $8 \text{ kg } ^{235}\text{U}$) in the melter, with glass frit metering interrupted and no glass pouring. Since glass frit metering is an integral part of the process and glass pouring a daily process, this sequence of initiating events is considered to be incredible. Nevertheless, the accumulated mass would be sub-critical as a homogeneous mixture.

Alternatively, high-density uranium precipitates could accumulate in the melter feed tank, if the feed tank is not adequately stirred and the extent of chemical denitration in the feed tank is significant. If good stirring were suddenly resumed, with a small volume left in the feed tank, rapid transfer of the accumulated material could potentially occur. A triple batch of $7.8 \text{ kg } ^{235}\text{U}$ is equivalent to more than 600 kg of uranium solids. It is unlikely that this abnormal condition would go undetected by an operator monitoring the reading of a load cell on the feed tank.

Accumulation of a sub-critical mass limit of ^{235}U in the melter, constrained to a melt volume of approximately 125 L, would be, for all practical purposes, incredible. The normal inventory of ^{235}U in the melter would be less than 1 kg, compared to the sub-critical limit of $19.8 \text{ kg } ^{235}\text{U}$ (some of the melter inventory is a slurry, in the cold cap).

Uranium is expected to be readily soluble in the reference borosilicate glass formulation. The absence of uranium in the glass, nominally 14% by weight, would be detectable by mass determination of the glass canisters. The accumulation of significant uranium precipitate in the melter would eventually interrupt the glass pour, and result in detectable changes to the glass electrical conductivity, long before a sub-critical limit (19.8 kg of ^{235}U) could accumulate in the melter. To put the sub-critical mass in perspective, it would represent 1730 kg UO_2 , accumulated in a volume ranging from 150 L to 275 L, assuming the melter plenum has a volume of 125 L. In the smaller volume (150 L), the normal combined volume of the melt and cold cap, this exceeds the theoretical density of UO_2 . There is no credible way to approach this condition.

The glass matrix is itself sub-critical. With the water content limited to 1.5 wt%, the SCL on enrichment is 3.2 wt%. The glass also contains a high concentration of boron.

It was concluded that downblending of the fissile solution to 1.37 wt% ^{235}U and vitrification of a 'maxi-blend' of all conditioned stored liquid wastes could be conducted in a critically safe manner, providing that appropriate batch controls and measures to limit balance after processing were instituted. Process equipment with conventional geometry can be used. There is no need for critically safe-by-geometry equipment.

Waste Blending and Conditioning

Evaluation of waste storage configurations suggest that keeping the number of storage tanks to a minimum and using shared leak confinement structures is cost effective. Co-storage of caustic wastes and acidic slightly enriched uranium wastes introduces the potential for erosion of criticality safety margins, by inadvertent addition of caustic solution to the SEU solution. Inadvertent transfers could potentially occur during waste consolidation operations, abnormal operating conditions such as leak management, and during future waste transfer operations from the facility.

The AECL design concept decision is to store all of the acidic high-level wastes in one storage tank (the Slightly Enriched Uranium or SEU tank) and all of the intermediate-level wastes, as an acidic blend, in a Consolidation Tank. This separation also cleanly segregates the waste types. The SEU tank will contain 98% of the beta/gamma activity, 99.7% of the dissolved mercury, 70 % of the total alpha activity and 95% of the total uranium, in 1-2 mol/L nitric acid. AECL presently anticipates blending the two waste types prior to solidification. It is recognized that the mercury concentration of the SEU solution, from current and historic dissolution of aluminum clad and aluminum/uranium alloy fuel, is many times the concentration in typical vitrification plant feed streams. Pre-treatment to remove this mercury may be required. Partitioning the wastes on the basis of mercury content therefore makes sense. The effect of high uranium content on potential mercury separation processes is discussed later in this paper (under 'Impact of Selected Waste Consolidation Decisions on Possible Future Mercury Removal').

The leak management philosophy is to place both of the storage tanks, together with a spare tank capable of holding the entire contents of the consolidation tank (the larger of the two), in one

stainless steel lined vault. The stainless steel liner is also sized to hold the entire contents of the consolidation tank. The two tanks also share a common waste receiving system, consisting of a receiving tank, used to receive the bulk of the wastes from the legacy waste tanks, and a holding tank of the same size, used to support waste conditioning processing. The process flow scheme is shown in Figure 2.

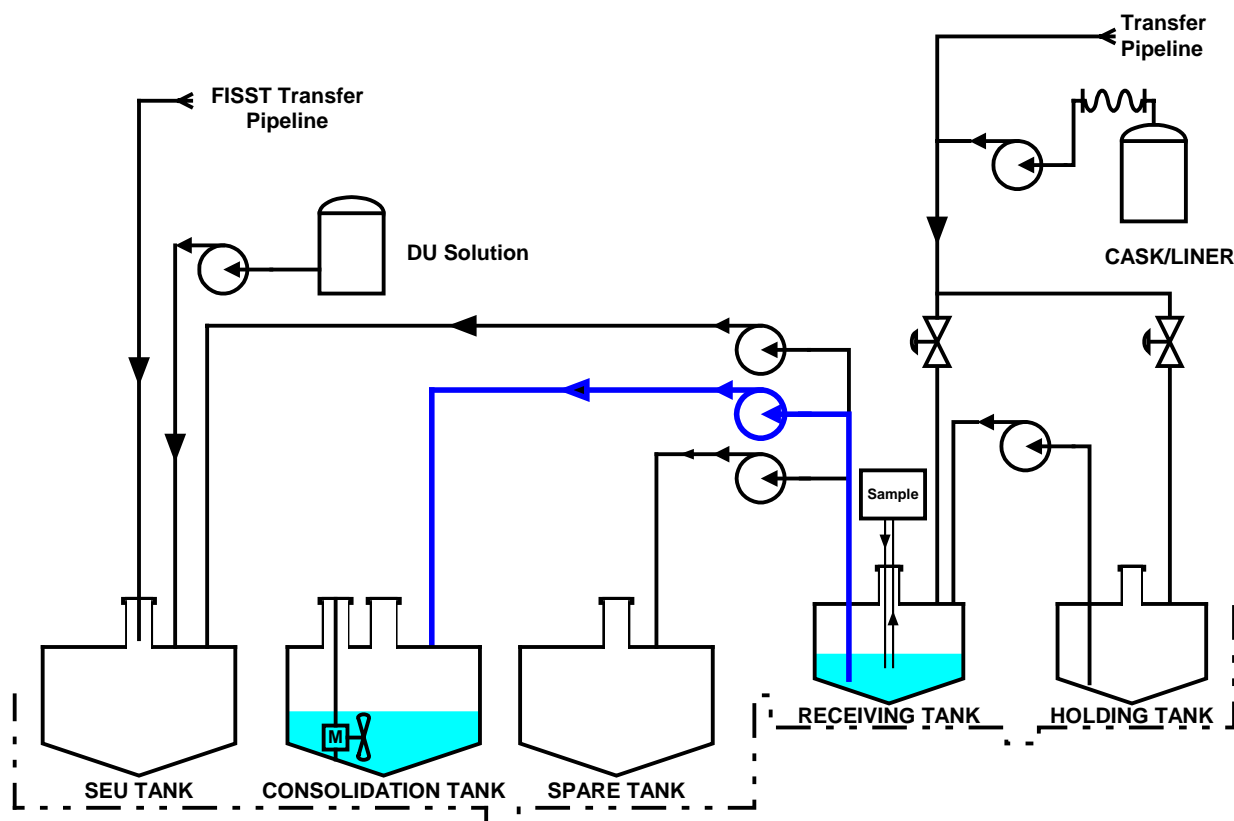


Fig. 2. Simplified flow diagram of stored liquid waste consolidation and conditioning process.

The solutions destined for the SEU tank are all acidic and therefore miscible. Blending of the wastes in the intermediate-level waste consolidation tank is more complex, due to the wide range of acidity. The proposed intermediate-level waste consolidation sequence is summarized in Table II. The acidic and near neutral IXRW solutions will be consolidated first, to form an acidic heel ($\text{pH} < 1$). The LDW, including their sludges, will then be retrieved, and sludges will dissolve in the acidic ion exchange solution. The pH of this blend is expected to be in the region of 1. Retrieval of the caustic CPW follows.

Table II. Planned Retrieval Sequence.

Sequence #	Building	Number of Tanks	Waste Stream	Waste Volume (m ³)
1	B	3	Ion Exchange Regeneration Waste	105
2	C	4	Loop Decontamination Waste	10
3	A	4	Loop Decontamination Waste	2
4	A	2	Cobalt Processing Waste	60
5	WTF	3	Ion Exchange Regeneration Waste	48
6	FISST Tank	1	High-level Medical Isotope Waste	23
7	WTF	3	Historic Fuel Reprocessing Waste	17
8	B	1	Isotope Processing Waste	22

Test blends with surrogate solutions followed by confirmatory tests with actual waste samples have demonstrated that the high aluminum content CPW, mixed with the IXRW and LDW blend, results in the formation of a viscous gel in a caustic supernatant. Aluminum hydroxide is an amphoteric compound, insoluble in the pH range 4-9. Even when sufficient concentrated acid is added to dissolve the aluminum hydroxide, forming an acidic mixture, high shear mixing is required to promote the dissolution of the metastable solids. High shear mixing in a large storage tank is not practical.

Storage of a caustic mixture in the same facility as acidic wastes, which for criticality safety and chemical safety reasons require exclusion of 'foreign' caustic materials, would require relatively expensive segregation of process equipment, storage tanks, and confinement structures. Hence, the design concept decision is to acidify the CPW in small batch volumes in the receiving tank.

Controlled acidification requires that the waste (or acid) be metered into the acid (or waste). Since the target solution is acidic, and Al is amphoteric, it is logical to meter the waste into the acid, and pH does not rise above 4 for the bulk of the mixture, where Al has negligible solubility. This means that gel formation will be a local effect only. Allowing the pH to rise above 4 could cause the entire aluminum inventory to gel, which could be difficult to recover from, particularly if a mixer failed mid-process. The acidification process is therefore to transfer 2 m³ batches of CPW into a 10 m³ holding tank, and to meter this waste into approximately 1 m³ of concentrated nitric acid in the receiving tank. The heat of reaction will raise the mixture to approximately 80°C, without cooling. It may be possible to simply transfer the hot mixture into the consolidation tank with no adverse effects, although this may create design challenges for a pumping system, since vapour pressure will limit suction lift. Cooling of the receiving tank is therefore under consideration.

Acidification of small batches of CPW will provide effective batch and chemistry control of caustic wastes in the facility. CPW is received in the holding tank, which is not connected directly to the storage tanks. Under normal operating conditions, transfers of acidified CPW into the consolidation tank will occur from the receiving tank. Inadvertent transfer of a significant volume of unconditioned CPW into the SEU tank, rather than the consolidation tank, would require three independent, unlikely abnormal conditions, that is: waste is received in the wrong process tank; waste is not acidified; and, waste is transferred to the wrong storage tank. This more than meets the double-contingency principle for criticality safety. This further supports batch acidification of the CPW.

The intermediate-level waste infrastructure is older than the high-level waste storage infrastructure. Current operational planning indicates that intermediate-level waste retrieval, waste conditioning and waste consolidation will occur before fissile solution is transferred into the facility. With this retrieval sequence, there will be no potential to inadvertently transfer intermediate-level wastes into the SEU tank.

Management of Rinses

Tank rinses and water to mobilize sludge during waste retrieval and transfer operations from existing tanks to the Waste Storage System will add to waste volume. Rinses of retrieval and transfer equipment, and rinses of waste handling equipment within the waste storage system are required between waste transfers and to support maintenance activities. The total rinse and mobilizing water volume has been estimated to be approximately 10% of the total waste volume. The wastes are relatively close to saturation, since they were, in general, subjected to volume reduction prior to, or as part of the existing storage operations. A cost benefit study was used to assess the viability of rinse volume reduction. It was determined that volume reduction would not be cost effective for a short-term waste consolidation operation, since the evaporator would have to be designed to handle concentrates similar to the wastes, and therefore require a shielded structure and remote tooling; condensate would contain mercury and therefore require additional treatment; and the condensate transfer infrastructure cost would be significant. Rinse volume reduction is therefore not in project scope. Tank and equipment rinses will be added to the new storage tanks.

Detailed calculations were conducted to estimate the quota of rinse that will be allowed for each legacy waste tank, and the total to be accommodated in the Waste Storage System. Rinsing of legacy waste tanks, and dilution of tank heels is expected to be sufficient to remove most of the mobile radionuclide and chemical (e.g., mercury) content in the legacy waste tanks.

Impact of Selected Waste Consolidation Decisions on Possible Future Mercury Removal

The impact of downblending on the potential need to pre-treat the wastes for mercury removal, prior to waste solidification, was assessed with scoping laboratory tests. The majority of the mercury originates from mercury catalyst used in dissolving medical isotope irradiated targets and is therefore present in the Isotope Processing Wastes. The downblending process introduces added uranium and results in higher acid concentration, which have the potential to interfere with mercury removal methods.

Ion exchange was selected as the benchmark process for testing the effect of these two variables on Hg recovery. Ion exchange was one of the methods recommended by a consultant study commissioned by AECL. Commercially available acid tolerant ion exchange resins and an acid-tolerant proprietary resin prepared by a Canadian University at the request of AECL were tested. It was determined that the added uranium and higher nitric acid concentration would not preclude the use of ion exchange for pre-treatment of the SEU solution.

CONCLUSIONS

Ongoing storage of legacy and isotope production wastes, presently stored in 21 aging tanks, present a number of challenges. The existing storage infrastructure is aging, and no longer meets current design standards. Costly criticality safety constraints are required to ensure safe storage of medical isotope wastes containing fissile material.

As an interim measure, the liquid wastes will be consolidated into a low uranium content intermediate-level waste (ILW) storage tank and a high uranium content high-level waste (HLW) storage tank. Medical isotope production wastes will be isotopically downblended to reduce criticality safety constraints, and mixed with historic fuel reprocessing wastes. Intermediate-level wastes will be conditioned with nitric acid, if required, and blended into a single waste solution, essentially free of sludge. The two acidic waste streams will be chemically compatible, which simplifies the configuration of the Waste Storage System in the new Interim Liquid Waste Storage Building, as well as simplifying follow-on waste solidification processing.

Isotopic downblending of AECL medical isotope waste fissile material simplifies criticality safety for continued liquid waste storage, as well as during future waste solidification. The added uranium required for downblending is not expected to impede future mercury recovery processing. A vitrification process concept was developed which utilizes the synergy of the high uranium content of 'high level' wastes with the high sodium content of 'intermediate level wastes.' Blending of high uranium content wastes and high sodium content wastes will permit the use of a single glass formulation to vitrify the blend, using a low sodium content frit. Studies have shown that the glass volume produced by blending ILW and HLW wastes would be approximately half the glass volume produced if each stream were vitrified separately. The added uranium required for downblending will therefore have no net effect on the glass volume required to immobilize the liquid wastes.

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FOOTNOTES

- (a) P.L. Heeney and S. Wickware “In –tank Inspections of Buried and Sub-surface HLW Tanks” (WM'04).
- (b) CNSC, “Managing Radioactive Waste,” Draft Regulatory Policy P-290, 2003 April.