

## Review Article

# Immobilisation of Higher Activity Wastes from Nuclear Reactor Production of $^{99}\text{Mo}$

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A variety of intermediate- and low-level liquid and solid wastes are produced from reactor production of  $^{99}\text{Mo}$  using UAl alloy or  $\text{UO}_2$  targets and in principle can be collectively or individually converted into waste forms. At ANSTO, we have legacy acidic uranyl-nitrate-rich intermediate level waste (ILW) from the latter, and an alkaline liquid ILW, a U-rich filter cake, plus a shorter lived liquid stream that rapidly decays to low-level waste (LLW) standards, from the former. The options considered consist of cementitious products, glasses, glass-ceramics, or ceramics produced by vitrification or hot isostatic pressing for intermediate-level wastes. This paper discusses the progress in waste form development and processing to treat ANSTO's ILW streams arising from  $^{99}\text{Mo}$ . The various waste forms and the reason for the process option chosen will be reviewed. We also address the concerns over adapting our chosen process for use in a hot-cell environment.

## 1. Introduction

$^{99}\text{Mo}$  is produced in several countries; notably Belgium, Netherlands, Canada, and South Africa produce  $> 2,500$  6dCi. (This refers to the number of curies of  $^{99}\text{Mo}$  left 6 days after shipping from a production facility and is typically used during operation in allocating and pricing the shipment.) There are also smaller producers (300–1500 6dCi) in France, Russia, Czech Republic, Poland, Australia, and Argentina [1]. Wastes arising from  $^{99}\text{Mo}$  production using nuclear reactor irradiation of enriched U-bearing targets range from ILW to LLW in both liquid and solid forms, according to current International Atomic Energy (IAEA) Classifications [2]. In  $^{99}\text{Mo}$  production, the higher activity wastes would typically be classified as ILW, even after decaying for a few years. Traditionally [3], the boundary between ILW and high-level waste (HLW) was set at a heat output from the decay of radioisotopes of  $2\text{ kW/m}^3$  and the boundary between ILW and LLW was that at which shielding was required (contact dose of  $2\text{ mSv/hr}$ ).

Both HLW and ILW require shielding; however, ILW due to its lower heat output does not require controlled cooling during storage. In the updated version of the IAEA Classification System [2], the heat output has been omitted. This is because the new standard for classification and treatment is more closely related to the disposition options and the heat output limits for a waste package should now be linked to the safety cases for the storage/disposal facility.

Other methods of classification exist; for example, the British in determining the amount of waste to be returned to customers from its THORP reprocessing facility use the integrated toxic potential [5] methodology. This method is used as part of the UK waste allocation and substitution policy [6]. The USA operates under a different system to the IAEA. It developed prescriptive specifications for the operation of the Waste Isolation Pilot Plant (WIPP) [7] and the now halted Yucca Mountain geological repository [8] for high-level waste.

Typical waste compositions from  $^{99}\text{Mo}$  production can be found in [9]. For irradiated U-Al alloy targets dissolution

is achieved via an alkaline-route; typically, this produces a 3.4–4 M NaOH plus 1–1.5 M NaAlO<sub>2</sub> plus fission products intermediate-level liquid waste (ILLW), with an activity of ~10<sup>10</sup>–10<sup>11</sup> Bq/L after ~3 years decay time from processing (Figure 1 and Table 1). The ILLW is subsequently adjusted to 5–6 M NaOH for tank storage to prevent the precipitation of gibbsite (Al(OH)<sub>3</sub>). From a long-term waste form storage and disposition viewpoint, <sup>137</sup>Cs and <sup>90</sup>Sr dominate the activity, although in alkaline waste streams the bulk of the Sr (~90–95%) remains with the U-rich filter cake. Separation of Cs and Sr was considered by ANSTO, but was rejected on the grounds that it would lead to two ILW waste streams that would need to be treated as the ILLW activity would remain above LLW limits beyond the design life of the holding tanks. Furthermore, ANSTO is building one plant to treat both alkaline and acidic wastes and a separations approach would require the construction of a second ion exchange route to remove the Cs and Sr from that. The result would be four waste streams to treat, four waste forms to qualify, and expensive additional hot-cell plant with its associated secondary waste streams.

Also produced are secondary wastes; the most predominant of these are a short-lived high activity liquid waste that decays below the intermediate-level waste limit of 10<sup>8</sup> Bq/L after ~4–5 years (Figure 1), plus a Na-U-O residue that also contains fission products, notably Sr. The options suggested for this residue include recycling to extract the enriched U, followed by reuse in new targets for <sup>99</sup>Mo production or disposition, with appropriate safeguards to allow for the fissile content. The latter may include dilution with depleted U or treatment to form a criticality safe and proliferation-resistant waste form.

UO<sub>2</sub> targets were used by ANSTO until 2005 and were dissolved in nitric acid, resulting in an intermediate level liquid waste (ILLW) that consists mainly of uranyl nitrate solution plus fission products in 0.5–1 M nitric acid (Table 2). Typically this consists of primary waste at 120–200 gU/L and secondary waste (wash), ~20 gU/L. The treatment of the intermediate-level wastes and the uranium filter cake wastes will be the focus of this paper.

In addition to these streams, additional wastes such as ion exchange columns (resin and/or alumina based), noble gases and iodine in the off-gas, and general low-level waste associated with processing are produced [9]. In the future there is the possibility of silicide targets being introduced to increase the target density [10], particularly with the push to move <sup>99</sup>Mo production from using highly enriched uranium (HEU) to <20% <sup>235</sup>U low enriched uranium (LEU) [11].

While the ILLW wastes will be considered separately in the first instance, we will also consider whether a single technology platform could be used for the individual wastes or waste mixtures. Candidate solids for immobilisation of the intermediate ILW or LLW within scope can be described as ceramics, glasses, glass-ceramics, or cementitious materials. While asphalt-based materials have been used by Belgium to immobilise LLW (not arising from <sup>99</sup>Mo production), the flammability of such material is highly undesirable from a risk aspect.

## 2. The Development of Waste Forms and Processes to Treat Radioactive Wastes

As early as 1953, researchers were showing concern about the need to immobilise radioactive wastes arising from the recently constructed nuclear reactors [12]. The waste of most concern is used UO<sub>2</sub> fuel in which most of the original fissile U was still present but in which the fission products caused so much neutron absorption that the fuel was no longer efficient. However, large amounts of waste that were a lot more dilute from a radioactive aspect were also generated. The initial concept to immobilise waste radionuclides was to add them to appropriate precursors for incorporation in leach-resistant clay minerals, followed by consolidation and burial in deep holes, an approach initially favoured at Chalk River, Canada, later that decade. Good leach resistance was needed to prevent the transport of radionuclides to the biosphere by groundwater. However, from the 1960s the favoured method for immobilisation of high-level nuclear waste (waste arising from used nuclear power plant fuel or primary fuel reprocessing waste) was incorporation in borosilicate glasses that could be melted and poured at temperatures of 1000–1200°C. The waste was calcined at ~600°C to remove nitric acid, water, and organics and then combined with glass frit and vitrified. Table 3 shows the typical chemical composition of HLW reprocessing waste.

The advantage of borosilicate glass was the fact that most fission products and process chemical wastes after calcination could be incorporated in the glass structure and the glass was reasonably resistant to leaching by groundwaters characteristic of deep (~1 km) geological repositories, with such repositories being generally agreed by the 1970s as the best way to deal with vitrified high-level waste. As an aside, it has been generally agreed for many years that spent fuel itself only needs encapsulation in metal containers for disposal in deep geological repositories. In the mid-1970s, university researchers devised the idea of atomically incorporating waste radionuclides in the crystalline lattices of certain minerals that were known to be very resistant to water leaching, as such minerals that incorporated small amounts of natural radioactivity in their structures could be shown to have survived in hot, wet environments for millions of years [13]. These minerals could then be produced by ceramic technologies and became alternative (to borosilicate glass) candidates for HLW immobilisation.

The optimisation of waste form design is achieved by optimising the waste form chemistry to achieve high waste loadings and applying appropriate noncomplex process technologies to derive an integrated solution to achieve maximum cost savings, whilst still retaining waste form performance. The following several key requirements were identified for a suitable waste form for Pu [14] but could equally apply to U-doped wastes, particularly HEU.

(1) *High Waste Loading.* The waste loading must be sufficiently high to make the waste form economic to process. It is the volume of waste form and packaging produced that determines the efficiency of the process. For instance, ceramics such as Synroc can have almost double the density

TABLE 1: Typical ILLW from alkaline-route <sup>99</sup>Mo production at ANSTO > 10 years after production.

Chemical composition		Main nuclides present	Half-life	Typical activity in ILLW waste (Bq/L)
NaOH	4–6 M	<sup>137</sup> Cs	30.07 y	1E + 10
NaAlO <sub>2</sub>	1–1.5 M	<sup>137m</sup> Ba	2.552 m	1E + 10
<i>Corrosion products</i>		<sup>90</sup> Sr	28.78 y	5E + 08
Fe, Cr, Ni	Traces	<sup>90</sup> Y	64.1 h	5E + 08
		<sup>147</sup> Pm	2.6 y	1E + 08
		<sup>125</sup> Sb	2.77 y	1E + 07
		<sup>134</sup> Cs	2.07 y	9E + 6
		<sup>155</sup> Eu	4.96 y	1E + 07
		<sup>106</sup> Rh	29.92 s	3.5E + 06
		<sup>106</sup> Ru	1.02 y	3.5E + 06
		<sup>125m</sup> Te	58 d	3E + 06
		<sup>99</sup> Tc	213000 y	3E + 04

TABLE 2: Analysed ILLW compositions from tanks at ANSTO that were produced from irradiated LEU UO<sub>2</sub> target produced at ANSTO.

Chemical composition		Nuclide	Half-life	Analysed activity of primary ILLW waste (MBq/L)	Analysed activity of secondary ILLW waste (MBq/L)
U (primary waste)	70–200 g/L	<sup>144</sup> Ce	284 d	10–3500	16–6000
U (secondary waste)	8–35 g/L	<sup>134</sup> Cs	2.07 y	0.35–5.3	<DL–2.4
Mg	<0.02–0.6 g/L	<sup>137</sup> Cs	30.07 y	2600–8000	170–1800
Fe	< 0.05–0.4 g/L	<sup>60</sup> Co	5.27 y	0.6–2	0.1–1
NH <sub>4</sub> <sup>+</sup>	75–800 mg/L	<sup>155</sup> Eu	4.76 y	<DL–90	<DL–20
HNO <sub>3</sub>	0.6–0.8 M	<sup>95</sup> Nb	35.06 d	1–80	4–1100
Al	<DL–0.6 g/L	<sup>106</sup> Ru/ <sup>106</sup> Rh	1.02 y/29.6 s	<DL–970	<DL–420
		<sup>125</sup> Sb	2.77 y	<DL–13	<DL–18
		<sup>95</sup> Zr	64 d	0.6–50	1–610
		<sup>90</sup> Sr	28.78 y	2600–7700	120–1700
		<sup>141</sup> Ce	32.5 d	<DL–1.3	<DL–30
		<sup>91</sup> Y	58.51 d	<DL–125	<DL–380
		<sup>103</sup> Ru	39.35 d	<DL–1.5	<DL–32
		<sup>144</sup> Pr	17.2 m	nd	<DL–6

# Note: the data in this table are for from ~1 to 16 years after the tanks were filled. Lower activity values are generally from older waste. nd: not detected; DL: detection limit.

TABLE 3: Approximate composition (wt%) and half-lives<sup>&</sup> of main fission product and actinide oxides in PUREX fuel reprocessing HLW that has been stored for >10 years.

Fission product oxide Basis (wt%) <sup>§</sup>	Half-life of most abundant radioisotope (y)	Fission product oxide Basis (wt%) <sup>§</sup>	Half-life of most abundant radioisotope (y)
Cs <sub>2</sub> O (6)	30	TcO <sub>2</sub> (6)	210000
SrO (3)	30	*AnO <sub>2</sub> (6)	>10000
BaO (4)	—	RuO <sub>2</sub> (10)	—
RE <sub>2</sub> O <sub>3</sub> (15)	100 <sup>&amp;</sup>	PdO (6)	—
ZrO <sub>2</sub> (15)	—	Rh <sub>2</sub> O <sub>3</sub> (2)	—
MoO <sub>3</sub> (15)	—		

Water excluded; \* An: actinide. <sup>§</sup>Contains additional stainless steel corrosion products, RE: rare earth.

Group half-lives<sup>&</sup> are very approximate as they range from short to long times for different components. Absence of half-life value: stable elements.

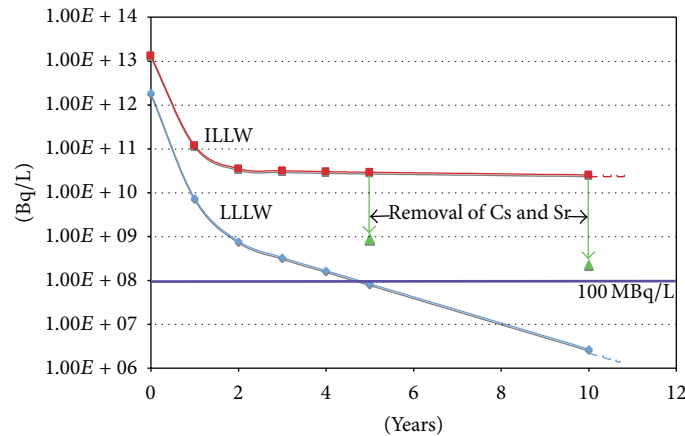


FIGURE 1: Typical calculated activity in Bq/L of the two liquid wastes from  $^{99}\text{Mo}$  as a function of postproduction time. The intersections of the triangles represent the activity of ILLW if all Cs/Sr is removed after 5 and 10 years of storage, showing the  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  dominate the ILLW activity.

of borosilicate glass and hence an equal waste loading will produce less waste volume in the ceramic compared to the glass. Waste volume reduction significantly reduces life-cycle costs, particularly storage, transport, and repository costs; for instance, the disposition of one glass canister at Yucca mountain was estimated to cost \$US 620,000 [15]. For instance, ANSTO demonstrated the production of a 40 kg hot-isostatically pressed waste form that had an 80 wt% waste loading of Idaho HLW calcines, far in excess of that achievable via glass melters [16]. The volume reductions achievable via this approach were independently estimated to have potential disposition cost savings over alternative routes for the calcines of \$2–4.8 billion [15]. There are some limitations to waste loadings beyond just how much waste a waste form can incorporate and still remain durable. These include limits due to criticality concerns and limitations on heat loadings for the waste form and repository. The former can be overcome by the incorporation of neutron absorbers (e.g., Hf, Gd, Sm) into the same ceramic waste form phase as the fissile material and such an approach could be employed for  $^{99}\text{Mo}$  production waste streams that contain HEU. Heat loading limits in HLW waste forms are constrained partly by the repository design and partly by the current baseline waste form technology, borosilicate glass, which undergoes devitrification at elevated temperatures and thus requires storage under controlled cooling for 30 years or more prior to disposition in a repository if it contains substantial amounts of HLW. The use of ceramic waste forms that are unaffected by moderate heat can enable higher levels of heat-producing isotopes; however  $^{99}\text{Mo}$  production does not produce HLW according to current classifications [2, 3].

(2) *The Waste Form must be Mechanically and Chemically Durable.* It is important that the waste form retains the radioisotopes under storage and repository conditions. The waste form's ability to contain the radioactive isotopes under repository conditions is often measured by short-term leach testing, but also required is a measure of the long-term durability of the material, particularly when radiation damage and

annealing processes will be occurring over the waste form's lifetime. Modelling of the leaching of radionuclides and movement of them through a geological repository become part of the safety case for the repository. Typically, repositories are modelled on an  $\sim 10,000$  y timeframe; however, recently there have been political drivers to have one million year time frames [17]. In the authors' opinion, this is likely to be unrealistic given the errors in potential models over such a time frame.

(3) *Chemical Flexibility.* The waste form has to be flexible enough to cope with "real," often variable, waste streams and processes. The waste form usually has to be able to incorporate significant amounts and types of impurities and process chemical additives without serious property degradation.

(4) *Ease of Processing.* Processing the waste to make the waste form needs to be cost effective, meet environmental and occupational health and safety norms (such as radiation doses to workers), and be technically feasible. Gamma emitting radioactive wastes, such as the ILLW from  $^{99}\text{Mo}$  production, impose the need for remote operations in a hot-cell, which is expensive to build, operate, and maintain. Furthermore, characterisation of such wastes is difficult and expensive. Therefore, the process chosen must have process parameters that are broad enough to be practical and to cope with changes in the waste stream and enable easy operation of the remote process line.

(5) *Proliferation Resistance.* For fissile materials, such as HEU used in Mo-99 production, the waste form must have a good resistance to theft or diversion and it must be difficult to retrieve the actinides for reuse. Physical security in terms of storage and inspection by safeguards officers is required. In the longer term rendering the material unattractive for reuse by converting it to a waste form for disposition is desirable. There are usually two approaches to this: providing a radiation barrier coupled with physical security, and producing a waste form from which it is more difficult to extract the fissile

materials, for example, by requiring techniques other than existing, well-known reprocessing routes.

In all cases the aim to be achieved in selecting the waste form and process selection is to reduce risk. The primary risks are economic and safety/environmental. Economic risk can be managed by reducing life-cycle costs and using technology assessment processes [18]. Environmental risk can be dealt with by ensuring the waste form is durable and stable over long-time frames while meeting the appropriate standards and criteria for disposition and safety (using safety assessment processes) and applying principles such as, as low as reasonably achievable (ALARA) or practical (ALARP) to the design and operation.

*2.1. Waste Forms for Molybdenum-99 Wastes.* Nearly all  $^{99}\text{Mo}$  producers use highly enriched U (HEU) and simply contain their waste in tanks (liquids) or as solids (e.g., used targets). However, from the 1970s to 2005, ANSTO produced  $^{99}\text{Mo}$  from ~1.8 to 2.2% enriched  $\text{UO}_2$  (LEU) targets irradiated in its HIFAR reactor at Lucas Heights. Until the early 1990s all the resultant nitric acid waste containing ~150–300 gU/L plus fission products was stored in tanks, but then a program was started to solidify this waste and contain the solids in metal cans [19]. ANSTO now has 560 kg of this solidified waste, but still has ~6000 L of liquid ILLW. The liquid waste consists of primary (95–195 gU/L) and secondary (9–35 gU/L) waste in tanks. In more recent times, however, plans have been made for immobilisation of this waste [20].

*2.1.1. Ceramic Waste Forms for Legacy U-Rich ILW Arising from the Acidic Route for  $^{99}\text{Mo}$  Production at ANSTO.* The waste from the acidic route is principally uranyl nitrate plus a small amount of fission products and mostly is classed as ILLW (Table 2). To immobilise this a pyrochlore-rich ceramic was developed [20], which was similar to the pyrochlore-zirconolite-brannerite ceramics developed by ANSTO and the Lawrence Livermore National Laboratory (LLNL) in conjunction with Savannah River National Laboratory (SRNL) for the immobilisation of 17–30 tons of surplus weapons grade Pu, the Plutonium Immobilization Project (PIP) [21]. Initially a zirconolite-rich formulation was developed for the Pu immobilisation, and it also included Ba-hollandite and rutile. The hollandite would enable the incorporation of radioactive Cs and would form a radiation barrier to reuse. The material was extremely durable [22]. The zirconolite-rich laboratory samples were prepared via cold-pressing and pressureless sintering, and via hot-uniaxial pressing in graphite dies. For production purposes ANSTO proposed that this material would be produced via hot-isostatic pressing (HIPing) [23], which involves the simultaneous application of heat and pressure to consolidate materials. For containment of waste forms in metal cans for HIPing ANSTO typically used stainless steel cans; however, other alloys may be used, for example, Ni [24, 25] (Figures 2 and 3). The powder is fed into the bellows; the bellows are evacuated and then hermetically sealed before HIPing. A hot-isostatically pressed metal bellows (~0.4 kg) that contained ~50 g of  $\text{PuO}_2$  plus several full-scale 9.5 kg



FIGURE 2: A hot Isostatic press located at ANSTO. This press can take up to a 30 cm diameter load. The machine consists of a pressure vessel in which a furnace is installed. Densification occurs under Ar at up to 200 MPa at the desired temperature.

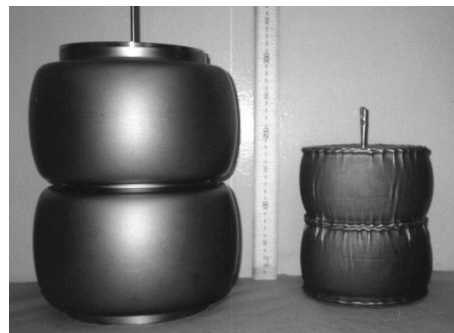


FIGURE 3: One of the many types of HIP can dumbbell designs showing how the can collapses to a near cylindrical shape (left before, right after HIPing). This 13.5 kg can contains Synroc-C. The HIPed can is 19 cm high by 15.5 cm in diameter.

bellows (12 cm dia.  $\times$  24 cm ht.) with Ce used as a Pu simulant were made.

Long-term criticality issues arising from the decay of  $^{239}\text{Pu}$  to  $^{235}\text{U}$  and the need to further discourage diversion led to the incorporation of significant amounts of depleted U. This reduced the waste loadings for Pu and hence pyrochlore-rich ceramics were developed containing ~10 wt% Pu, plus 20% U and equimolar amounts (to Pu) of Hf and Gd as neutron absorbers for criticality control both during processing and upon emplacement in a geological repository. A baseline formula of  $0.9 \text{Ca}_{0.89}\text{Gd}_{0.23}\text{Hf}_{0.23}\text{Pu}_{0.23}\text{U}_{0.44}\text{Ti}_2\text{O}_7 + 0.1 \text{Ti}_{0.9}\text{Hf}_{0.1}\text{O}_2$  was used [26]. This ceramic was shown to be capable of accommodating significant amounts of process chemicals and other variations in the Pu waste streams, having a wide range of ionic sizes and valences [27, 28]. The final formulations contained mixtures of pyrochlore, zirconolite, and brannerite (nominally  $\text{UTi}_2\text{O}_6$ ) depending upon the feed chemistry. The process chosen was cold pressing and sintering of ~500 g pucks using a route similar to that used for mixed oxide (MOX) fuel.

Ceramics were chosen ahead of lanthanide borosilicate (LABS) glass for PIP [29], which was also a possibility for use in immobilising  $^{99}\text{Mo}$  acidic ILLW if a melting-route

was chosen. While there were several factors influencing the decision to use a ceramic over a high-melting (1500°C) LABS glass [30] and one may have thought that the long-term durability of the ceramic phases (MCC-1 type leach tests produced very low normalized Pu leach rates of  $10^{-5}$  to  $10^{-6}$  g·m<sup>-2</sup>·d<sup>-1</sup> at 70°C in deionised water [22, 31]) would be critical, the two strong factors favouring the ceramic were its factor of ~7 lower neutron dose to workers (LABS glass contained boron which underwent ( $\alpha, n$ ) reactions); and its greater resistance to proliferation [32]; LABS could simply be dissolved in nitric acid and the Pu extracted by a PUREX-like process. Indeed, LABS glass was later developed as a means to store and transport actinides between US national laboratories [33, 34]. The processing options also favoured the ceramic in the fact that LABS glass was produced by melting at high temperatures (~1500°C) in costly platinum crucibles [35], and produced potential criticality risks from settling of PuO<sub>2</sub>, in the crucible, whereas the ceramic was proposed to be produced using a process similar to mature mixed oxide fuel manufacturing technology. The leach resistance of the ceramic, particularly for actinides and U, was far greater than that of LABS glass [36]. However, another long-term issue was the potential rapid loss of highly leachable B, which with Gd also serves as a neutron absorber, from LABS glass over geological time frames, rendering it less intrinsically safe from a criticality viewpoint than the ceramic [37]. The ceramic contained both Gd and Hf. The leach rates of these are low and with Gd leach rates being slightly higher than that of Pu, particularly if the pH is low, and Hf lower or similar to that of Pu. Furthermore, the ceramics were shown to be durable even when radiation-damaged, with accelerated testing on samples doped with <sup>238</sup>Pu carried out at the Pacific Northwest National laboratory (PNNL) [38, 39].

Therefore, from a Mo-99 viewpoint the ceramic-route offers advantages over LABS glass in terms of U-durability, criticality safety, proliferation resistance, and processing. The higher processing temperatures needed for LABS glass production would increase volatile losses of fission products and complicate the high temperature off-gas system. Furthermore, ANSTO needed to treat additional waste streams and required one process line for these, and LABS glass was not considered suitable for both streams. The choice of plant is discussed later in this paper.

Following on from the plutonium immobilisation and work on U-doped zirconolite, in-house research into treatment of ANSTO's U-bearing wastes started in the late 1990s [40]. This work showed that simply mixing the waste with the Synroc-B precursor developed for the original Synroc-C, designed for immobilising PUREX-type HLW from nuclear power plant fuel reprocessing [41], and then calcining and HIPing the material in a manner similar to that for Synroc-C produced a durable waste form. However, to increase the waste loading the design was shifted from zirconolite as a host for actinides to the related pyrochlore (nominally (Ca,Zr,U,Gd,Hf)<sub>2</sub>(Ti,Al)<sub>2</sub>O<sub>7</sub>) phase as a host for U [42, 43]. The waste form was somewhat similar to Synroc-F [44, 45], which was developed for the immobilisation of U-rich wastes such as those of the chemical composition of spent nuclear

fuel. The pyrochlore phase comprises ~80 wt% of the waste form. Hollandite and rutile (~10 wt% each) are present as secondary phases to assist in immobilising fission products present in ANSTO's legacy ILW [46], and small amounts of perovskite and brannerite may also form the final waste form matrix.

Although it would seem attractive to utilise a single ceramic phase for a given radwaste, real radwastes are inhomogeneous. So, the aim should be to create phase assemblages which can incorporate the full range of radionuclides, impurities, and process additives such that when the radwaste composition is variable the phase assemblage stays the same, but the phase proportions vary. Moreover, the waste form phase assemblage should be insensitive to variations in the waste/additives ratio as has been shown for Synroc-C and other Synroc systems.

The pyrochlore is nominally targeted as CaU<sub>0.47</sub>Zr<sub>0.53</sub>Ti<sub>2</sub>O<sub>7</sub> with U in the tetravalent state, but ANSTO researchers have found that due to the presence of U<sup>5+</sup> the pyrochlore contains additional Ca to maintain charge neutrality. This can also lead to the formation of brannerite. Figure 4 shows the microstructure of a sample produced via kneader drying. The sample was analysed in a scanning electron microscope and is composed of ~40–50 vol% pyrochlore (Ca<sub>0.95</sub>Zr<sub>0.09–0.12</sub>U<sub>0.83–0.84</sub>Ti<sub>1.99–2.04</sub>Al<sub>0.05–0.07</sub>O<sub>7</sub>); 30–40 vol.% brannerite (Ca<sub>0.02</sub>U<sub>0.97</sub>Ti<sub>1.9</sub>Zr<sub>0.04</sub>Al<sub>0.01</sub>O<sub>6</sub>); 5–10 vol% hollandite (Ba<sub>1.13</sub>Ca<sub>0.25</sub>Al<sub>0.76</sub>Ti<sub>6.72</sub>Zr<sub>0.02</sub>O<sub>16</sub>); 5–10 vol% Zr-doped rutile; plus ~1 vol% UO<sub>2</sub>. This is an initial test sample for scale-up and shows some segregation of TiO<sub>2</sub>, which explains the presence of more brannerite and some UO<sub>2</sub> than seen in laboratory samples which were more uniform [42]. This can be eliminated by improved drying techniques and improved precursor preparation. The samples produced were durable with low leach rates when tested using MCC-1 methodology (ASTM C1220-10 [47]). Measured leach rates for the HIPed sample shown in Figure 4 are given in Table 4. The result is consistent with unpublished data from small laboratory samples made earlier [4] (Table 4). The process is currently undergoing scale-up with full-scale testing to produce a 30L HIP can. The processing system will enable more homogeneous powders to be produced than those produced so far using small-scale and available mixers.

It has been shown at the laboratory scale that 100% dense ceramic samples containing around 40 wt% of U oxide plus fission products can be produced by HIPing at 1250°C/100 MPa for 2 h [20, 42] and that quite large variations in the additives and waste loading have little effect on the excellent leach properties. The advantages of HIPing have been described many times [16, 48, 49] and will be discussed below. In the process, an alkoxide-hydroxide precursor mix is prepared external to the hot-cell line. The preparation route for this precursor is the same as that used to produce Synroc-B [50, 51], the precursor used for the production of Synroc-C.

*2.1.2. Ceramic and Glass-Ceramic Waste Forms for Alkaline ILLW Arising from <sup>99</sup>Mo Production.* With the closing down of the Australian Research Reactor in 2005 and

TABLE 4: Leach rates for the HIPed sample shown in Figure 4. MCC-1 replacement test 0-1 and 1-7 day periods, 90°C, deionised water. Data from earlier work (0-7 days) [4] are also given; note that after the 7 d leach period the leach rates drop to less than or close to the detection limit for all elements.

Route	Normalised release rate ( $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ )						
	Latest data		Preliminary pyrochlore-rich work <sup>#</sup> [4] small-scale				
	Kneader dried		Alkoxide-route		Microsphere		
Waste loading	40 wt%	40 wt%	25 wt%	35 wt%	40 wt%	44 wt%	40
Leach period	0-1 d	1-7 d	0-7	0-7	0-7	0-7	0-7
Al	<DL	<DL	<0.01	0.05	<0.02	nm	0.05-0.3
Ba	0.65	0.11	0.04-0.1	0.005	<0.004	0.02	0.003-0.08
Ca	0.12	0.03	<0.01	0.01	0.02	nm	0.006-0.4
Cs	np	np	0.03-1	0.08	nm	0.10-0.13	0.2-7.3
Sr	np	np	0.04-1.4	0.08	0.03	0.08-0.12	0.04-0.3
Ti	0.005	0.00017	<0.01	<0.0001	<0.0001	<0.0001	<0.0001
U	0.008	0.0006	<0.01	<0.0001	<0.0001	<0.0001	<0.0001
Zr	0.010	0.0002	<0.01	<0.0001	<0.0001	<0.0001	<0.0001

Nm: not measured; np: not present.

<sup>#</sup>Note: data are varied because several different routes that produced differing degrees of homogeneity and some different processing conditions were tested. In addition variations in the waste composition were also tested. Only in a few samples where the redox was not controlled or the sample was inhomogeneous did the Cs and Ba leach rates increase. In all cases the U-leach rates remained low.

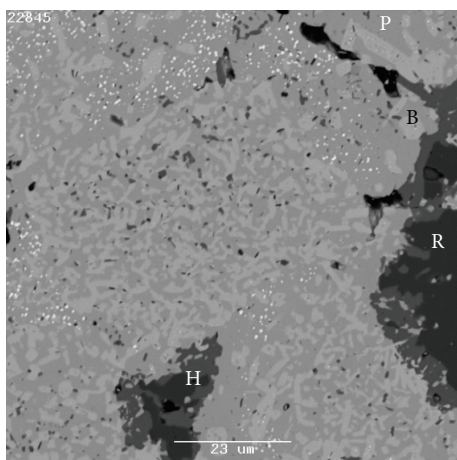


FIGURE 4: Microstructure of a baseline waste form designed to immobilise U-rich legacy waste at ANSTO. B = brannerite, H = hollandite, P = pyrochlore, R = rutile.

the construction of the new research reactor OPAL in 2006, ANSTO is now using 3% enriched UAl alloy targets and the Argentine/S. Africa/Belgium <sup>99</sup>Mo extraction methods, yielding alkaline ILW typically consisting of 5-6 M NaOH (after the addition of more NaOH for tank storage) plus 1.14-1.5 M NaAlO<sub>2</sub>, plus fission products (Table 2). The waste form chemistry and its waste loading limits are therefore dominated by the Na in the waste stream.

Sodium can be incorporated into several ceramic phases. In Synroc-C, the waste loading is limited to ~2.5 wt% Na<sub>2</sub>O, above which the leach rate increases as Na concentrates at the grain boundaries [52]. Other alternatives examined by the authors and others include, for example, perovskite (Ca,Na,RE(III))TiO<sub>3</sub> [53], freudenbergite (Na<sub>2</sub>(Al,Fe)<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>) [54], nepheline (NaAlSi<sub>3</sub>O<sub>8</sub>) [55], NZP

(NaZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub>) [56, 57], and NTP (NaTi<sub>2</sub>P<sub>3</sub>O<sub>12</sub>) [58]. However, the waste loading for Na in ceramics, especially after additional phases are added to host the waste ions, is limited, increasing the waste volumes produced, limiting plant throughput, and increasing life-cycle costs. Alternatives such as borosilicate glasses and glass ceramics were therefore examined.

Following initial forays into boroaluminosilicate glass consolidated by HIP rather than vitrification, we are now working with a glass-ceramic which can be HIPed at 1000°C/35 MPa with a 26 wt% oxide waste equivalent loading [20]. This has satisfactory leaching properties insofar as it will pass the Product Consistency Test (PCT) for HLW borosilicate glass [59] at 40 and 90°C and further optimisation and scale-up is in progress. We will discuss this further below.

Another alternative is bitumisation, carried out in Belgium [9] Japan, and elsewhere. However, such a plant did not match ANSTO's technical expertise and concerns exist about the storage and flammability and potential for self-ignition of such material, with accidents having already occurred [60]. Thus, there was no advantage in considering this route. Furthermore, from a long-term storage and repository perspective, the inclusion of large quantities of flammable materials may be deemed problematic.

*2.1.3. Cementitious Options for ILLW and LLLW Arising from <sup>99</sup>Mo Production.* The alkaline-route <sup>99</sup>Mo production process also produces a similar amount of lower activity wastes to the volume of ILW produced. This waste is initially highly active but decays over ~3 years to below the ILW/LLW level. Of course cement is a popular solid waste form for low-temperature solidification and/or encapsulation of LLW. However, homogeneous incorporation of waste has some risk associated because the waste might seriously perturb the cement setting process. The cement cannot be dehydrated

by heating without detriment to its physical integrity, so radiolytic gas buildup as storage and disposal time is a serious factor to contend with. Also the fact that this waste is rich in Na is not a positive feature for cement; the large Na content would probably give rise to high leachability (the well-known alkali reaction problem for cement) unless the waste loading is kept very low. As a consequence, the waste volume would be considerably higher.

Alternative routes to ceramic immobilisation include drum drying of liquid waste followed by overpacking in concrete, which also acts as radiation shielding. This route is used by COVRA in The Netherlands. ANSTO looked at using this route but found that it would create 50,000 L/y of concrete waste for the ~2000 L/year production from its existing plant and much more (~112,000 L/y) from its planned future plant. The hot-isostatic pressing route chosen by ANSTO would produce only ~500 L per year of unshielded waste. The package size meant that the waste could be stored in existing facilities and hence eliminated the need to build a multimillion dollar waste store every 10 years. Furthermore, the number of shipments required to a future national store would be reduced by at least an order of magnitude. Given the several 1,000 km transportation distance in Australia, this cost saving was significant, but the decrease in political, environmental, and security risks by fewer shipments was also considered important. In addition, any final repository volume would also be significantly reduced, leading to life-cycle cost savings. While there are no published costs for an Australian repository/store the effect of volume reduction can be illustrated by considering the published US cost of \$US602,000 per glass canister for disposition at Yucca Mountain [15] and around £18,000/m<sup>3</sup> to dispose of ILW in UK [61]. Using the UK figure the disposition savings from volume reduction alone would be around \$3-4 million/yr. There are also other calculated benefits such as a reduction in life cycle CO<sub>2</sub> emissions. The Synroc route shows a significant reduction in CO<sub>2</sub> emission over the cementation process, although from an operational perspective the power consumption of producing synroc versus cement waste forms is similar with synroc being about 20% lower in the life cycle to storage. The significant CO<sub>2</sub> savings come from the size of the repository that is needed to be built to house and store the treated wastes, where the difference is around 20 times less for the synroc process compared to the cement option.

Geopolymers are low-temperature ceramics made by the action of highly alkaline silicate solutions on reactive aluminosilicate precursors, so the alkaline LLLW (Table 2) is attractive from this aspect. Geopolymer processing has many similarities to that of cement. Geopolymers are generally superior to cement in the radioactive context with respect to leachability (in addition to the absence of the alkali reaction problem). Cements are subject to radiolysis from nuclear waste and consequent weakening of the hydrous binding phase, whereas geopolymers do not rely on hydrous material for strength and can be carefully dehydrated by not-too-rapid heating without decrepitation or significant strength loss problems. It has been shown [62] that both the ILLW and LLLW from <sup>99</sup>Mo production can be incorporated in a metakaolin-based geopolymer and can pass the PCT leach

test for deep disposal; however, the waste loadings on an oxide basis were somewhat below 10 wt% in both cases. The sulphate was precipitated as BaSO<sub>4</sub> to inhibit the SO<sub>4</sub><sup>2-</sup> from interfering with the geopolymerisation process. More fundamental aspects of geopolymer leaching, notably temperature, pH dependence, and solution/volume ratio, have also been published by ANSTO workers [63]. The alkaline nature of geopolymers would suppress any potential for cyanide gas emissions from the KSCN present in the liquid LLW, even during dehydration at temperatures of ~300°C for example. Further optimisation studies are in progress.

However, nitrate waste streams are highly problematic for cement and geopolymer production would require front end treatment, calcination, or other denitrations, which would complicate the process. In addition the presence of water would also have criticality implications for HEU wastes requiring very low waste loadings and hence would produce large waste volumes if used to immobilise the U-rich wastes.

*2.1.4. Immobilisation of Used UAl Alloy Targets.* These consist mainly of UO<sub>2</sub> + Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>, plus some fission products. A ceramic waste form approach could be the addition of Ca, rare earth, and Ti oxides to allow conversion into a perovskite-structured (Na,RE)TiO<sub>3</sub> + brannerite ceramic (nominally UTi<sub>2</sub>O<sub>6</sub>). Preliminary experiments have demonstrated the general feasibility of this approach. Depending on the enrichment of the U, the preferred rare earth would be Gd as a neutron absorber to inhibit the likelihood of criticality. While the U in the nominal brannerite is tetravalent, U<sup>5+</sup> can also be accommodated, with the charge compensation provided by the addition of Gd<sup>3+</sup> and other ions such as Ca<sup>2+</sup> on the U site and Al<sup>3+</sup> on the Ti site. Another alternative is a ceramic to immobilise U in brannerite and the Na in freudenbergite (Na<sub>2</sub>(Al,Fe,Cr,Ti)<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>).

A different approach would be to immobilise the Na in a glass and the uranium in a zirconolite/pyrochlore to make a glass-ceramic, similar in principle to work being undertaken by the UK National Nuclear Laboratory and ANSTO to immobilise Pu-residues wastes [64, 65].

*2.1.5. Separation of Cs and Sr.* Recent work appears to show highly efficient separation of Cs and Sr from ILLW [66], and several routes for both alkaline and acidic streams have been examined [67]. Also, IONSIV [68], the commercially available NaSiTiOx ion exchanger for separation of Cs and Sr from alkaline wastes, can be converted to a high-temperature ceramic with excellent leach resistance [69] or a glass [70]. The removal of the Cs and Sr may reduce the activity of the ILLW close to or below that of LLLW and the Cs and Sr could be incorporated in a relatively very small volume of waste form. Of course IONSIV is not able to immobilise the solid cake or any of the other ILW and the production of the highly radioactive waste form, such as the hollandite phase, would not be easy.

The principal disadvantage of separation technology is the fact that it requires the additional expensive hot-cell unit operations and you end up with two waste streams to treat,



plus additional secondary wastes. The reasons we did not pursue this option at ANSTO have already been summarised above.

**2.2. ANSTO's Waste Treatment Plant for Treating ILLW.** ANSTO undertook an assessment of options to treat both its legacy and alkaline wastes prior to commencement of the project. Some of the benefits have been discussed above in Part 3.1, in particular the life-cycle cost savings from waste volume reduction. After an assessment ANSTO chose a production route that included similar unit process operations to that used in the original Synroc Demonstration Plant (SDP), which was designed to process 10 kg/hr of Synroc-C [41]. Given the need to treat both acidic and alkaline streams and the desire to avoid costly off-gas systems, plus the relatively low throughput and currently proposed intermittent plant operation (3-4 days/week) compared to HLW glass melters, a melting-route was ruled out. As discussed above cementation was also ruled out on a life-cycle cost basis, because it could not handle all of the potential waste streams to produce a durable waste form and would therefore require additional front-end processing, produce a considerably larger waste volume, and could not use existing storage facilities. Given the lack of repository specification it was felt that an encapsulation approach was undesirable in an Australian context and that the fission products should be bound in the waste form.

HIPing, a technology that has matured considerably since the SDP was run in the 1980–90s, was employed as the consolidation step and its advantages are discussed below. In the SDP a hydraulic hot uniaxial press with induction heating was wed with metal bellows containing the processed synroc powder. The plant capital and operation have been costed for a plant with a 30-year design life with a planned maintenance schedule. The plant is designed to produce 150 30L HIP cans per year with a conservative maintenance and availability regime, but that is operating on a 3-4 day working week schedule and the plant has at least double that capacity. In addition, the plant could also be used to treat the lower activity liquid waste from the alkaline route and the U-rich filter cake. ANSTO is currently storing the latter with a view to either disposition or reuse after treatment.

Currently, the project is moving into the detailed design stage and the Environmental Risk Assessment is with the Australian regulator, the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) and has successfully undergone independent technical readiness level (TRL) assessment [71].

Although the compositions of the final waste forms for the legacy and alkaline wastes are different, the waste treatment steps are the same. Figure 5 illustrates the steps in the modern SYNROC HIP process. The durable synroc waste form is not produced until the calcined precursor powder has been HIPed. The process line is divided into sections for contamination control. In the first section the liquid waste is mixed with additives to get the chemistry of the waste form correct. This slurry is then dried to a free flowing powder. The front end will use fairly standard stainless steel tanks, mixing

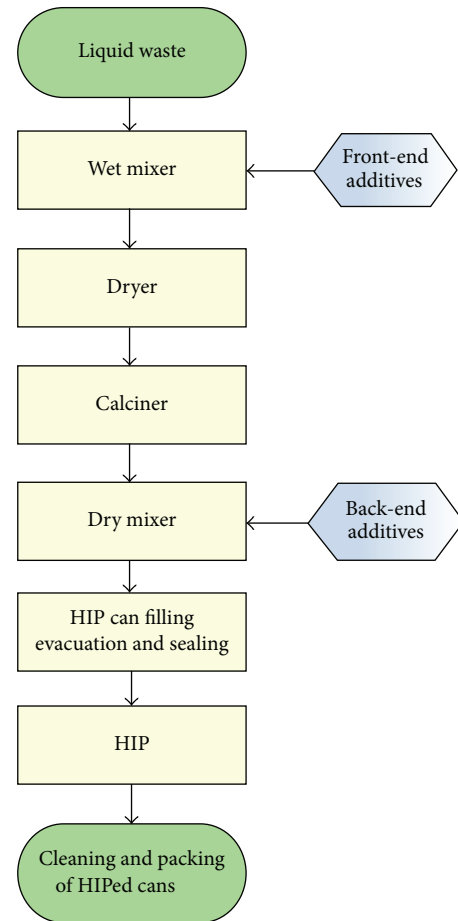


FIGURE 5: Schematic of the waste treatment steps.

and transfer systems that have been nuclearised for hot-cell maintenance and longevity. The powder is then heated in a calciner to remove species that may decompose and generate gas upon heating, such as chemically bound water, nitrates, and carbonate. ANSTO has examined a number of calciner options and has developed a proprietary system to replace the traditional rotary calciner. This system has a smaller footprint and will not require seal maintenance to prevent air ingress, as is the case with rotary calciners.

By using 3.5%  $H_2$  in  $N_2$ , reducing conditions are maintained during calcination to reduce fission product volatility. There are limited data available at this stage on the specific plant dryer; however, work employing  $^{134}Cs$  and  $^{103}Ru$  radioactive tracers to measure volatilisation during the Synroc-C process, which has similar unit process steps and operating conditions to the current plant design (wet mixing, drying, calcining and hot-pressing), was undertaken. The dryer was a flash dryer with a measured loss of  $\sim 0.006\%$  of Cs and  $0.05\%$  of Ru, but some of this was likely to be in fine particulates. The Cs loss during calcination during calcination at  $750^\circ C$ , in  $3.5\% H_2/N_2$ , was measured at  $0.11\%$  and this was mainly due to entrainment in/on the fine powder carried through by the process gas into the off-gas system [41]. In additional work by Woolfrey and Cassidy [72] the fines

were filtered from the off-gas and the measured Cs loss due to volatilisation was found to be much lower (0.0001%) and the Ru volatilisation was also lower (0.004%). We have undertaken some laboratory-scale work with nonradioactive Ru and have found little if any loss from the alkaline stream when dried and calcined. Further work is planned to be undertaken at scale to confirm this. As the plant off-gas will be filtered and the fines recycled, so the volatilisation is expected to be similar to the Synroc-C test figures. Technetium levels in the waste are small and the losses will also be minimised by processing under reducing conditions. ANSTO has prepared via sintering  $^{99}\text{Tc}$  samples that retain the bulk of the Tc [73, 74]. Iodine is absent from the alkaline ILLW, but the off-gas system will be designed to remove I and any other volatiles carried over. The carryover waste will be treated via ANSTO's site management lines. With the use of HIPing inside a metal can for consolidation there will be considerably less off-gas compared to a melter route and hence the off-gas system for the ANSTO plant is considerably smaller than melters.

The resulting powder can then be mixed, if required, with back-end additives, such as metal getters for redox control; Ni and/or Ti are the most commonly used in Synroc. The calcined powder will be then loaded into the metal HIP can using ANSTO's proprietary designed filling and sealing system, that prevents contamination spread of the powder. The can is evacuated and sealed, and the seal welded. The can is decontaminated and passed through a lock into the next cell. For some plants there is the option to preheat the can or bake-out during evacuation, but this is not required for wastes in ANSTO's plant. The HIP can is placed inside an ACOP (Active Containment Over-Pack) [48] that provides another layer of protection for the HIP machine and the surrounding environment from the spread of contamination and damage to the furnace or pressure vessel should an unexpected failure of a HIP can occur.

The ACOP containing the filled HIP can is transferred to the HIP and processed under heat and pressure (using Ar) to produce a dense, durable glass-ceramic, or ceramic with a high waste loading. This is discussed in more detail below. The HIPed cans go through a further decontamination and check and are then loaded into bins for transfer to ANSTO's storage facilities.

The Synroc waste treatment plant will be operated to process around 5000 L of liquid waste per year with a higher capacity possible. The plant uses industrially mature plant and equipment that has been modified to be able to be operated remotely. The focus of the Synroc team's work in the past 2 years has been on developing the design to a high TRL to minimise technical risk involved in a "first of a kind" plant, and to optimise the processing parameters and determine the process windows. Preliminary engineering is at completion and the plant construction and commissioning is expected to be completed by 2016.

A conceptual design is shown in Figure 6. This design utilises a front-end with process equipment to mix the waste stream with additives and dry and calcine the product. The calcined powder is placed in a HIP can, which is then evacuated, sealed, and moved through decontamination cells into the HIP cell. The HIP cell is located such that contamination

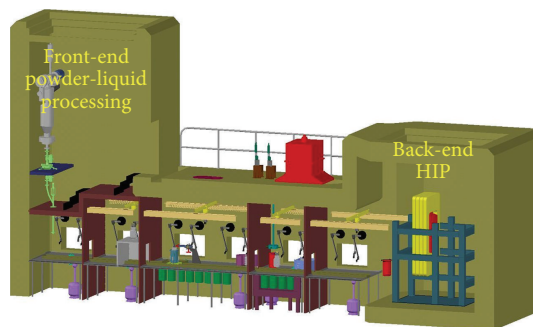


FIGURE 6: Initial conceptual plant design for the treatment of ILLW wastes at ANSTO.

control is maintained and access for maintenance is feasible. This design was ~18 m long. The final design will have triple the capacity to this design and will be only ~4 m longer and a little wider.

#### 2.2.1. The Use of Hot-Isostatic Pressing to Treat Nuclear Waste.

Hot-isostatic pressing (HIPing) technology was invented in the 1950s at the Battelle Memorial Institute (US) [75] and was used throughout the late 1950 and early 1960s as a research tool for fabricating experimental fuels and reactor materials [76, 77]. It involves the simultaneous use of heat and pressure to densify a material. Argon is the traditional gas medium used in commercial HIPs, but other gases have been employed for speciality materials or research purposes. The use of gas to transmit the pressure means that the material must either be contained within a sealed layer or first sintered to closed porosity, in order for densification to occur. To avoid high-pressure gas in pores or voids the container must be evacuated. The use of HIPing for the manufacture of radioactive waste forms was first proposed in the 1970s [78]. HIPing has been validated at the Idaho National Laboratory in the US as a credible (and advantageous) method of consolidating radioactive ceramic waste forms, with HIPing at the 100 kg scale of a zeolitic-type waste form and the use of an in-cell hot-isostatic press [79]. Moreover, the method is widely used in industry for preparing inactive ceramics. In the radioactive waste form field, Swedish workers were the first to use HIPing [80]. US workers HIPed experimental waste forms targeted to Savannah River wastes in the late 1970s and early 1980s [81] with Synroc-D developed at LLNL for US defence wastes [82, 83]. This was consolidated via HIPing or hot-uniaxial pressing in metal containers, which were favoured over pressureless sintering because this route gave a wider process window in which to achieve the required density rapidly (10 min. at 4000 psi (28 MPa) at 1100°C [84]) and could produce larger blocks of waste form. The cans also reduced the spread of contamination in the process line. HIPing demonstrations at 0.45 m dia. by 0.5 m high (50 kg) were undertaken [82] and bellows 26 "(0.67 m) in diameter by 58" (1.47 m) high proposed for a HIP plant [85]. A preliminary engineering layout was developed for

the Synroc-D process consisting of a wet mixer, a fluidised bed calciner, and a HIP to consolidate the material after it was loaded and welded into metal bellows [86]. The plant design capacity was ~1.45 tons/day.

For waste form processing ANSTO uses Ar as the pressure transmission medium. HIPs can be designed to operate above 2000°C, but processing temperatures for ceramic and glass-ceramic waste forms lie typically between 900 and 1300°C. HIP pressures up to 1000 MPa are possible with most general purpose laboratory HIPs operating around 100 MPa. Typical processing widows for waste forms are 20–100 MPa.

The metal HIP can is usually stainless steel, but it can be mild steel, nickel, or other metal as desired as mentioned in Section 2.1.1. The cans themselves are a few mm thick. The HIP can shape is tailored to suit the properties of the powder feed, the time-temperature-pressure cycle in the HIP, and the behaviour of the waste form during heating. It is advantageous to maximise the density of the calcined powder on loading the HIP can, to avoid undue rippling and substantial deviations from cylindrical geometry of the HIPed can; however, special designs are available for low-density powders. The dumbbell shaped can is designed to collapse to a near-cylindrical shape (Figure 3). The dumbbell design replaces earlier bellows designs and has the advantage of having the joins/welds in the can under compression. If a dumbbell can should fail or pinhole, high pressure gas can enter the can; on depressurisation of the HIP a dumbbell can will only expand to slightly bigger than its original shape and will therefore not damage the HIP furnace. ANSTO has undertaken experimental work to verify this. The bellows designs on the other hand are prone to failure at the tips of the bellows and if they fail they will expand considerably when depressurisation occurs, destroying the HIP furnace.

The can serves several roles. Its primary function is to act as a seal between the gas and powder allowing densification to occur during HIPing; it assists in maintaining the desired redox conditions during processing; it contains the waste form, preventing contamination spread, with minimal interaction. Testing has shown HIP that can interactions between the ceramic and glass-ceramic waste forms are minimal and not deleterious to the integrity of the waste form of HIP can [87, 88]. The can also retains volatile radioisotopes such as <sup>99</sup>Tc, <sup>104</sup>Ru, and <sup>137</sup>Cs during high-temperature consolidation. So the entire process produces off-gas only in the calcination stage where temperatures, <750°C, are much lower than those in the final consolidation, and reducing conditions further reduce the loss of volatile radioisotopes. While some credit may be possible for containment during storage of the waste form, ANSTO's approach is to rely on the waste form chemistry and use a transport container or overpack to provide mechanical protection.

For laboratory samples, the HIP can is usually evacuated after filling. The laboratory small cans typically contain a lid to which is attached an evacuation tube. However, production cans have a filling port and welding occurs on the lid. In laboratory samples the can often undergoes a bakeout cycle prior to sealing where it is heated to 300–600°C for several hours to remove gases adsorbed by the calcined powder when exposed to atmosphere. However, in production lines,

where the unit process operations are interconnected and the atmosphere is controlled, this step may often be dispensed with.

*2.2.2. Addressing Production Concerns Surrounding Use of HIPing in a Radioactive Environment.* Concerns have been expressed about the use of a high-pressure system in a radioactive environment and about the capacity of a HIP line to treat the volumes of nuclear waste, possibly because HIPing is a batch process, whereas its main competitor, glass melting, is semicontinuous and produces tonnes per day of glass waste form. Industrially large HIPs with hot zones of up to 2 m diameter with tonnes per day throughputs are in commercial operation. ANSTO has demonstrated that cans containing 100 kg of waste form are feasible (Figure 7) and has produced concept designs for treating ~10,000 m<sup>3</sup> per year of fuel pond sludges with two HIP units and another series of designs to treat the 6,600 tonnes of Idaho HLW calcines over a 6–12 year time frame. Industrially, cans containing several tons of material are processed.

The initial cans used in HIPing were of the bellows design used in hot uniaxial pressing. In the early 1980s ANSTO and LLNL [82, 89] studied synroc densification during HIPing using these types of cans and cylindrical tubes. These designs suffered from being inefficient in their use of space. Cylindrical cans deformed preferentially in the middle to give a “dog-bone” type shape. Bellows collapsed vertically leaving a relatively thick layer of compressed convolutions around the waste form. Bellows had an additional disadvantage in that the welds were placed in tension and if failure occurred (typically a pinhole failure), the Ar gas could enter the can. Upon decompression of the HIP this internal pressure would force the bellows to expand well beyond their original length often destroying the HIP furnace. To overcome this design deficiency ANSTO developed a dumbbell design [90]. These cans were designed to place the welds in compression to substantially reduce the risk of pin holing and if a dumbbell can failed it expands back to close to its original size and shape. The failed can may then be simply placed inside a bigger can, evacuated, sealed, and re-HIPed. ANSTO has tested this by deliberately inducing failure by putting a defect in the can wall; we have also examined failures due to defective welding. Once the waste form has densified there is no dust to leak out of the can. The dumbbell design had an added bonus of much more efficient packing. The dumbbell HIP cans have been designed with a 1/10,000 failure rate. They will be leak tested and the weld will be tested before use and the can marked for traceability.

The prevention of the loss of volatiles has also been mentioned and this considerably simplifies the off-gas system compared to a melter route. Recent laboratory-scale experiments at ANSTO have shown that the alkaline waste form process retained essentially all of the Cs and Ru from the wet mixing to the final HIPed waste form. Further tests at scale are planned. The segmented hot-cell design and decontamination systems also serve to mitigate the spread of contamination. As with all hot-cells the ANSTO line is connected to active ventilation systems that remove activity.



FIGURE 7: An ANSTO dumbbell design HIP can (100 L capacity) containing over 170 kg of Synroc waste form, before HIPing (a) and after HIPing (b), which was produced to demonstrate the scalability of HIPing.

The vent gases from the HIP are also passed through filtered systems. Water cooling in the HIP vessel design removes the heat from the vessel and hence the ventilation rates and temperature in the HIP hot-cell are within the normal operating parameters for hot-cells.

Control of radioactive contamination when handling powders is another concern. Dust is controlled by microfiltration on the dryer and calciner that recycles the particles back to the feed. The process lines are sealed with the units interconnected. The only decoupling occurs during HIP can filling or maintenance. Valving, and coupling design, plus washing procedures will be used to allow decoupling of equipment for removal or maintenance. ANSTO has a proprietary designed can filling system that replaces the earlier crimping and cutting system and prevents the calcined powder escaping during can filling. The use of an ACOP also provides another layer of protection for the HIP machine and the surrounding environment from the spread of contamination and damage to the furnace or pressure vessel, should an unexpected failure of a HIP can occur, containing both the can and its contents.

The two main HIP vessel designs are monolithic forged and wire wound pretensioned. The wire wound vessel has some fabrication advantages for the very large HIPs when compared to a monolithic forged vessel in terms of weight and size. However, ANSTO chose not to use a wire wound vessel because of some key potential risks, especially for radioactive environments. Concerns about the use of pressure needed to be addressed during the safety case for the ANSTO HIP. There have been two major vessel failures in the HIP industry. One was a noncoded monolithic pressure vessel that was improperly used, and the other, was a coded wire wound pressure vessel. Both resulted in damage to the surrounding infrastructure with the latter incident resulting in the death of a worker. In a radiological application the potential energy stored in a HIP system could in the event of failure pose a

hazard to the hot-cell structure and has the potential risk of the release of radioactive material to the surrounding building. ANSTO worked with the US HIP manufacturer American Isostatic Presses Inc. (AIP) to develop designs that mitigate the risk and make it possible to safely utilise HIP technology in a radioactive environment. ANSTO chose to use a forged vessel due to reasons discussed in detail in [48].

The ANSTO-AIP approach was to significantly increase the level of conservatism built into the pressure vessel design. By doing this, the subsequent major inspection interval for the vessel could be extended, even to the point that a properly designed hot-cell HIP that could complete the cleanup mission/campaign well before the first major vessel inspection is required. The additional cost of this is more than compensated for by reduced maintenance, replacement, and inspection costs, plus the reduced risk of radiation exposure to workers from such activities, even though the segregated hot-cell design and associated contamination control is such that it allows workers to enter the hot-cell that contains the HIP.

The first step in ensuring safety was to mandate the use of coded vessels designed, built, and tested in accordance with demanding specifications of the American Society of Mechanical Engineers (ASME) Pressure Vessel and Boiler Code, Section VIII, Division 2 and 3. ASME designed vessels can be designed for lives of 10,000–100,000 cycles at the maximum operating pressure, which would give a vessel 20–100 years of operation depending upon its duty cycles. The ASME lifetimes for a vessel are conservative and based on a presumed flaw in a pressure vessel. Such Division 2 coded vessels have a burst pressure of 2.4 times the design pressure, or roughly 2.5 times the normal operating pressure. The HIP in-built safety systems initiate well before the burst pressures are reached. A leak before burst design is also incorporated into the forged shell and heads without any high prestressing

requirements. In addition, it is possible to monitor crack growth in a forged vessel and hence determine its design life, repair the surface crack, or derate the vessel. The hot-cell is also designed against catastrophic failure. The ANSTO-AIP proprietary design has a design life of 10,000 cycles and will operate at a pressure well below its failure pressure. It also incorporates the leak before burst design which means that catastrophic failure is not possible. Safety analysis has indicated that failure of the proposed design nuclear HIP system is not credible.

While a pretensioned wire wound vessel, in theory, may also afford the leak before burst feature in the event of overheating, for example, due to cooling water loss, stress relaxation in the pre-tensioned wire winding could lead to significant distortion of the vessel. While one could put designs and systems in place to enable a wire wound vessel to have some of the advantages of the forged vessel, ANSTO's approach has been to use the passive safety implicit in a forged vessel design rather than rely solely on active systems, an approach that underpins the nuclear industry approach to design.

HIPing has several other advantages for use in a hot-cell: the process has a relatively small footprint, arising in the first instance because of the absence of off-gas in the hot-consolidation step. The HIP cans contain the fission products and, in conjunction with other methods, the HIP vessel can be kept relatively contamination free. The HIP pressure vessel is designed to exceed the life of the plant and because it is monolith contamination will be limited to the surface, which can be readily decontaminated. Thus, the secondary waste from the HIP plant will be far less than that from a glass melting route, which would produce several used glass melters, plus highly contaminated off-gas lines. The plant decommissioning will therefore be simpler.

For radioactive ceramic waste forms a prime advantage of HIPing is to achieve theoretical density of the waste form with minimum temperature and therefore minimum grain size, thereby adding to the overall strength and leaching resistance as well as reducing the potential of microcracking via polymorphic structural changes or radiation damage when the waste form contains a substantial amount of alpha-emitting waste actinides.

The HIP process is scalable and can treat batches from a few grams to tons in the same unit. Because of this one process line could be used to treat multiple waste streams and ANSTO has design options to treat the ion exchangers, filter cake, and LLLW in the one plant. The scalability also means that small to large plants, tailored to a client's requirements, could be built.

For hot-cell operation ANSTO and AIP have designed remote loading and unloading systems, with a bottom loading approach used for the ANSTO line.

### 3. Conclusions

Higher activity LLLW and ILLW streams arising from  $^{99}\text{Mo}$  production can be incorporated into several types of waste forms: ceramics, glass-ceramics, glasses, and in some cases

cements or geopolymers. ANSTO is currently entering the detailed design stage of a Synroc plant to treat its legacy, current and future liquid wastes from  $^{99}\text{Mo}$  production at its Lucas Heights site. For the legacy waste, which is mainly uranyl nitrate plus some fission products, ANSTO has chosen to use a pyrochlore-rich ceramic in which the U and fission products will be incorporated into titanate Synroc phases, pyrochlore, brannerite, hollandite, rutile, and perovskite. For the current and future waste arising from an alkaline route ANSTO will use a glass-ceramic. Both waste types will be processed in the one line, which has broadly similar unit operations to the original Synroc processing designs—liquid mixing, drying, calcining, and consolidation via hot-pressing. The plant will be the “first of a kind” incorporating a hot-isostatic press into the design. This was chosen because the route had significant life-cycle cost benefits for ANSTO and Australia, including a significant reduction in the volume of the waste that would need transporting to a National Store and future repository. The option of using the plant or similar designs to process other waste streams has also been examined and it is possible to utilise the technology to process other waste streams from  $^{99}\text{Mo}$  production or from other waste inventories. The plant at ANSTO is currently entering the detailed design stage with a view to finishing construction by 2016.

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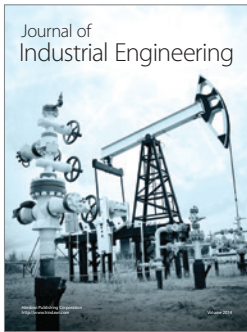
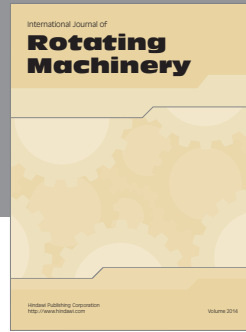
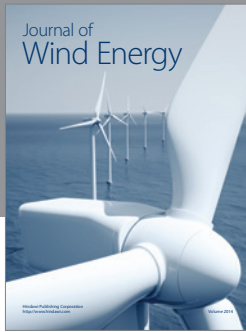
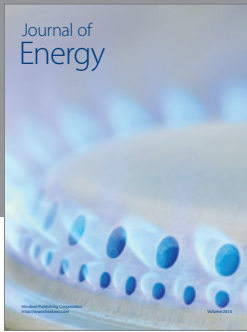
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