Technical Support for Waste Management of Fission-Based Mo-99 Production

Basic Ordering Agreement No. 4J-30041

Work Order 1: Feasibility review of immobilization and disposal of generated waste streams

FINAL REPORT

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EXECUTIVE SUMMARY

Molybdenum-99 (Mo-99), is the parent nuclide for the most widely used radioisotope in nuclear medicine Technetium-99m (Tc-99m); it is produced primarily from the fission of Uranium-235 (U-235). The current global demand for Mo-99 is 622 000 6dCi/year (where 6dCi refers to the number of curies of Mo-99 remaining 6 days after shipping from a production facility). Reactors that currently provide more than 90% of global Mo-99 supply are 43 to 52 years old. Recently supply shortages have been experienced due to unscheduled shutdowns and will continue into the near future as these reactors are decommissioned. Therefore, several countries are in the course of planning the development their own capabilities to produce Mo-99.

The majority of Mo-99 is currently produced in research, test or isotope production reactors by the irradiation of highly enriched uranium (HEU) targets. The U.S. Department of Energy's (DOE) National Nuclear Security Administration (NNSA) manages the Global Threat Reduction Initiative (GTRI) reactor Conversion Program, a continuation of the Reduced Enrichment for Research and Test Reactors (RERTR) Program that was established by the DOE in 1978 to reduce and eliminate the use of HEU.

The GTRI-Reactor Conversion Program mission supports the minimization and, to the extent possible, elimination of the use of highly-enriched uranium (HEU) in civil nuclear applications by working to convert research reactors and radioisotope production processes to the use of low enriched uranium (LEU) fuel and targets throughout the world. Argonne National Laboratory (ANL) has provided technical support for RERTR since its inception. Conversion from a HEU to an LEU Mo-99 production process will decrease the efficiency of Mo-99 production, and result in an increase in waste volumes and associated treatment costs. The demonstration of practical and economically feasible technologies, to treat the waste arising from Mo-99 production from HEU and LEU target material, is likely to provide an additional incentive for Mo-99 producers to convert from HEU use to LEU.

The production of Mo-99 in which the targets are dissolved in a sodium hydroxide or nitric acid solution and then processed to remove the Mo-99, results in several operational waste streams. The focus of this current body of work is the uranium containing waste streams generated during the production of Mo-99 via an alkaline-route; the waste streams generated by acidic methodology are summarized in the introductory chapter for completeness. The possible co-processing of waste streams, by using the same plant and equipment to process a variety of different waste streams, could provide significant overall waste treatment cost savings. Therefore, the waste generated by a variety of means will be considered for future co-processing during the final recommendation of waste forms; this will include: (i) the acid production method wastes as well as (ii) the caustic intermediate-level liquid waste streams that do not contain uranium (the highest volume of waste generated from the alkaline process). Note, co-processing defined as the mixing of different waste streams to be processed simultaneously will not be considered in this work.

The production of Mo-99 via an alkaline-route in which the targets are dissolved in a sodium hydroxide solution, results in several waste streams. One of these is the uranium filter cake (residue), which contains fission products and minimal process chemicals, and is the subject of this project. Two possible routes are envisaged for the encapsulation and immobilization of the residue for disposal in-line with the NNSA's GTRI objectives are: (i) direct waste processing and (ii) waste produced after the addition of a uranium recovery process.

The first is the direct processing of the residue to incorporate it into suitable immobilization matrices that reduce proliferation risks (for example titanate ceramics). This treatment will include the option of down-blending prior to treatment for HEU residues.

The second proposed processing methodology is based on the recovery of the valuable enriched uranium, for reuse as LEU. This process will generate various waste streams that will need to be immobilized. The process is envisaged to be a two-step process. The first process step, inside a hot cell, involves the dissolution of the residue and performing an initial separation. The second step involves the transfer of the uranium in a nitric acid medium to a glove box for final purification using known UREX liquid-liquid extraction technology. Based on current available experimental results, the generated radioactive waste streams that need to be encapsulated are: (i) possible undissolved residues, (ii) active ion exchange columns, and (iii) active liquid solutions.

The contracted ***"Work order 1: Feasibility review for immobilization and disposal of waste streams"*** is a literature based feasibility study regarding the encapsulation of the above waste streams (original residue and uranium recovery process wastes). It is structured around the following series of inter-related chapters with technical details:

Chapter 1: Identification and description of all waste streams resulting from fission Mo-99 production

An outline of the various processing routes for Mo-99 is described. This section presents detailed characterization results of waste generated from Mo-99 production by both alkaline and acid processing of uranium target plates. It also includes detailed proposals for the generation of suitable surrogate materials for lower activity preliminary waste encapsulation studies.

Chapter 2: Nuclear waste form candidates for the immobilization of waste streams from fission-based Mo-99 production

The aim of turning waste into a waste form is to render it into a stabilized solid matrix suitable for safe storage or disposal at a final site, such as a geological repository. In this chapter the historical development and properties of candidate glasses, ceramics and glass-ceramics for nuclear high- (HLW) or intermediate- level waste (ILW) are reviewed. Cementitious waste form materials are also discussed specifically in the context of waste arising from Mo-99 production. The chapter is a survey of the research and development efforts in these materials for use as nuclear waste forms as well as their various production technologies.

Chapter 3: The application of waste acceptance criteria to waste forms used to immobilize waste from Mo-99 production

Waste Acceptance Criteria (WAC) are the standards against which a radioactive waste package is assessed. It sets the limits for acceptance of a waste package into a store or repository and these criteria are developed with reference to a safety case for the store or repository. Given the lack of open repositories for radioactive waste arising from Mo-99 production, the most practical approach for this project is to focus on generic criteria that are directly related to the waste form and its production, with some assessment of its compatibility with its container. In this chapter the classification of radioactive waste is discussed from a global perspective and is applied to waste produced from the production of Mo-99. The generic concepts outlined by the IAEA are introduced, including waste characterization and properties used to assess conformance of the waste form. A brief overview of guidelines and standards used in each of the key Mo-99 producing countries has been given. Specific waste acceptance criteria and tests for the waste forms generated in this project for Mo-99 waste have been proposed.

Chapter 4: Proposed criteria for encapsulation technology and preliminary screening of waste forms

In order to evaluate or compare the level of maturity of a technology, it is proposed to use the applicable parts of US-DOE guidance document Technology Readiness Assessment DOE G 413.3-4A, 9-15-2011. Additional criteria and methodology specifically targeting the waste form performance and WAC will also be used. This will allow for a more complete evaluation of not only the proposed technologies but it will be in conjunction with the end product performance.

Chapter 5: Recommended waste form selections for waste streams resulting from fission Mo-99 production

There are four waste streams that will be considered for encapsulation in this work package; (i) uranium filter cake from the alkaline processing, (ii) undissolved residue after uranium recovery dissolution, (iii) alumina ion exchangers from uranium recovery process and (iv) nitric acid solutions. From the established compositions for each of these waste streams, literature surveys and in house experience, recommendations have been made in this chapter for the deployment of encapsulation technologies. Several technologies have been considered and down-selected to what are believed to be the most feasible waste form options. Immobilization matrices for the wastes must demonstrate proliferation resistance and are assessed against the generic Waste Acceptance Criteria.

ABBREVIATIONS AND DEFINITIONS

AHA	Acetohydroxamic acid
ALARA	As low as reasonably achievable
ANL	Argonne National laboratory
ANS	American Nuclear Society
ANSTO	Australian Nuclear Science and Technology Organization
ARPANSA	Australian Radiation Protection and Nuclear Safety Agency
ASTM	American Society for Testing and Materials
AVM	Atelier de Vitrification Marcoule
BADT	Best available demonstrated technology
CANDU	Canada Deuterium Uranium reactor
CAS	Chemical Abstracts Service
CBPC	Chemically Bonded Phosphate Ceramic
CCD	Charged Coupled Device
CCIM	Cold crucible induction melter
CFR	Code of Federal Regulations
COVRA	Centrale Organisatie Voor Radioactief Afval
CRWMS	Civilian Radioactive Waste Management System
CT	Computerized tomography
DC	Direct current
DL	Detection limit
DOE	Department of Energy
DU	Depleted uranium
DWPF	Defense Waste Processing Facility, Savannah River Site, USA
EA	Environmental assessment
EDX	Energy Dispersive X-ray spectroscopy
EPMA	Electron-probe microanalysis
FISST	Fissile Solution Storage tank waste
FOW	Field of view
GCM	Glass composite material
GSG	General Safety Guide

HEU	Highly enriched uranium
HIP	Hot Isostatic Pressing
HLW	High level waste
IAEA	International Atomic Energy Agency
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICRP	International Commission on Radiological Protection
IHC	Induction hot crucible
IHPT	Induction heated pot type melter
ILLW	Intermediate level liquid waste
ILW	Intermediate level waste
IR	Infrared
IST	Intermediary storage tank
JHCM	Joule heated ceramic melter
LABS	Lanthanide borosilicate
LET	Linear energy transfer
LEU	Low enriched uranium
LLNL	Lawrence Livermore National Laboratory
LLW	Low level waste
LLWR	Low-Level Waste Repository
MEU	Medium enriched uranium
MKP	Magnesium potassium phosphate
NDE	Non-destructive examination
NEA	Nuclear Energy Agency
NBO	Non-bridging oxygen
n.d.	Not detected
Necsa	South African Nuclear Energy Corporation SOC Limited
NFC	Nuclear fuel cycle
NNSA	National Nuclear Security Administration
NPP	Nuclear power plant
NR	Normalized leaching rates
NRAD	Neutron radiography
NTP	NTP Radioisotopes SOC Limited, a subsidiary company of Necsa

OCRWM	Office of Civilian Radioactive Waste Management
OPC	Ordinary Portland cement
ORIGEN	Oak Ridge Isotope Generation Code (computer code developed at Oak Ridge National Laboratory)
PAL	Pelindaba Analytical Laboratories
PCT	Product Consistency Test
PFA	Pulverised fuel ash
PIP	Plutonium Immobilization Project
PNNL	Pacific Northwest National laboratory
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride
RF	Radiofrequency
SCALE	Standardized Computer Analyses for Licensing Evaluation (computer software system developed at Oak Ridge National Laboratory)
SDP	Synroc demonstration plan
SRO	Short-range order
TCLP	Toxicity Characteristic Leaching Procedure
TRU	Transuranic
UK	United Kingdom
UV	Ultraviolet
PUREX	Plutonium and Uranium Extraction process
RCRA	Resource Conservation and Recovery Act
RFETS	Rocky Flats Environmental Technology Site
SEM	Scanning electron microscopy
SRL	Savannah River National Laboratory, USA
SSV	Self-sustaining vitrification
TEC	Thermal expansion coefficient
UK	United Kingdom
UREX	Uranium Extraction process (a variant of the PUREX process developed at Argonne National Laboratories that separates uranium from spent fuel without recovering pure plutonium)
USA	United States of America

UTS	Universal Treatment Standard
UV	Ultraviolet
VIS	Visible
VOC	Volatile organic compound
WAC	Waste Acceptance Criteria
WAPS	Waste Acceptance Product Specifications
WASRD	Waste Acceptance System requirements document
WIPP	Waste Isolation Pilot Plant
WVP	Waste Vitrification Plant, Sellafield, UK
XRD	X-ray diffraction
XRF	X-ray fluorescence

Table of Contents

CHAPTER 3: THE APPLICATION OF WASTE ACCEPTANCE CRITERIA TO WASTE FORMS USED TO IMMOBILIZE WASTE FROM MO-99 PRODUCTION

CHAPTER 1: IDENTIFICATION AND DESCRIPTION OF ALL WASTE STREAMS RESULTING FROM FISSION MO-99 PRODUCTION

1. Introduction

Molybdenum-99, as the parent nuclide for the most widely used radioisotope in nuclear medicine (Tc-99m), is produced primarily from fission of U-235. Global demand for Mo-99 is currently 622 000 6dCi/year (6dCi refers to the number of curies of Mo-99 remaining 6 days after shipping from a production facility) [1]. Several countries produce Mo-99 commercially via this method. Information on the production capacities and processing methods of the major Mo-99 producing countries is listed in Table 1-1.

Table 1-1 Countries currently producing Mo-99 [2, 3, 4, 5, 6]

Country	Reactor (age)	Production per week (6dCi)	Processing facility	Processing facility capacity (6dCi)	Target type	Processing
Canada	NRU (57)	4680	MDS Nordion	7200	HEU	Acid (HNO_3)
Netherlands	HFR (53)	4680	Mallinckrodt	3500	HEU	Alkaline (NaOH)
Belgium	BR-2 (53)	7800	IRE	2500	HEU	Alkaline (NaOH)
South Africa	Safari-I (49)	3000	NTP	3000	LEU	Alkaline (NaOH)
Australia	OPAL (8)	1000	ANSTO Health	1000	LEU	Alkaline (NaOH)
Argentina	RA-3 (47)	400	CNEA	900	LEU	Alkaline (NaOH)
France	OSIRIS (48)	1200	IRE		HEU	
Czech Republic	LVR-15 (57)	2800	IRE		HEU	
Poland	MARIA (40)	1920	Mallinckrodt		HEU	
Russian Federation	RIAR (40)	900	IPPE	unknown	HEU	Acid (HNO_3)

For irradiated U-Al alloy targets the most common processing method involves dissolution of the target plates using an alkaline sodium hydroxide solution, as can be seen in Table 1-1. This processing method results in three waste streams; a solid filter cake, intermediate level liquid waste (ILLW), as well as solid waste from the sorbent columns used for Mo-99 extraction [5]. Another processing option is to dissolve UO_2 targets in nitric acid, resulting in ILLW (usually in two streams) as well as solid waste from the sorbent columns used for Mo-99 extraction [5]. Uranium silicide targets are an alternative to U-Al alloy that is being investigated for LEU targets for Mo-99 production, but requires sodium hydroxide, sodium nitrate and hydrogen peroxide for dissolution [5], or alternatively hydrofluoric acid, hydrogen peroxide and potassium iodate [7].

Since the five reactors that provide >90% of global Mo-99 supply are 43 to 52 years old, supply shortages due to unscheduled shutdowns have been recently experienced and are expected to continue in the near future as these reactors are shut down [1]. Therefore, several countries are planning to develop their capabilities to produce Mo-99. Table 1-2 lists the countries that are planning to develop potential new conventional research reactor-based irradiation capacity and clearly indicates the move towards LEU targets. The USA and Belgium are also planning to develop Mo-99 production capabilities using other facilities such as aqueous homogeneous reactors, deuterium-tritium accelerators, subcritical aqueous homogeneous reactors and accelerator-driven system research reactors [4].

Table 1-2 Countries planning future or expanded Mo-99 production via conventional research reactor irradiation [4]

Country	Reactor	Production per week (6dCi)	Target type	Full production to begin (year)
Russian Federation	RIAR	1800-2000	HEU	2014-
USA	Northstar/ MURR	750-3000	Non-fissile	2014-
Germany	FRM-II	1950	LEU	2016
China	China Advanced RR	1000	LEU	2017
Australia	OPAL	3600	LEU	2017
Brazil	Brazil MR	1000	LEU	2018
Korea	-	1000	LEU	2018
France	Jules Horowitz reactor	2400	LEU	2019
Argentina	RA-19	2000	LEU	2019
Netherlands	PALLAS	7300	LEU	2025
South Africa	Safari-II	3000	LEU	2026

The purpose of this chapter is to provide an overview of the waste streams that arise from Mo-99 production using both alkaline and acidic target processing routes. The descriptive and quantitative results presented here are based on Necsa and ANSTO's combined experience in characterization of waste streams from both types of processes. Although Necsa/NTP has recently started converting its Mo-99 production process to LEU target plates (19 % enriched uranium), the results presented here for the alkaline process are based on measurements of waste from processing of target plates containing 46 % enriched uranium, since this is the only type of waste which has thus far been characterized. These uranium target plates are classified as "medium-enriched uranium" (MEU) by Necsa. However, the intention of this report is to provide generic guidelines for possible methodologies that can be used for immobilization of waste from both LEU and MEU/HEU Mo-99 production processes. In Section 5 a description is therefore given of what adjustments are needed for generating surrogate materials for investigating the encapsulation of LEU waste streams, based on theoretical knowledge of the composition of LEU target plates.

2. Characterization of waste from alkaline route processing of Mo-99 (Necsa process)

2.1 Background

The initial production of fission Mo-99 in South Africa was performed using target plates consisting of a uranium-aluminum alloy (containing 46% enriched uranium) clad with aluminum. Plates were irradiated in the 20 MW SAFARI-1 reactor at Pelindaba with an average neutron flux of (1-2).10^{14} n.cm^{-2}.s^{-2} for 50-200 hours, depending on customer demand.

Currently Mo-99 is produced by NTP Radioisotopes SOC Ltd, a subsidiary company of Necsa, using low-enriched uranium (LEU) target plates. The operational waste streams generated during the purification of the Mo-99 are the same as for the previous MEU (46% U-235) target plates, with the exception that the volume of waste is increased.

The process flowsheet for recovery of Mo-99 from uranium-aluminum alloy target plates is shown in Figure 2-1. The process can be described as follows: Target plates are dissolved in concentrated sodium hydroxide containing an oxidizing agent in order to form a residue with the non-fissioned uranium. After precipitation of the residue the filtrate consists of Mo-99 and a limited amount of dissolved radioisotopes. This Mo-99 solution is then purified using a number of ion exchange resins (anionic and chelating resins) as indicated in Figure 2-1. The precipitated uranium residue, which still contains approximately 44% enriched uranium, is currently being stored in stainless steel canisters.

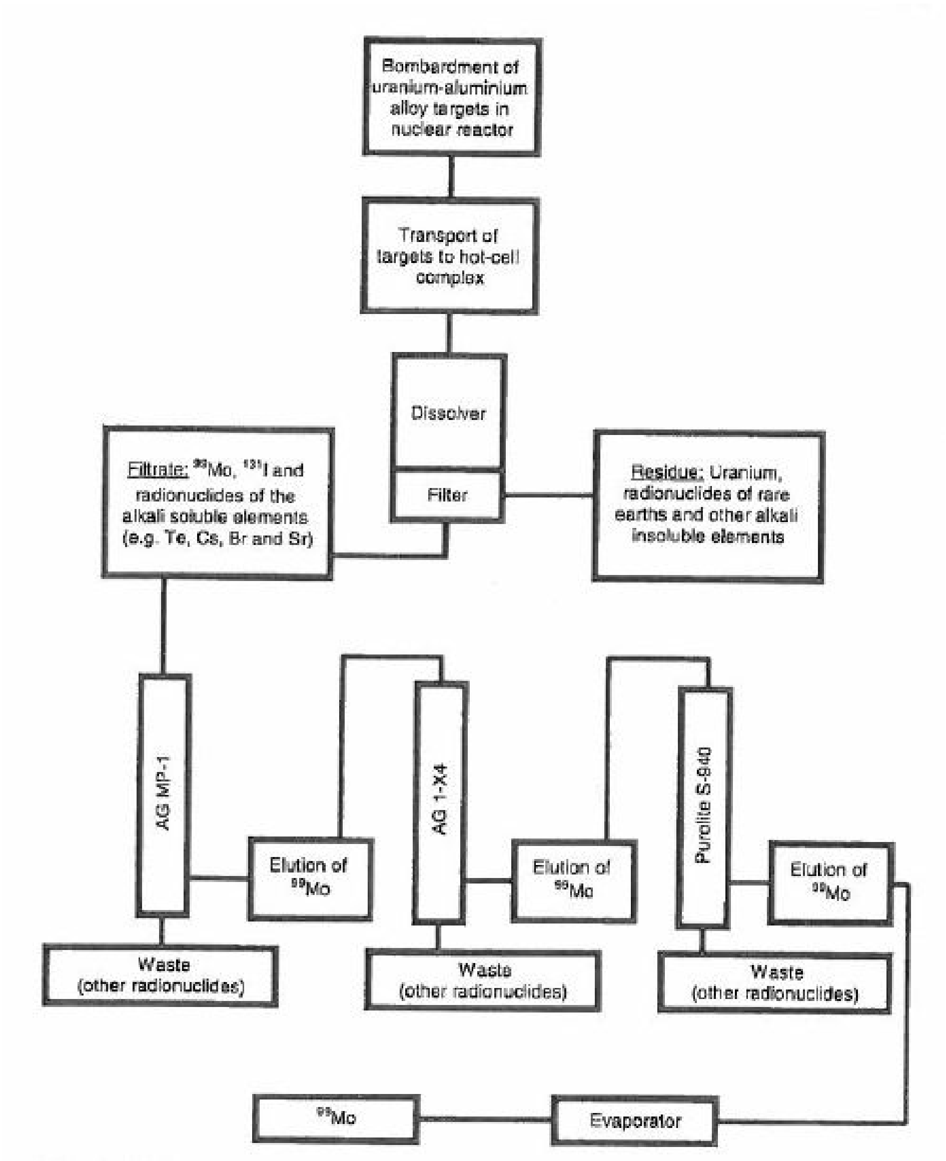

Figure 2-1 Schematic representation of the alkaline route processing of irradiated uranium target plates to recover Mo-99

As well as describing the operational waste streams generated during recovery of Mo-99 from targets, this chapter also presents results from characterization work and process development carried out at Necsa on the uranium residue waste generated from the alkaline processing of target plates. It includes a summary of the characterization of residue generated from unirradiated depleted uranium (DU) target plates (0.5% enriched U), with exactly the same dimension, U and Al content and U density as the MEU plates used in the commercial production process. Also results from the characterization of processed and unprocessed residue waste streams generated from the actual MEU Mo-99 production process, from residue batches with a decay age between 5 and 11 years, are presented. The process for recovery and purification of uranium from the irradiated residue that is currently being developed at Necsa is shown in Figure 2-2. It involves dissolution of the residue in an ammonium carbonate / hydrogen peroxide leach solution followed by initial purification using alumina columns. The carbonate medium is then converted to a nitric acid medium using a “steam-stripping” method, where ammonia and carbon dioxide are volatilized by heating, yielding a $UO_3 \cdot 2H_2O$ precipitate which is re-dissolved in nitric acid. No secondary waste is generated by this conversion process, since the carbon dioxide and ammonia are re-absorbed in water to regenerate the leaching reagent. The final purification of uranium can be achieved via a solvent extraction process such as the UREX process, or an ion exchange purification process.

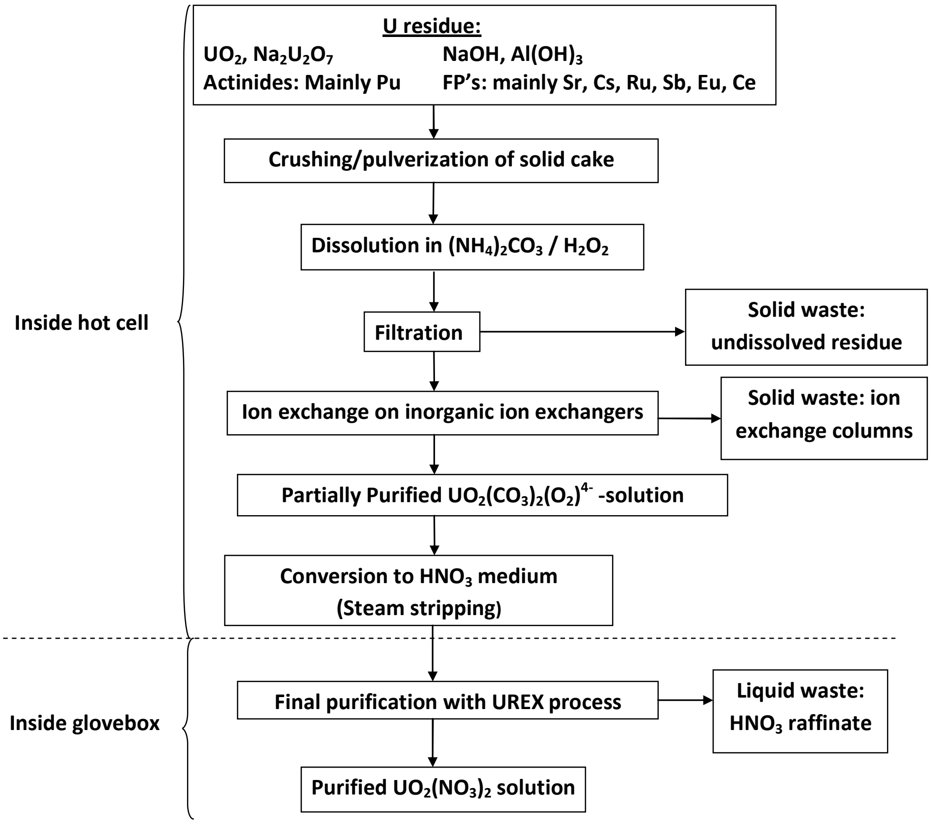

Figure 2-2 Schematic representation of the process for recovery of uranium from Mo-99 production process solid residue

The results from characterization of the waste streams can be used to design surrogate matrices for the development of encapsulation technologies for the various waste streams. The waste streams that will be considered for encapsulation are:

1. Unprocessed residue: In case of final disposal of the uranium residue without processing for recovery of uranium
2. Processed residue: In case of processing of the irradiated residue to recover and purify uranium for re-use; the following waste streams are generated:
    a. Undissolved residue after the carbonate leaching process
    b. Alumina ion exchangers used for retention of fission products in the initial purification step of the uranium
    c. Nitric acid solutions after the final purification of uranium.

The development of encapsulation technologies for the waste arising from LEU (19.8% enriched U) target processing for Mo-99 production is also considered. No experimental characterization results are available yet for this waste at Necsa.

2.2 Description of routine operational waste streams from Mo-99 production process

2.2.1 Decontamination solutions resulting in precipitate formation

The floors of the dissolution cells are periodically decontaminated using decontamination solutions and paper towels that are discarded as solid waste into specialized containers. Should decontamination liquid leak into the liquid waste tanks during the decontamination process, alumina present in the liquid waste tank could precipitate and settle to the bottom of the tank. This precipitate will contain small amounts of cesium and strontium as co-precipitation products. This precipitate can be filtered and discarded as solid waste into specialized containers for disposal.

2.2.2 Resin material generated during purification of Mo-99

The generated Mo-99 solution is purified using a number of commercial available ion exchange resins (anionic and chelating resins) as shown in Figure 2-1. Every purification step consists of adsorption of Mo-99 and removal of source solution followed by the elution of Mo-99. Unconditioned spent resin materials (generated during the purification process) are discarded as solid waste into specialized containers for storage.

2.2.3 Intermediary liquid alkaline waste generated during purification of Mo-99

The caustic soda and aluminate solution generated during the dissolution of target plates contains various fission and decay products that are adsorbed onto resin material as a first purification step. These adsorbed radionuclides are then eluted from the resin material using different eluate media, for example NaOH, LiOH, Li_2SO_4 and others. These eluents are collected in an intermediary storage tank (IST, so called due to temporary nature of storage until encapsulation). This waste stream is therefore mainly a sodium hydroxide/sodium aluminate solution at a concentration of 4-5 M. The contents of the intermediary storage tank (IST) are currently cemented for safe disposal at a waste disposal site.

Only a few measurements of the content of this intermediary liquid alkaline waste stream at NTP are currently available. Also, the results of these measurements can only be regarded as qualitative as the dilution technique used in the production hot cell is not accurate enough to be used for quantitative analysis and the homogeneity of the waste solution after mixing cannot be guaranteed. The theoretical activity levels of radionuclides in 46% enriched uranium irradiated in a thermal neutron flux of 1.0 x 10^{14} n.cm^{-2}.s^{-1} for 196 h were therefore calculated, using the computer code ORIGEN-S, which is part of the SCALE 4.4 system. The measured radionuclide content of the uranium residue, presented in Table 2-3, has been subtracted from these theoretical values, and the remaining activity is assumed to be present in the intermediary liquid alkaline waste generated during purification of Mo-99. This is a conservative assumption, since the theoretical values are usually higher than measured activities. For example, the Mo-99 yield obtained during production at NTP is usually lower than the calculated values and uranium isotopic analysis on a sample of residue from actual Mo-99 production, showed less U-235 burning than theoretically calculated.

The long list of nuclides produced by ORIGEN-S has been filtered to report only those that remain in this waste stream at a level of >3x10^{7} Bq (1mCi) per target plate, at 5 years decay, and are reported in Table 2-1. The radionuclide content collected in the intermediary storage tank (IST) per gram uranium, per dissolved target plate and per litre of solution in the IST is indicated in Table 2-1 for decay ages of 1 and 5 years.

Table 2-1 Estimated radionuclide content in intermediary liquid alkaline waste

Nuclide	**Bq/g residue**		**Bq/target plate**		**Bq/L solution**	
	1 a	**5 a**	**1 a**	**5 a**	**1 a**	**5 a**
^{90}Sr ($t_{1/2}$ = 28.8 y)/ ^{90}Y ($t_{1/2}$ = 2.67 d)	3.55x10^{8}	3.24x10^{8}	4.52x10^{9}	4.12x10^{9}	3.95x10^{9}	3.60x10^{9}
^{99}Tc ($t_{1/2}$ = 2.1x10^{5}y)	9.45x10^{4}	9.45x10^{4}	1.20x10^{6}	1.20x10^{6}	1.05x10^{6}	1.05x10^{6}
^{103}Ru ($t_{1/2}$ = 39.3 d)	2.46 x10^{8}	1.56 x10^{3}	3.12x10^{9}	1.98x10^{-2}	2.73x10^{9}	1.73x10^{-2}
^{106}Ru ($t_{1/2}$ = 1.02 y)/ ^{106}Rh ($t_{1/2}$ = 30 s)	6.66 x10^{8}	4.16 x10^{7}	8.47x10^{9}	5.29x10^{8}	7.41x10^{9}	4.63x10^{8}
^{125}Sb ($t_{1/2}$ = 2.76 y)	2.19 x10^{7}	8.08 x10^{6}	2.78x10^{8}	1.03x10^{8}	2.43x10^{8}	8.99x10^{7}
^{125m}Te ($t_{1/2}$ = 57.4 d)	1.15 x10^{7}	4.28 x10^{6}	1.46x10^{8}	5.44x10^{7}	1.27x10^{8}	4.76x10^{7}
^{134}Cs ($t_{1/2}$ = 2.07 y)	7.49 x10^{6}	1.95 x10^{6}	9.52x10^{7}	2.48x10^{7}	8.33x10^{7}	2.17x10^{7}
^{137}Cs ($t_{1/2}$ = 30.1 y)	1.13 x10^{9}	1.03 x10^{9}	1.44x10^{10}	1.31x10^{10}	1.26x10^{10}	1.15x10^{10}
^{141}Ce ($t_{1/2}$ = 32.5 d)	1.44 x10^{8}	4.25 x10^{6}	1.83x10^{9}	5.40x10^{-5}	1.60x10^{9}	4.72x10^{-5}
^{144}Ce ($t_{1/2}$ = 285 d)	9.29 x10^{9}	2.64 x10^{8}	1.18x10^{11}	3.35x10^{9}	1.03x10^{11}	2.93x10^{9}
^{144}Pr ($t_{1/2}$ = 17.3 m)	1.62 x10^{10}	2.75 x10^{8}	2.06x10^{11}	3.50x10^{9}	1.80x10^{11}	3.06x10^{9}
^{147}Pm ($t_{1/2}$ = 2.62 y)	3.78 x10^{9}	1.32 x10^{9}	4.81x10^{10}	1.67x10^{10}	4.21x10^{10}	1.46x10^{10}
^{151}Sm ($t_{1/2}$ = 90 y)	2.56 x10^{7}	2.48 x10^{7}	3.25x10^{8}	3.15x10^{8}	2.84x10^{8}	2.76x10^{8}
^{155}Eu ($t_{1/2}$ = 4.75 y)	8.73 x10^{6}	5.20 x10^{6}	1.11x10^{8}	6.61x10^{7}	9.71x10^{7}	5.78x10^{7}

Although the presence of relatively high levels of especially the lanthanide elements according to these calculations could be questionable, it was compared to a few measured values from samples taken from the IST tanks, which did show these nuclides at relatively high levels, although an exact comparison cannot be made since the age of the solution in the IST tank at the time of sampling is unknown. The highest values measured were as follows:

Isotope	**Bq per liter**
Nb-95	1.14E+10
Zr-95	6.68E+09
Ru-103	2.73E+09
Cs-137	2.95E+10
La-140	7.43E+08
Ce-141	3.23E+09
Ce-144	4.88E+09

It should be noted that the focus of this report is not on the development of immobilization technologies for these operational waste streams.

2.3 Description of uranium residue waste

2.3.1 Summary of results of characterization of unirradiated depleted uranium (0.5% U-235) residue

Characterization work was performed using unirradiated uranium residue, since more extensive characterization techniques can be applied using this material as it poses a low radiation hazard and no shielding is required. The unirradiated uranium residue was obtained through dissolution of unirradiated U/Al target plates with the same configuration and dimensions as the irradiated target plates being used in the Mo-99 production process; they contained depleted uranium (DU, 0.5% U-235) as opposed to enriched uranium. The dark grey residue that formed contained most of the uranium in the form of hydrated oxides. Once the residue was dried completely, it was homogenized into a very fine powder for further use. The main conclusions from the characterization of unirradiated depleted uranium residue are:

- The uranium content of the residue is about 70% by mass, based on XRF analysis of the residue.
- The uranium is present in the residue at a U(IV)/U(VI) ratio of about 15:85, based on UV/VIS spectrophotometry of phosphoric acid solutions of the residue.
- A definitive characterization of the uranium compounds present in the residue was not possible, but based on XRD results, analysis of U and Na content and determination of the U(IV)/U(VI)-ratio, one of the main compounds could be sodium diuranate ($Na_2U_2O_7$).
- The main chemical impurity in the residue is sodium, with about 5.5% of the residue mass consisting of sodium, based on ICP-OES analysis of the residue.
- Another significant chemical impurity is aluminum at around 1% of the residue by mass, but less than 0.5% of the aluminum originally present in the target plates remains in the residue.
- Other significant impurities are carbon, phosphorus and silicon of which the origin is unknown, and elements such as iron, manganese and chromium which could be from the steel vessel in which the target plates were dissolved, with some scraping required to get the last bit of residue out of the vessel.

Although these results were obtained with unirradiated DU residue, a large difference in chemical characteristics was not expected for the irradiated MEU residue, since the target plates from which the residue is generated had exactly the same dimensions, density and uranium mass and the same dissolution process was used. Differences were however seen specifically for uranium content, which will be discussed in Section 2.3.2.2 below.

Since the density as well as uranium and aluminum content of LEU target plates are different from MEU target plates, it is uncertain whether the chemical characteristics of uranium residue generated from the dissolution of LEU target plates will be the same as that from MEU. Further discussion and recommendations on preparing surrogates for studying encapsulation of waste from LEU target plates are given in Section 5.2.

2.3.2 Summary of results of characterization of irradiated MEU (46% U-235) residue

Characterization studies were also performed on small (1 g) samples of actual irradiated MEU residue from batches with ages between 5 and 11 years, in a small experimental hot cell facility. Due to the limitation on analytical methods available for irradiated uranium samples at Necsa, not all of the analytical measurements performed on the unirradiated DU residue could be repeated on the actual residue samples.

2.3.2.1 Uranium isotopic composition

A sample from one of the irradiated uranium residue runs performed on the residue batch with decay age of 11 years was analyzed for the uranium isotopic composition with Thermal Ionization Mass Spectrometry. The following results were obtained:

- U-234: 0.487% by mass
- U-235: 45.57% by mass
- U-236: 0.167% by mass
- U-238: 53.77% by mass

A theoretical calculation has been completed by Necsa’s Radiation and Reactor Theory department using the ORIGEN-S code, for U target plates with an enrichment level of 46%, irradiated for 196 h at a thermal neutron flux of 1.0 x 10^{14} n.cm^{-2}.s^{-1}. These calculations yielded a U-235 level of 44.29%. The measured results therefore indicate a higher U-235 level (lower burn-up) than the theoretical values, possibly due to a lower neutron flux, or position of irradiation, or a shorter irradiation period.

2.3.2.2 Uranium content

The uranium content for three different irradiated residue samples was measured at Pelindaba Analytical Laboratories (PAL) using ICP-OES. The following results were obtained:

- 11 year-old residue: 47.2% by mass
- 10-year-old-residue: 47.0% by mass
- 5-year-old residue: 49.3% by mass

The uranium content of 47 - 49% in the irradiated residue samples is at least 20% lower than the uranium content of between 68 and 73% measured in the characterization work on uranium residue from unirradiated DU target plates. This large difference could be partly attributed to the large amount of iron present in the irradiated residue which is thought to be caused by corrosion of the stainless steel canisters in which the uranium residue is being stored (a value of up to 7% iron content per mass of residue was measured). Stainless steel also contains a large chromium content of up to 20% and a nickel content of up to 14 %, and a significant amount of these elements could also be present in the residue, although a full impurity analysis of the irradiated residue has not yet been completed. It is estimated that up to 10% of the residue mass could therefore consist of corrosion products from the stainless steel canisters, causing a decrease of 10% in the U content of the irradiated residue. The residual 10% difference in U content in the irradiated vs. unirradiated residue cannot at this stage be fully explained. One possibility is analytical error due to the large dilution factor required for sample analysis at PAL, which can only handle samples at dose limits below 0.025 mSv/h. This analytical error cannot be quantified at this stage. Only once a large number of irradiated samples have been processed and enough data collected to enable accurate statistical analysis, can this discrepancy be fully investigated.

2.3.2.3 Chemical impurities

Samples from the irradiated uranium residue runs have been analyzed for Fe and Al using ICP-OES, and the results are given in Table 2-2 for the total mass in the residue, in the leach solution, in the undissolved residue and in the HNO_3 waste solution at the end of the purification process. Due to interference from uranium, it was not possible to analyze the samples for Na.

The average iron content in the residue of 4% by mass in the 11-year-old sample (ranging from 1 to 7% in the four sub-samples analyzed), is much higher than found in the unirradiated DU residue, and could be due to corrosion (“rusting”) of the steel canisters in which the irradiated uranium residue is being stored.

The aluminum content of the residue of about 1% by mass is similar to what was previously found for the unirradiated DU residue, and represents about 0.2% of the total aluminum present in the target plates plus cladding.

Table 2-2 Measured aluminum and iron chemical impurities in residue samples

Sample age (a)	**Aluminum**				**Iron**			
	g/g residue	**g/g residue in CO_3^{2-} leach**	**g/g residue remaining undissolved**	**g/g residue in HNO_3 waste stream**	**g/g residue**	**g/g residue in CO_3^{2-} leach**	**g/g residue remaining undissolved**	**g/g residue in HNO_3 waste stream**
11	$1.10\text{x}10^{-2}$	$1.52\text{x}10^{-3}$	$9.47\text{x}10^{-3}$	$< 2.21\text{x}10^{-3}$	$4.15\text{x}10^{-2}$	$2.73\text{x}10^{-4}$	$4.14\text{x}10^{-2}$	$< 1.38\text{x}10^{-3}$
10	$1.36\text{x}10^{-2}$	$7.49\text{x}10^{-4}$	$1.29\text{x}10^{-2}$	$< 7.58\text{x}10^{-4}$	$1.55\text{x}10^{-2}$	$< 7.16\text{x}10^{-4}$	$1.55\text{x}10^{-2}$	$< 1.37\text{x}10^{-3}$
5	$1.70\text{x}10^{-2}$	$1.29\text{x}10^{-3}$	$1.57\text{x}10^{-2}$	$< 1.72\text{x}10^{-3}$	$3.65\text{x}10^{-3}$	$< 1.62\text{x}10^{-3}$	$3.65\text{x}10^{-3}$	$< 3.10\text{x}10^{-3}$

2.3.2.4 Radioactive impurities

Samples from the irradiated uranium residue runs were analyzed using γ-spectrometry with a high-resolution Ge/Li detector, chromatographic separation and liquid scintillation counting for ß-emitting nuclides (Sr-90), and chromatographic separation and α-spectrometry for α-emitting nuclides (Pu-239). The results in Table 2-3 give the activity values for all measurable radionuclides, per gram of residue. Activity values are given for the total activity in the residue, in the leach solution, in the undissolved residue, retained on the alumina inorganic ion exchange column used as initial purification step and in the HNO_3 waste solution at the end of the purification process.

Table 2-3 Measured radionuclide impurities in residue samples

Nuclide	**Sample age (a)**	**Bq/g residue**	**Bq/g residue in CO$_3^{2-}$ leach**	**Bq/g residue remaining undissolved**	**Bq/g residue on Alumina column**	**Bq/g residue in final HNO$_3$ waste stream**
^{60}Co (t$_{1/2}$ = 5.27 y)	11	1.67x10^{4}	1.44x10^{3}	1.53x10^{4}	1.61x10^{3}	1.44x10^{3}
	10	2.95x10^{4}	5.72x10^{3}	2.37x10^{4}	1.64x10^{3}	4.08x10^{3}
	5	3.89x10^{4}	5.23x10^{3}	3.37x10^{4}		5.23x10^{3}
^{95}Nb (t$_{1/2}$ = 35.2 d)	11	3.14x10^{4}	2.92x10^{4}	2.22x10^{3}	1.32x10^{4}	2.19x10^{4}
	10	1.17x10^{4}	9.03x10^{3}	2.66x10^{3}	1.79x10^{3}	7.24x10^{3}
	5	3.27x10^{4}	3.27x10^{4}		1.28x10^{4}	2.00x10^{4}
^{95}Zr (t$_{1/2}$ = 64 d)	11	2.32x10^{4}	2.06x10^{4}	2.57x10^{3}	3.75x10^{3}	1.97x10^{4}
	10	1.41x10^{4}	9.37x10^{3}	4.74x10^{3}	1.20x10^{3}	8.17x10^{3}
	5	2.66x10^{4}	2.66x10^{4}			2.66x10^{4}
^{106}Ru (t$_{1/2}$ = 1.02 y)/ ^{106}Rh (t$_{1/2}$ = 30 s)	11	4.08x10^{5}	2.37x10^{5}	1.72x10^{5}		2.07x10^{5}
	10	5.32x10^{5}	2.77x10^{5}	2.55x10^{5}	6.08x10^{4}	2.16x10^{5}
	5	2.08x10^{7}	1.35x10^{7}	7.33x10^{6}	2.21x10^{6}	1.12x10^{7}
^{125}Sb (t$_{1/2}$ = 2.76 y)	11	1.33x10^{6}	1.14x10^{6}	1.99x10^{5}	3.35x10^{5}	6.09x10^{5}
	10	1.95x10^{6}	1.63x10^{6}	3.18x10^{5}	7.41x10^{5}	8.87x10^{5}
	5	6.65x10^{6}	5.20x10^{6}	1.45x10^{6}	1.64x10^{6}	3.56x10^{6}
^{137}Cs (t$_{1/2}$ = 30.1 y)	11	3.04x10^{6}	2.73x10^{6}	3.06x10^{5}	1.73x10^{5}	2.66x10^{6}
	10	4.74x10^{6}	4.45x10^{6}	2.93x10^{5}	4.17x10^{6}	2.73x10^{5}
	5	1.17x10^{7}	1.06x10^{7}	1.14x10^{6}	7.89x10^{6}	2.67x10^{6}
^{144}Ce (t$_{1/2}$ = 285 d)	11	8.46x10^{5}	5.20x10^{5}	3.26x10^{5}	3.35x10^{5}	
	10	1.18x10^{6}	1.34x10^{5}	1.05x10^{6}	1.34x10^{5}	
	5	1.37x10^{8}	2.89x10^{7}	1.08x10^{8}	2.82x10^{7}	7.41x10^{5}
^{144}Pr (t$_{1/2}$ = 17.3 m)	11	7.54x10^{5}	4.36x10^{5}	3.18x10^{5}	2.82x10^{5}	
	10	8.83x10^{5}	3.36x10^{4}	8.50x10^{5}	3.36x10^{4}	
	5	1.29x10^{8}	2.69x10^{7}	1.02x10^{8}	2.62x10^{7}	6.89x10^{5}
^{154}Eu (t$_{1/2}$ = 8.6 y)	11	5.95x10^{4}	3.43x10^{4}	2.52x10^{4}	2.09x10^{4}	
	10	9.13x10^{4}	4.38x10^{4}	4.75x10^{4}	4.38x10^{4}	
	5	1.44x10^{5}	8.23x10^{4}	6.22x10^{4}	8.23x10^{4}	
^{155}Eu (t$_{1/2}$ = 4.75 y)	11	2.27x10^{6}	1.31x10^{6}	9.61x10^{5}	7.28x10^{5}	3.98x10^{4}
	10	2.92x10^{6}	1.39x10^{6}	1.54x10^{6}	1.35x10^{6}	3.36x10^{4}
	5	6.20x10^{6}	3.64x10^{6}	2.57x10^{6}	3.59x10^{6}	4.84x10^{4}
^{90}Sr (t$_{1/2}$ = 28.8 a)	11	3.71x10^{8}	2.70x10^{8}	1.01x10^{8}	2.50x10^{8}	1.99x10^{7}
	10	4.74x10^{8}	3.25x10^{8}	1.49x10^{8}	3.22x10^{8}	2.31x10^{6}
	5	4.92x10^{8}	3.84x10^{8}	1.09x10^{8}	3.65x10^{8}	1.89x10^{7}
^{239}Pu (t$_{1/2}$ = 2.4x10^{4} y)	11	3.46x10^{5}	3.00x10^{5}	4.55x10^{4}	2.97x10^{5}	3.06x10^{3}
	10	3.77x10^{5}	1.85x10^{5}	1.92x10^{5}	1.82x10^{5}	2.36x10^{3}
	5	4.23x10^{5}	2.64x10^{5}	1.59x10^{5}	2.59x10^{5}	5.70x10^{3}

The activity levels of radionuclides measured in this study have been compared against the theoretical values calculated for 46% enriched uranium irradiated in a thermal neutron flux of 1.0×10^{14} $n.cm^{-2}.s^{-1}$ for 196 h, using the computer code ORIGEN-S, which is part of the SCALE 4.4 system.

The average measured to calculated ratio is about 0.5, which seems quite plausible taking into account the uncertainties in the parameters used in the calculation, and also considering; (i) the U isotopic analysis reported in Section 2.3.2.1 showed less U-235 burnup than theoretically calculated, (ii) a fraction of these nuclides could remain in the sodium hydroxide operational waste stream due to partial dissolution during the target plate dissolution process (see Section 2.2.3).

3. Characterization of waste from alkaline route processing of Mo-99 from LEU target plates (ANSTO process)

Currently Mo-99 is produced by ANSTO Health via alkaline processing of irradiated low-enriched uranium (LEU) target plates (19-20% enriched). The processing methodology is very similar to that shown in Figure 2-1, i.e. the irradiated target plates are dissolved in concentrated sodium hydroxide followed by filtration to separate the uranium-containing residue from the molybdenum-containing filtrate. The uranium-rich residue was assumed by INVAP to be composed of approximately 90% UO_2 and 10% $Na_2U_2O_7$ [10]. In agreement with this assumption, X-ray diffraction of the fresh filter cake derived from an unirradiated alloy plate yielded a very broad pattern characteristic of UO_2 [10]. However on ageing this filter cake for 21 days, the X-ray pattern indicated that the predominant phase was well-crystallized $Na_2U_2O_7$ [10]. More detailed characterization data on the U valence are not available, but it would be simple to carry out X-ray photoelectron spectroscopy to resolve the U valence question. Having said this however, the U valence in any waste form will be dictated by the processing route and not the starting U valence in the waste. Compositional data are available for the intermediate level liquid waste (ILLW) stream, which is formed from the eluents of further ion-exchange purification of the Mo-99-containing filtrate. This alkaline ILLW consists predominantly of fission products. The chemical composition of this waste stream varies from 5-6 M NaOH and 1.1-1.4 M $NaAlO_2$. As a representative example, the concentration of radioactive impurities (after 1 year decay) in 5 M NaOH/1.2 M $NaAlO_2$ ILLW is given in Table 3-1.

Table 3-1 Measured radionuclide content in intermediate liquid alkaline waste (irradiated LEU target plate processing)

Nuclide	Bq/L
^{89}Sr	5.91×10^{7}
^{90}Sr	7.93×10^{8}
^{90}Y	7.54×10^{8}
^{91}Y	2.82×10^{8}
^{95}Zr	2.15×10^{9}
^{95}Nb	4.12×10^{9}
^{99}Tc	3.53×10^{4}
^{103}Ru	1.96×10^{7}
^{106}Ru/ ^{106}Rh	6.80×10^{8}
^{123}Sn	6.13×10^{6}
^{125}Sb	1.06×10^{8}
^{125m}Te	2.41×10^{7}
^{127m}Te	2.46×10^{7}
^{127}Te	2.41×10^{7}
^{134}Cs	1.41×10^{8}
^{137}Cs	1.65×10^{10}
^{147}Pm	1.08×10^{9}
^{155}Eu	3.81×10^{7}

4. Characterization of waste from acid route processing of Mo-99 (ANSTO process)

Acid processing involves the full dissolution of irradiated UO_2 HEU targets in concentrated nitric acid (HNO_3). The processing is then continued in two stages; stage 1 molybdenum adsorption onto an alumina column and stage 2 cleaning and subsequent removal of purified molybdenum. Each stage produces an intermediate level liquid waste (ILLW) stream. A flow diagram of the acid route processing of irradiated targets to recover Mo-99 is given in Figure 4-1.

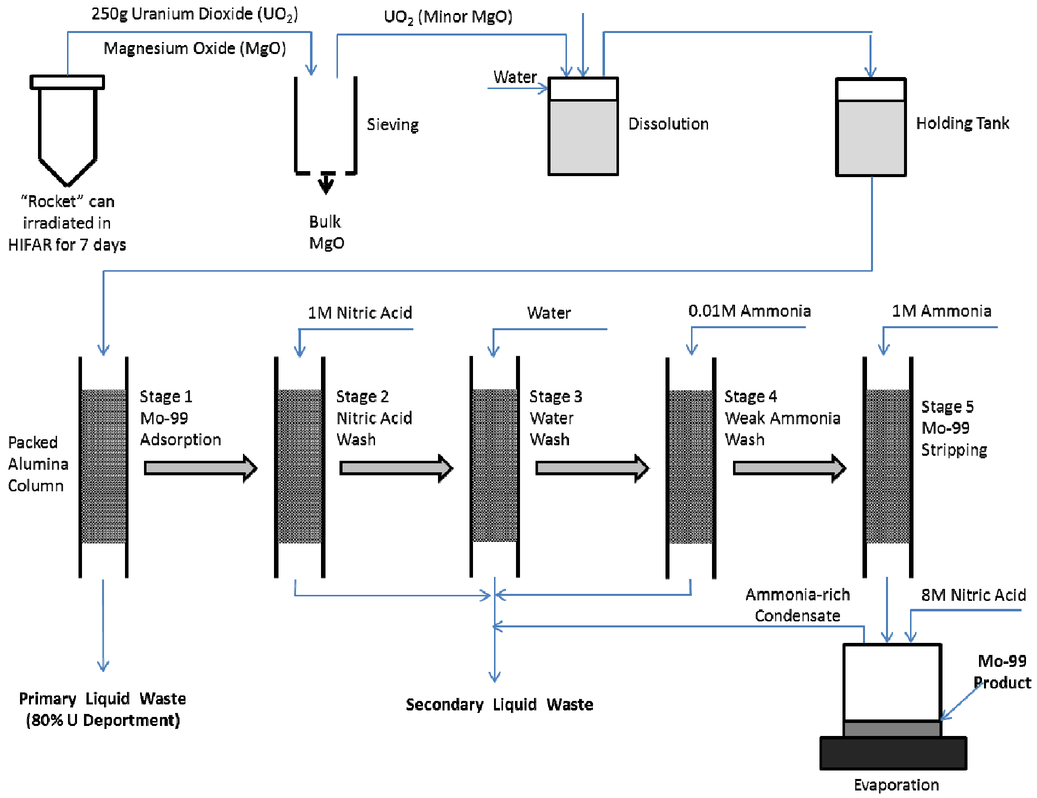

Figure 4-1 Schematic representation of the acid route processing of irradiated uranium target plates to recover Mo-99

Stage 1 produces primary ILLW and Stage 2 produces secondary ILLW, with the activity of the waste from Stage 1 higher than that of Stage 2. There is a deportment of approximately 80% of the uranium to the primary waste stream along with unwanted fission products. The secondary waste stream is a collection of the solutions used to wash the columns and purify the molybdenum. This secondary ILLW contains residual uranium, fission products and other contaminants. Details of the composition of each waste stream are provided in Table 4-1.

Waste collection options for ILLW can be

- as a liquid (0.5-1 M HNO_3),
- as a solid where solvent evaporation methods have been used, and
- as a calcine, where solid oxide phases are produced.

Table 4-1 Analyzed ILLW compositions from tanks at ANSTO that were produced from irradiated UO_2 targets produced at ANSTO [8, 9].

Chemical composition	**Concentration**
U (primary waste)	70–200g/L
U (secondary waste)	8–35g/L
Mg	<0.02–0.6 g/L
Fe	<0.05–0.4 g/L
NH_4^+	75–800 mg/L
HNO_3	0.6–0.8M
Al	<DL–0.6 g/L

Nuclide	**Analyzed activity of primary ILLW waste (MBq/L)**	**Analyzed activity of secondary ILLW waste (MBq/L)**
^{144}Ce ($t_{1/2}$ = 285 d)	10–3500	16–6000
^{134}Cs ($t_{1/2}$ = 2.07 y)	0.35–5.3	<DL–2.4
^{137}Cs ($t_{1/2}$ = 30.1 y)	2600–8000	170–1800
^{60}Co ($t_{1/2}$ = 5.27 y)	0.6–2	0.1–1
^{155}Eu ($t_{1/2}$ = 4.75 y)	<DL–90	<DL–20
^{95}Nb ($t_{1/2}$ = 35.0 d)	1–80	4–1100
^{106}Ru ($t_{1/2}$ = 1.02 y)/^{106}Rh ($t_{1/2}$ = 30 s)	<DL–970	<DL–420
^{125}Sb ($t_{1/2}$ = 2.76 y)	<DL–13	<DL–18
^{95}Zr ($t_{1/2}$ = 64 d)	0.6–50	1–610
^{90}Sr ($t_{1/2}$ = 28.8 y)	2600–7700	120–1700
^{141}Ce ($t_{1/2}$ = 32.5 d)	<DL–1.3	<DL–30
^{91}Y ($t_{1/2}$ = 58.5 d)	<DL–125	<DL–380
^{103}Ru ($t_{1/2}$ = 39.3 d)	<DL–1.5	<DL–32
^{144}Pr ($t_{1/2}$ = 17.3 m)	nd	<DL–6

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

5. Proposed surrogate wastes for waste encapsulation studies

Due to the cost and hazardous nature of working with large amounts of activity, initial waste encapsulation studies will be performed using "surrogate" materials consisting of depleted or natural uranium and non-radioactive equivalents of the fission products. The results from these encapsulation studies will be used for down-selection of waste forms. Only the subset of chosen waste forms will be further tested using radioactive waste requiring the use of a hot cell.

5.1 Alkaline process waste from MEU (46% U-235)

5.1.1 Intermediary liquid alkaline waste

Based on the theoretical values of nuclide activities in the intermediary liquid alkaline waste stream at the 5-year decay level given in Table 2-1, a proposal is made in this section for generation of a surrogate mixture which can be used for encapsulation studies. Using the estimated values in Table 2-1, calculations were done to yield masses of chemical compounds to use in a surrogate mixture, and the results are given in Table 5-1. If a chemical compound simulating each nuclide is to be used in a surrogate mixture, its mass should be representative of the total mass of all the nuclides of that specific element formed due to fission or activation reactions, or radioactive decay. However, the nuclides and their activities given in Table 2-1 were calculated from total theoretical activities given by the ORIGEN code for these nuclides, with the actual measured activities subtracted. Other nuclides of the same element could be present at low activity levels, or even stable nuclides formed due to the decay of other nuclides over time. To obtain an estimate of the total mass of each element, the theoretical calculations performed with the ORIGEN code at the 5 year decay stage were used to scale these values, since the masses of all the radionuclides as well as their activities, are given in the output of the code. In Table 5-1 the results are given for the total mass per element, represented by the nuclide analyzed in the irradiated sample.

Since both ^{99}Tc and ^{147}Pm have no non-radioactive equivalent chemical compound, Re_2O_7 is proposed as a surrogate compound for ^{99}Tc and Sm_2O_3 for ^{147}Pm due to chemical similarity. Based on the dissolution reaction of the aluminum in the target plates:

$$2Al\ (s) + 2NaOH\ (aq) + 6H_2O \rightarrow 2Na^+\ (aq) + 2[Al(OH)_4]^- + 3H_2(g),$$

the final waste solution will contain 1.4 M $Na(Al(OH)_4)$ and 3 M NaOH.

Table 5-1 Final surrogate mixture proposed for 1 L of intermediary liquid alkaline waste (oxide equivalent)

Element/Nuclide	Surrogate compound	Mass of surrogate (g)
Na	NaOH	120
Al	$NaAlO_2$	115
^{90}Sr	SrO	1.37×10^{-3}
^{99}Tc	Re_2O_7	2.17×10^{-3}
^{103}Ru/ ^{106}Ru	RuO_2	3.96×10^{-3}
^{125}Sb	Sb_2O_3	1.17×10^{-5}
^{125m}Te	TeO_2	1.41×10^{-3}
^{134}Cs/ ^{137}Cs	$CsOH.H_2O$	9.03×10^{-3}
^{141}Ce/ ^{144}Ce	CeO_2	3.36×10^{-3}
^{144}Pr	Pr_6O_{11}	2.82×10^{-3}
^{147}Pm	Sm_2O_3	
^{151}Sm	Sm_2O_3	3.42×10^{-3}
^{155}Eu	Eu_2O_3	6.07×10^{-5}

5.1.2 Uranium residue without processing

Based on the information gained on the uranium residue characteristics through investigations on both unirradiated DU residue and the actual irradiated MEU residue, a proposal is made in this section for generation of a surrogate residue which can be used for encapsulation studies. The exact chemical composition of the uranium in the real residue could not be determined. However, a ratio of U(VI) to U(IV) (85:15), with the U(VI) compound possibly being $Na_2U_2O_7$, was measured for the unirradiated DU residue. The starting material will use U in the form of uranyl nitrate for waste forms, since as noted above (Section 3) the starting U valence will bear little relation to that in the candidate waste form which will depend on the processing route. However for unheated cementitious materials or other unheated systems, there will be little U valence change and efforts will be made to use realistic filter cake materials. In Table 5-2 the proposed composition of the surrogate residue in terms of uranium compounds is given, per 1 g residue surrogate. However, it has been observed that during ageing of uranium residue from alkaline Mo-99 processing, the uranium is converted from UO_2 to $Na_2U_2O_7$ according to XRD. That is, the uranium is oxidized from U(IV) to U(VI) and there is a corresponding weight increase of 6 wt% due to uptake of oxygen [10]. Therefore, the age of the uranium residue should be taken into consideration when proposing surrogate compositions for this waste stream.

It is also proposed to add iron to the maximum level that was measured in one of the 11-year-old irradiated residue samples, i.e. 7%, and to use Fe_2O_3 as surrogate compound. Although a measurement of Cr and Ni was not done on the irradiated residue, it is proposed to add it to the level of 1.5% and 1% respectively by mass, since it would be present if the iron content measured in the irradiated residue was due to the corrosion of the stainless steel canisters in which the residue is being stored. The level of 1.5% Cr is equivalent to Cr being present at 18% by mass in the corroding stainless steel. Cr_2O_3 is proposed as the surrogate compound. The level of 1% Ni is equivalent to Ni being present at 14% by mass in the corroding stainless steel. NiO is proposed as the surrogate compound. Finally, addition of Al to a level of 1% by mass is recommended as this amount was measured in both unirradiated and irradiated residue. $Al(OH)_3$ is proposed as a surrogate compound. In Table 5-2 the proposed composition of the surrogate residue in terms of the chemical impurities Na, Fe, Cr, Ni and Al is given, per 1 g residue surrogate.

With this amount of chemical impurities added, the U content in the surrogate mix comes to between 62 and 65% by mass, somewhat lower than what was measured in the unirradiated residue, but substantially higher than what was measured in the irradiated residue. Since the lower U content measured in the irradiated residue must still be confirmed with measurements in future, the proposed formulation for surrogate mixtures in the rest of this chapter will be based on 65% U content. Based on the Necsa process where each target plate contains 9 g uranium and a uranium content of 65 % in the residue, the volume of waste to be treated for this scenario would be about 14 g of residue per target plate processed for Mo-99 production.

The addition of fission products, activation product ^{60}Co and actinide Pu-239 (at the higher levels measured in the 5-year-old irradiated residue sample), to the surrogate mixture, must be considered. If it is not possible to add radioactive nuclides at the required activity levels in the surrogate mixture, inactive chemical surrogates could be used. Since no inactive chemical compound of Pu exists, CeO_2 is proposed [11].

If a chemical compound simulating each nuclide is to be used in a surrogate mixture, its mass should be representative of the total mass of all the nuclides of that specific element formed due to fission or activation reactions, or radioactive decay. However, the nuclides given in Section 2.3.2.4 are the only ones which could be measured in the irradiated residue sample. Other nuclides of the same element could be present at low activity levels, or even stable nuclides formed due to the decay of other nuclides over time. To obtain an estimate of the total mass of each element, the theoretical calculations performed with the ORIGEN code at the 5 year decay stage were used, since the masses of all the radionuclides as well as their activities, are given in the output of the code. In Table 5-2 the results are given for the total mass per element, represented by the nuclide analyzed in the irradiated sample.

In the theoretical output from the ORIGEN code, the activities and masses of many nuclides are given, which were not observed during measurements of the irradiated samples, due to their activities probably being below the minimum detectable values. To enable a more accurate definition of a surrogate mixture including the masses of all elements which could be expected in the uranium residue, the masses of all the elements not measured as radioactive impurities are also included in Table 5-2 based on their theoretical ORIGEN values. For neptunium, no additional surrogate is required, since its most suitable surrogate in immobilized waste forms is uranium [12], which is already present in the surrogate mixture in high quantity.

Table 5-2 Final surrogate mixture proposed for 1 g unprocessed residue (oxide equivalent)

Element/ Nuclide	Surrogate compound	Mass of surrogate (g)
7% Fe	Fe_2O_3	0.100
1.5% Cr	Cr_2O_3	0.022
1% Ni	NiO	0.013
1% Al	$Al(OH)_3$	0.029
U(VI)	$Na_2U_2O_7$	0.725
U(IV)	UO_2	0.109
^{60}Co	CoO	6.30×10^{-8}
^{95}Nb	Nb_2O_5	1.26×10^{-9}
^{95}Zr	ZrO_2	2.45×10^{-3}
^{106}Ru	RuO_2	9.14×10^{-4}
^{125}Sb	Sb_2O_3	3.41×10^{-6}
^{137}Cs	$CsOH.H_2O$	1.03×10^{-5}
^{144}Ce/ ^{239}Pu	CeO_2	1.59×10^{-3}
^{144}Pr	Pr_6O_{11}	6.15×10^{-4}
^{154}Eu/ ^{155}Eu	Eu_2O_3	2.13×10^{-5}
^{90}Sr	SrO	5.73×10^{-4}
Se	SeO_2	3.72×10^{-5}
Y	Y_2O_3	3.35×10^{-4}
Mo	MoO_3	6.34×10^{-4}
Rh	Rh_2O_3	2.45×10^{-4}
Pd	PdO	1.24×10^{-4}
Ag	AgO	2.38×10^{-6}

Table 5-2 Final surrogate mixture proposed for 1 g unprocessed residue (oxide equivalent)

Element/ Nuclide	Surrogate compound	Mass of surrogate (g)
Cd	CdO	5.32×10^{-6}
Sn	SnO_2	1.34×10^{-5}
Te	TeO_2	1.81×10^{-4}
La	La_2O_3	6.42×10^{-4}
Nd	Nd_2O_3	2.13×10^{-3}
Sm	Sm_2O_3	3.72×10^{-4}
Gd	Gd_2O_3	4.99×10^{-6}
Total surrogate mixture mass		**1.010**

5.1.3 Uranium residue with processing to recover and purify uranium

5.1.3.1 Undissolved residue

For the surrogate mixture of the undissolved residue after the leaching process for recovery of uranium (see Figure 2-2), a conservative amount of 5% uranium remaining undissolved is proposed, that is 0.05 g per 1 g of dissolved residue. Based on the Necsa process where each target plate contains 9 g uranium and a uranium content of 65 % in the residue, the volume of waste to be treated for this scenario would be about 0.7 g of residue per target plate processed for Mo-99 production. Since no information is known at this stage about the chemical composition of the uranium remaining undissolved, it is proposed to use the same composition as for the original residue not yet subjected to leaching, while the solubility constants of uranium in ammonium carbonate are being investigated. In Table 5-3 the proposed composition of the surrogate undissolved residue in terms of uranium compounds is given, per 1 g residue surrogate.

It is also proposed to add iron to the maximum level that remained undissolved in one of the irradiated residue runs, that is 4% of the original residue mass, and to use Fe_2O_3 as a surrogate compound. It is proposed to add chromium to the level of 0.7% and nickel to the level of 0.5% by mass of the original residue, since it would be present if the iron content measured in the irradiated residue was due to the corrosion of the stainless steel canisters in which the residue is being stored. The level of 0.7% is equivalent to Cr being present at 18% by mass in the corroding stainless steel. Cr_2O_3 is proposed as the surrogate compound. The level of 0.5% Ni is equivalent to Ni being present at 14% by mass in the corroding stainless steel. NiO is proposed as the surrogate compound. Finally, the addition of Al to a level of 1.5% by mass of the original residue is recommended as the highest measured amount remaining undissolved in the irradiated residue runs. $Al(OH)_3$ is proposed as the surrogate compound. As such, the chemical impurities iron and aluminum will be present in this residue at the levels given in Table 2-2. In Table 5-2 the proposed composition of the surrogate residue in terms of all chemical impurities is given, per 1 g residue surrogate.

In addition, based on results from the irradiated residue process runs, the undissolved residue will contain radionuclide impurities at the levels given in Table 2-3 for 5-year-old residue.

Similarly to Section 5.1.2, calculations were done to yield masses of chemical compounds to use in a surrogate mixture, and the results are given in Table 5-3.

The activities and masses of elements from the theoretical output of the ORIGEN code, which were not observed during measurements of the irradiated samples, cannot be quantified for the undissolved residue surrogate mixture as was done for the residue in Table 5-2 since it is not known to what extent these elements will remain undissolved without further experimental work.

Table 5-3 Final surrogate mixture proposed for undissolved residue waste per 1 g residue processed (oxide equivalent)

Element/ Nuclide	Surrogate compound	Mass of surrogate (g)
4% Fe	Fe_2O_3	0.057
0.7% C r	Cr_2O_3	0.010
0.5% Ni	NiO	0.006
1.5% Al	$Al(OH)_3$	0.043
U(VI)	$Na_2U_2O_7$	0.057
U(IV)	UO_2	0.009
^{60}Co	CoO	5.45×10^{-8}
^{106}Ru	RuO_2	3.22×10^{-4}
^{125}Sb	Sb_2O_3	7.43×10^{-7}
^{137}Cs	$CsOH.H_2O$	1.00×10^{-6}
^{144}Ce/ ^{239}Pu	CeO_2	9.14×10^{-4}
^{144}Pr	Pr_6O_{11}	4.87×10^{-4}
^{154}Eu/ ^{155}Eu	Eu_2O_3	8.83×10^{-6}
^{90}Sr	SrO	1.26×10^{-4}
Total mass of surrogate mixture		**0.184**

5.1.3.2 Alumina ion exchanger used for initial purification

The leach solution from the residue will be sent through alumina inorganic ion exchange columns for initial purification of the uranium. Uranium is not retained by the column, but the fission products are. The spent alumina exchanger will therefore be a major waste form arising from the processing of the residue to recover and purify uranium. The exact volume of this waste stream must still be determined by break-through capacity testing of the alumina columns during up-scaled testing of the uranium recovery process, but is estimated to be about 0.5 g of alumina per 1 g residue processed using current conservative estimates based on measured distribution coefficients (K_D values) of the fission products on alumina. The calculated activities and surrogate masses of all radionuclide impurities will therefore be mixed with 0.5 g alumina. The alumina used for this process is weakly acidic aluminum oxide with pore size 58 Å, ~150 mesh (CAS Number 1344-28-1). Based on the Necsa process where each target plate contains 9 g U and a U content of 65 % in the residue, the volume of waste to be treated for this scenario would be about 7 g of alumina waste per target plate processed for Mo-99 production.

Based on results from the irradiated residue process runs, the alumina exchanger will contain radionuclide impurities at the levels given in Table 2-3 for the 5-year-old residue. Similarly to Section 5.1.2, calculations were done to yield masses of chemical compounds to use in a surrogate mixture, and the results are given in Table 5-4.

The activities and masses of elements from the theoretical output of the ORIGEN code, which were not observed during measurements of the irradiated samples, cannot be quantified for the alumina surrogate mixture as was done for the residue in Table 5-2 since it is not known to what extent these elements will be retained on alumina without further experimental work.

Table 5-4 Final surrogate mixture proposed for alumina waste per 1 g residue processed (oxide equivalent)

Element/ Nuclide	Surrogate compound	Mass of surrogate (g)
Al	Al_2O_3	0.5
^{95}Nb	Nb_2O_5	4.91×10^{-10}
^{106}Ru	RuO_2	9.72×10^{-5}
^{125}Sb	Sb_2O_3	8.38×10^{-7}
^{137}Cs	$CsOH.H_2O$	6.93×10^{-6}
^{144}Ce/ ^{239}Pu	CeO_2	6.57×10^{-4}
^{144}Pr	Pr_6O_{11}	1.25×10^{-4}
^{154}Eu/ ^{155}Eu	Eu_2O_3	1.23×10^{-5}
^{90}Sr	SrO	4.24×10^{-4}
Total mass of surrogate mixture		**0.501**

5.1.3.3 HNO_3 waste stream generated after final purification

The resulting raffinate waste stream after the extraction of uranium for final purification (solvent extraction process such as the UREX process), will be ≈ 0.7 M HNO_3, also containing AHA (acetohydroxamic acid) at an estimated concentration of ≈ 0.1 M (in the UREX process it is added in the first scrub at a concentration of 0.47 M [13], but is diluted by the extraction feed and second scrub containing no AHA). It is used in the UREX process to complex plutonium and suppresses its extraction. However, it rapidly hydrolyzes in acidic medium to acetic acid according to the following reaction [14]:

$CH_3CONHOH(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + NH_3OH^+(aq)$

Hydroxyl amine will react with nitrate and will no longer be present. By the time this waste stream must be treated, only acetic acid will remain as a by-product from the AHA originally present.

The raffinate waste solution will contain no uranium (which is extracted into the TBP solvent) or chemical impurities such as Fe and Al (which are removed by the alumina purification process in carbonate medium), but will contain fission products and plutonium.

Based on results from the irradiated residue process runs, radionuclide impurities at the levels given in Table 2-3 for the 5-year-old residue will be present in the alumina column eluate going forward into the final HNO_3 purification process, and are assumed to be present in the raffinate waste stream from the UREX process. Similarly to Section 5.1.2, calculations were done to yield masses of chemical compounds to use in a surrogate mixture, and the results are given in Table 5-5.

Based on an estimated uranium concentration of 75 g U per litre of HNO_3 solution in the final purification process and a U content of 65 % in the residue, the surrogate masses given below will be contained in a volume of about 8.7 ml HNO_3. Based on the Necsa process where each target plate contains 9 g U, the volume of waste to be treated for this scenario would be about 120 ml of HNO_3 per target plate processed for Mo-99 production.

Table 5-5 Final surrogate mixture proposed for HNO_3 waste stream per 1 g residue processed (oxide equivalent)

Element/Nuclide	Surrogate compound	Mass of surrogate (g)
H	HNO_3	0.38
C	CH_3COOH	0.052
^{60}Co	CoO	8.45×10^{-9}
^{95}Nb	Nb_2O_5	7.68×10^{-10}
^{95}Zr	ZrO_2	2.60×10^{-3}
^{106}Ru / ^{106}Rh	RuO_2	4.94×10^{-4}
^{125}Sb	Sb_2O_3	1.83×10^{-6}
^{137}Cs	$CsOH.H_2O$	2.34×10^{-6}
^{144}Ce	CeO_2	4.15×10^{-6}
^{144}Pr	Pr_6O_{11}	3.28×10^{-6}
^{155}Eu	Eu_2O_3	1.67×10^{-7}
^{90}Sr	SrO	2.20×10^{-5}
^{239}Pu	CeO_2	1.10×10^{-5}

5.2 Alkaline Process Waste from LEU (19.8% U-235)

No experimental studies have been performed yet at Necsa or ANSTO on the characteristics of LEU (19.8% enriched U) residue from the Mo-99 production process, and no detailed information can therefore be given regarding the composition or characteristics of uranium residue waste arising from processing of LEU Mo-99 target plates. However, based on the data provided in Section 3 regarding the composition of intermediary liquid alkaline waste generated during the Mo-99 production process at ANSTO using LEU, a proposed surrogate mixture radionuclide composition has been calculated and is given in Table 5-6. The chemical composition of this surrogate mixture would be 5 M NaOH and 1.2 M $NaAlO_2$.

Table 5-6 Final surrogate mixture proposed for intermediate level liquid alkaline waste from LEU per L (oxide equivalent)

Element/Nuclide	Surrogate compound	Mass of surrogate (g)
Na	NaOH	200.0
Al	$NaAlO_2$	98.4
$^{134}Cs/^{137}Cs$	$CsNO_3$	$7.4x10^{-3}$
^{155}Eu	Eu_2O_3	$8.5x10^{-7}$
^{95}Nb	Nb_2O_5	$4.1x10^{-6}$
$^{103}Ru/^{106}Ru/^{106}Rh$	RuO_2	$7.1x10^{-6}$
^{125}Sb	Sb_2O_3	$2.4x10^{-6}$
^{95}Zr	ZrO_2	$3.7x10^{-6}$
$^{89}Sr/^{90}Sr$	SrO	$1.7x10^{-4}$
$^{90}Y/^{91}Y$	Y_2O_3	$4.9x10^{-7}$
$^{125}Te/^{125m}Te/^{127m}Te$	TeO_2	$6.6x10^{-8}$
^{147}Pm	Pm_2O_3	$3.6x10^{-5}$

In addition, despite the lack of experimental data, a proposal is made here for the generation of surrogate material for uranium residue waste streams with and without processing based on the characterization studies of the MEU waste and theoretical calculations of fission and activation products in LEU target plates, and some assumptions regarding the LEU waste.

A MEU target plate used for Mo-99 production at NTP has a uranium/aluminum ratio of 0.22 (aluminum including cladding mass), whereas this ratio is 0.58 in a LEU target plate, and the U density in an MEU target plate is also much lower, at 1.3 g/ml versus 3 g/ml in a LEU target plate. It is therefore debatable whether the uranium and aluminum content in the uranium residue generated from the dissolution of LEU target plates will be the same as that from MEU, but due to lack of experimental evidence at this stage, it is proposed to generate a surrogate mixture for encapsulation studies of LEU residue containing the same masses of uranium and the chemical impurities iron, chromium and aluminum as reported above for MEU.

The content of radioactive impurities in the LEU residue waste can be estimated from theoretical calculations using the ORIGEN code for LEU (19.8% enriched U), irradiated for the same length of time and same neutron flux as was done for MEU (46% enriched U), and used to compare with the experimental results reported in the sections above. The ORIGEN calculations show that all of the fission products are produced in an LEU target plate at a ratio of 0.43 of the levels in MEU, per gram of uranium (due of course to the fact that the levels of U-235 is at a ratio of 0.43 of the value in LEU). Assuming the uranium content of LEU residue is the same as that of MEU residue, it is therefore proposed to scale the values of surrogates for the fission products based on the different MEU waste streams by 0.43, to generate surrogate mixtures for LEU waste.

Due to the fact that the main transuranium element in the waste, Pu-239, is formed by a transmutation reaction from neutron capture of U-238, the levels of Pu-239 in LEU waste should be scaled by 1.5 times relative to that in MEU waste, because of the fact that the levels of U-238 is 1.5 times higher in the LEU target plate vs the MEU plate. The other significant transuranium element in the waste, Np-237 is produced at yet another ratio in LEU, which is 0.54 of the value produced in MEU, because it is produced both from U-235 and U-238:

- When a U-235 atom captures a neutron, it is converted to an excited state of U-236. About 81% of the excited U-236 nuclei undergo fission, but the remainder decay to the ground state of U-236 by emitting gamma radiation. Further neutron capture creates U-237 which has a half-life of 7 days and thus quickly decays to Np-237 as follows: during ß decay, the excited U-237 emits an electron, while the atomic weak interaction converts a neutron to a proton, thus creating Np-237.
- Np-237 is also the product of α decay of Am-241, which is the daughter product of Pu-241, in turn produced through successive neutron capture reactions from Pu-239, which is formed by a transmutation reaction from neutron capture of U-238.

The ratio of 0.54 of Np-237 in LEU vs MEU is therefore a combination of the scaling factor of 0.43 for U-235 and 1.5 for U-238.

Assuming the uranium content of LEU residue is the same as that of MEU residue; it is therefore proposed to scale the values of surrogates for plutonium based on the different MEU waste streams by 1.5 and that for neptunium by 0.54, to generate the final surrogate mixtures for LEU waste.

5.3 Acidic process waste

Based on the data in Table 4.1 regarding the composition of primary and secondary liquid acidic waste from acid processing of target plates, a proposed surrogate mixture composition has been calculated using the maximum measured concentration of uranium, chemical impurities and radionuclides in the intermediate level liquid waste (ILLW) tanks at ANSTO. This surrogate composition, given in Table 5-7, is proposed to be used for encapsulation studies. All the uranium in this waste stream was assumed to be present as U(VI) due to the oxidizing conditions of approximately 0.9 M HNO_3. The surrogate chosen for uranium was therefore UO_3 ($Na_2U_2O_7$ was not considered as this waste stream does not contain measurable quantities of Na). All other surrogates have also been calculated on an oxide basis.

Considering that approximately 80% of uranium is deported to the primary waste stream and each target plate contains 9 g uranium (based on the Necsa process), the volume of primary liquid acidic waste to be treated would be about 30 mL per target plate processed for Mo-99 production. Assuming the remaining 20% of uranium is deported to the secondary waste stream, the volume of secondary liquid acidic waste to be treated would be about 43 mL per target plate processed for Mo-99 production.

Table 5-7 Final surrogate mixture for ANSTO's liquid acidic waste per L HNO_3 produced from irradiated UO_2 targets (oxide equivalent) †

Element/ Nuclide	Surrogate compound	Primary Waste Mass of surrogate (g)	Secondary Waste Mass of surrogate (g)
U	UO_3	240.580	42.101
Mg	MgO	0.995	0.995
Fe	Fe_2O_3	0.572	0.572
NH_4^+	NH_4NO_3	3.550	3.550
H	HNO_3	56.7	56.7
Al	Al_2O_3	1.134	1.134
$^{144}Ce/^{141}Ce$	CeO_2	$3.6x10^{-4}$	$6.2x10^{-4}$
$^{134}Cs/^{137}Cs$	$CsNO_3$	$3.6x10^{-3}$	$8.1x10^{-4}$
^{60}Co	CoO	$6.2x10^{-8}$	$3.1x10^{-8}$
^{155}Eu	Eu_2O_3	$2.0x10^{-6}$	$4.5x10^{-7}$
^{95}Nb	Nb_2O_5	$7.9x10^{-8}$	$1.1x10^{-6}$
$^{103}Ru/^{106}Ru/^{106}Rh$	RuO_2	$1.0x10^{-5}$	$4.4x10^{-6}$
^{125}Sb	Sb_2O_3	$3.0x10^{-7}$	$4.2x10^{-7}$
^{95}Zr	ZrO_2	$8.7x10^{-8}$	$1.1x10^{-6}$
^{90}Sr	SrO	$1.6x10^{-3}$	$3.6x10^{-4}$
^{91}Y	Y_2O_3	$1.7x10^{-7}$	$5.2x10^{-7}$
^{144}Pr	Pr_2O_3	-	$2.5x10^{-12}$

† It should be noted that the composition is based on ANSTO's liquid acidic waste and will differ depending on the Mo-99 producer as composition is process dependent.

6. Conclusion

A summary has been presented of the characteristics of the waste arising from the processing of both MEU and LEU target plates for Mo-99 production, using both alkaline and acidic processes. This information was successfully used to make proposals for generating surrogate mixtures for encapsulation studies for the following main waste streams from Mo-99 production:

- For the alkaline target plate dissolution process:
  1. Unprocessed residue: In case of final disposal of the uranium residue without processing for recovery of uranium
  2. Processed residue: In case of processing of the irradiated residue to recover and purify uranium for re-use; the following waste streams are generated:
     a) Undissolved residue after the carbonate leaching process
     b) Alumina ion exchangers used for retention of fission products in the initial purification step of the uranium

  c) Nitric acid solutions after the final purification of uranium.

- For the acidic target dissolution process (ANSTO's irradiated UO_2 pellets in a MgO matrix)
  a) Nitric acid solutions in the primary and secondary intermediate level liquid waste (ILLW) containing residual uranium, fission products and other contaminants.

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CHAPTER 2: NUCLEAR WASTE FORM CANDIDATES FOR THE IMMOBILIZATION OF WASTE STREAMS FROM FISSION-BASED MO-99 PRODUCTION

1. Introduction

Low- and intermediate-level wastes from Mo-99 production need to be treated to immobilize them for future final disposal. The wastes have been produced from nuclear irradiation of high-enriched uranium (HEU) and low-enriched uranium (LEU) targets which are then chemically processed to extract the Mo-99. They are variable in nature, ranging from liquids, U-rich "cake" arising from alkaline treatment of the uranium targets, ion exchangers and activated charcoal. The radioactivity of the wastes under consideration largely derives from fission products.

The technical aspects of immobilization of nuclear waste in general have been studied around the world for over 50 years, although socio-political issues are still widely debated and very little nuclear waste has actually been immobilized and disposed. While there are advantages in delaying treatment insofar as the activity of the waste decreases with time, delay also creates the impression that immobilization is very difficult and costly. This would further suggest that Mo-99 production is unsustainable. Since Mo-99 production for radiopharmaceutical purposes is becoming increasingly in demand, because of a broadening customer base, treatment of the waste should be done as soon as possible to establish sustainability for the process.

Immobilization requires the conversion of solid and liquid nuclear waste to a solid material that displays high resistance to leaching by water insofar as ultimate disposal will likely be carried out in a shallow geological repository and transport of radionuclides via groundwater back to the biosphere is very undesirable. Such a solid can be created by the use of selected additives to the waste and various processing methods. Also, this type of solid should be created by simple, reliable technology and there should be a high proportion of the waste in the final solid, typically 20 wt% or more. Secondary wastes arising from the processing technique need to be minimized and fed back into the process. As well as being leach resistant, the solids should have reasonable strength, be refractory and fire resistant and be essentially immune to self-irradiation processes over very long periods of time as some of the fission products have half-lives of Myr, albeit with correspondingly low activity.

The types of potential immobilization solids can be broadly classified as glasses, ceramics, glass-ceramics and cementitious materials. The following chapter is a survey of the research and development efforts in those materials for use as nuclear waste forms as well as their production technology. Low-level wastes which do not contain HEU are not the focus of the current initiatives.

1.1 Historical background

As early as 1953, researchers were showing concern about the need to immobilize radioactive wastes arising from the recently-constructed nuclear reactors [1]. The waste of most concern was used UO_2 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 immobilize 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 favored 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 favored method for immobilization 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.

The advantage of borosilicate glass was 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 groundwater characteristic of deep (~1 km) geological repositories, 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 [2]. These minerals could then be produced by ceramic technologies and became alternative (to borosilicate glass) candidates for high level waste (HLW) immobilization.

1.2 Waste form Design

The optimization of waste form design is attained through the overall waste form chemistry to achieve high waste loadings and applying appropriate 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 [3], but could equally apply to U-doped wastes, particularly enriched uranium:

1. *High Waste Loading* – This should be sufficiently high to make the waste form economic to process and minimize the volume of waste produced. Waste volume reduction will significantly reduce life-cycle costs particularly storage, transport and repository costs. To maximize waste loading the use of non-baseline technology may be required, e.g. glass melters are limited by viscosity, crystal content and temperature; however, by adopting alternatives, significant increases in waste loadings can be achieved. For instance, 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 [4] has been demonstrated. The volume reductions achievable via this approach were independently estimated to have potential disposition cost savings over alternative routes for the calcines of $2 to 4.8 billion [5][1]. However, there are some limitations to waste loadings such as limits due to criticality concerns and limits on heat loadings for the waste form and repository. The former can be overcome by the incorporation of neutron absorbers (Hf, Gd, Sm) into the waste form phase. Careful consideration of the heat loading is required as this may lead for example to glass devitrification.

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[1] Based on disposal cost charges of $620,000 per waste canister at Yucca Mountain.

2. *The waste form must be durable* - it is important that the waste form retains the radioisotopes. 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.
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. Generally, a single phase does not make a satisfactorily flexible ceramic waste form unless the waste is a "clean" single phase thus a multiphase system or a glass is usually required.
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. Moreover, the process chosen must have process parameters that are broad enough to be practical and to cope with changes in the waste stream.
5. *Proliferation resistance* - for fissile materials, the waste form must have a good resistance to theft or diversion and it must be difficult to retrieve the actinides for reuse. There are usually two approaches to this: a radiation barrier coupled with physical security; and producing a waste form from which it is more difficult to extract the fissile materials, e.g. by requiring techniques other than existing, well-known, reprocessing routes.

In all cases the aim of waste form and processing 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 [6]. Environmental risk can be managed by ensuring the waste form is durable and stable over long time frames while meeting the appropriate standards and criteria for disposition and safety by utilizing processes that are safe and applying principles such as ALARA.

2. Glass waste forms for Immobilization of Radioactive waste

2.1 Glasses and the vitreous state [7]

Glassy and vitreous are synonyms and moreover the word vitreous comes from the Latin word for glass. Glass is an amorphous solid, i.e. glass is an amorphous material below the glass transition temperature (T_g) which is the temperature where the properties of the material change continuously from those of a solid to those of a liquid. A material is amorphous when it has no long-range order, that is, when there is no regularity in the arrangement of its molecular constituents on a scale larger than a few times the size of these groups. For example, the average distance between silicon atoms in vitreous silica (SiO_2,) is ~ 3.6 Å, and there is no order between these atoms at distances above ~ 10 Å. A solid is defined as a material having a definite shape and volume that is neither liquid nor gaseous e.g. a material the degree of connectivity between its molecular constituents of which ensures that the geometry of its connecting bonds is 3-dimensional.

Glasses can be formed by several methods: melt quenching, physical vapour deposition, solid state reactions via thermochemical or mechanochemical methods, liquid state reactions e.g. sol-gel method, under action of high pressures (pressure amorphization). Irradiation of crystalline solids can also result in formation of amorphous solids. Glasses are however most frequently produced by a melt cooling below its glass transition temperature sufficiently fast to avoid formation of crystalline phases. Because of that, the International Commission on Glass defines the glass as a uniform amorphous solid material, usually produced when the viscous molten material cools very rapidly to below its glass transition temperature, without sufficient time for a regular crystal lattice to form. Glass-forming materials such as dioxides do not require fast cooling whereas quickly crystallizing materials such as metals require a very fast cooling (quenching) e.g. the early metallic glasses had to be cooled extremely rapidly ~10^6 K/s to avoid crystallization.

Below the T_g amorphous materials have a 3-dimensional geometry of bonds as crystals do and therefore a solid like behavior. Above the T_g fractal structures are formed by broken bonds. T_g depends on the rate of cooling, however it can be roughly assessed from Kauzmann's relation:

$$T_g \approx (2/3) T_L \tag{1}$$

where T_L is the liquidus temperature at which a phase diagram shows a crystal-free melt. A higher T_L provides a higher T_g, but high processing temperatures are not acceptable for an efficient waste immobilization process. A more exact method to calculate T_g is to consider melting as a percolation via broken covalent bonds with T_g dependent on quasi-equilibrium thermodynamic parameters of bonds e.g. on enthalpy (H_d) and entropy (S_d) of formation:

$$T_g = H_d / \left[S_d + R \ln[(1-\theta_c)/\theta_c] \right] \tag{2}$$

where R is the universal gas constant and θ_c is the percolation threshold, e.g. θ_c = 0.15 for vitreous silica. Although actual H_d and S_d value depend on the cooling rate they can be found from available experimental data on viscosity of glasses and melts. The viscosity of melts and glasses is given by universal equation

$$\eta = A_1 T \left[1 + A_2 \exp(B/RT)\right] \left[1 + C \exp(D/RT)\right] \tag{3}$$

where R is absolute gas constant, T is temperature and coefficients A_1, A_2, B, C and D are directly related to the parameters of broken bonds (termed configurons) such as enthalpies (H_d, H_m) and entropies (S_d, S_m) of formation and motion (designation – m). The viscosity of melts at high temperatures is typically characterized by a low activation energy of flow η~exp(Q_L/RT) with Q_L = B = H_m~80– 300 kJ/mol whereas that of glasses by a high activation energy of flow:

η~ exp(Q_H/RT) with Q_H = (D + B) = (H_d + H_m) ~ 400– 800 kJ/mol.

Although, compared to crystalline materials of the same composition, glasses are metastable materials, their relaxation to a thermodynamically stable crystalline structure is kinetically impeded. The metastability of silicate glasses commonly used by various industries is rather theoretical than practical issue as most of oxide glasses are stable for times much longer than any imaginable timescale of our Universe. In practice there is no stress relaxation at room temperatures e.g. high permanent internal stress is preserved in glass articles made more than several millennia ago. Relaxation processes are controlled by viscosity with a characteristic relaxation time required to attain stabilized parameters (Maxwell's relaxation time) given by:

$$\tau_M = \eta / G \tag{4}$$

where G is the shear modulus and η is the viscosity. The higher the viscosity the longer the relaxation time. Viscosity change is thermally-activated and glass-forming amorphous oxides are characterized by high activation energies and very high viscosities under normal conditions. E.g. fused silica has an activation energy of viscosity at low temperature of Q_H=759 kJ/mol, shear modulus = 31 GPa, giving relaxation times as long as $\tau_M = 10^{98}$ years incommensurably longer than even the lifetime of the Universe which is about $14 \cdot 10^9$ years.

2.2 Glasses for nuclear waste immobilisation [8]

Michael Faraday described the glass as a solution of different substances one in another which can still stand as a characterization of a multicomponent glass. Glasses as solid state solutions are tolerant to compositional changes, e.g. properties of glasses changes continuously and smoothly (in most cases linearly) with variations of composition. Because of that, vitrification is almost non-sensitive to slight compositional variations typical of most wastes. Physical and chemical durability of glasses combined with their high capability to incorporate into their structure most elements make them irreplaceable when highly toxic wastes such as long-lived and highly-radioactive wastes need reliable immobilization for safe long-term storage, transportation and consequent disposal. Waste vitrification is attractive because of:

(a) High capability of glass to reliably immobilize a wide range of elements;
(b) Simple production technology adapted from glass manufacture;
(c) Small volume of the resulting glassy waste form;
(d) High chemical durability of glassy waste forms in contact with natural waters and
(e) High tolerance of glasses to radiation damage.

Two main glass types are currently used for nuclear waste immobilisation: borosilicate and phosphate glasses (Table 2-1). The exact compositions of nuclear waste glasses are tailored for easy preparation and melting, avoidance of phase separation and uncontrolled crystallization, and acceptable chemical durability, e.g. leaching resistance.

High waste loadings and high chemical durability can be achieved in both borosilicate and aluminophosphate glasses. Moreover such glasses immobilize well large quantities of actinides, for example borosilicate glasses can accommodate up to 7.2 mass% of PuO_2. Phosphate glasses can accommodate large amounts of aluminium oxides, however in contrast to borosilicate melts molten phosphate glasses are highly corrosive to refractory linings, behavior which has limited their application. Currently this glass is used in Russia, which has immobilized HLW from nuclear fuel reprocessing in alumina-phosphate glass since 1987. Recently prospective borosilicate glasses have been developed to host Hanford high-Al radioactive waste (SRNL glass, Table 2-1).

The most important parameters of nuclear waste glasses are: radionuclide leaching rates NR_i (g/cm^2 day), mechanical strength (MPa), density ρ (g/cm^3), thermal expansion coefficient κ (1/K), specific heat C_p (J/kg K) and thermal conductivity λ (W/m K).

Important glass processing parameters are melting temperature T_m, viscosity η (Pa.s) and electrical conductivity σ (1/ Ωcm) near the melting temperature. Vitrification can be performed efficiently at T_m values below 1200°C so avoiding excess radionuclide volatilization and maintaining viscosities below 10Pa·s to ensure high throughput and controlled pouring into canisters. Some typical data on parameters of HLW borosilicate and phosphate glasses are shown in Table 2-2.

Table 2-1 Compositions of nuclear waste glasses [8]

Country	**Oxide, wt.%**								
	SiO_2	**P_2O_5**	**B_2O_3**	**Al_2O_3**	**CaO**	**MgO**	**Na_2O**	**Misc**	**Waste oxides**
R7/T7, France	47.2	-	14.9	4.4	4.1	-	10.6	18.8	28
DWPF, USA	49.8	-	8.0	4.0	1.0	1.4	8.7	27.1	33
SRNL, USA	30.5	1.1	15.2	25.0	6.1	0.1	9.6	13.5	45***
WVP, UK	47.2	-	16.9	4.8	-	5.3	8.4	17.4	25 (up to 35-38)
Pamela, Germany Belgium	52.7	-	13.2	2.7	4.6	2.2	5.9	18.7	30
Mayak, Russia	-	52.0	-	19.0	-	-	21.2	7.8	33*
Radon K-26, Russia	43	-	6.6	3.0	13.7	-	23.9	9.8	35**
P0798, Japan	46.6	-	14.2	5.0	3.0	-	10.0	20.2	
GC-12/9B, China	46.2	-	13.4	4.2	2.5	1.5	9.1	23.1	

DWPF – Defense Waste Processing Facility, Savannah River Site, US; SRNL – Savannah River National Laboratory, US; WVP – Waste Vitrification Plant, Sellafield, UK; * ≤10 for fission products and minor actinide oxides; ** This glass is designed for sodium-containing LLW and ILW; ***This glass has been developed to host Hanford high-Al radioactive waste.

Table 2-2 Basic properties of borosilicate glasses and glass composite materials [9]

Parameter		**Borosilicate glasses for high sodium waste**	**Glass-ceramics**
Waste oxide content, wt.%		30-35	30-35 + up to 15vol.% of yellow phase[a]
Viscosity, Pa s, at 1200°C		3.5-5.0	3.0-6.0
Resistivity, Ω m, at 1200°C		0.03-0.05	0.03-0.05
Density, g/cm³		2.5-2.7	2.4-2.7
Compressive strength, MPa		80-100	50-80
Leach rate, g/(cm² day), (28-day IAEA test at 25 °C)	^{137}Cs	10^{-5}-10^{-6}	~10^{-5}
	^{90}Sr	10^{-6}-10^{-7}	10^{-6}-10^{-7}
	Cr, Mn, Fe, Co, Ni	~10^{-7}-10^{-8}	10^{-7}-10^{-8}
	REE, An	~10^{-8}	~10^{-8}
	Na	10^{-5}-10^{-6}	10^{-4}-10^{-5}
	B	<10^{-8}	≤10^{-8}
	SO_4^{2-}	~10^{-5} -10^{-6}	~10^{-4}-10^{-5} at content up to 15vol.% of yellow phase[a]

[a] Yellow phase refers to an undesirable separate glass phase that segregates and floats on the melt [10].

The leaching resistance of nuclear waste glasses is a paramount criterion as it ensures low release rates for radionuclides on any potential contact with water. Vitrified radioactive waste is a chemically durable material which reliably retains active species. Typical normalized leaching rates (NR) of vitrified waste forms are below 10^{-5} – 10^{-6} g/cm^2 day. Moreover, as glasses are highly corrosion resistant, their high nuclide retention is expected to last for many millennia. The excellent durability of vitrified radioactive waste ensures a high degree of environment protection.

Vitrification has been used for nuclear waste immobilization for more than 40 years in France, Germany, Belgium, Russia, UK, Japan and the USA. The total production of all vitrification plants by the end of 2000 was ~10,000 tonnes of radioactive glass in ~20,000 canisters.

Vitrification is also currently used for immobilisation of intermediate-level and low-level radioactive wastes from operation and decommissioning of nuclear power plants. Plans are in place to vitrify vast volumes of waste in the future; for example the vitrification of the low activity radioactive waste at Hanford, USA is expected to produce over 200,000 m^3 of glass. A bulk vitrification process is used at Hanford, USA in which liquid waste is mixed with controlled-composition soil in a disposable smelter. Electrodes are inserted to vitrify the mixture and when cooled the smelter, its contents and the embedded electrodes will be buried as LLW. An *in situ* vitrification process was attempted in the cleanup of heavily-contaminated soil at a nuclear weapons test site at Maralinga in Australia in the late 1990's but this was abandoned.

2.3 Immobilization mechanisms

Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro- and micro-structure. Nuclear waste glasses are not completely homogeneous vitreous materials but contain significant amounts of bubbles, foreign inclusions such as refractory oxides and other immiscible components. Hazardous waste constituents are immobilized either by direct incorporation into the glass structure or by encapsulation. In the first case, waste constituents are dissolved in the glass melt, some being included into the glass network on cooling while others are confined as modifiers. The solubility limits of elements as oxides in silicate glasses are given in Table 2-3.

Table 2-3 Approximate solubility limits of elements in silicate glasses [11]

Element	Solubility limit, wt.%
Al, Si, P, Pb	25
Li, B, Na, Mg, K, Ca, Fe, Zn, Rb, Sr, Cs, Ba, Fr, Ra, U	15 -25
Ti, Cu, F, La, Ce, Pr, Nd, Gd, Th, Bi, Zr	5 - 15
Mn, Cr, Co, Ni, Mo	3 - 5
C, S, Cl, As, Se, Tc, Sn, Sb, Te	1 - 3
H, He, N, Ne, Ar, Br, Kr, Ru, Rh, Pd, Ag, I, Xe, Pt, Au, Hg, Rn	< 0.1

Encapsulation is applied to elements and compounds which have low solubility in the glass melt and do not fit into the glass microstructure either as network formers or modifiers. For example, immiscible constituents which do not mix easily into the molten silicate glass are typically sulphates, chlorides and molybdates as well as noble metals such as Rh and Pd, refractory oxides with high liquidus temperatures such as PuO_2, noble metal oxides and spinels. In the case of these elements, encapsulation is carried out either by deliberate dispersion of insoluble compounds into the glass melt, immiscible phase separation on cooling or by sintering of glass and waste powders so that the waste form produced is a glass composite material (GCM).

2.3.1 Borosilicate glasses

Borosilicate glasses are the first choice of material worldwide for immobilizing both HLW and Low- and Intermediate-level waste (LILW). This selection is based on the flexibility of borosilicate glass with regards to waste loading and the ability to incorporate many different kinds of waste elements, coupled with good glass-forming ability, chemical durability, mechanical integrity, and excellent thermal and radiation stability. Borosilicate glasses generally have SiO_2 as the major component, relatively high B_2O_3, CaO, MgO, Na_2O and Al_2O_3 content and minor amounts of many other oxides. SiO_2, B_2O_3 and Al_2O_3 are generally network formers because they form strong covalent bonds involving SiO_4, AlO_4 and BO_4 tetrahedra and BO_3 triangles.

Silicon is the main glass-forming element in a borosilicate waste glass and its basic elements are SiO_4 tetrahedra, which comprise bridging or cross-linking and non-bridging atoms of oxygen (NBO). In a silicate glass the SiO_4-tetrahedra vertices connect these elements to each other through bridging oxygen atoms so that the network consists of chains of various lengths. The glass network is not regular as in the case of crystalline silica, for example the bond angle Si–O–Si can range from 120^o to 180^o while in quartz it is a constant. However, the Si-O bond length remains constant (1.62 Å) as well as the bond angle O-Si-O ($109^o28'$). Alkali, alkaline earth ions, transition metals, and ions of high charge and large size including actinides cannot readily substitute for Si, B or Al and so are network modifiers entering the gaps in the network structure. They generally have coordination numbers of 6 and higher, form weaker bonds to oxygen than the network formers and act to charge-balance the negatively charged borosilicate or alumina-borosilicate network. This leads to break up of Si-O-Si bonds producing NBO e.g. SiO^- ions localized to modifying ions.

Both glasses and melts possess short-range order (SRO) with a typical radius about several angstroms. SRO structural groups in commercial glasses are usually tetrahedral Si, B, Al, Fe, P surrounded by 4 oxygen atoms (tetrahedral coordination) or B surrounded by 3 oxygen atoms (trigonal coordination). Moreover glasses are typically named based on predominant tetrahedral species such as borosilicate glasses which have primarily B and Si species. The tetrahedra and trigonal species in glass link to each other via bridging oxygen bonds. The remaining non-bridging (NBO) atoms effectively carry a negative charge and ionically bond positively charged cations such as Na^+ or Ca^{+2}. The atomic structure of oxide glasses is most exactly represented by Greaves' modified random network (MRN) model. The MRN has two interlacing disordered sublattices: one is the network region and another consists of regions comprised of large concentrations of atoms which do not enter in the network e.g. network modifiers. These may form percolating channels at higher concentrations of network modifiers. The tetrahedra define the network regions, while NBO define depolymerized regions that can form percolation channels. Percolation channels are defined by the NBO atoms at the edges of the highly ordered network regions, which ionically bond to the alkali, alkaline earths or other modifier species in a glass. Moreover these channels can be revealed as they act as ion-exchange paths for elements that are less well bonded to the NBO. It has been also found that for small length scales the alkali pathways are fractal in structure with Hausdorff [12] dimensionality D_f in the range from 1.5 to 2.0 whereas on macroscopic scales the D_f rapidly increases to three-dimensional. This structural feature of oxide glasses explains the well-known mixed alkali effects in glasses as caused by effective blocking by immobile unlike cations due to low dimensionality (< 3) pathways on local length scales.

2.3.2 Phosphate glasses [13]

Phosphate glasses have been intensively studied in Russia, at the Eurochemic Corporation at Mol, Belgium, at Oak Ridge National Laboratory and the University of Missouri-Rolla in the USA. Russia has immobilized HLW from nuclear fuel reprocessing plant RT-1 in the Ural region in alumina-phosphate glass since 1987. Molten phosphate glasses are highly corrosive to refractory linings, behavior which has limited their application. Novel Fe-Pb-phosphate glasses are particularly attractive due to their ability to accommodate enhanced amounts of refractory oxides and their high chemical durability. A number of Na-Al-phosphate, Fe-Al-phosphate and zinc phosphate compositions exhibit improved chemical durability. Fe-Pb-phosphate glasses which melt from 800 - 1000°C are not as corrosive as earlier phosphate compositions.

The phosphate glass structure is built around PO_4 tetrahedral units described using the Q_n designation (Figure 2-1).

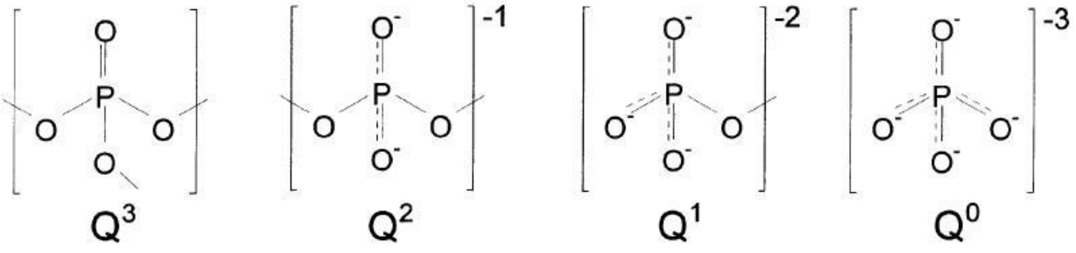
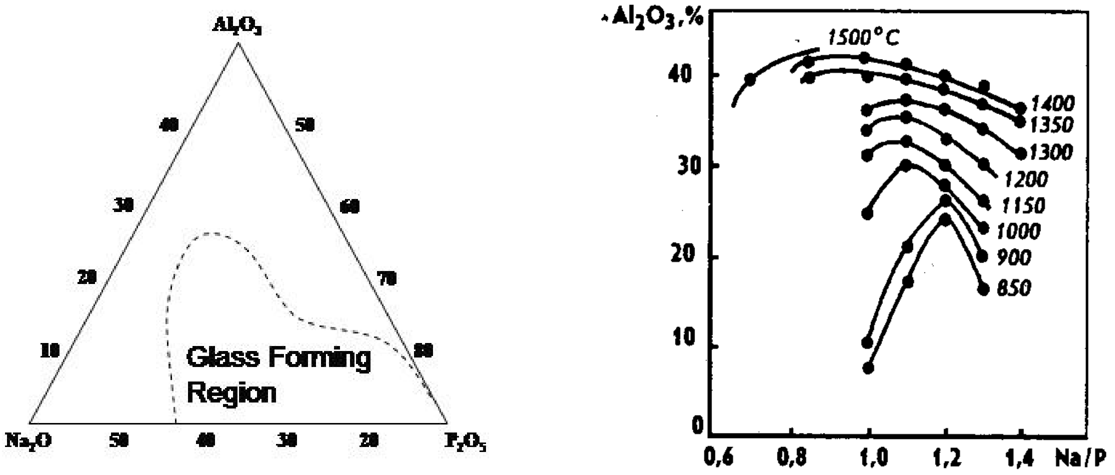


Figure 2-1 Structural units of phosphate glasses.

In a pure P_2O_5 system, the glass is a 3-dimensional network of branching Q_3 units with 3 bridging oxygens and one doubly-bonded oxygen per tetrahedral unit. Addition of modifying alkali or alkaline earth cations replaces Q_3 units with Q_2 units with the cations creating ionic cross-links between the phosphate units. At a P_2O_5 concentration of approximately 50 mol%, the Q_3 units disappear and the structure consists of only Q_2 units in the form of linear phosphate chains. Further addition of modifying cations at concentrations greater than 50 mol % begins to convert Q_2 units to Q_1 units and finally Q_0 units.

Phosphate glass is particularly attractive for immobilisation of high Al and Na wastes. Figure 2-2 shows the glass forming regions of the Na_2O-Al_2O_3-P_2O_5 system.



(a) (b)

Figure 2-2 *Phosphate glass for immobilization of high Al and Na wastes. (a) glass formation in the system Na_2O-Al_2O_3-P_2O_5 at 1000 ^{O}C (compositions in wt%) and (b) the content of Al_2O_3 as a function of (Na/P) ratio.*

Table 2-4 *Solubility of elements in the phosphate glass*

Element	Solubility limit, ppm
Ru	20 – 60
Rh	20 – 60
Pa	300 – 600
Ag	$\geq 2.6\ 10^3$
Te	$\geq 10^3$
Zr	$\geq 7\ 10^3$
Mo	$\geq 7\ 10^3$
La	$(11 – 14)\ 10^3$
Ce	$(12 – 16)\ 10^3$
Nd	$(20 – 24)\ 10^3$
Sm	$(28 – 32)\ 10^3$
Fe	$5\ 10^3$
Cr	500 - 2000
Ni	500 - 2000

For low-to-moderate melting temperatures, the optimum range of the Na to P ratio is from 1.0 to 1.3. This ratio can be increased at higher temperatures, and at 1400-1500°C phosphate glasses can be made with up to 40% Al_2O_3. In contrast to borosilicate glasses phosphate glasses incorporate significantly larger amounts of corrosion products as well as actinide oxides, molybdates and sulphates. Lanthanides and actinides in phosphate glasses tend to complex strongly with phosphate ions. Table 2-4 gives data on solubility of some HLW components in melted phosphate glass at 1000°C.

2.4 Glass options for Mo-99 Production Waste

The composition of the identified waste streams consists mainly of uranium (the major component of some of the waste streams) and therefore the literature regarding the encapsulation of uranium or spent fuel into glass can be used as a basis.

For instance fourteen U-bearing borosilicate glass samples containing 0, 15, and 30 wt % uranium produced by melting were studied using X-ray photoelectron spectroscopy [14]. Results indicated that the uranium occurs as $U^{4+}$and U^{6+} and up to 5 wt % and UO_2 is believed to be uniformly dissolved inside the glass structure. By increasing the waste loading (up to 15 wt %), small regions of possible crystallization (nuclei of uranium-oxygen composition) were observed. With 30% waste loading, grains of UO_2 were observed inside the glass structure.

In contrast with these above observations, in another study a multi-component 55 wt % SiO_2, 10 wt % B_2O_3, 25 wt % Na_2O, 5 wt % BaO and ZrO_2 borosilicate host glass with a waste loading of 30 wt% UO_3 was studied by Fourier transformation Raman technique and reverse Monte Carlo simulation [15]. Structural information from this study indicated that the basic network structure consists of tetrahedral SiO_4 units and of mixed tetrahedral BO_4 and trigonal BO_3 units, similar to the corresponding host glass. The uranium ions act as network formers, which may be the reason for the observed good glassy stability and hydrolytic properties that were found.

Waste form properties of Ca-Mg-Al-silicate glasses are controlled by the bulk composition, equipment, temperature, time, atmosphere, and cooling rate during the manufacturing of the glass. However, the incorporation of uranium in Ca-Mg-Al-silicate glasses resulted in the formation of U(VI), U(V), and U(IV) as a function of the redox environment in the glass. For instance, the influence of Ce(IV) and Mn(III) [16] as well as Cr(VI) and Fe(III) [17] as potential oxidising agents and Cr(II) as a potential reducing agent [18] during the vitrification of uranium into borosilicate glass (doped with iron) were investigated. Results indicated that independently of the different oxygen concentrations at the melting temperature of 1150 ^{0}C, the iron performed a redox buffer role as the Fe(III)-Fe(II) couple protects the U(VI)-U(V) couple from oxidation by either Ce(IV) or Mn(III). The mechanism postulated is that the oxidising agents, Ce(IV) or Mn(III), preferentially oxidises the Fe(II), before any excess oxidising agent interacts with U(V). The Fe(III)-Fe(II) couple also protects the U(V)-U(VI) couple from reduction by Cr(II), as it first preferentially reduces Fe(III) in the melt, before any excess reducing agent interacts with Uranium. However, at higher concentrations of the Cr(VI) and Mn(III) the uranium will be oxidized, while limited oxidation was observed with Ce(IV).

In another study, the leaching performance of two glass encapsulation matrices, a mixed alkali borosilicate glass and a lead borosilicate glass were determined as possible candidate encapsulation glasses for UO_3 powder [19]. The term encapsulation refers to physically surrounding the waste in a glass matrix rather than using the conventional high level waste (HLW) vitrification process where radionuclides are dissolved into the glass and are chemically immobilized by substitution into the glass structure. The composition of the two glass encapsulants (1) 57.2 wt.% SiO_2, 20.3 wt.% B_2O_3, 10.1 wt.% Na_2O, 4.6 wt.% Li_2O, 3.5 wt.% Al_2O_3 and (2) 4.3 wt.% ZnO and 10.4 wt.% SiO_2, 10.2 wt.% B_2O_3, 0.7 wt.% Al_2O_3 and 78.7 wt.% PbO were used to encapsulate waste consisting of up to 75 wt.% UO_3. Leaching results indicated that the alkali borosilicate glass was very poor in comparison to that of the Pb-glass. This demonstrate in principle the use of a Pb-glass as an encapsulant for UO_x powders.

Twenty-four iron phosphate compositions were evaluated regarding their suitability for the vitrification of spent nuclear fuel (SNF) using a 15 wt% waste loading a basis [20]. These iron phosphate glasses were manufactured by melting at 1150°C and the final waste forms were free from any crystalline uranium phases compared to the solid phases had been found in borosilicate glasses with 4.4 wt% UO_2. Results confirmed that all twenty-four compositions were homogeneous in structure and the results of the chemical durability (measured by the product consistency test (PCT)) determinations were in many cases up to 15 times better than borosilicate glass.

The uranium waste streams that form part of this study contain multivalent radionuclides that could constrain the waste loading of these waste streams in glass due to redox chemistry and uranium crystallization within the glass matrix. However, the possibility does exist that certain waste streams, for instance the undissolved residue (iron and uranium) and alumina waste stream (no uranium), could be considered for glass encapsulation and thus need to be investigated.

3. Ceramic and Glass-Ceramic Candidates for Immobilization of Radioactive Waste

3.1 Ceramics for Immobilizing HLW and ILW

Ceramics of interest in the present context to immobilize waste radionuclides are fully crystalline and refractory with melting points usually well in excess of ~1000°C. They are also very resistant to aqueous dissolution because groundwater transport is the predominant means of transport of the radionuclides away from the ceramics when they are emplaced in a shallow trench or a deep geological repository, depending on the class of the waste. Typical common ceramics are mullite ($Al_6Si_2O_{13}$), stabilized zirconia {$(Zr,Y,Ca)O_2$}, aluminosilicate bricks etc. Their densities are typically 70-98 % of theoretical and they are made by high temperature consolidation of pressed mixed powders.

The ceramic materials which have application in the immobilization of nuclear waste will now be reviewed. Emphasis is given to waste forms for different types of actinide, high- and intermediate level wastes, with particular focus on wastes which are problematic for glass matrices or existing vitrification process technologies. The first mineral-modelled ceramics for reprocessing waste immobilization were the Pennsylvania State University supercalcines [21], in which additives such as Ca and Al hydroxides and carbonates, plus phosphate and silicate, were added to the reprocessing waste, followed by calcination at around 700°C and sintering at ~1100°C. Supercalcines were based on a composite of ceramic aluminosilicate and phosphate mineral phases such as monazite, apatite, pollucite and feldspars. Synroc, or "Synthetic Rock", based on titanate minerals-perovskite, hollandite, zirconolite and rutile - appeared soon after [22,23], and had the advantage that the titanate minerals were much more leach resistant in water than the silicates and phosphates in supercalcine. Synroc technology has been developed for over 30 years at the Australian Nuclear Science & Technology Organisation (ANSTO) and now extends well beyond the original titanate formulations. Today the Synroc process is applied to a variety of waste form technologies (e.g. ceramic, glass-ceramic or glass) depending on specific requirements, to result in a tailored waste form for the immobilization of components in a range of intermediate- or high-level wastes.

3.1.1 Ceramic Waste Form Development

Since the supercalcines work, researchers from many countries have devised an extensive range of crystalline candidate phases for HLW immobilization. Table 3-1 shows many of these and the principal radionuclides that they can incorporate. This development has occurred since the 1970s with a steady increase in research on candidate ceramic and glass-ceramics for immobilization of HLW and ILW, both from the aspects of crystal-chemical design and processing technology. Although, after the US Department of Energy decision in 1982 to immobilize Savannah River National Laboratory HLW in borosilicate glass (the best demonstrated available technology from the points of view of scale, use of actual HLW and properties at that time), waste form research on alternatives to glass, at least in the US, slowed down to some extent. Vitrification development in the US and elsewhere has continued however.

Other ceramic or glass-ceramic waste forms continued to be pursued around the world and included apatite [24,25], murataite [26], sphene glass-ceramics [27] and sodium zirconium phosphate (NZP)-structured $Ca(Ti/Zr)_4(PO_4)_6$ [28], and to a lesser extent double actinide phosphates [29]. An important boost for alternative waste forms (and Synroc technologies, see section 3.1.2) came in the late 1990s when waste form candidates were sought by the US Department of Energy for immobilization of ~50 tonnes of impure surplus Pu [30,31].

A variety of ceramics and glass-ceramics have since been designed for different types of HLW, actinide wastes and ILW, notably those which are problematic for glass matrices or existing vitrification process technologies. Wastes can be problematic to glass processing for a number of reasons: they may contain large proportions of refractory elements that limit the waste loading; similarly they may require an increase in the processing temperature with commensurate increases in volatile fission product losses; the chemistry of the waste may cause problems in controlling the viscosity or conductivity of the melt; some wastes promote crystallization (of e.g. spinels, or actinide oxide) which can hinder processing; and some wastes have a highly variable composition that can restrict the processing window. The economic effect of the problematic species is to limit the waste loading and hence increase the waste volume and disposition costs. The potential phase systems for wastes arising from acidic route Mo-99 production are discussed in section 3.2.

Table 3-1 Partial 'library' of ceramic host phases.

Phase and nominal composition	**Radionuclide**
Pollucite, $CsAlSi_2O_6$	Cs
Hollandite, $(Cs,Sr,Ba,Rb)_{1.14}(Al,Ti^{3+},Fe)_{2..28}TiO_{16}$	Cs, Rb,Sr,Ba
Feldspar, $CaAl_2Si_2O_8$	Sr ,Ba
Apatite, $Ca_{10}([P,Si]O_4)_6(OH,F,Cl)_2$	RE,An,Sr,Ba
NZP $(Na,Ca_{0.5})(Zr,Ti)_2(PO_4)_3$	Many
Monazite, $REPO_4$	RE,An
Zircon, $ZrSiO_4$	RE,An
Xenotime, YPO_4	RE,An
Zirconolite, $CaZrTi_2O_7$	RE,An
Perovskite, $CaTiO_3$	Sr, RE, Tc, An
Fluorite, $(RE,An)O_2$	RE,An
Pyrochlore, $RE_2Ti_2O_7$	RE, Zr, An
Titanite, $CaTiSiO_5$	RE,An,Sr
Rutile, TiO_2	Tc
Sodalite, $Na_4Al_3Si_3O_{12}I$	I

RE= Rare Earth; An = Actinide

3.1.2 Synroc-type Waste Form Development

The original Synroc-type titanate ceramics were specifically targeted towards immobilization of PUREX type PW-4b type waste from the reprocessing of spent nuclear power reactor fuel [32]. The variety of waste ions present in such HLW meant that a multiphase approach was required to treat the waste. Table 3-2 shows the approximate composition of the HLW resulting from PUREX fuel reprocessing following storage for over ten years.

Table 3-2 Approximate composition (wt%) and halflives[&] of main fission product and actinide oxides in PUREX fuel reprocessing HLW that has been stored for > 10 years.

FP Oxide (wt%)[$]	Half-life of Most abundant radioisotope (yr.)	FP Oxide (wt%)[$]	Half-life of Most abundant radioisotope (yr.)
Cs_2O (6)	30	TcO_2 (6)	210000
SrO (3)	30	*AnO_2 (6)	>10000
BaO (4)	-	RuO_2 (10)	-
RE_2O_3 (15)	100[&]	PdO (6)	-
ZrO_2 (15)	-	Rh_2O_3 (2)	-
MoO_3 (15)	-		

Water excluded; *An = actinide. [$] Contains additional stainless steel corrosion products.

Group halflives[&] are very approximate as they range from short to long times for different components. Absence of halflife value = stable elements

Typical waste loadings were 20 wt% of HLW oxides and the production technology was the addition of TiO_2, ZrO_2, CaO, BaO and Al_2O_3 to the PUREX-type HLW, calcination of the waste/precursor mixture in a reducing atmosphere, followed by hot uniaxial pressing at ~1100-1200°C (Figure 3-1) to produce “Synroc-C”.

Synroc-C can accommodate PW-4b type reprocessing waste at levels of ~5-35 wt% solids without changing the basic rutile + hollandite + perovskite + zirconolite phase assemblage (Figure 3-1) [33]. Table 3-3 shows the phases and the radionuclides that can be accommodated in them. Several variations of Synroc were developed for different types of waste and these are summarized in Table 3-4.

Table 3-3 Phase assemblage of Synroc-C.

Phase	Nominal Composition	wt% [$]	Key Radionuclides in lattice
Hollandite	$Ba(Al,Ti)_2Ti_6O_{16}$	30	Cs, Rb
Zirconolite	CaZrTi2O7	30	RE, An
Perovskite	$CaTiO_3$	20	Sr, RE, An
Ti oxides Rutile, Magnéli and Ca-Al-Titanates (e.g. loveringite)	TiO_2, $TinO_{2n-1}$, Ca-Al-Ti (CAT) phases [34]	15	
Alloy phases		5	Tc, Pd, Rh, Ru etc.

RE = rare earths; An = actinides; [$] = Wt.% of phase in Synroc-C with 20 wt.% HLW

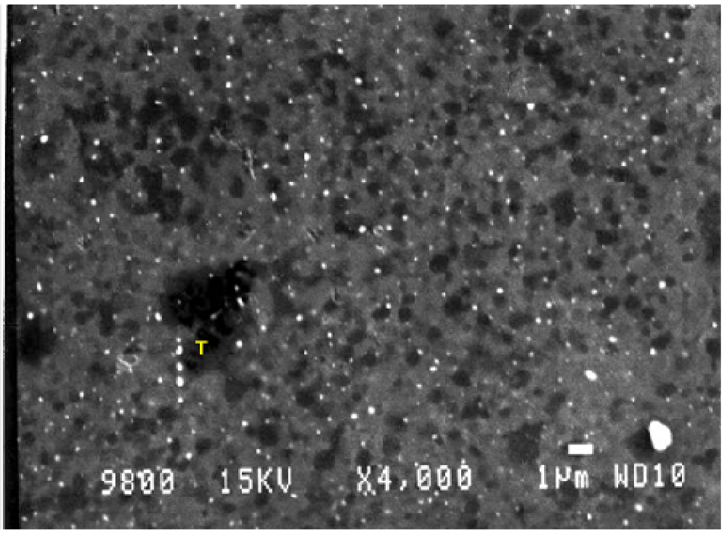


Figure 3-1 Back scattered SEM micrograph of hot-pressed Synroc-C (in this case 10% waste loading), showing the fine sub-micron and dense grain structure achieved. The microstructure consists of a mixture of similarly contrasting zirconolite and Ba-hollandite (lighter of the phases); perovskite (mid-grey) and rutile (dark-grey-black). One can also see fine metallic alloy phase at the grain boundaries and triple points (white). Residual titanium oxide (Magnéli phases, marked T)) from the oxidation during hot-pressing of the added Ti metal powder can also be seen.

Table 3-4 Summary of the types of Synroc investigated since 1978.

Synroc Type	**Description**
Synroc-A	A titanate-silicate ceramic formed by melting [35]
Synroc-B[2]	Standard Synroc precursor composition [23,35]. Forms a Ba-hollandite, zirconolite, perovskite and titania mixture on sintering.
Synroc-C[3]	Synroc-B plus PUREX type HLW typically 20 wt. % [23,35]. Forms the same phases as Synroc-B but with an additional metallic alloy phase.
Synroc-D	Specially designed for the US defense program for a HLW containing large amounts of processing contaminants at Savannah River, SC. Its phase assemblage is nepheline, spinel, zirconolite and perovskite [36].
Synroc-E	Synroc formulation with no Ba or Al, containing 5-7 wt. % HLW, which follows the strategy of micro-encapsulation of the Synroc phases in a rutile matrix [35]
Synroc-F	Formulation designed for direct incorporation of spent fuel. It consists of pyrochlore (~80 wt%), rutile and hollandite – uraninite and perovskite may also form [23,37].
Synroc-FA	Modified Synroc-F for a CANDU amine process high-level liquid waste [38,39].
Synroc-JW-A	Synroc containing Japanese HLW. This waste is similar to PUREX waste but contains Na as a processing contaminant. Typically leads to the formation of freudenbergite, loveringite and β-alumina in addition to the major Synroc-C phases [40,41].

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[2] Synroc-B is the reference Synroc precursor composition.

[3] Synroc-C is the reference Synroc for PUREX type HLWs.

Table 3-4 Summary of the types of Synroc investigated since 1978.

Synroc Type	**Description**
Synroc-Modified-JW-A	Similar to Synroc-JW-A but with additional processing contaminants, namely Al [42,43].
Synroc-JW-K	The Na in the Modified JW-A HLW is substituted by K with the aim of forming K-hollandite instead of Na-rich phases [44].
High-Zirconolite	A zirconolite-rich Synroc (80-90 wt. %) with hollandite, rutile and perovskite in different combinations. Designed for waste streams high in actinide elements [45,46,47,48], but also capable of immobilizing fission products.
High-Pyrochlore	A 95 % pyrochlore + 5 % hafnia-doped rutile ceramic for actinide immobilization [49,50].
Perovskite-rich	An alternative approach to encapsulating Na rich wastes by adding rare-earth elements to form $(Na,RE)TiO_3$ perovskite instead of the standard Na phases [51].
Low-perovskite Synroc	Attempt to reformulate Synroc-C with a lower perovskite content [51].
Synroc /glass composite	Originally designed for Hanford Waste. Consists of main Synroc phases plus additional phases such as spinel, nepheline, glass and ulvospinel [52].
Synroc for Cs/Sr	A Synroc with ~ 70 wt. % hollandite, 20 wt. % perovskite and 10 wt. % rutile [53].
Synroc for Tc and Tc-bearing wastes	Tc has been immobilized in Synroc minerals in either the alloy-phase, perovskite or rutile [54].
Freudenbergite-containing Synroc	Developed to incorporate (Na, Al, Fe, U)-rich waste [55].
Pu-residues glass-ceramic	A zirconolite rich glass ceramic designed for Pu-residues wastes [56,57].

A considerable amount of development work was carried out on Synroc-C [58]. This included scientific studies on the behavior of the material under various leaching conditions [59,60], natural analogues of Synroc's titanate phases [61,62], phase chemistry [23,63,64] and radiation damage [65]. The processing technology was also developed from laboratory to demonstration plant. The demonstration plant was assembled and operated at ANSTO and an alkoxide-route became the standard feed producing 100-150 kg batches.

In 1997, the pyrochlore-structured ceramic Synroc derivative and its associated processing routes developed by ANSTO and the Lawrence Livermore National Laboratory (LLNL) in conjunction with Savannah River National Laboratory (SRNL) for the disposition of surplus US plutonium was chosen ahead of borosilicate glass [31,66]. The baseline ceramic contained ~10 wt% Pu, plus twice as much as U as Pu to discourage diversion potential, 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. The baseline formula was: $Ca_{0.89}Gd_{0.23}Hf_{0.23}Pu_{0.23}U_{0.44}Ti_2O_7 + 0.1\ Ti_{0.9}Hf_{0.1}O_2$ [67], the former having the pyrochlore structure. This ceramic could also accommodate significant amounts of process chemicals in the Pu waste streams, having a wide range of ionic sizes and valences. A simplified version of the phase system is given in Figure 3-2. The material was designed to primarily form pyrochlore, however the varied Pu waste streams contained elements that could shift the mineralogy. Those compositions higher in actinides, or if the waste loading was higher would tend to form some brannerite, $(U,Pu)Ti_2O_6$. The presence of transition metals resulted in the formation of zirconolite; excessively reducing conditions resulted in the formation of perovskite. Extensive testing showed that with the baseline composition chosen, a wide variation in expected impurities, including some glass formers, could be tolerated without reducing the durability (Figure 3-3) [68,69].

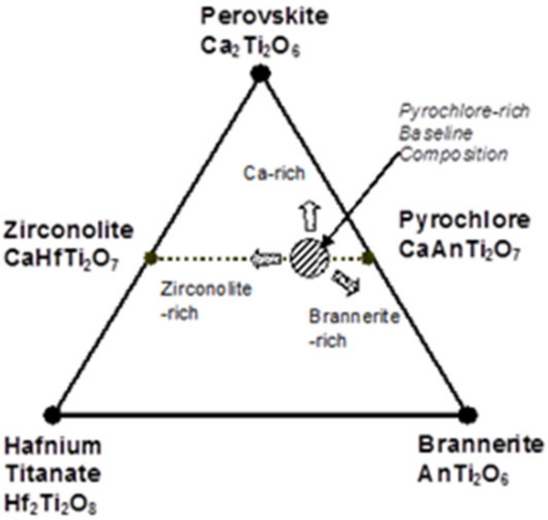

Figure 3-2 Simplified phase representation of the compositions studied in this work. It is a projection perpendicular to the TiO_2 direction. An = U^{4+}, Pu^{4+}, Th^{4+}, and Ce^{4+} (Ce is used for analogue studies). Gd^{3+} ions also present in the system can substitute in the Ca^{2+} and An^{4+} sites ($2Gd^{3+} \leftrightarrow An^{4+} + Ca^{2+}$).

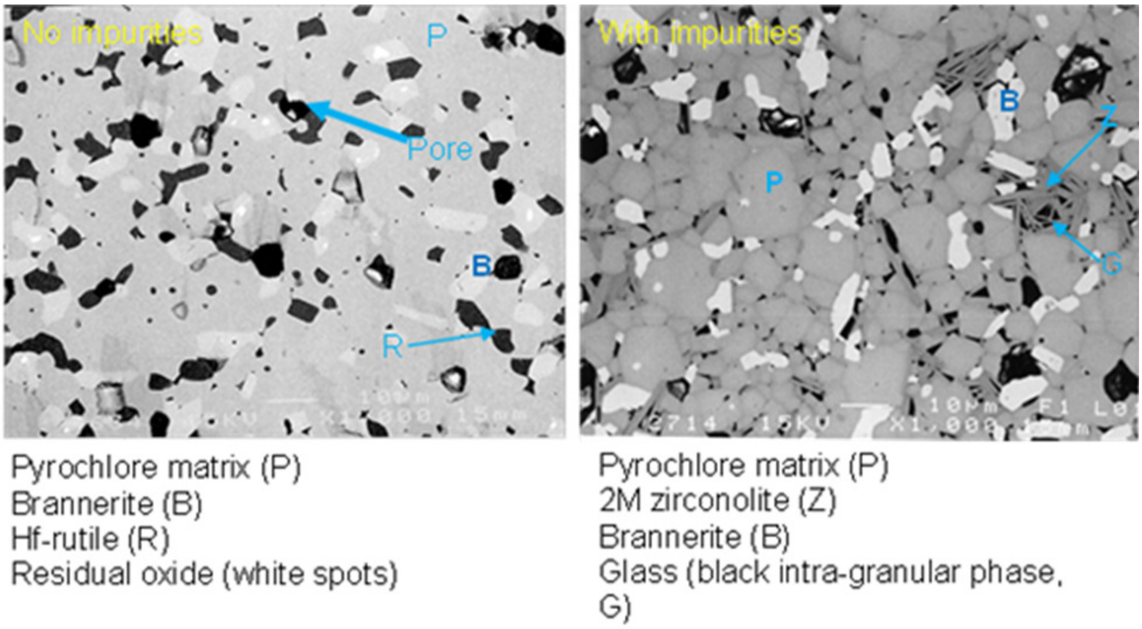

Figure 3-3 Typical matrix structure of the pyrochlore-rich ceramics designed for excess weapons Pu. The sample on the left is a pure baseline material made via an oxide-route. It consists of a pyrochlore matrix, brannerite and rutile, and there is some residual actinide oxide in the cores of some brannerite grains. The sample on the right contains 15 wt% of a mixture of impurities. The predominant differences are the formation of zirconolite due to the presence of transition metals and Al, and the presence of intragranular glass due to glass formers.

Samples were in the form of ~500g “hockey pucks” of ~75 mm diameter by 10 - 15 mm high and were prepared via cold pressing and then sintering in air or argon between 1250 and 1350℃ (Figure 3-4). ANSTO also demonstrated the use of HIP as an alternative production-route with samples including a hot-isostatically pressed metal bellows (~ 0.4 kg) that contained ~ 50 g of PuO_2 plus an ~ 5 kg bellows with Ce used as a Pu simulant (Figure 3-5) [70].

The plan was to emplace the pucks or HIP can inside a Defense Waste Processing Facility (DWPF) glass canister and surround them with radioactive – HLW glass to inhibit diversion. This would then be disposed of at Yucca Mountain. The process was written into version 4 of the *Waste Acceptance System Requirements Document* [71].

While there were several factors influencing the decision to use a ceramic over a lanthanide borosilicate (LABS) glass [30] such as 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} $g.m^{-2}.d^{-1}$ at 70°C in deionized water [72,73,74]), two significant factors favoring the ceramic were its factor of ~ 7 lower neutron dose to workers (LABS glass contained boron which underwent (α,n) reactions) and its greater resistance to proliferation [75]; although this does not disqualify glass for this application, 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 [76,77]. Another issue was the loss of highly leachable B (which along with Gd form the neutron absorbers in LABS glass) from LABS glass over geological time frames which rendered it less intrinsically safe from a criticality viewpoint than the ceramic [78]. The ceramic contained both Gd and Hf. The leach rates of these are low with Gd leach rates being slightly higher than Pu, particularly if the pH is lower, 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 Pu-238 carried out at the Pacific Northwest National laboratory (PNNL)[79,80].

The processing options also favored the ceramic in that LABS glass was produced by melting at high temperatures (~ 1500°C) in platinum crucibles [81], whereas the ceramic was proposed to be produced using a process similar to mature mixed oxide fuel manufacturing technology.

The higher processing temperatures needed for LABS glass production [81] would increase volatile losses of fission products and complicate the off-gas system.

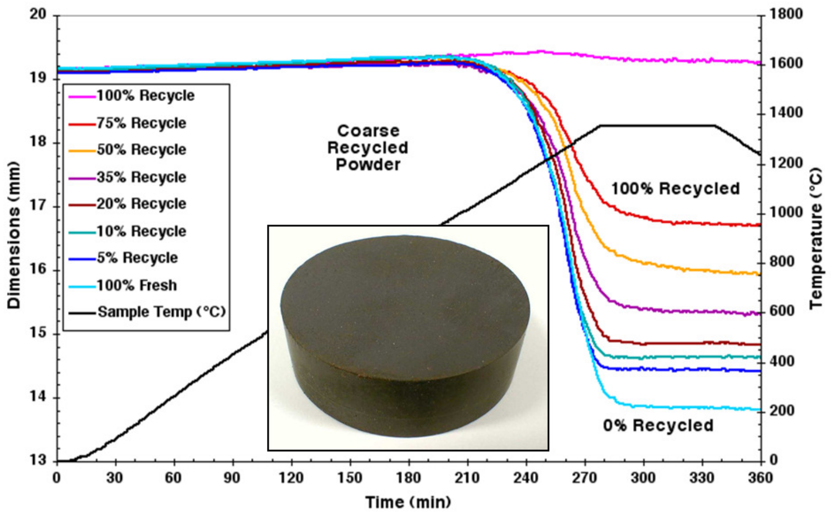

Figure 3-4 Scanning Laser Dilatometer trace for pyrochlore-rich waste form developed for PIP showing the effect of coarse (< 500μm) recycled material on the sintering behaviour of the ceramic. Similar type curves were produced examining the effects of binder burnout on shrinkage. Inserted is a picture of a Th/U-doped puck (~ 67 mm dia.) produced from attrition milled powders in a scanning laser dilatometer by sintering at 1350 ℃ for 4 hours.

Figure 3-5 Hot-isostatically pressed dumbbell-type cans used for Pu-doping work. The can uncut on the left contained ~ 370 g of zirconolite-rich Synroc containing ~ 50 g of PuO_2 and 18 wt% Gd, Sm and Hf neutron absorbers. The can is ~ 6 cm diameter by 4 cm high. The can on the right is a non-radioactive 5 kg scale up, ~ 9 cm diameter by 18 cm high. The final size can be tailored by adjusting the starting geometry of the cans.

3.2 Synroc options for Mo-99 Production Waste

ANSTO has developed a pyrochlore-rich ceramic for its legacy waste that had arisen from Mo-99 production from an acidic route. This waste is mainly uranyl nitrate plus a small amount (~ 0.1 wt%) of fission products. In-house research into treatment of ANSTO's U-bearing wastes started in the late 1990s [82,83]. The waste form was somewhat similar to Synroc-F [39,84], a pyrochlore-rich waste form, which was developed for the direct immobilization of spent nuclear fuel.

Internal ANSTO work showed that simply mixing the waste with the precursors (additives) developed for Synroc-C 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 $(Ca,Zr,U)_2(Ti,Al)_2O_7$) phase as a host for U. The pyrochlore phase comprises ~ 80 wt% of the waste form. As discussed above this phase was selected for the disposition of weapons grade plutonium by the US Department of Energy, and has been shown to be extremely durable and proliferation resistant. Hollandite and rutile (~ 10 wt% each) are present as secondary phases to assist in immobilizing fission products, and small amounts of perovskite and brannerite may also form in the final waste form matrix (Figure 3-6).

The pyrochlore is nominally targeted as $CaU_{0.47}Zr_{0.53}Ti_2O_7$ with U in the tetravalent state, but ANSTO researchers have found that due to the presence of U^{5+} the pyrochlore contains additional Ca to maintain charge neutrality. This can also lead to the formation of the durable brannerite (nominally, UTi_2O_6) phase. All of these phases are well investigated and known to be durable titanate minerals and were also part of the phase system developed for the immobilization of surplus weapons plutonium (PIP).

The waste form is designed to accommodate the small amounts of fission products present in the ANSTO intermediate level liquid waste (ILLW) waste produced from acidic route processing, e.g. transition metals substitute for Ti and Al in the phases and rare earths can substitute into the pyrochlore and perovskite. The primary role of Ba-hollandite in the design is to incorporate the caesium. Hollandite has a variable composition, but is nominally targeted as $Ba_{1.2}(Al,Ti)_8O_{16}$ for Synroc applications. Sr can be incorporated into Ba-hollandite and will also be incorporated into perovskite (nominally $CaTiO_3$). Titanium oxides such as rutile (TiO_2) are present as a buffer and from oxidation of the added Ti metal. Under reducing conditions Magnéli phases (Ti_nO_{2n-1}) form. Minor amounts of other phases such as traces << 1 vol.% of metallic alloys, typically containing Rh, Pd, etc. encapsulated in the waste form and minor titanate phases such as loveringite, etc, can also be present, but none of these limit the durability of the waste form.

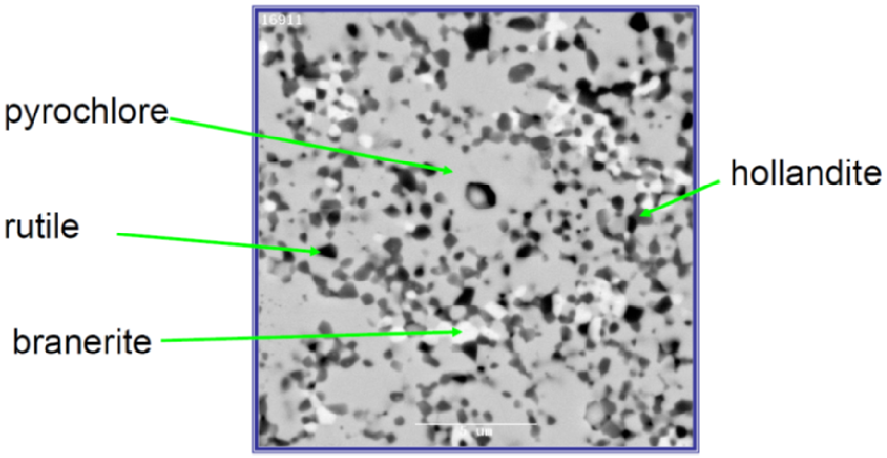

Figure 3-6 Microstructure of a baseline waste form designed to immobilize U-rich legacy waste from Mo-99 production at ANSTO.

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 [85,86] the precursor used for the production of Synroc-C. The samples proved to be durable with leach rates comparable to Synroc-C (Table 3-5).

Table 3-5 MCC-1 Leach rates (0-7 days at 90 °C; g/m^2/day) for two waste forms at varying waste loadings that were developed for the immobilization of U-rich wastes from acidic route Mo-99 production [87].

Sample	25%	44%	35%	20 wt% Synroc-B	30 wt% Synroc-B	40 wt% Synroc-B
Element						
U	n.m.	n.m.	n.m.	0.00015	0.00001	0.00022
Ba	0.04	0.015	0.005	0.002	0.001	0.007
Ca	n.m.	n.m.	n.m.	Below blank	0.013	0.009
Cs	0.03	0.10	< 0.08	0.261	0.117	0.024
Sr	0.04	0.08	0.08	0.007	0.007	0.059

Although it would seem attractive to utilize a single ceramic phase for a given radioactive waste, real radioactive wastes are inhomogeneous. So the aim is to create phase assemblages which can incorporate the full range of radionuclides such that when the radioactive waste 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.

3.3 Glass-ceramics

Glass-ceramics are composites (glass composite materials, GCM) consisting of mixtures of glass and crystalline material and they can be made either by subsolidus sintering or controlled cooling from the melt, perhaps followed by a reheat at lower temperatures to enhance the amount of crystalline material if this enhances their properties. An illustration of nuclear waste forms of this type used and developed for industrial application is given in Figure 3-7. All efforts are aimed at retaining durable crystals in the waste form and, if present, to isolating nondurable crystals by encapsulation in durable glass.

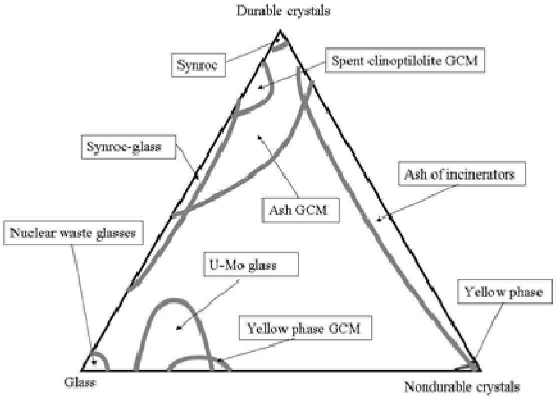

Figure 3-7 Phase composition of nuclear waste forms [10]

Depending on the intended application, the major component may be a crystalline phase with a vitreous phase acting as a bonding agent, or, alternatively, the vitreous phase may be the major component, with particles of a crystalline phase dispersed in the glass matrix. Glass-ceramics may be used to immobilize glass-immiscible waste components such as sulphates, chlorides, molybdates and refractory materials requiring unacceptably high melting temperatures. Further they have potential to immobilize long-lived radionuclides (such as actinide species) by incorporating them into the more durable crystalline phases, whereas the short-lived radionuclides are accommodated in the less durable vitreous phase. Historically, crystallisation of vitreous wasteforms had been regarded as undesirable as it has the potential to alter the composition (and hence durability) of the remaining continuous glass phase which would (eventually) come into contact with water. However, there has been a recent trend towards higher crystallinity in ostensibly vitreous wasteforms so that they are more correctly termed GCMs [10]. This is particularly apparent in the development of hosts for more difficult wastes or where acceptable durability can be demonstrated even where significant quantities of crystals (arising from higher waste loadings) are present such as the high sodium Hanford wastes. Acceptable durability will result if the active species are locked into the crystal phases that are encapsulated in a durable, low activity glass matrix.

Probably the most intense program on development of glass-ceramics was the Canadian program in the 1980s on sphene ($CaTiSiO_5$) glass-ceramics [27]. The basic composition was (wt%): Na_2O (6.6); Al_2O_3 (5.1); CaO (16.5); TiO_2 (14.8) and SiO_2 (57.0). The original development targeted waste loadings of only a few wt% but later efforts examined higher loadings. The materials were first melted at 1350^{o}C, then cooled and reheated at ~1000^{o}C to maximize the formation of sphene.

Workers at the Hahn-Meitner Institute in Germany studied the properties of borosilicate glasses containing PUREX-type HLW and which were devitrified. Different formulations yielded celsian ($BaAl_2Si_2O_8$), fresnoite ($Ba_2TiSi_2O_8$), diopside ($CaMgSi_2O_6$) or perovskite as major crystalline phases [88,89]. The best versions were the materials yielding celsian and these were also studied in the US. In the US, different groups studied the glass-ceramics derived from melting mixtures of natural basalt powder and HLW calcines [90,91]. Hanford (WA, US) tank wastes are rich in alkali nitrates and transition metal hydroxides, and a range of glass-ceramics was designed for these [92,93].

The 4400 m^3 of calcines stored at the Idaho National Laboratory, ID, US are rich in alumina, zirconia and CaF_2. Whereas only about 30 wt% of these calcines can be incorporated in glass [94], glass-ceramics studied in the late 1980s and early 1990s and produced by HIPing to immobilize the calcines had waste loadings of as high as 80 wt% [95]. These utilized SiO_2-rich frit additives. Subsequently, ANSTO workers in unpublished reports have recently developed separate glass-ceramics for immobilization of the alumina-rich and the zirconia-rich Idaho Chemical Processing Plant calcines, again having waste loadings in excess of 80 wt% [4] (Figure 3-8).

Actinides in various HLWs have been preferentially partitioned towards titanate phases, principally zirconolite, in boroaluminosilicate glass ceramics (unpublished work at ANSTO [96,97]. These glass-ceramics have waste loadings of 30-80 wt% and leach rates are often 10-100 times lower than those for standard US EA glass [98], the baseline glass to pass the PCT leach test. These glass-ceramics were prepared by melting as well as the HIP method.

Glass-ceramics have also been developed for Pu-residues wastes at Sellafield [99]. These have been developed to handle a very heterogeneous waste stream [100]. In this material the Pu is immobilized in the durable zirconolite phase (Figure 3-9). Impurities are found in the glass; occasionally minor secondary phases such as spinel were found.

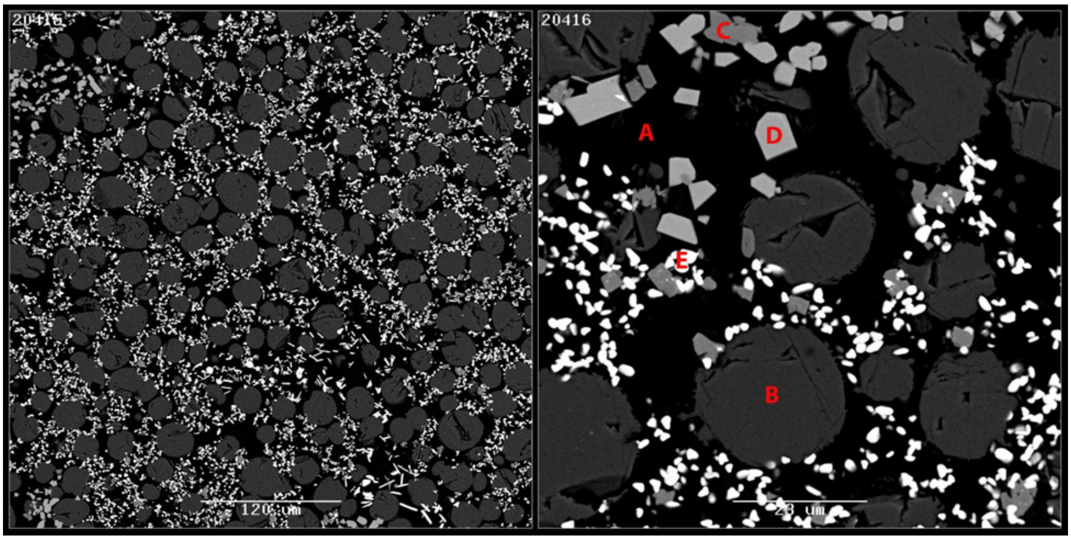

Figure 3-8 Backscattered electron images of baseline treated Idaho Chemical Processing Plant zirconia calcine with 80 wt% waste loading at magnifications 200x & 1000x respectively showing the phases formed in the bulk ceramic. (A) glass, (B) calcium fluoride, (C) $Fe(Cr,Al)_2O_4$ spinel, (D) zircon, (E) zirconia.

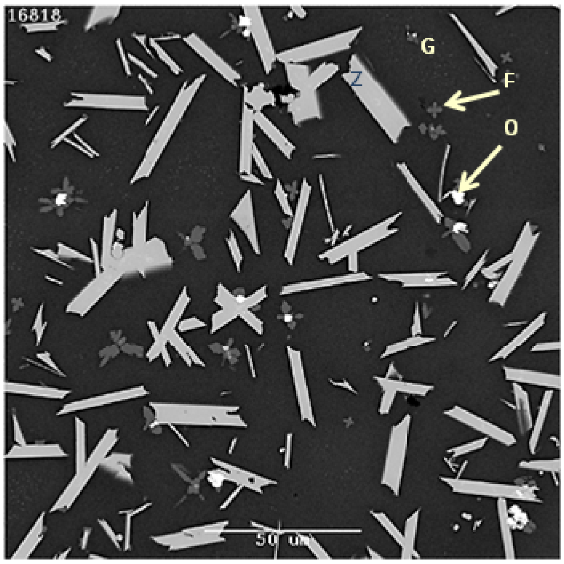

Figure 3-9 SEM backscatter electron micrograph of a glass-ceramic developed at ANSTO at 100x magnification. (Z) zirconolite - light abundant platy crystals in all samples, (F) fluorite - common grey dendrites, (G) glass - enclosing dark matrix, (O) U-Th oxide - small white particles.

Other systems of interest include the French U-Mo glass-ceramic to immobilize Mo-rich HLW and the glass-ceramic developed to immobilize sulphur-rich waste streams in Russia [101]. The latter contains conventional borosilicate glass vitreous phase with uniformly distributed particles comprising up to 15% by volume of yellow phase. The durability of this glass-ceramic is similar to that of conventional waste form glasses. Further, glass-ceramics are potential host materials for highly volatile radionuclides such as ^{129}I. Such systems can be produced by sintering an intimate mixture of glass powders and iodine-containing sorbents, possibly under applied pressure [101].

4. Cementitious Materials for Waste Arising from Mo-99 Production

4.1 Introduction to cement

Cement has long been a strong candidate for immobilization of low- and even intermediate level nuclear waste and will be briefly discussed here. As a potential waste form, cement has favorable chemical properties such as high pH when in contact with water and forms hydration products which favour sorption and ion substitution. Physically, cement is a durable solid material with a low permeability in its hardened state with adequate compressive and tensile strength to protect the radioactive waste in transport and storage without cracking or disintegration [102,103]. Importantly, cement is inexpensive and readily available, fluid when cast and by and large tolerant to waste in both solid and liquid forms, although there are several compounds which can inhibit or unduly accelerate setting (see below). As a result cementitious materials have been used for several decades to immobilize low-level radioactive wastes [103], as well as for engineered structures associated with storage and disposal facilities. Portland cement, waste and water is the conventional cement system for immobilization of radioactive waste. The order of mixing with the waste is often important and in many applications a portion of the cement is substituted by a supplementary cementing material, for example fly ash or slag. There are also novel cement systems such as geopolymers, high alumina and, calcium sulfoaluminate, as well as MgO based or phosphate (acidic) cements. There are three types of cementation process used for cementation of various types of liquid wastes; (1) in drum/container cementation where the components including waste are mixed in a standard drum with a disposable or removable stirring unit, (2) cementation using a unit where the cement and waste are mixed and, when homogenized, poured into a standard drum or container and (3) in-situ cementation where immobilization in cement is carried out inside large conditioning tanks. In situ cementation is often done at large scale, for example in the USA, where very large tanks up to several million litres have been cement filled.

4.2 Chemically bonded phosphate cements

The initial application of magnesium phosphate cement as a repair material for concrete occurred in the US in the early 1970s. An enormous increase in road and air travel at that time meant there was a need for a fast setting low shrinking material for rapid repair of heavily used surfaces. In 1982, FEB Ltd launched a commercially available magnesium phosphate cement product called Febset 45. FEB Ltd is now owned by BASF Construction Chemicals and continues to manufacture magnesium phosphate cement as “off-the-shelf” product ranges called Feblab and Devlab.

The commercially available magnesium phosphate cements are normally based on the reaction between magnesia and ammonium dihydrogen phosphate. This reaction produces the mineral struvite, $(NH_4)MgPO_4.H_2O$. Struvite is a yellow/brown crystalline substance which is found in nature, especially in rock strata containing ancient guano deposits. Commercial magnesium phosphate cements typically reach a compressive strength of about 13.8 MPa after 1 hour, with an ultimate strength of 55 MPa, and they do exhibit good durability [104].

Since the mid 1990s ANL have recognized the potential of magnesium phosphate cements for radioactive and mixed waste encapsulation [105]. The technology has been commercialized as a brand known as Ceramicrete. The name Ceramicrete was given to the material by ANL because it exhibited features of both a ceramic and a concrete, and hence it is named after both types of material.

Ceramicrete contains both highly crystalline material with ionic and covalent bonds, as well as non-crystalline material with hydrogen bonding. The material is often referred to as a Chemically Bonded Phosphate Ceramic (CBPC). The majority of scientific research available in open literature regarding the encapsulation of waste using a CBPC system has been conducted by ANL.

ANL’s research program has centered on the encapsulation of volatile low level radioactive and transuranic mixed waste streams using Ceramicrete [106,107]. ANL has principally tested Ceramicrete to encapsulate plutonium contaminated ashes that reside at the Rocky Flats site. Wagh et al. [107] showed through bench-scale feasibility studies that powdered oxidized cerium (a surrogate which is chemically similar to plutonium and uranium) could be readily incorporated into Ceramicrete. The samples were found to be leach resistant, have low porosity and the radiolytic gas evolution yields were comparable to conventional cement systems.

Studies have indicated that samples which incorporated actinide species appeared stable, suggesting that the system is stable to alpha radiation [108].

Research at ANL has mainly focused on product development and acquiring patents for the use of Ceramicrete in specialized applications. Patents have been obtained by ANL for the encapsulation of low level radioactive species and hazardous metals at room temperatures including Cr, Ni, Zn, Pb, As, Ag, Cd, Ba and Hg. In 1998, a major patent [109] was issued to ANL for its method of waste encapsulation using CBPC.

In 2009, a study undertaken by AMEC Nuclear UK Ltd [110] assessed the effect on the corrosion behavior of encapsulating aluminium tokens in magnesium phosphate cements. This work used a conventional ILW encapsulation matrix, 3:1 PFA:OPC 0.42 w/s, as a reference cement to compare the effect. In this case a direct hydrogen gas measurement technique was used to assess the extent of corrosion over a 28 day testing period. The results showed a large difference in hydrogen gas generation, especially at early age. The magnesium phosphate cement formulations outperformed the control by a considerable margin. Approximately two orders of magnitude less H_2 gas was liberated from the magnesium phosphate cement waste forms compared to that of the control over the 28 day test period. This finding is similar to the results reported by Hayes and Godfrey [111], in which pressure transducer equipment was used to monitor gas evolution. These results are significant and indicate that similar results may be gained when encapsulating uranium containing Al or Alumina resin.

Table 4-1 Solubility product constants of magnesium potassium phosphate and uranium phosphate compounds [112,113,114].

Compound	**Formula**	**K_{sp} (25°C)**	**pK_{sp}**
Magnesium Potassium	$MgKPO_4$	2.4×10^{-11}	10.6
Uranyl Hydrogen Phosphate	UO_2HPO_4	2.1×10^{-11}	10.6
Uranyl Phosphate	$(UO_2)_3(PO_4)_2$	2.0×10^{-47}	46.7
Uranyl Potassium Phosphate	UO_2KPO_4	7.76×10^{-24}	23.1

The relatively stable tetravalent uranium complexes often come in the form of hydroxides, hydrated fluorides and phosphates. Many metals, including uranium, will be precipitated as insoluble phosphates when encapsulated using magnesium phosphate cement. Encapsulating uranium in magnesium phosphate cement is likely to produce uranyl hydrogen phosphate, uranyl phosphate and uranyl potassium phosphate as the corrosion products. The formation of insoluble uranium phosphate compounds is preferable in the case of radioactive waste immobilisation because the movement of the radioactive species is limited. The solubility of a compound is indicated by its solubility product constant. This constant is expressed as the equilibrium constant (K_{sp}) between a solid and its respective ions in a solution. The constant can be also expressed as a base-10 logarithm (pK_{sp}) value, useful for comparative purposes. Its value indicates the degree to which a compound dissociates in water. As the solubility product constant increases, so does the solubility of the compound. Table 4-1 shows the solubility product constants for each likely uranium phosphate product, as well as the constant for the encapsulant material.

It can be seen from Table 4-1 that the solubility of the magnesium potassium phosphate encapsulant material is similar to the solubility product of uranyl hydrogen phosphate. Furthermore, the solubility product constants of uranyl phosphate and uranyl potassium phosphate indicate that these compounds are considerably more insoluble than the encapsulant.

4.3 Cement options for Mo-99 Production Waste

The alkaline-route Mo-99 production process produces a similar volume of lower activity waste to that of the main operational ILW stream. Although initially highly active this waste decays over ~3 years to below that of the defined ILW/LLW level [115]. As discussed cement is a popular solid waste form for low-temperature solidification and/or encapsulation of LLW, however there are several drawbacks for its use in higher activity wastes such as ILLW from Mo-99 production.

- Homogeneous incorporation of waste has some risk associated because the waste might seriously perturb the cement setting process. The set process and set strength can be greatly affected by water soluble substances and waste additives.
- The strength-creating agent in regular Portland cement is tobermorite which is hydrated. Thus a danger with cement is radiolytic hydrogen gas build-up during storage and disposal time resulting in expansion, cracking and potential release of the radionuclides, which is obviously a serious factor to contend with. While this risk can be removed by cement dehydration through heating, this is at detriment to its physical integrity.
- The alkaline route waste is mainly NaOH plus $NaAlO_2$ plus fission products (see Chapter 1). It is therefore rich in Na ions, which may be problematic for cement waste forms. The high Na content is likely to give rise to attack on any aggregates present which can cause expansion and cracking leading to loss of durability (the well-known alkali reaction problem for cement) unless the waste loading is kept very low [116]. As a consequence, the waste volume would be correspondingly high.
- Nitrate waste streams are also problematic for cementitious waste form production and require front end treatment, calcination, or other denitration methods. This may complicate the process.
- Criticality implications also need to be considered for the immobilization of HEU U-rich wastes due to the presence of water in the process. As a result very low waste loadings would again be necessary and result in large waste volumes.

Currently COVRA in the Netherlands drum dry the liquid waste from alkaline processing of Mo-99 followed by overpacking in concrete, which also acts as radiation shielding. ANSTO have investigated this route but found that it would create 50,000 L/y of concrete waste from the ~2000 L/year waste produced from its existing plant and much more (~112,000 L/y) from its planned future plant [115]. By comparison the hot-isostatic pressing route results in only ~500L/y of unshielded waste. This decrease in volume has huge benefits in terms of waste storage facility footprints and transport costs to future national waste storage facilities. This is not only of financial benefit but also reduces political, environmental, and security risks. Any final repository volume would be significantly reduced, leading to lifecycle cost savings. Based on UK figures of £ 18,000/m^3 for the disposal of ILW in UK [117], the disposition savings from volume reduction alone would be around $3-4 million/yr by using the HIP process. Other benefits which result from the smaller size of the repository include reduction in life cycle CO_2 emissions, where the difference is around 20 times less for the Synroc process compared to the cement option [115]. As a result of the above, the use of regular cements such as ordinary Portland cement can effectively be ruled out when considering a waste treatment plant for Mo-99 production 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, and as it produces considerably larger waste volumes. On the other hand, successful encapsulation of different types of radioactive waste (including selective waste streams from the production of Mo-99) using modified phosphate cements have been demonstrated at Necsa and will be considered further in this project.

4.4 Geopolymers

Geopolymers are being increasingly researched as a potential improvement over cement in regard to greenhouse emissions in production, and fire and acid resistance [118,119,120]. They can be represented as porous two- or three-dimensional aluminosilicate networks, depending on the precise composition, with alkali ions providing charge compensation for the replacement of Si^{4+} by Al^{3+} [118,119,120,121]. Samples with alkali/Al and Si/Al molar ratios of ~1 and 2 respectively are also candidates for immobilization of toxic and radioactive wastes [122,123,124,125,126,127]. Thus such geopolymers can pass regulatory tests such as the TCLP test for hazardous waste incorporation [128] and ANS 16.1 [129], and also in some cases the PCT-B test (ASTM C1285-04 (2004) protocol) [130] for radioactive wastes. Alkali ions are the constituents that exhibit the highest releases [122]. Geopolymer processing has many similarities to that of cement. They are made by the action of highly alkaline silicate solutions on reactive aluminosilicate precursors, so the alkaline low level liquid waste (LLLW) from Mo-99 production using an alkaline processing route is attractive from this perspective. As with cement however, nitrate waste streams are highly problematic for geopolymer production and would also require front end treatment. Geopolymers do not rely on hydrous material for strength and can be carefully dehydrated by slow heating to avoid cracking or significant strength loss problems. As their strength derives from the aluminosilicate network, careful dehydration can suppress radiolytic gas production without significant strength losses. Geopolymers also have advantages over cement with respect to leachability (in addition to the absence of the alkali reaction problem).

It has been shown at the laboratory scale [127] that both the ILLW and LLLW from the alkaline route Mo-99 production can be incorporated in a metakaolin-based geopolymer. The waste form passes the PCT leach test for deep disposal in both cases, although waste loadings are less than 10 wt% on an oxide basis. A further advantage in using geopolymers is their alkaline nature which would suppress any potential for cyanide gas emissions from KSCN present in the LLLW waste stream.

5. Polymeric Materials considered as a waste forms for Waste Arising from Mo-99 Production

Polymer materials can be classified into three major categories: thermoplastics, thermosets, and elastomers. These categories associate the polymers by their initial synthesis, production methodology and subsequent final properties. Polymer materials may be applied as single polymers or as composite materials where other materials or polymers are used as fillers to enhance the final properties [131]. Polymeric materials exposed to ionizing radiation undergo a variety of complex reaction and degradation mechanisms; including chain scission and cross linking. The extent of the degradation depends on the polymer and the total dose of radiation emitted from the specific radionuclide. As a consequence research has been undertaken over a long time frame to develop stabilisation of polymeric materials to ionizing radiation [132].

The physical properties of polymers (thermoplastics, thermosets and elastomers) that have been exposed to radiation will vary and are dependent upon properties such as: section thickness; molecular weight distribution [132]; morphology [132]; moisture [133]; oxygen levels [134]; and temperature [132,133]. Residual or functional stress also plays a role in the radiation stability as stresses effects morphological properties, for example crystallization which in turn effects the stability [135]. To complicate matters further chemical reactivity of polymers is also altered under a radiation field and synergistic effects can be generated in these environments [132,136]. Additionally, there are no absolute values of radiation stability for elastomeric polymers as radiation tolerance is affected by both the base polymer and the curing system used in preparation; under a radiation field all elastomers are subject to additional cross-linking [132]. Therefore after an initial selection process, in regards to both chemical and radiolytic stability, each polymer or polymer blend must be tested in the specific application under consideration [133,136].

Some thermoplastic polymers like high and low density polyethylene have been applied in the immobilization of low-level and intermediate-level waste by encapsulation. The typical radiation stability of polyethylene to gamma dose is approximately 10^7 rads [137]. Polyethylene has excellent moisture barrier properties which make it ideal to encapsulate ion-exchange resins which contain Cs-137 and Ru-106 radionuclides [138]. However, polymer resins that exhibit good radiation resistance may be considered as candidates for the immobilization of radioactive waste. Examples of polymer resins with demonstrated radiation resistance include phenol formaldehyde and epoxy resins (139,140). Furthermore, the incorporation of certain inorganic fillers like carbon fiber [141] and glass fibre [142] can improve the radiation resistance of polymers [143].

6. High-Temperature Processing Technologies for Immobilization of Radioactive Waste

6.1 Vitrification technology

Vitrification technology comprises several stages, starting with evaporation of excess water from liquid radioactive waste, followed by batch preparation, calcination, glass melting, and ending with pouring and cooling of vitrified waste blocks with some small amounts of secondary waste. Thin film evaporators are used to evaporate the water. There are two types of nuclear waste glass preparation processes currently used:

A. one-stage vitrification and
B. two-stage vitrification.

Table 6-1 Summary of melter design and characteristics [144,145]

Melter	Comments
Pot processes	• A batch process • Waste and glass frit melted on a pot which also served as the storage container • Original UK FINGAL and HARVEST processes, later abandoned in favour of the AVM process • Used in France in the PIVER process, later abandoned in favour of the AVM process • Currently employed in India
Induction furnace continuous melting	• A continuous process; also known as the AVM process • Calcined waste and glass frit melted in an inductively heated Inconel furnace • Molten glass fed via a freeze-thaw valve into separate storage canisters • Limited furnace life due to corrosion • Employed by France and the UK
Joule-heated ceramic melting	• A continuous process • Either calcined waste and glass frit or a slurry of waste and glass frit melted in a Joule-heated ceramic melter • A viscous glassy layer is formed on the walls of the furnace, this minimizing corrosion of the refractory lining and thus extending furnace life • Molten glass fed via a freeze-thaw valve into separate storage canisters • Employed in many countries including USA, Germany, Belgium, Russia, Japan and Canada
Cold crucible induction processes	• A continuous process; also known as induction skull melting • Employs a water cooled induction furnace • A layer or ‘skull’ of solid glass forms on the walls of the furnace; therefore there is no contamination from metal furnace components or refractories and furnace life is greatly extended • Molten glass fed via a freeze-thaw valve into separate storage canisters • Employed in Russia, with new plants being commissioned in France, Italy and Korea
Plasma arc melters	• Melting in a plasma with very high temperatures possible • Short plasma torch life and severe melter corrosion are disadvantages • Has been employed in the USA for vitrifying contaminated soils
Microwave processing	• A batch process; melting container also used as storage container • Facilities are portable and wastes can be treated *in situ* • An energy efficient methods • Has been employed in Russia and Italy
In situ melting	• A batch process • Used for melting contaminated soil *in situ* by the passage of an electric current via electrodes in the ground • Pioneered in the USA
Bulk vitrification	• A batch process • Waste melted in a very large metallic refractory lined box which becomes the container • Has been employed in the USA
Alternative methods	• Electrodeless induction melter • One-stage melting converter-burial-bunker system

In the one-stage vitrification process glass forming additives are mixed with concentrated liquid wastes and so a glass-forming batch is formed (often in the form of a paste). This batch is then fed into the melter where further water evaporation occurs, followed by calcination and glass melting, which both occur directly in the melter.

Table 6-2 Current operational data on radioactive waste vitrification facilities

Facility	Waste type	Melting process	Operational period	Performance
R7/T7, La Hague, France	HLW	IHC[1]	Since 1989/92	5573 tonnes in 14045 canisters to 2008, 6430x10^6 Ci
AVM, Marcoule, France	HLW	IHC	1978 – 2008	1138 tonnes in 3159 canisters, 45.67x10^6 Ci
R7, La Hague, France	HLW	CCM[2]	Since 2003	GCM: U-Mo glass
WVP, Sellafield, UK	HLW	IHC	Since 1991	1800 tonnes in 4319 canisters to 2007, 513x10^6 Ci
DWPF, Savannah River, USA	HLW	JHCM[3]	Since 1996	5850 tonnes in 3325 canisters, 40x10^6 Ci.
WVDP, West Valley, USA	HLW	JHCM	1996 – 2002	~500 tonnes in 275 canisters, 24x10^6 Ci
EP-500, Mayak, Russia	HLW	JHCM	Since 1987	~8000 tonnes to 2009, 900x10^6 Ci
CCM, Mayak, Russia	HLW	CCM	Pilot plant	18 kg/h by phosphate glass
Pamela, Mol, Belgium	HLW	JHCM	1985-1991	~500 tonnes in 2200 canisters, 12.1x10^6 Ci
VEK, Karlsruhe, Germany	HLW	JHCM	2010 – 2011	~60 m^3 of HLW (24x10^6 Ci)
Tokai, Japan	HLW	JHCM	Since 1995	> 100 tonnes in 241 canisters (110 l) to 2007, 0.4x10^6 Ci.
Radon, Russia	LILW	JHCM	1987-1998	10 tonnes
Radon, Russia	LILW	CCM	Since 1999	> 30 tonnes
Radon, Russia	ILW	SSV[4]	2001-2002	10 kg/h, incinerator ash
VICHR,Bohunice, Slovakia	HLW	IHC	1997-2001, upgrading work to restart operation	1.53 m^3 in 211 canisters
WIP, Trombay, India	HLW	IHPT[5]	Since 2002	18 tonnes to 2010 (110x10^3 Ci)
AVS, Tarapur, India	HLW	IHPT	Since 1985	
WIP, Kalpakkam, India	HLW	JHCM	Under testing & commissioning	
WTP, Hanford, USA	LLW	JHCM	Pilot plant since 1998	~ 1000 tonnes to 2000
Taejon, Korea	LILW	CCM	Pilot plant, planned 2005	?
Saluggia, Italy	LILW	CCM	Planned	?

[1]IHC - Induction, hot crucible, [2]CCM – Cold crucible induction melter, [3]JHCM – Joule heated ceramic melter, [4]SSV - Self-sustaining vitrification, [5]IHPT – Induction heated pot type melter.

In a two-stage vitrification process, the waste is calcined prior to melting. After calcination the required glass-forming additives (usually as a glass frit) together with the calcine are fed into the melter. Some data on melters used are given in Table 6-1.

Two types of melters are most frequently used at waste vitrification plants: Joule heated ceramic melters (JHCM) and induction-heated melters which can either be hot (IHC) or cold e.g. cold crucible melters (CCM). Melting of nuclear waste glasses can be performed efficiently at temperatures below 1200^{o}C because of the volatility of the fission products, notably Cs, Tc and Ru, so avoiding excess radionuclide volatilization and maintaining viscosities below 10 Pa·s to ensure high throughput and controlled pouring into canisters. A more fluid glass is preferred to minimize blending problems, however higher fluidity is associated with higher carryovers of volatile radionuclides (Cs, Ru, Tc). Phase separation on melting is most important for waste streams containing glass-immiscible constituents however these can be immobilized in form of isolated and phase separated disperse phases (in glass composites).

Two streams come from the melter:

- the glass melt containing most of radioactivity and
- the off gas flow, which contains off gases and aerosols.

The melt waste glass is poured into containers (canisters) typically made of stainless steel when immobilizing HLW or carbon steel for vitrified LILW. These may or may not be slowly cooled in an annealing furnace to avoid accumulation of mechanical stresses in the glass.

The second stream from the melter goes to the gas purification system, which is usually a complex system that removes from the off gas not only radionuclides but also chemical contaminants. Operation of this purification system leads to generation of a small amount of secondary waste. For example, the distribution of beta gross activity at the PAMELA waste vitrification plant was (%):>99.88 in waste glass, and the rest in secondary waste, e.g. <0.1% in intermediate level waste, <0.01% in cold waste and <0.01% in off gas.

6.2 Ceramic and Glass-Ceramic processing

The production of ceramic phases typically involves the initial mixing of raw materials in either a dry or wet process, followed by calcination and compaction and finally sintering at high temperature to form a well consolidated ceramic. Sintering is often time- and energy-consuming and as such prohibitively expensive or impractical at production scales. A variety of alternative processing routes have been utilized to produce ceramic waste forms, including hot-pressing, melting and more recently hot-isostatic pressing. The front-end processes can also vary depending upon the nature of the waste feed (e.g. liquid or solid, particle size, etc). Melt processing of waste forms is advantageous since melters are already in use for High-Level Waste vitrification in several countries, the equilibrium of the system can be attained relatively quickly, and melter technology greatly reduces the potential for airborne contamination as compared to processes involving extensive powder handling operations [146]. However, one of the challenges of such a process is attaining the high melting temperatures of most potential host ceramic phases, although this is effectively lowered for polyphase ceramic materials. For example, attempts have been made to form Synroc-type waste form phases using induction melters at 1550-1600°C [147]. The formulation contained 20 wt% simulated plant waste from

"Mayak" reprocessing plant and the resulting waste form consisted of mainly zirconolite and hollandite (about 80-85 vol.%) as well as minor phases of rutile, perovskite, a U-enriched mineral and glass (< 5 vol.% each). Very small amounts of zirconia and barium feldspar phases were also observed. Preliminary leach data suggested uranium dissolution from the waste form was similar to that for UO_2 under the same experimental conditions [147]. ANSTO has been working on the development of hot isostatic pressing (HIPing), to enable optimal processing of problematic wastes and is utilizing it in its Synroc plant, which is currently entering the detailed design phase [161,148].

The essential process steps during the HIP cycle will be outlined below. Effective consolidation of a wide variety of tailored glass-ceramic and ceramic waste forms has been demonstrated. The principal advantages of the HIP technology include negligible off-gas during the high temperature consolidation step because the can is sealed, the equipment has a relatively small footprint, and high waste/volume loadings can be achieved, which translate to significant economic benefits. An area of concern is that there must be no substantial emission of gas on heating after the HIP container is sealed.

Since a major feature of ceramic waste forms is relative insolubility in water, open porosity must be suppressed to restrict water access. Therefore densification of the ceramics is necessary. While melting could in principle assure high densities, the relatively slow cooling rates that are likely for sample sizes of practical dimensions may lead to large grain sizes which could impact on mechanical properties. For example, if radiation damage from incorporated actinides was significant, the anisotropic expansion of non-cubic crystals would lead to microcracking and potential disintegration. Over the last 20 years hot isostatic pressing technology has been developed in which a ceramic or glass-ceramic waste form is consolidated at subsolidus temperatures by heat and pressure to produce materials with sufficiently fine grains to obviate negative mechanical and radiation damage effects.

Calcined waste and additives are first mixed and emplaced in a metal can. Then the can is evacuated to remove sorbed gases and sealed before being heated to temperatures of 1000-1200°C under pressures of 30-100MPa. Samples weighing in excess of 200 kg have been produced and even larger samples are contemplated.

HLW and ILW from nuclear power and weapons production exist in many chemical forms. While borosilicate glass is acceptable in general for most of these wastes, the general approach in ANSTO [149,150] is based on the recognition that there are wastes that are problematic for vitrification because they consist largely of refractory oxides such as alumina or zirconia that do not readily enter silicate glasses or elevate the melting point to very high temperatures, or form crystals that disrupt Joule melter operations. Thus rather than being a competitor to vitrification technology, ANSTO is complementary in the sense that it targets wastes that are problematic for vitrification. Examples of nuclear wastes that are less tractable for Joule melting will be discussed in Section 6.2.2.1.

6.2.1 Synroc Process Development

During the past 25-30years, Synroc's processing technology has developed from laboratory to demonstration plant scale (Figure 6-1). ANSTO is currently designing a plant based on this experience in order to treat wastes arising from its Mo-99 production. The following briefly outlines the historical development of Synroc's processing technology.

Subsequent to laboratory scale demonstrations of Synroc's titanate phases, a conceptual plant design was produced in the 1980s; featuring a mixer-dryer, rotary calciner and with consolidation of the waste form achieved via a bank of hot-presses to press Synroc bellows. The process consisted of mixing the liquid waste (a non-radioactive simulant was used for the Synroc demonstration plan (SDP)) and a precursor (termed Synroc-B as it formed the Synroc phases even when waste was absent).

Figure 6-1 The Synroc Demonstration Plant, designed to produce 10 kg/hr of Synroc. At the top are the mixing tanks for the simulated waste and precursor; this was fed into a rotary calciner (red). In the foreground are the preheating and cool-down furnaces (yellow). The plant also contained a cone blender into which Ti metal was blended with the product exiting the calciner, a filling station which filled the metal bellows, a prepress, robotic arms to move the cans, and an induction heated hot-press (Figure 6-2). On the left is a smaller rotary calciner (yellow and blue) for a dry-feed route.

Varieties of the Synroc-B composition precursor were examined; each produced by a different method including:

1. *Oxide-route* – used commercial oxides of Ti, Al and Zr and carbonates of Ba and Ca [23,151].
2. *High surface area anatase-route* (sometimes referred to as "*oxide-route revisited*") – this route utilized a specially prepared anatase powder with a surface area of 25 m^2/g – compared to ~ 5 m^2/g for most TiO_2 powders at the time. Its main advantage over oxide-route was greater homogeneity, less sticking on mixing and drying and a lower hot-pressing temperature (~ 1200°C as opposed to ~ 1250°C for conventional oxide-route) [152,153].
3. *Harwell sol-gel-route*- This route involved making separate sols of Ti, Zr and Al, blending them and then adding solutions of Ba and Ca nitrates and then spray drying and calcining

the sol to produce 10 – 25 μm spherical particles. Intra-particle sintering tended to occur during heating (i.e., the particles became "hard" agglomerates) and hence temperatures of ~ 1250°C were needed to densify large monoliths [23,154]. At lower temperatures monoliths tended to have regions of low density.

4. *Sandia-route* – utilized a "chemical" process developed at Sandia National Laboratories [23,155]. In this process a Ti, Zr, Al hydrolysate was formed by reacting alkoxides with an NaOH-methanol solution, then hydrolysing it with an acetone-water mixture. The Na was then ion exchanged with Ca and Ba. The hydrolysate is then washed to remove the acetone. It had the disadvantage of being very difficult to scale-up due to the dilute nature of the process and the large quantities of acetone involved. Large batches made by sub-contractors were variable in composition. The route also resulted in a precursor with ~ 0.5 wt. % Na2O processing contamination [1,2]. The presence of Na resulted in a material that densified at a slightly lower temperature 1100-1150°C.
5. *Alkoxide-route* – this route used alkoxides of Ti, Zr and Al in ethanol mixed with hydroxides of Ca and Ba, and water to produce homogeneous powders with surface areas of ~ 400 m^2/g on scales of up to 100 kg/batch [23,156,157]. This route was sometimes referred to as hydroxide-route.
6. *Sol-gel microspheres*- an immature technology at the time of commencement of this work that has now been developed to a large scale [158,159]. This precursor consists of porous microspheres about 20-50 μm in dia., designed to "soak-up" the liquid HLW.

The alkoxide-route became the standard feed for the demonstration plant; its high surface area improved the adsorption of the waste ions compared to the oxide-route and it was easier to make than the Sandia-route material. A plant producing 100-150 kg batches was assembled and operated at ANSTO.

Several options for drying and calcination were studied, but rotary calcination, similar to the French AVM module, was chosen for the SDP, primarily because of its existing industrial maturity at that time (late 1980s) and its existing use in hot-cell borosilicate glass plants. Initially a wet feed into the calciner was used, but later a separate dry mixer was introduced and a dry feed adopted for the conceptual plant design. This resulted in a considerable reduction in the calciner footprint, as can be seen in Figure 6-1.

At the backend several processing routes were investigated including sintering [160] and various modes of hot-pressing, before a bellows mode of hot pressing was adopted for the SDP. The bellows provided the lateral restraint during compaction and eliminated the need for a die (Figure 6-3). Later as the technology matured, hot-isostatic pressing (HIPing) was chosen as the preferred route for many Synroc and its derivative waste forms [161,162] (see below).

In addition to the inactive laboratory work and the SDP development, Synroc samples were made doped with Cs and Sr in hot-cells at ANSTO's Lucas Heights Facility [163] (Figure 6-4)

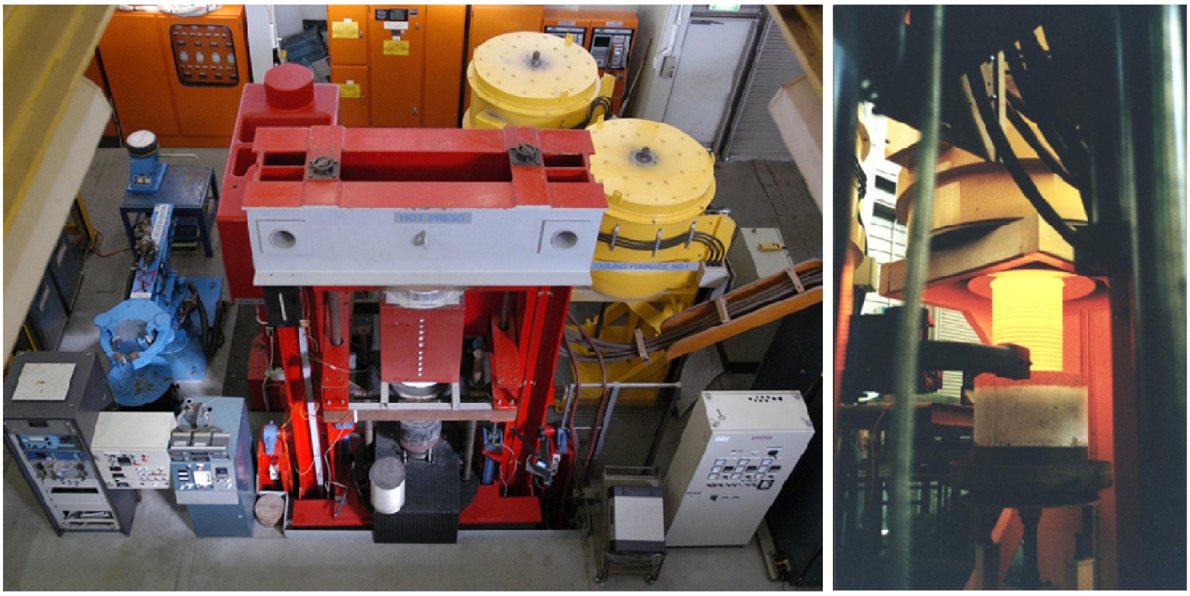

Figure 6-2 The back-end of the Synroc process, the hot-uniaxial press that hot pressed up to 40 cm diameter metal bellows containing Synroc. The bellows were robotically moved between the filling station, pre-heat/cool-down furnaces and the hot-press. A preheated bellows can be seen in the picture on the right; it is about to be transferred to the hot-press unit.

Figure 6-3 An early hot-uniaxial pressing bellows containing ~ 40 Kg of Synroc-C showing the bellows before (left) and after (right) hot pressing. The ruler is 40 cm long.

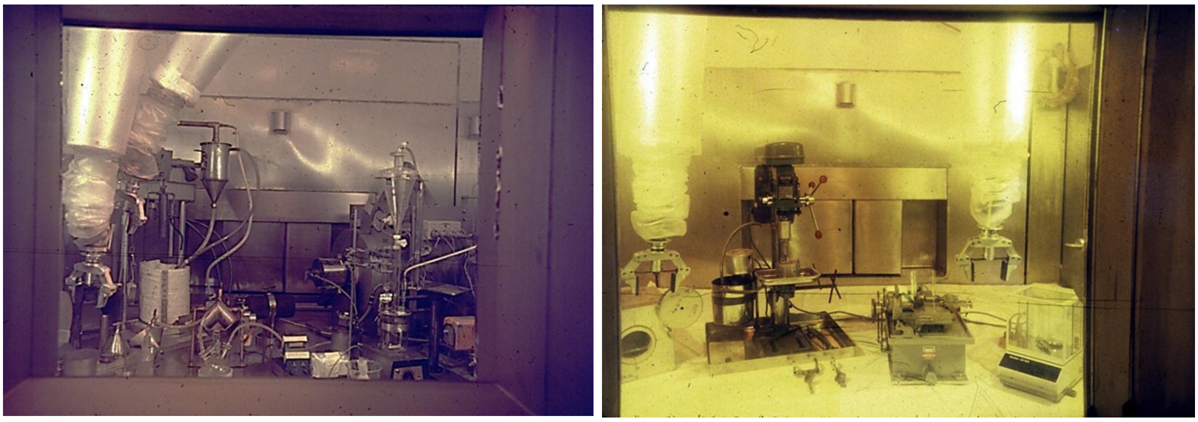

Figure 6-4 Two of the hot-cells used to produce Cs-137 and Sr-90-doped Synroc at ANSTO. The top cell was the processing cell; it contained a pot mixer dryer, a rotary calciner, a V-blender, hot-press and other ancillary equipment. The second cell was the test sample preparation cell with sample coring, cutting, weighing, density measurement and leach test apparatus.

Synroc-C with ^{244}Cm for irradiation damage studies, was also fabricated in a hot-cell at the Japan Atomic Energy Research Institute (JAERI) [41,65] and other samples with ^{238}Pu were also made at the UKAEA, Harwell [164]. The latter samples were retested 20 years after manufacturing and found to be intact [165].

6.2.2 Hot-isostatic Pressing

Hot-isostatic pressing (HIPing) technology was invented in the 1950s at the Battelle Memorial Institute (US) [166,167]. It was initially developed as a technique to diffusion bond the zircalloy cladding for nuclear fuel rods. HIPing was used throughout the late 1950s and early 1960s as a research tool for fabricating experimental fuels and reactor materials [168,169]. The use of HIPing for the manufacture of radioactive waste forms was first proposed in the 1970s [170] and here we discuss the development of HIPing for nuclear application in particular as a means of producing radioactive waste forms. 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 achieved [171]. 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 and they have been HIPing copper cans containing spent fuel since the mid-1970s [172,173,174] and this work is ongoing. US workers HIPed experimental waste forms targeted to Savannah River wastes in the late 1970s and early 1980s [175,176]. Similarly, the Synroc-D formulation was developed at LLNL for US defense wastes [177]. It was a modification of Ringwood's original Synroc-C concept with nepheline ($NaAlSiO_4$) and spinel [$(Mg,Fe)(Al,Fe)O_4$] added to incorporate Na, Al and Fe that are abundant in many US tank wastes [178,179]. For the Savannah River sludge (Synroc-D) waste loadings of 60 – 65 wt% were achieved. Hot-pressing and cold-pressing + sintering were examined as consolidation steps. Hot-uniaxial pressing [176] or HIP [180] were favored by the LLNL developers over sintering because they gave a wider process window in which to achieve the required density and meant that densification could be achieved rapidly; 10 minutes at 4000 psi (28 MPa) at

1100°C [181,182], thus shortening the process cycle over a sintering-route. In addition much larger blocks of waste form could be reliably produced compared to sintering and the material could be contained within the metal cans, reducing the spread of contamination in the process line. Furthermore, hot pressing routes do not require binders or lubricants to be added to the powder, as is the case with sintering. HIPing was identified to be capable of producing larger canisters than HUPing, with bellows 26” (0.67 m) in diameter by 58” (1.47 m) high proposed for a HIP plant and demonstrations at 0.25 m diameter for rapid HUPing and 0.45 m diameter by 0.5 m high (50 kg) for HIPing undertaken [36]. A preliminary engineering layout was developed for the Synroc-D process consisting of a mixer to add the additives to the liquid tank waste, a fluidized bed calciner to calcine the mixture and a HIP to consolidate the material after it was loaded and welded into metal bellows [183]. It was estimated that for a waste loading of 60 wt% and a powder particle packing density of 35%, that two of the 26” diameter by 58” HIP canisters could be processed per day [180]. The plant design capacity was ~ 1.45 tons/day.

HIPing work at ANSTO began in the early 1990s and schematics of the process are given in Figure 6-5 and Figure 6-6. Currently ANSTO is designing a plant to treat wastes arising from its Mo-99 production (Figure 6-7) and this will contain a HIP [161,148].

In HIPing of ceramics or glass-ceramics for radioactive waste immobilization the reactive calcined waste form (waste + additives) material is in the form of near dust-free powder or granules that is first packed by vibratory means inside a relatively thin-walled metal can. This is then evacuated after welding on a lid to which is attached an evacuation tube and often heated to 300 - 600°C for several hours to remove gases adsorbed by the calcines. The evacuation tube is then sealed, and the can is consolidated to full density by compressing it with several tens or even hundreds of MPa of argon gas during a further heating cycle. The metal container, prevents any direct reaction between the waste and HIP process equipment, and of course prevents off-gas escape. So the entire process produces off-gas only in the calcination stage where temperatures are much lower (~ 600-700°C) than those in the final consolidation (roughly the same as those used for vitrification, i.e. 1000-1200°C in most cases). The HIP can shape is tailored to suit the properties of the powder feed and waste form. The dumbbell shaped can is designed to collapse to a near-cylindrical shape (Figure 6-8), with the can geometry allowing the cans to occupy a maximum of space in a cylindrical transport container (60 cm internal diameter x ~3m high in the US).

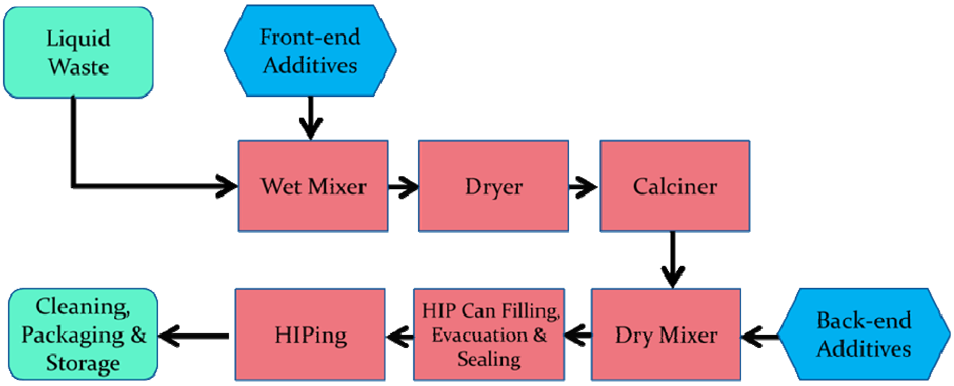

Figure 6-5 Synroc process schematic for a wet feed waste.

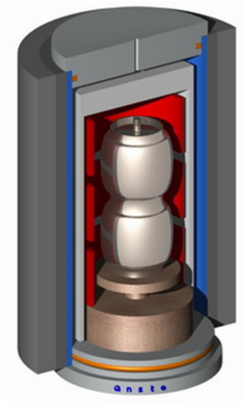

Figure 6-6 Schematic of a Hot-isostatic press and ANSTO's Eagle HIP apparatus.

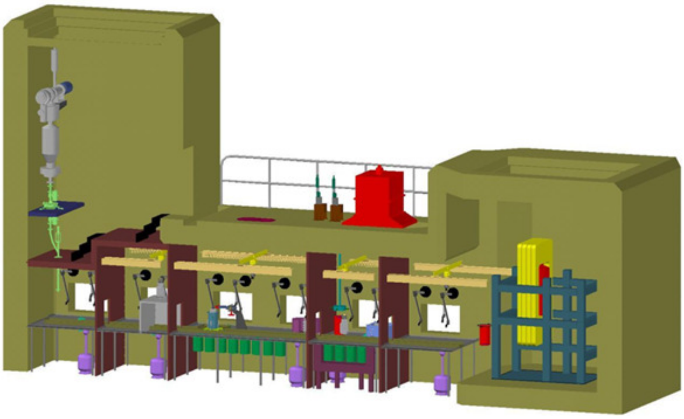

Figure 6-7 An initial conceptual plant design of a series of hot cells in which powder and additives are mixed and transferred.

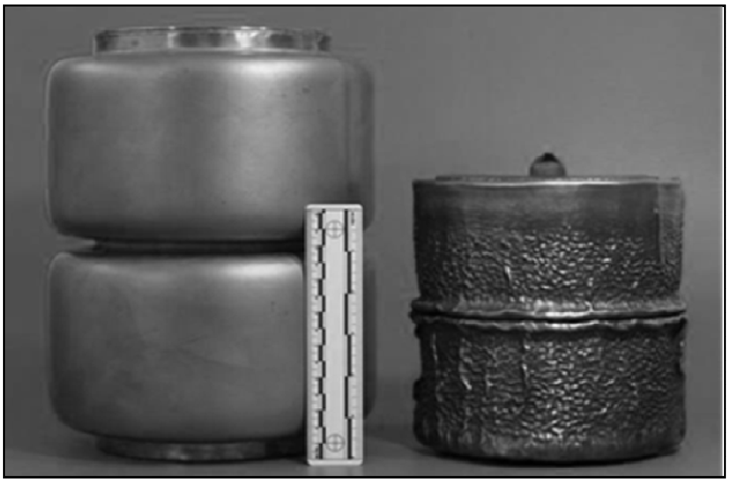

Figure 6-8 One of the many types of HIP can dumbbell designs showing how the can collapses to a near cylindrical shape. This 10 kg can contains a waste form with a Magnox sludge simulant [184]. Ruler is ~ 30 cm long.

HIPing is a batch approach and cans containing more than ~ 100 kg of waste form are feasible, with a processing time of ~ 10 h. Industrially large HIPs with hot zones of up to 2m diameter with tonnes per day throughputs are in commercial operation. ANSTO has produced concept designs for treating ~10,000 m^3 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.

A large advantage is the relatively small footprint of HIP equipment, arising in the first instance because of the absence of off-gas in the hot-consolidation step. The HIP cans contain the contamination and in conjunction with other methods the HIP vessel can be kept relatively contamination free. Further, the HIP vessel is designed to exceed the life of the plant and is much easier to decontaminate: hence, there is much less secondary waste compared to vitrification, i.e. used melters.

The HIP process can be used for encapsulation in a metal waste form for some wastes. Other than the Swedish work, examples that have been demonstrated inactively are Sn encapsulation of ^{129}I sorbed on zeolites [185,186] and work on Cu and other metal encapsulation has been carried out at ANSTO and demonstrated in-cell at Idaho national laboratory (Figure 6-9) [187]. This process was later scaled up to 100 kg-scale. Encapsulation in ceramic phases such as highly durable rutile [188] or glass [189] has also been proposed (Figure 6-10).

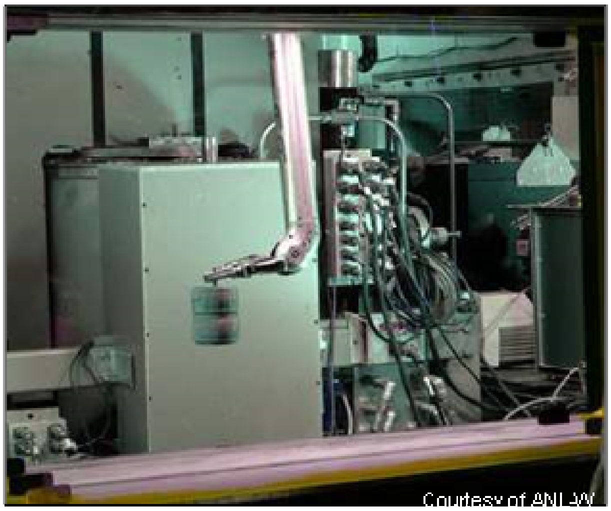

Figure 6-9 A dumbbell HIP can containing a zeolite-type waste form after HIPing in the hot-cell facility at the Idaho National Laboratory (formerly Argonne National Laboratory-West).

Figure 6-10 Sectioned HIPed copper metal encapsulation waste form containing uranium-aluminium alloy, cermets, steel and graphite. Note the U-metal (Mo-99) target emplaced in the sample.

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 radiation damage when the waste form contains a substantial amount of alpha-emitting waste actinides.

6.2.2.1 HIPing wastes that are problematic for borosilicate glass

To reiterate, by problematic, we mean wastes that (a) can only be incorporated in borosilicate at very low loadings, (b) because there are extensive problems of waste volatility at the melting conditions or (c) because the waste is so refractory that very high temperatures would be necessary, say in excess of ~1500°C. Here we give some examples.

- Idaho HLW Calcines. These wastes consist of partly calcined powders from the reprocessing of naval reactor fuel in the US. These wastes, that only contain ~1 wt% of fission products, can be problematic for borosilicate glass as they consist mainly of alumina, zirconia, alkalis and CaF_2. While the alkalis can readily be incorporated in borosilicate glass, alumina raises the melting point considerably and zirconia is highly refractory and has limited solid solubility. For these wastes the limiting waste loading for Joule melters is in the order of 20 wt%, and the CaF_2 would tend to give hazardous F-rich emissions at high temperatures in open melting systems, not to mention the volatile fission products. Furthermore, crystallization in high alumina and zirconia melts can restrict Joule melter operation. In contrast HIPing at ~ 1150°C can yield waste loadings of ~70 wt% and in some cases up to 80 wt% (Figure 6-11) [190], with phase assemblages consisting mainly of zirconia, alumina, CaF_2, zircon and glass. The US Resource Conservation and Recovery Act (RCRA) elements such as Hg, Cd, Pb and Cr are also present in these wastes and these are adequately contained in the HIPed waste forms (unpublished ANSTO work). The work package also included the HIPing of samples inside the hot-cell facilities at the Idaho National laboratory (Figure 6-12).

Figure 6-11 First non-optimized 30 kg scale HIP demonstration of the Zr-calcine (80 wt% waste loading) simulant. HIP can before and after (left) and cut section (right).

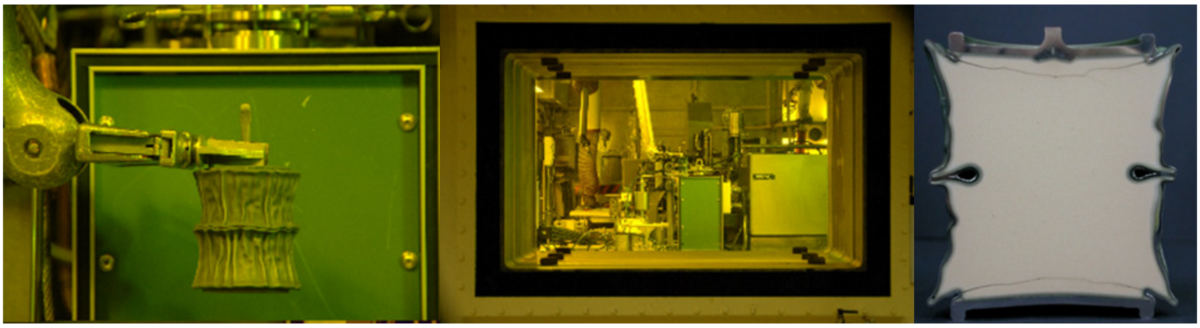

Figure 6-12 Photographs of the direct HIP zirconia calcine within the HFEF hot-cell at Idaho national laboratory, together with a cross-section of the equivalent can HIPed at ANSTO.

- Pu-bearing wastes. Tetravalent Pu is not very soluble in borosilicate glass although vitrification at elevated temperatures (~1500°C) using Pt crucibles has been argued to be an alternative means of processing to form a La-rich borosilicate glass (see above) [191] to immobilize Pu^{4+}. Although reducing conditions can allow Pu to form Pu^{3+} with extensive solubility, U accompanies Pu in such wastes and remains tetravalent under such conditions and so still has quite limited solubility in borosilicate glass. Moreover the use of Pt crucibles under reducing conditions is not feasible. Sintering is viable [66] for Pu-rich wastes if the impurities do not lead to severe volatile losses of other waste components. Also, wastes containing ~ 10 wt% Pu have been shown at ANSTO (unpublished work) to be amenable to glass-ceramic formation with ~ 99% of the Pu and U partitioned into crystalline zirconolite. Pyrochlore and brannerite glass-ceramics containing Pu and/or U have also been made at ANSTO.
- Cs/Ba/Sr/Rb heat-producing waste from reprocessing. Radiogenic heat production imposes severe limitations on waste loading for geological repository disposal, where a key requirement is to maintain temperatures in the repository walls below ~ 100°C to

avoid compromising waste form (particularly borosilicate glass) leachability in water. The smaller size of HIPed waste-bearing containers relative to full glass canisters such as the US transport containers, allows more even distribution of heat-producing waste in a repository if a relatively small amount of heat-producing waste can be judiciously mixed with processed HLW that produces relatively little heat. Moreover HIPed hollandite-rich (Synroc-C phase) waste forms containing ~10 wt% of these heat-producing isotopes have considerably more aqueous durability than borosilicate glasses [192] and this has notable benefit for the long-lived ^{135}Cs in such waste.

- Pyroprocessing waste. The fission products in chloride salt wastes from pyroprocessing can be removed for salt reuse in principle by selective ion exchange processes or even crystallization [193]. The waste can also be vitrified when mixed with borosilicate glass frit [194] but in this case HCl and Cl_2 emissions are severe and would impose critical materials limitations on the vitrification and off-gas plant. High-temperature halide losses can be reduced or eliminated via HIPing. The chloride (or fluoride)-bearing waste pyroprocessing salts are incorporated in zeolite [195] or mixed with $NaAlO_2$ and fine silica [196]. After the addition and mixing of 10-20 wt% borosilicate glass, HIPing at 850°C allows the formation of sodalite + glass waste forms [195,196]. Apatite + glass composites may also be possible [197]. Pu-residues wastes doped with lesser amounts of Cl (2 wt%) have also been shown to be treatable using a glass-ceramic and a HIP process route [198] with minimal effects on the HIP can interface.
- ^{129}I. ^{129}I with a half life of ~16 Myr is a difficult radionuclide to immobilize for times comparable with its halflife but the specific activity of ^{129}I is correspondingly small. Iodine immobilized in Ag-zeolite can be incorporated in tin and HIPed at 200°C to encapsulate it [97]. Also iodide sodalite can be made fairly readily from $NaAlO_2$, silica and NaI [199], although unpublished leaching studies of material HIPed at 900°C/100MPa at ANSTO did not look very encouraging. Sheppard et al. [200] and Maddrell [201] have also carried out HIPing experiments on silver iodide sodalites and viewed their results as positive.
- ^{99}Tc. While Tc in its highest valence states as e.g. pertechnate (+7) is very volatile at modest temperatures (a few hundred °C;[202]) reduction to the tetravalent state or to metal allows the potential for HIPing at ~1100°C to produce leach-resistant waste forms. Thus Tc metal can be alloyed with stainless steel and Tc^{4+} can be substituted for Ti4+ in Synroc-type waste forms [203,204]. Sintered $MgTi_2O_4$-based waste forms in which Tc^{4+} was substituted for Ti have also been studied in this connection [205].
- Sludges. In partly published ANSTO work [206], dried and heat-treated simulated K-basin (Hanford) [207] and Magnox sludges (UK) have been successfully HIPed at very high waste loadings at ~ 1000°C/100MPa to produce a dense waste form with the concentrated sludge volume reduced by ~ 60-70%. ANSTO demonstrated a sludge treatment option and produced 10 kg full scale HIP cans of simulated Magnox sludge waste form [184].
- Can-ceramic interactions. At the metal can/ceramic interface, over distances of a few tens of microns at most, the metal tends to be oxidized and the ceramic reduced. Thus the main reactions are that Cr is transferred from stainless steel cans to the ceramic and Fe-rich oxides occur on the inner can surface. It has been shown for several types of ceramic waste forms based on Synroc phases that HIP can/ceramic interactions are not deleterious [208,209] to the immobilization quality of the ceramic.

6.2.3 Glass-ceramics from Melting Routes

Glass-ceramics can also be made via melting-routes. The preferred route is to use cold crucible melting. The French have developed commercial cold crucible melters for the manufacture of vitrified wastes and are currently installing one at AREVA's R7 vitrification line in which a cold-crucible melter has replaced the previous glass- melter [210]. In this line they will produce a glass-ceramic from spent UMo fuel that was reprocessed during the 1970s in the UP2-400 plant in La Hague [211]. CEA[4] and AREVA developed a new formulation for this waste. They also needed to adopt cold crucible melting technology to make this waste form as it requires processing temperatures of 1200-1300°C, which exceeded the design limits for existing melters. In addition, the chemistry of the CSD-U waste was corrosive to the existing R7T7 glass melter material of construction. The waste loading targeted by COGEMA was 10 wt.% Mo and given that Mo is ~ 66 wt.% of the waste stream this would equate to a waste loading of ~ 15 wt.%. To do this they added calcium to form $CaMoO_4$ [212]. The reference glass composition is given in Table 6-3. Cold crucible melting has also been used to make ceramic phases, such as muratatite [213], titanate ceramic phases [214,215] and powellite [216]. Recently published work has demonstrated that a UMo powellite glass–ceramic that was very similar to the French composition was quite leach resistant in water at 90°C with the dissolution of Cs, Mo, Na, B and Ca not exceeding 2 g/L in normalized PCT tests [217].

Table 6-3 UMo reference glass composition (oxide basis) from Reference [211].

Oxide	Wt.%	Oxide	Wt.%
SiO_2	38.7	MoO_3	10.0
Na_2O	9.4	ZnO	6.0
B_2O_3	13.9	ZrO_2	3.3
Al_2O_3	7.1	CaO	6.1
P_2O_5	3.1	Other	2.4

Vitrification of NPP operational LILW was carried out at Moscow SIA "Radon" vitrification plant using high frequency cold crucible melters. Waste concentrates of about 1000 g/l were intermixed with glass forming additives in the form of loam, datolite, bentonite, and silica. Both calcinations and melting processes were carried out in the same cold crucible melter apparatus. Glasses and glass composites produced were examined applying X-ray diffraction (XRD), optical microscopy, infrared (IR) spectroscopy, and electron-probe microanalysis (EPMA). Glasses were characterized as vitreous with no crystalline phases. At present liquid radioactive wastes from facilities in parts of Russia are vitrified [218].

From the work reported by Rutledge [219], it was demonstrated that glass ceramic waste forms tailored to immobilize fission products can be processed using cold crucible induction melting (CCIM) technology. The advantageous higher temperatures reached with the CCIM compared to the Joule-heated melter allow the lanthanides, alkali, alkaline earths, and molybdenum to

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[4] CEA is the French Atomic Energy Commission (Commissariat à l' énergie atomique).

dissolve into a molten glass. Upon controlled cooling they enter targeted crystalline phases to form a glass ceramic waste form with higher waste loadings than achievable with borosilicate glass waste forms.

Tsuyoshi Usami et al. [220] determined the properties of crystalline phases formed using Mo and Re waste streams. The chemical forms of the constituents were determined by XRD and SEM-EDX. In the Mo waste stream where Mo is dominant, crystalline material is mainly composed of molybdates of Na, Li, Ba and Ca, Na_2SO_4 and $CsReO_4$. In the Re waste stream where Re is dominant, $(Na_xCs_{1-x})ReO_4$ were observed. The density of this waste form is larger than that of molten glass, and increases with Re content. The molten waste form of Mo-type and its simulant showed a density of 2.73 - 2.79 g/cm^3 at 700°C - 850°C, slightly decreasing with temperature. In the case of the Re-type simulant, the density increased with Re content, and was 3.06 - 3.15 g/cm^3 at 500°C - 650°C. Since the density of the molten waste form is greater than that of molten glass, it drops to the bottom of the melt in the glass melter under the influence of gravity.

6.3 Deposition of a SiC layer by plasma spraying

Necsa has developed various methods of nuclear waste treatment and immobilisation as part of the nuclear fuel cycle (NFC). The Republic of South Africa is bound by the non-proliferation treaty, which prohibits the re-processing of post-reactor waste to partition radionuclides for immobilisation. Encapsulation in polymer, glass and ceramic matrices is however difficult and radiation effects can cause cracking due to helium built-up. The application of an additional permeation barrier such as silicon carbide can mitigate the possible release of waste from the immobilization matrix. An effective barrier layer should completely eliminate the possible permeation of any radionuclides or gases from the waste matrix. It should also be able to maintain stability under high temperatures and aggressive environmental conditions. The additional barrier might also be applied directly onto HLW particles depending on the waste properties.

Various methods can be used to produce low permeability, corrosion resistant barriers (such as SiC, Si_3Ni_4, TiC, TiN, TiO_2, etc.) onto various substrates (polymer, glass, “cold” ceramic, ceramic, synthetic rock, etc.). Chemical vapor deposition is widely applied to obtain thin layers of such barriers. Due to the high temperature and high energy density, plasma techniques are also widely applied for this purpose. Plasma spraying has the advantage that the technology is used in industry to manufacture a wide range of layers onto different materials/components. Plasma torches used for spraying can be operated inside a hot cell during layer spraying which can be considered as the most attractive aspect for the treatment of HLW.

Various aspects of plasma spraying using the equipment as indicated in Figure 6-14, have been investigated at Necsa. The plasma sprayed coatings are affected by variables relating to the powder injection into the plasma [221]. These include:

- the feed material
- the powder feeder
- the carrier gas
- the position of the powder injectors
- the injector geometry

The coating properties also depend mainly on the adhesion between splats (melted particles) and between splat and substrate. Therefore, the contact between the first splats and the substrate is crucial and determines the adhesion properties of the deposition layer [222]. The substrate roughness and the substrate temperature also affect the bond strength [223,224].

Figure 6-13 Use of microwave technology to apply SiC coatings onto substrates

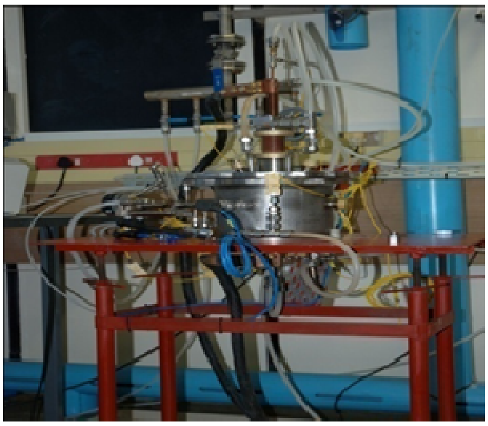

Figure 6-14 Use of plasma sputtering to apply SiC coatings onto substrates

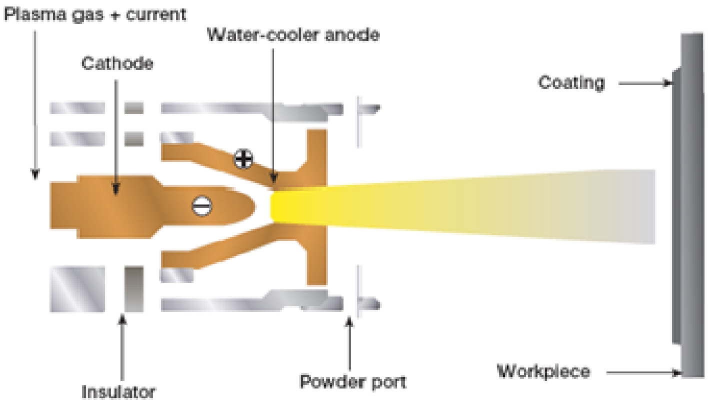

Figure 6-15 Plasma spray

The plasma spray technology used at Necsa, Figure 6-15, is a plasma torch whereby the powder (material composition of the barrier layer) is introduced into the tail flame of the plasma. The advantage of this system is that the plasma gas can also only contain inert gas (such as He, H_2, N_2 or mixtures).

Various methods can be used to obtain SiC powders or to apply a SiC layer onto a substrate. Due to the very high temperature and high energy density, plasma techniques are widely applied for SiC powder production. The injection of chlorosilanes ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2) into induction plasmas containing C_2H_4 and NH_3 will result in the formation of ultrafine powders composed of Si, SiC, Si_3N_4 and C [225]. Induction plasma synthesis of other carbide powders (such as WC) by means of radio frequency (RF) thermal plasmas is also possible [226].

Plasma spraying of SiC and Si_3N_4 containing powders or powder mixtures using argon/hydrogen atmospheric can be employed to produce composite coatings [227], Commercially available SiC powder can also be plasma sprayed onto substrates by feeding the powder inside a plasma flame stream obtained by a direct current (DC) plasma torch. Argon gas (and in most instances a small amount of hydrogen gas) is used to prevent oxidation of the SiC to SiO_2 and CO [228]. The substrate temperature is one of the key parameters that affect coating quality in many coating processes. The temperature can be controlled in most instances by adjusting the substrate distance from the plasma flame [229].

The use of plasma spraying/sputtering that was successfully demonstrated at Necsa to create a coating barrier on different substrates will be extended to the creating of a SiC layer on the suggested waste forms.

7. Conclusions

The aim of turning waste into a waste form is to render it into a stabilized solid matrix suitable for safe storage or disposal at a final site, such as a geological repository. For example, taking a radioactive liquid waste stored in tanks and converting that into a durable solid waste form such as a glass, ceramic or cement, reduces the risk to the environment, the workforce at the facility and the local community. The types of potential waste form materials for radioactive waste can be broadly classified as glasses, ceramics, glass-ceramics, cementitious materials and polymers. In this chapter the historical development and properties of candidate glasses, ceramics and glass-ceramics for nuclear high- (HLW) or intermediate- level waste (ILW) are reviewed. Cementitious waste form materials are also discussed specifically in the context of waste arising from Mo-99 production. This chapter is a survey of the research and development efforts in these materials for use as nuclear waste forms as well as their various production technologies, including melting, sintering and hot isostatic pressing.

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CHAPTER 3: THE APPLICATION OF WASTE ACCEPTANCE CRITERIA TO WASTE FORMS USED TO IMMOBILIZE WASTE FROM MO-99 PRODUCTION

1. INTRODUCTION

The aim of turning waste into a waste form is to render it into a stabilized solid matrix suitable for safe storage over the long-term or disposed of at a final site, such as a geological repository or other engineered disposition facility. For example, taking a radioactive liquid waste stored in tanks and converting that into a durable solid waste form such as a glass, ceramic or cement, reduces the risk to the environment, the workforce at the facility and the local community. In this chapter the classification of radioactive waste is discussed from a global perspective and is applied to waste produced from the production of Mo-99. Specific waste acceptance criteria and tests for the waste forms generated in this project for Mo-99 waste are proposed at the end of the chapter.

1.1 Classification of Radioactive Waste

As radioactive waste is generated in a number of different kinds of facilities, there is a variety of current, legacy and future radioactive waste streams to be classified. They have different chemical compositions and physical forms with levels of radioactivity ranging from just above background to those that are extremely hazardous to human health. Coupled to this, some wastes contain fissile materials that add additional criticality, safeguards and security concerns. The international concept of classifying wastes is to first consider the level of activity and the half-lives of the radioisotopes present (Figure 1-1 and Figure 1-2). The most internationally common overlying standard is the International Atomic Energy Agency (IAEA) General Safety Guide[i] (GSG) *Classification of Radioactive Waste* [1]. However while some countries follow such guides [2], others such as the USA have historically developed their own standards. Classification is further complicated by the inclusion of toxic non-radioactive materials, organics, etc. in some wastes, and such wastes are commonly referred to as "mixed wastes". For instance Hg is/was sometimes used as an aid in dissolution of Al-clad fuels and U-Al alloy targets and hence is present in some wastes from Mo-99 production.

Further complications arise from the presence of long-lived isotopes, typically transuranic ones. In Mo-99 production, the U-rich filter cake from an alkaline leaching process would be classified as "long-lived". While transuranics such as Pu-239 are also present in the Mo-99 wastes, the short irradiation period for Mo-99 targets, typically 7-10 days, means their levels are very small and well below what one would find in, e.g. used fuel.

In Mo-99 production the higher activity wastes would typically be classified as intermediate-level waste (ILW), even after cooling off for a few years. Traditionally [3], the boundary between ILW and high level waste was set at a heat output from the decay of radioisotopes of 2 kW/m^3 and the boundary between ILW and low level waste (LLW) was that at which shielding was required (contact dose of 2 mSv/hr). In addition, there is a distinction made between short

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[i] An IAEA Safety Guide is a set of recommendations on what constitutes good practice, which if followed will enable the organisation owning the waste to comply with safety requirements.

and long-lived wastes with the boundary between them typically set at 4000 Bq/g of long-lived isotopes [3]. There are also exempt wastes, defined as waste with levels of radioactivity that are so small they are exempt from regulatory control. Additional categories have been created such as "very short lived waste" and "very low level waste". From a disposal perspective short lived waste is considered suitable for near-surface facilities and long lived waste (and HLW) requires a more permanent solution, such as an engineered or geological facility.

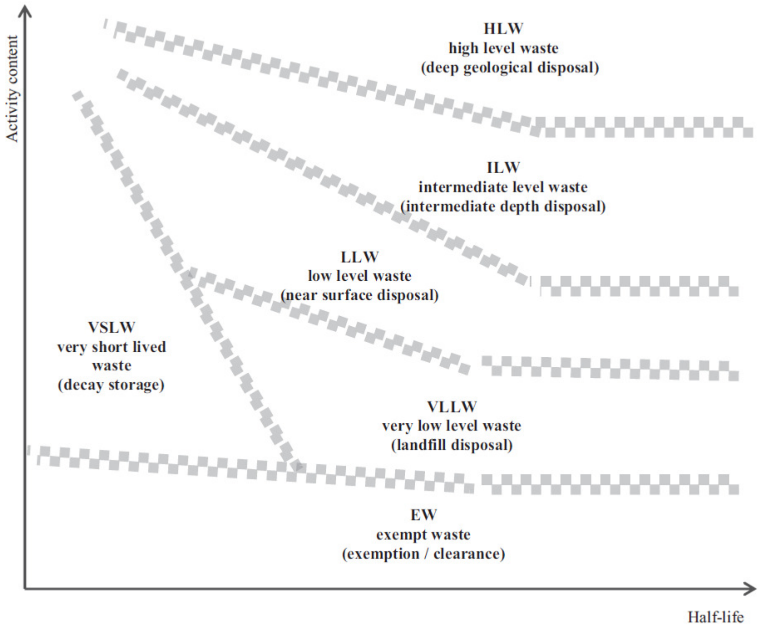

Figure 1-1 The IAEA concept of radioactive waste classification, taken from Reference 1

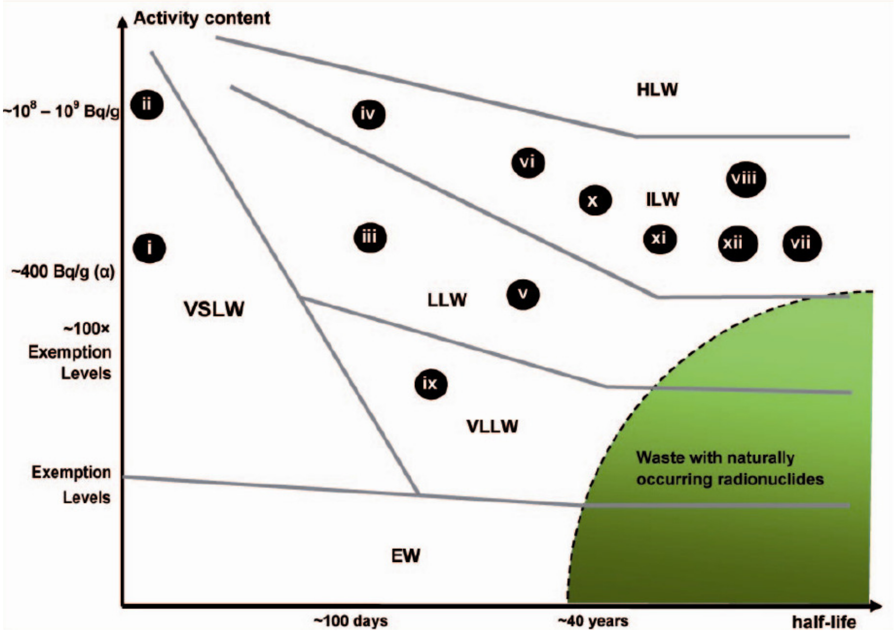

Figure 1-2 An example of the waste classification scheme adapted from Figure 1-1 above by the Australian Radiation Protection and Nuclear Safety Agency taken from reference 2. The roman numerals refer to examples in the reference.

While both HLW and ILW require shielding, ILW due to its lower heat output does not require “provision for heat dissipation”. In the updated version of the Classification System [1] the heat output has been omitted. This is because the new standard for classification and treatment is more closely related to the disposition options. Hence the heat output limits for a waste package should now be linked to the safety cases for the disposal facility.

Other methods of classification exist, for example, the British in determining the amount of waste to be returned to the customers of the THORP reprocessing facility use the integrated toxic potential [4] methodology. The toxic potential is derived from data within the International Commission on Radiological Protection (ICRP) and is defined as “the volume of water into which 1 m^3 of the waste would have to be completely dispersed so that the water is still considered safe to drink” [4,5]. The integrated toxic potential is derived by integrating this toxic potential over a period and in the UK 500 to 100,000 years was used. This gives a “nominal value” for the toxicity of the waste over the longer term. This method is used as part of the UK waste allocation and substitution policy [6].

1.2 Generic Waste Acceptance Criteria Concepts

Waste Acceptance Criteria (WAC) are the standards against which a radioactive waste package is assessed. Radioactive waste package is defined as the waste form, any overpack and the canisters/containers, into which the waste is emplaced for storage or disposal. The IAEA describes the nature of waste acceptance criteria in its General Safety Requirements Part 5 Document *Predisposal Management of Radioactive Waste* [7] (pp. 19-20) as:

> “…
>
> ***Requirement 12: Radioactive waste acceptance criteria***
>
> *4.24. Waste acceptance criteria have to be developed that specify the radiological, mechanical, physical, chemical and biological characteristics of waste packages and unpackaged waste that are to be processed, stored or disposed of; for example, their radionuclide content or activity limits, their heat output and the properties of the waste form and packaging.*
>
> *4.25. Adherence to the waste acceptance criteria is essential for the safe handling and storage of waste packages and unpackaged waste during normal operation, for safety during possible accident conditions and for the long term safety of the subsequent disposal of the waste. Waste packages and unpackaged waste that are accepted for processing, storage and/or disposal shall conform to criteria that are consistent with the safety case.*
>
> *4.26. The operators’ procedures for the reception of waste have to contain provisions for safely managing waste that fails to meet the acceptance criteria; for example, by taking remedial actions or by returning the waste. …”*

Therefore, WAC set the limits for acceptance of a waste package into a store or repository and these criteria are developed with reference to a safety case for the store or repository. The primary aims of the WAC are to ensure that the underpinning nuclear safety principles [8] are adhered to. This is stated on page 29 of the IAEA general safety requirements document, *Predisposal Management of Radioactive Waste* as:

> *"… on various elements of predisposal management of radioactive waste stipulate that the waste generated is required to be kept to the minimum practicable and that interdependences among all steps and the application of waste acceptance criteria are required to be taken into consideration, in compliance with Principles 5, 6 and 8. …"*

Of course the other principles still apply. Principle 5 is the "optimization of protection", principle 6 is the "limitation of risks to the individual" and principle 8 is the "prevention of accidents". Therefore, WAC must strive to meet the ALARA (as low as reasonably achievable) principle with the waste form/package and the process to convert the waste to a stable form suitable for storage, minimizing the risks to the individuals and the environment. This will require oversight, a robust process, and management, quality, security and safety systems to ensure the safe storage of the waste. The overall aim of radioactive waste management is to protect both people and the environment [9] with a need to meet Principle 7 "protection of present and future generations" [8]. Therefore WAC criteria must also address the long-term aspects of radioactive waste, such that it is converted into a form that has long-term stability, e.g. conversion of a liquid to a solid in the first instance.

Given the variety of wastes and potential waste forms, plus the variations in local standards/ regulations, environmental conditions and means of storage/disposal, the WAC developed by the IAEA are of necessity generic (Table 1-1). Specific WAC are developed by local regulators to meet the requirements of each situation. Often underlying specifications for the waste form and process used to produce the waste form are developed to ensure the waste form produced meets the WAC. These are sometimes referred to as Waste Product Specifications or Waste Acceptance Product Specifications (WAPS). These are supported by quality systems that ensure the waste meets these specifications. For example, the US Department of Energy (DOE) developed WAPS for its vitrified waste forms [10] and a waste acceptance document [11] supported by a quality system [12] for the now halted Yucca Mountain Repository.

The WAC should be such that they assist in producing a waste form that can be handled when moved, does not degrade during storage, can be transported safely to the site of final disposition and will perform acceptably when emplaced.

A challenge for waste producers is the changing nature of regulations/criteria or the absence of criteria, if their country has yet to finalize a disposition path. Producers should anticipate future requirements such that once the waste is conditioned to create a waste form, further costly treatment is unnecessary. This will require discussions with relevant parties [13,14].

1.3 Characterization of Radioactive Waste

A fundamental requirement in the treatment of radioactive waste is the characterization of the waste [7,14]. This applies to all categories of waste: low, intermediate [14] and high level [13]. Classification not only serves to provide the information necessary to initially design the waste treatment process and waste form, but also provides the information necessary to validate the actual treatment process and hence meet quality assurance standards. Some form of testing and characterization will also be required for the entire waste package system in order to meet regulatory requirements and satisfy the operators of the store or repository. The most fundamental aspect of the characterization process is to determine the classification of the waste [1]. Another fundamental aspect of any characterization data, and data gathered for the WAC is the need for traceability. The WAC for the form may vary over the life cycle of the waste and require different characterization methodologies and criteria for each phase, notably production, conditioning, treatment, storage, transport and disposal. The overpacks, containers/canisters and transport flasks will also have to undergo a design and testing process to ensure their suitability. IAEA characterization requirements are stated as [9]:

> ***"Requirement 9: Characterization and classification of radioactive waste***
>
> *4.10. Radioactive waste has to be characterized in terms of its physical, mechanical, chemical, radiological and biological properties.*
>
> *4.11. The characterization serves to provide information relevant to process control and assurance that the waste or waste package will meet the acceptance criteria for processing, storage, transport and disposal of the waste. The relevant characteristics of the waste have to be recorded to facilitate its further management.* ***At various steps in the predisposal management of radioactive waste, the radioactive waste shall be characterized and classified in accordance with requirements established or approved by the regulatory body.***
>
> *4.12. Radioactive waste may be classified for different purposes, and different classification schemes may be used in the successive steps in waste management. The most common classification is that made from the perspective of its future disposal ..."*

As the chemistry, radiological and physical forms of the many radioactive waste streams which exist vary, the method applied to characterization the data will also vary. Furthermore, the testing of radioactive materials is costly; hence a cost benefit assessment is needed to determine the appropriate level of testing, such that sufficient testing is carried out to be able to design the storage/disposal facility and associated overpacks, canisters, containers or flasks.

In some cases indirect methods of control may be feasible when operating treatment processes [14]:

> *"… However, it may be possible to apply indirect methods of characterization based on process control and process knowledge instead of or in addition to sampling and the inspection of waste packages in order to avoid undue occupational exposure. …"*

If a process is well defined, with known inputs and with sufficient valid test data that define the process window which produces an acceptable waste form, then provided the plant is operated within the process window and the inputs to the plant do not vary, or remain within specified ranges, then the plant may operate and produce acceptable packages without extensive testing. The process of sampling and then testing materials from a radioactive process is not without risk to human health or the environment. In addition, the funds available to treat radioactive waste are limited. This clause provides a means of balancing the costs and risks associated with testing and treating radioactive wastes with the aims of treatment, which is to transform the waste into a stable form. If the prescribed process becomes prohibitively expensive then this may discourage efforts to treat the waste e.g. liquid radioactive wastes in tanks are difficult to characterize fully, but if left untreated due to prohibitively difficult characterization requirements or costs, then the hazard to the environment and humans will remain and increase as the tank ages.

1.4 Application of Generic Waste Acceptance Criteria

The WAC developed by the IAEA are of necessity generic and descriptive (Table 1-1). For this work however, it is essential to develop a succinct performance-based WAC criteria, with defined tests and acceptance values. Performance-based criteria allow comparison of a variety of forms (ceramic, glass, glass-ceramic, cementitious etc.) enabling selection of the most appropriate waste form from a risk-based approach. Prescriptive requirements, such as the amount of crystallinity allowed in a waste form for example, are discouraged as this does not allow comparison of ceramics, glass-ceramics and glass.

A list of generic specifications for waste packages is provided in Annex II of IAEA safety guide [14] and IAEA TECDOC [15], contains information on the predisposal management of LLW and ILW. However, the parameters given such as permeability of the waste form, curing, shrinkage and percentage water incorporated are targeted at cement/grout type waste forms, so modifications would be required for other forms e.g. a vitreous waste form. A danger in setting waste acceptance criteria for waste packages targeted to a repository is to be so specific that improved waste forms are consequently excluded. For example, one might set a waste criterion such as a water content range that produces acceptable cement; consequently, a more durable waste form such as a glass would not meet the specification as it is essentially free of water.

The waste acceptance criteria apply not only to the waste form, but also the container for the waste form (e.g. the drum for grout based waste forms or canister for HLW glass) and the overpack (e.g. a flask, drum, or in some cases a shielded storage facility). As stated above, throughout the life cycle of the waste form different WAC can apply. Hence a WAC being specific not only for the produced form, but also the waste package during storage, transport and final disposition at a geological repository. To illustrate the waste form may be placed in a transport flask during transport, in which case the cask forms part of the WAC for transport. For this current package of work the focus is on WAC for the waste form, however, generic criteria for the overpack and container are also given in Table 1-1 for reference. One needs to consider material compatibility when matching the waste form and container.

Underpinning the technical criteria is the need for robust quality control and traceability systems, applied to the characterization, testing procedures and processes; in order to produce valid data and information. This includes a labeling system that can survive the storage period and that identifies the waste package and its contents. In addition any work needs to be carried out by staff with appropriate training, skills and experience.

The IAEA has also published technical documents on the establishment of criteria specific to ILW with comments on “Methods for demonstrating compliance with Waste Acceptance Criteria” [15]. At the time of publication the main matrices for immobilizing ILW were cement-based, bitumen, some polymers and borosilicate glass. Immobilization was achieved by encapsulation or intimate mixing. For the former, the waste components/particles were contained within such matrices, either by direct contact or by encapsulation in a container that contained ILW, in which case permeability of the encapsulation matrix became important. For the latter, the waste, usually liquid, was mixed with additives (e.g. grout) to achieve a near homogeneous monolithic mix, which was cast in the container. The method chosen depended upon the physical and chemical form of the waste.

Hence, a considerable portion of such specifications were devoted to the container. In particular because such containers were usually stacked in an interim store, the specifications emphasized the need for mechanical strength to enable stacking. Also important are the interaction of the container with the waste/waste form and the resistance of the container to corrosion. For example, the UK developed 560 L stainless steel drums for the immobilization of its intermediate level wastes via a cementitious route [16] with plants operating at Dounreay and Sellafield treating liquid ILW and Magnox cladding respectively.

With regards to ILW waste, IAEA recommends setting limits (threshold recording limits) on the input wastes, such as activity and fissile content, below which the conditioned waste will meet acceptance criteria [15].

The key to meeting WAC is to demonstrate that the waste package and constituent components comply with the criteria. Four methods of gathering quantitative data or information were identified [15]:

1. Direct measurement/testing of the waste package or its components during or after processing, for example, a radiological or chemical analysis of the waste form.
2. Calculation using suitable models of criteria from data obtained from waste or components of the waste package.
3. Correlation of measured values with the criteria, e.g. based on a test program if it can be shown that the process parameters are kept within certain limits an acceptable waste form is produced. So e.g. controlling the melting temperature and time which has been shown to ensure that the components have been reacted to produce a homogeneous glass.
4. Correlation to basic research, development or commissioning data, e.g. fundamental R&D on cements enables the use of mixtures that have been well documented to produce acceptable products.

Table 1-1 IAEA Generic Waste Acceptance Criteria – measured properties.

IAEA ILW and LLW [14,15]	**IAEA HLW [14] (excluding spent fuel)**	**Comments**
Criteria for the Waste Inputs		
Records of the waste		Use of process records, engineering/process designs, R&D. Need to also consider the retrievability of records over the storage lifetime.
Source		Details of the source and supporting documentation. In particular, determination of the depth and reliability of the records, the validity of the records, gap analysis and the need for additional testing or retesting. Used to determine the amount of characterization necessary.
Radioactivity of the waste Dose	Radiological properties – Activity, dose rate	Measurement of α, β, γ and neutron production of samples or on-line. Dose limits for treatment facilities, such that there is sufficient shielding and distance to prevent unnecessary occupational exposures. Application of ALARA principle.
Fissile content	criticality safety – fissile component	Content of fissile material U-233, U-235, Pu-239 and calculations or measurement of inventory. Assessment of criticality potential and determination of physical and procedural requirements to eliminate the risk of criticality. E.g. vessel design, dimensions, waste loading limits, weight limits, waste form shape and dimensions, etc.
	Any surface contamination of vessels, etc.	Setting of limits, container designs and transfer systems and procedures that reduce the risk of the spread of contamination during processing, preconditioning or transport of the waste. Measurement of fixed and non-fixed contamination, by swabs, etc.
Nuclides present		Radiological analysis of the waste. Identification of radioisotopes or calculation of content with time based on burn-up of fuel/target and decay time or source age and decay time. Samples may be taken or on-line monitors installed. Used for life-cycle analysis to determine optimum time to treat the waste. Identification of key radionuclides and their impact on design of the process and waste form. Changes in dose with time. Note the focus should be on key radioisotopes; there may be little benefit in the cost of identifying radioisotopes present in trace amounts.
	Thermal properties – heat output	Calculated or measured heat output and determination of its impact on the processing and final waste form.
Chemical composition of the waste components	Chemistry of the waste – composition, pH, presence of toxic or corrosive species.	Chemical analysis of the waste, including radionuclides. Boundaries on waste composition based upon studies of waste chemistry variation on the properties of the waste form.

Table 1-1 IAEA Generic Waste Acceptance Criteria – measured properties.

IAEA ILW and LLW [14,15]	IAEA HLW [14] (excluding spent fuel)	Comments
Physical nature of the waste components	Physical properties – viscosity and density	Description of the nature of the waste, solid, liquid, gas, sludge, slurry, etc. Data will feed into initial waste treatment process design, but will also provide limits for the input beyond which the waste will not be capable of being processed. For example, particle size < x mm to prevent pipe blockage, viscosity within a range that a pump may handle. The nature of the physical property criteria for the waste may therefore vary from plant to plant. For solids - particle size and distribution, particle shape, agglomeration, flow properties, etc. For Liquids - concentration, pH, viscosity, etc.
Volume/weight of waste		In conjunction with chemical/radiological and physical properties is used to determine the maximum weight per package. Also links to engineering design limitations of the plant. The degree of variability in the radiological, chemical, physical characteristics.
Criteria for the Conditioning/Treatment Process		
Details of the process – technical description, process flow diagrams, critical parameters.		Identify key parameters during processing that impact upon the properties and performance of the waste form or have safety implications for plant operation.
“Means of controlling free liquids, powders, explosives and compressed gasses, toxic metals and compounds, hazardous materials, complexing agents, organics, fissile content, activity content.”		Identify potential hazard and develop safety measures to mitigate the risk. Identify components which may impact upon the properties of the waste form produced. Obtained via records or direct measurement.
Details of any pretreatment		Records and/or characterization
Description of how the process will enable compliance with the product WAC, e.g. fissile content, radioactivity, etc.		Safety/Risk assessment for the process, plus test data to back the analysis
Chemical Physical Properties of the Waste Form		
Input Raw Materials	Chemical and physical properties of the input additives	Develop specifications for raw materials from R&D program. Application of QA and analysis (in-house or by the supplier) to ensure raw materials meet specifications. Direct measurement of properties or use of certified materials. Need to also understand the effect of age on materials and “use by” date. Need to control storage conditions to prevent spoilage.

Table 1-1 IAEA Generic Waste Acceptance Criteria – measured properties.

IAEA ILW and LLW [14,15]	IAEA HLW [14] (excluding spent fuel)	Comments
Waste Loading	Mass fraction of waste. , Waste limits	Target waste loading derived from experimental research program. Waste loading variation studies to define range of acceptable waste loading. Requires documented evidence to ensure compliance. Will require process control to ensure waste loading limits are not exceeded, possibly with testing.
Chemical composition of the waste form/waste	Chemical composition	Chemical composition and acceptable variation ranges. Key analyses are also required for components of the waste that present additional, non-radioactive hazards, e.g.: combustible/flammable liquids and solids, oxidizers, corrosives (also for plant and equipment life), explosive materials, toxic materials (e.g. Cd and Hg, these can require additional WAC), reactive materials, gas evolving materials or those capable of evolving gas, organics, asbestos, biological components, components that may require regulatory notification. Require systems to identify and if possible exclude such materials, or if present the process renders them into a form that is suitable for disposal/storage.
Density, porosity		Measurement of the density and porosity of the product or correlation of size and dimensions of container with development and commissioning test program densities.
	Relevant properties of form during processing – e.g. viscosity of glass.	Identify key properties of the waste form as it is processed and control methodologies and measurement parameters of process equipment and inputs to ensure they are met.
Permeability to water and permeability to gases		Density and porosity of the product, direct or indirect measurement of permeability, degree of interconnected porosity. For certain waste forms, such as cement, the permeability of the material to liquids and/or gases is a key parameter.
Its homogeneity and the compatibility of the waste with the matrix;	Homogeneity of the waste form – distribution of radionuclides.	Measured homogeneity of the product at the micro and macro scales either by direct measurement of the waste form product or by utilizing data from a research/commission program.
Its thermal stability		Calculated or measured radiogenic heat and modeling of storage/repository conditions to derive expected temperature profiles and heat evolution from the waste form/package. Thermal tests on matrix stability at temperatures likely to be encountered, under storage conditions or in the repository.
The percentage of water incorporated, exudation of water under compressive stress, shrinkage and curing[ii]		Applicable only to certain waste forms, e.g. grouts, geopolymers, etc. Direct measurement of waste form or utilization of data from a test program.

[ii] These are related mainly to cement/grout materials

Table 1-1 IAEA Generic Waste Acceptance Criteria – measured properties.

IAEA ILW and LLW [14,15]	IAEA HLW [14] (excluding spent fuel)	Comments
The leachability/corrosion rate of the waste form	The stability of the waste form, its corrosion/leaching behavior under conditions relevant to a repository. Leaching of important radionuclides.	Measured short term and long term leach tests. Quality Assurance tests such as PCT under deionized water, or other medium. Long-term tests to determine leaching mechanisms and develop models for behavior of the waste form/package under geological repository conditions.
Chemical and Physical Properties of the Container		
Container dimensions	Container dimensions	Direct measurement and comparison with specifications.
Materials of construction	Materials of construction	Certified materials or direct testing.
Its porosity, permeability to water and permeability to gases. The characteristics of the lidding and sealing arrangements	quality of seal, e.g. weld	Test data, e.g. leak tests, to measure such properties. Engineering design and testing of the container to ensure compliance with sealing criteria.
Its thermal conductivity	Thermal conductivity of container material	Test data on actual container material or reference to specifications for certified materials. Possible application of models to show heat evolution from the waste package.
Container solubility and corrosion in corrosive atmospheres or liquids such as water or brines.	Corrosion resistance of container	Corrosion resistance of the container under storage and repository conditions. Measurement and modeling of behavior of the container material. Either from test data or with the use of certified materials with known corrosion behavior.
	Compatibility of container material with the waste form	From R&D test data and reports
Physical Properties of the Waste Package		
Labeling of package for quality assurance purposes	Labeling of package for quality assurance purposes	Requires an appropriate QA system, including records required for each package and records storage procedures. Labels with long-term life (may require a test system). Need to also consider the retrievability of records over the storage lifetime.
Package weight		Maximum weight specified for handling, transport and storage. In the case of fissile materials there may be a maximum weight associated with the amount of fissile materials per unit volume of the store.
The number of voids in the container (which are to be minimized)	Dimensions of container or package	Drawings of the package including spaces and means of fixing the waste form.

Table 1-1 IAEA Generic Waste Acceptance Criteria – measured properties.

IAEA ILW and LLW [14,15]	IAEA HLW [14] (excluding spent fuel)	Comments
Its sensitivity to changes in temperature.		Assumed to mean both thermal cycling that may be experienced during storage, e.g. night-day, summer-winter, plus changes due to radiogenic heat. It may also include sensitivity to thermal conditions encountered in a repository. Can be done directly by testing response to thermal cycles or indirectly via modeling.
Mechanical properties of the waste form and package		
The mechanical properties of the waste form include its tensile strength, compressive strength and dimensional stability.		Direct measurement of appropriate mechanical properties of the waste form with possible application of mechanical models to determine the behavior of the waste form and package under load.
The mechanical properties of the waste package include its behavior under mechanical (static and impact) or thermal loads.	The strength of the package in relation to stackability and handling – e.g. drop test	Load bearing test on the waste package. Impact tests on waste package system, fire resistance, for transport, storage and disposition safety scenarios
Radiological Properties Of The Waste Form And Package		
Surface contamination		Maximum level for waste form and package exiting from the process line and maximum level for contamination on over-pack or flask. Determined by direct measurement of fixed (if possible) and non-fixed contamination
Radiation Stability	Radiation Stability	Stability of the package to radiation damage it will experience over its lifetime. The package must retain sufficient stability to last through its period of storage. When disposed of under geological conditions, the key parameter is the effect of radiation damage on the ability of the waste form/package to retain the long-lived radionuclides. Transmutation effects on the waste form should also be considered.
Dose rate		Dose rate at surface of package with target such that the dose not exceed regulatory limits. Requires limits for two safety scenarios: (i) handling during process and transport of individual packages; and (ii) conditions in the storage facility, where multiple packages are likely to be present. Note this varies depending on the store design, degree of shielding, how many packages are in the store, whether and how often inspection is required.
The Containment Capability of the Waste Package System		
The capability for the fixation and retention of radionuclides; and the diffusion and leaching of radionuclides in an aqueous medium		See leach testing for waste form above. Testing/assessment of waste package under geological conditions. Assessment of the release rates of key radionuclides from the package under repository conditions. Repository modeling of release scenarios. Interrelated compatibility of package materials, waste form and repository materials.

Table 1-1 IAEA Generic Waste Acceptance Criteria – measured properties.

IAEA ILW and LLW [14,15]	IAEA HLW [14] (excluding spent fuel)	Comments
The release of gas and tritium under standard atmospheric conditions or the conditions in a repository		Measurement and calculation of potential gas generation and releases from the package.
The water tightness and gas tightness of the package sealing device.		Measurement of water and gas tightness of package under relevant safety scenarios for transport, storage and disposition.
Stability of the Waste Package System		
The overall stability of the waste package with respect to: (a) Its behavior under temperature cycling (b) Its sensitivity to elevated temperatures and behavior in a fire (c) Its behavior under conditions of prolonged radiation exposure; (d) The sensitivity of the matrix to water contact (e) Its resistance to the action of micro-organisms; (f) The corrosion resistance in a wet medium (for metal containers); (g) Its porosity and degree of gas tightness; (h) Its potential for swelling due to the internal build-up of evolved gases.		This part of the IAEA document reiterates specific tests for package components (see above): This section refers to an overall assessment of the packaging system under various scenarios. References to engineering and regulatory guides and codes. Design specifications to ensure the package meets stability requirements. *"… The results of work carried out to assess and demonstrate the integrity of the waste package against each of the identified requirements should be reported"* [15]

2. General Waste Criteria situation in Mo-99 producing Countries

The following is a brief overview of the situation in key Mo-99 producing countries. Most refer to the generic IAEA criteria and many have not yet developed specific criteria for the waste from Mo-99 processes as they have not decided upon the disposition route. Some case examples are given below.

2.1 South Africa

South Africa like most countries has broadly adopted the IAEA waste acceptance criteria methodology. Necsa have internal "commercial-in-confidence" documents of waste acceptance criteria for Vaalputs. However, this is currently under review with the government enacting legislation to form the National Radioactive Waste Disposal Institute, independent of Necsa, to oversee radioactive waste management in South Africa [17].

The classification is mainly related to low level wastes. Criteria are similar to those of the IAEA, include classification of the waste, restrictions on liquids – only solid wastes allowed, contact dose limits for packages, activity limits for the wastes, restrictions on hazardous materials (pyrophoric, explosive), no pressurized containers allowed. There are also limits on package materials, dimensions and weight. Quality measures such as labeling, verification systems and records. There is also provision for a qualification process.

2.2 Australia

Australia has adopted IAEA Guidelines and Standards with some editing for local conditions. Australia produces Mo-99 from low enriched uranium. Mo-99 that ANSTO produces is classified as ILW and LLW [2]. Australia has no HLW. Australia has produced a Code of Practice for near-surface disposal, but has no specific criteria for a repository. It is suggested that the following criteria [18] would likely apply for a near surface facility [19]:

"…

- is a solid;
- has stable chemical and physical properties;
- contains no free liquid;
- is compatible with concrete and natural barriers;
- does not contain compressed gases;
- contains no hazardous material, such as PCBs, infectious waste, putrescible materials;
- contains no organic liquids or chelating agents;
- is structurally stable and has long term compressive strength;
- will not generate gases;
- does not contain flammable material (excluding paper, plastics or cloth which may be included within normal radioactive waste);
- contains less than 10 percent voidage; and

- can be placed into a package that meets the *Code of Practice for the Safe Transport of Radioactive Material* (ARPANSA 2008). …"

For geological disposal the criteria are generic [18]:

- is a solid;
- has stable chemical and physical properties;
- is small enough to fit in a borehole;
- contains no free liquid;
- is structurally stable; and
- can be placed into a package that meets the *Code of Practice for the Safe Transport of Radioactive Material* (ARPANSA 2008).

The current plan in Australia is for a long-term store [20]. But as such a store does not exist the criteria are generic. Criteria categories given in Section 3.2 for waste acceptable for a store are

(a) the radionuclides should be immobile

(b) the waste form and its container should be physically and chemically stable

(c) thermal energy should be removed from the waste form, where required

(d) a multi-barrier approach should be adopted in ensuring containment

(e) the waste form and its container should be resistant to degradation

(f) the storage environment should optimize waste package lifetime

(g) the need for active systems to ensure safety and security should be minimized through use of passive controls

(h) the need for monitoring and maintenance to assure safety should be minimized through use of passive controls

(i) the need for human intervention to assure safety should be minimized through use of passive controls

(j) the storage building should be resistant to foreseeable hazards

(k) access should be provided for response to incidents

(l) there should be no need for prompt remedial action in the event of an incident

(m) the waste packages should be able to be inspected

(n) the waste packages should be retrievable for inspection or reworking

(o) the design life of the storage building should be appropriate for the storage period prior to disposal

(q) the waste packages should be acceptable for ultimate disposal or at least not preclude future disposal options

From a waste form perspective, points (a) to (e), and (q) are the most relevant to the waste form, although inspection and monitoring will be important if safeguard materials are present. For wastes that will be produced in the ANSTO Synroc plant, Waste Product Specifications adopted from these criteria have been developed for verifying product quality. For example, the leaching specification that has been suggested is based on a PCT-B type tests at 40°C for 7 days [21]. It should be noted that this test is designed for assessing glass waste forms, and for acceptance the mean concentrations of lithium, sodium, and boron in the leachate, after normalization for the concentrations in the glass, must be less than those of the benchmark glass. It is suggested this test be applied to all waste forms with pass limits applied to all elements.

2.3 Europe

There are several European countries that produce or plan to produce Mo-99, or have active repository assessment processes. Countries have developed their own waste management policies, but those in the European Union are also subject to directives from the European Commission [22]. For long-lived ILW, which is the major Mo-99 waste category, ANDRA policy e.g. requires a "definition of waste-package: acceptance criteria, disposal specifications and control modalities" [23], but there is a lack of detailed specifications.

Those specifications available for Mo-99 waste are not all publicly available; some are classified as commercial-in-confidence. ANSTO has access to specifications for cemented ILW being returned to it from former UKAEA, Dounreay, and vitrified ILW from AREVA in France, as part of the contracts for the reprocessing of spent research reactor fuel.

2.4 Canada

Canada has substantial volumes of waste from HEU Mo-99 production including the Fissile Solution Storage tank Waste (FISST), 175 kg of 93% enriched HEU as 7.2 g/L liquid. Currently AECL is looking at shipping the waste to the Savannah River Site in the US for treatment. Currently the Canadian option is to cement the wastes, as an interim storage measure [24].

2.5 The USA

The USA currently has no domestic production of Mo-99, however as it is planning future production a general perspective is given here. The USA operates under a different system to the IAEA. It developed prescriptive specifications for the operation of Waste Isolation Pilot Plant (WIPP) [25] and the now stalled Yucca Mountain repository [11].

Details of the WIPP WAC are outlined elsewhere [25], which also references other US CFRs (Code of Federal Regulations) that apply to the process. The criteria are discussed in Sections 3 (contact handled waste), 4 (remote handled waste) and Appendix A of Reference [25]. Criteria of interest to this project include [25]:

- The requirement for a quality system to be implemented that provides a manifest of the waste contents, container and data for each package, plus a system to control such records.

- The waste needs to be characterized – the preferred method is direct measurements although in some cases, because of the variability, age and nature of the waste streams, the concept of "acceptable knowledge" is applied using accessible records and data.
- The highest level of categorization of the waste packages separates packages that can be contact handled from those requiring remote handling and this is defined by dose rates from the waste packages.
- The need for regulatory oversight is emphasized - in WIPP's case there are five oversight bodies.
- The repository has cumulative limits for "specified radionuclides (^{241}Am, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{233}U, ^{234}U, ^{238}U, ^{90}Sr, and ^{137}Cs), free water, ferrous metals, non-ferrous metals, and CPR (cellulose, plastic, rubber). Interestingly ^{235}U is not present on the list.
- There is provision for allowing appropriate PCB contaminated wastes to be disposed of at WIPP.
- There are criteria for acceptable types of waste containers, their weight, center of gravity, surface contamination, labeling/identification, dunnage, and required filter vents to prevent gas buildup and pressurization.
- The radiological criteria in the WAC for WIPP relate to the ten "WIPP-tracked" radionuclides with the TRU content set with a lower limit, to ensure the repository capacity is effectively used, of > 100 nCi/g (3.7 kBq/g) and payload containers for alpha emitting TRU isotopes with a > 20 year half-life of waste producing > 100 nCi/g.
- The ten tracked radionuclides (^{241}Am, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{233}U, ^{234}U, ^{238}U, ^{90}Sr, and ^{137}Cs) and other radionuclides that contribute significantly to the activity, shall be measured and quantified – using methodologies qualified by WIPP and discussed briefly in the document.
- The fissile material content is limited and is calculated using the "^{239}Pu Fissile Gram Equivalent" methodology/"^{239}Pu Equivalent Activity" calculated with limits set per container type.
- There are decay heat criteria to ensure thermal limits for the repository are not exceeded.
- There are limits on the amount of free water, pyrophoric materials, and hazardous materials.
- It is unacceptable to have materials incompatible with each other or that contain explosives, corrosives or compressed gases.

The US also developed criteria for Yucca Mountain, which was designed for holding spent fuel; plus vitrified HLW from Department of Energy – Environmental Management (DOE-EM) operations. Waste Acceptance Product Specifications (WAPS) were developed for the vitrified wastes that had been planned to be sent to Yucca Mountain [10]. WAPS are:

> *".. The technical specifications of the waste forms producers are required to meet in order to ensure acceptance of their vitrified high level waste (HLW) into the Civilian Radioactive Waste Management System (CRWMS). …" [10]*

These specifications were developed prior to the issuing of the Office of Civilian Radioactive Waste Management (OCRWM) waste acceptance system. However, the systems are partly integrated with the WAPS rolled into the Waste Acceptance System requirements document (WASRD) [11] in the form of prescriptive requirements for borosilicate glass. There are also prescriptive requirements for spent fuel. The disadvantage of such a system is that it tended to discourage alternative waste forms as they did not meet the specifications set for borosilicate glass, e.g. glass-ceramics, which may have crystals in proportions above that allowed in the specification. The problem was that these crystals in designed glass-ceramic waste forms are durable ceramic phases, whereas the crystals referred to in the glass specifications included soluble cesium molybdate. Ceramics were also excluded, except for spent fuel and a pyrochlore-rich ceramic developed for the immobilization of plutonium, which was listed in Revision 4 of the WASRD [26], but was removed from Revision 5 [11]. Despite this, some of the criteria given in these documents could be adapted to form a specification for ILW. It should be noted that the leaching specification that has been suggested is based on a PCT-B type test with acceptance based on the mean concentrations of lithium, sodium, and boron in the leachate with no defined release rates for any key waste stream radionuclides.

The requirements contain criteria that are broadly similar to those for WIPP such as dose rate limits, container/canister design, etc. From a waste form viewpoint additional requirements were instituted with respect to toxic/hazardous materials covered under the Resource Conservation and Recovery Act (RCRA) 1976 [27], such as Hg[iii], Cd[iv], etc. In the US unless the repository is exempt from RCRA, radioactive wastes containing toxic metals (called "mixed-wastes") have to meet not only the regulations set by the relevant nuclear regulatory body, but also those set by the Federal [28] and often State Environmental Protection Agencies. In order to delist the waste forms for Yucca Mountain they had to either pass the Universal Treatment Standard (UTS)[v] or seek an exemption. The test method for this is the Toxicity Characteristic Leaching Procedure (TCLP)[vi], however the test method does not reflect the conditions experienced in a repository. Materials that fail the test are classified as toxic and would need to be disposed of as hazardous waste, which typically involves some prescribed treatment, such as amalgamating[vii] (for Hg-bearing waste) or cementing followed by disposal at a prescribed facility, such as an underground mine (repository).

For mixed HLW the vitrification treatment is considered acceptable [29,30,31]. This is stated in the Table in 40 CFR, Subpart D, 268.40 – *Applicability of treatment standards*.

2.6 Other Countries

The Russian Safety Regulatory Authority has also adopted many of the principles from IAEA, NEA and ICRP and this is discussed in Reference [32]. The Russian situation is like the US in that it has a multitude of varied waste streams from many different sources. At the specific level, the need for defining the waste input characteristics; characterization of samples of

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[iii] http://www.epa.gov/osw/hazard/tsd/mercury/regs.htm#debri

[iv] According to the EPA the best available demonstrated technology (BADT) for mixed wastes is vitrification and the BADT for radioactive contaminated mercury is amalgamation. Cd is classified as D006 treatment[iv]; this is discussed in the document in pp. 22562-22563 of reference [iv]. The proposed TCLP limit in this document is 1.0 mg/L, which is 9 times the UTS limit although it does mention the possibility of lower limits. BADT determination for Cd wastes was considered to be thermal recovery.

[v] http://www.epa.gov/osw/hazard/tsd/ldr/268_48.pdf

[vi] Method 1311, Toxicity Characteristic Leaching Procedure

[vii] Treated according to 55 FR 22569. (June 1, 1990).

conditioned waste and the establishment of process parameters to ensure the compliance of the waste form is included. Specific examples for cemented, bituminized and vitrified wastes are given. Key measures for the waste form are;

- Activity - type and amount
- Chemical composition
- Homogeneity
- A measure (test) of the durability/leachability/stability of the waste form in aqueous media
- Heat output
- Thermal stability – to radiogenic heat
- Thermal stability under store/repository conditions – e.g. thermal cycling (freeze-thaw)
- Radiation resistance
- Mechanical properties
- Thermal properties
- In the case of bitumen, biological stability

It should be noted however that these basic quality measures for the waste form do not consider fire resistance. Criteria are also given for the waste package and the repository.

Argentina has adopted criteria consistent with IAEA standards with CNEA tasked to "…Propose waste acceptance criteria and conditions for the transfer of radioactive wastes to high, intermediate and low level repositories". However, Argentina has decided to store its spent nuclear fuel and hence has not completed the development of criteria for geological repositories.

3. Waste Acceptance Criteria for Mo-99 wastes

Given the lack of operating repositories for radioactive waste arising from Mo-99 production, the most practical approach for this project is to focus on generic criteria that are directly related to the waste form and its production, with some assessment of its compatibility with its container (the drum for cement, glass canister, etc.). Consideration of criteria for the complete waste package including flasks or other over-pack is beyond the scope of this work. Hence, the focus is on waste form properties, such as the stability, durability, mechanical properties, homogeneity, etc. as the waste form is primary barrier for radionuclide release. Criteria such as absence of explosive, corrosive and pyrophoric materials and compressed gases in the waste form are taken as being present. It should be noted that waste inputs may contain these materials and appropriate precautions need to be taken to ensure their mitigation. Some Mo-99 wastes contain toxic materials, e.g. Hg, and this may require the establishment of some criteria, e.g. a measure of the ability to retain the toxic elements. With the down selection of options, specific processing criteria can also be considered. For example, from a practical operational viewpoint at scale one would prefer a processing route and waste form that would have broad process windows.

3.1 Classification of Mo-99 Waste Streams

The waste streams identified in the sections above would be classified as low level waste or intermediate level waste, with those containing U being long-lived intermediate level wastes. The U-wastes would also be subject to safeguards control, particularly if present as high enriched uranium. Ideally the treatment process would be such that it would render any HEU resistant to extraction by conventional means. ANSTO is currently in consultation with the regulator as to the inspection requirements for its legacy U-bearing ILW once it has been treated. The results of this, if authorized, may be used in this project.

3.2 Waste Form Acceptance Criteria and testing

Specific waste acceptance criteria, specifications and suggested tests are given in Table 3-1 and Table 3-2. Note the tests are to allow comparative testing of various options with each other and with published data to enable an assessment of the waste form options. The tables focus on the waste form. The input waste will have to be characterized for its physical and chemical properties and each process will have specifications/criteria that will need to be met to ensure the waste form produced is acceptable. Table 3-1 provides the succinct performance based WAC criteria, with defined tests and acceptance criteria, Table 3-2 outlines general waste form characterization testing to be performed, stipulating testing standards and expectations for viable products. Other key additional evaluation criteria that are to be considered, for example waste loading, life-cycle costs, and nuclear engineering maturity, are discussed in Chapter 4.

Table 3-1 Specific waste form acceptance criteria for the current project.

Criteria	Testing/Characterization Methods	Demonstration of Compliance
The waste form shall be in solid form over the designated lifetime and placed in a canister		A solid form in a canister. Documented evidence to assure solidity.
Durability and phase stability	All waste forms will be subjected to the MCC-1 leach test *ASTM C1220-98.* "Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste". ASTM International 1998. *Ceramics, glass-ceramics and glass:* *ASTM C 1285 – 02.* "Standard Test Methods for Determining Chemical durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)". ASTM International. 2002. *Cements and Geopolymers:* ANSI/ANS-16.1-2003;R2008 (R=Reaffirmed): Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure.	MCC-1 leach test: Release of all elements and simulated dilute radionuclides is less than $1\text{gm}^{-2}\text{d}^{-1}$ category I). PCT-B type leach test at 40°C (category II) or 90°C (category III) for 7 days: Release of all elements and simulated dilute radionuclides is less than those found for benchmark (EA) glass [33] (geometric surface area). Cements and Geopolymers: The derived value of diffusion coefficient, $D > 6$.
Thermal stability	a) At the macroscopic scale thermal cycling tests up to 300°C, with observation for cracking, etc. b) Differential thermal analysis and thermogravimetric analysis for weight loss and phase change data with off-gas analysis, up to 300°C? Aimed at ensuring that the package remains stable under storage Test methods: ASTM E2550 and ASTM E1356	Absence of changes in structure and chemical composition upon reheating up to 300°C that compromise waste form performance.[a] No expected volatile content that creates pressure build-up No weight loss that would compromise waste form up to 300°C.
Non-flammable	a) Composition analysis	No known flammable composition
Thermal properties	As required, but waste is not heat generating. Would typically include a) Thermal diffusivity/conductivity (ASTM E1461) b) Heat capacity (ASTM E1269) c) Thermal expansion (ASTM E228) These are more important for HLW forms but some confirmation of the expected radiogenic heat output and effect on the integrity of the repository.	Calculated total heat generation rate for canisters shall not exceed 1500 watts per canister. Waste form thermal expansion will not breach packaging.
Mechanical properties	Compressive strength test. The material must be of sufficient strength to withstand handling and storage conditions.	Compressive strength of waste form >5 MPa[c]

Criteria	Testing/Characterization Methods	Demonstration of Compliance
Radiation stability over lifetime	The criterion to assess is not whether the sample undergoes transformation during damage, but whether the sample loses its ability to retain the radionuclides. Therefore tests would involve the leach testing of damaged samples. The assessment of the effects of radiation on the waste package and its contents is based on mathematical models and R&D calculations and experiments. For example a Co-60 source can be used for assessment of radiation effects. Alpha-radiation tolerance is to be considered but not part of the testing regime.	γ radiation tolerance > 10^8 Gy Irradiated sample must pass aqueous durability tests above.
Fissile content	Provide qualified data to ensure radioactive waste can demonstrate critical safety.	Confirmation/modeling to demonstrate no criticality concern in processing or in the repository.
Non-proliferation	Resistance to plutonium extraction via dissolution in 4 M HNO_3 [34]	Fissile material cannot be extracted by conventional PUREX reprocessing.
Water incorporation and exudation on compression	Loss on Ignition tests (ASTM D7348) Neutron Imaging (NRAD)[b]	< 0.5% free water
Waste Form Compatibility	Assessment or testing of the compatibility of the waste form with can, overpack, package materials. To ensure that no detrimental effects such as corrosion and weakening of the packaging occur before final emplacement.	Waste form is chemically compatible with storage container

[a] ILLW requires limited provision for heat dissipation during its storage and disposal [1], thus 300°C is considered conservative. [b] See Appendix A for a description of NRAD. [c] Based on WAC requirements for cement materials in reference 32.

Table 3-2 General Waste Form Characterization Testing and Expectations[a].

Criteria	Testing/Characterization Methods	Expectations
Density and porosity	Water displacement methods, utilizing Archimedes' principle. AS 1774.5-2001 "The determination of density, porosity and water absorption"	Applicable to ceramic, glass or glass-ceramic waste forms. The aim is to produce a dense, durable waste form e.g. < 5% closed porosity and < 1% open porosity. <15% open porosity for cementitious materials
Permeability	Standard permeability testing [35,36,37] As above, one prefers a dense waste form that has a low permeability such that groundwater will not easily penetrate and accelerate leaching of soluble radioactive species from it.	Applicable to cementitious materials. Permeability is required < 10^{-6} cm^2/s.
Homogeneity and chemistry of the waste form	A suite of methods may be utilized depending upon the waste form type: These include, e.g.: a) X-ray diffraction b) Scanning electron microscopy with analytical analysis c) Image analysis techniques d) Optical Microscopy e) X-ray fluorescence f) NRAD[b] Homogeneity is to ensure that secondary phases that may decrease durability do not form. It also serves to measure the effectiveness of the processing conditions. Section samples from various points of the bulk sample will be assessed.	Ensure even distribution of radionuclides at the 100 µm scale. No deleterious secondary phases formed. Chemically homogenous at the 100 µm scale and larger. Demonstrate no stratification
Mass balance	Chemical analysis techniques utilizing, for example: a) X-ray fluorescence b) Analytical chemistry techniques with appropriate spectroscopy or mass spectrometry c) Analytical SEM d) Gamma/alpha spectroscopy These serve as a quality control measure and also ensure that radionuclides are retained in the waste form and not lost during processing. One wishes to minimize secondary waste volumes	Ensure no loss of radionuclides during processing. A demonstration to show that starting and final chemistries are identical is required.
Waste loading	Calculation based on input data, verified where necessary by chemical analysis and SEM/EDS Waste loading should be given as both a weight (wt%) and volume (volume of waste form per unit of waste input). This should be used to calculate the waste volume change. Disposal and storage costs are dependent upon the waste volume. The aim is to minimize the waste volume, whilst maintaining product quality	Ceramics, glass-ceramics and glass: waste loading > 20 wt% Cement/geopolymers: waste loading >5 wt% Values given as oxide wt%
Volume Change	Measure change in storage volume of initial waste compared to final waste form volume for disposal.	Dimensional

[a] Additional information with regard to the various characterization testing can be found in Appendix A. [b] See Appendix A for a description of NRAD.

4. Conclusions

Waste Acceptance Criteria (WAC) are standards against which a radioactive waste package is assessed. It sets the limits for acceptance of a waste package into a store or repository and these criteria are developed with reference to a safety case for the store or repository. Given the lack of operating repositories for radioactive waste arising from Mo-99 production, the approach taken to develop a suitable WAC for this work package has been to focus on generic criteria that are directly related to the waste form and its production. Further, some assessment of its compatibility with its container must be undertaken. In this chapter the generic concepts outlined by the IAEA have been reviewed and a brief overview of guidelines and standards used in each of the key Mo-99 producing countries has been given. These have been utilized as guides to produce a specific set of waste acceptance criteria that are considered vital for the integrity of a waste form. Further, expectations from essential characterization testing for the waste forms generated in this project for Mo-99 waste have been outlined.

5. References

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CHAPTER 4: PROPOSED CRITERIA FOR ENCAPSULATION TECHNOLOGY AND PRELIMINARY SCREENING OF WASTE FORMS

1. Introduction

Implementation of new or novel technology can often be fraught with high risk. Even known or mature technologies applied to new applications carry a degree of risk. However often it is only through the implementation of new or novel technologies that true solutions to problems can be found. They can provide substantial life cycle cost saving and efficiencies that the current base line technologies could never achieve.

The aerospace and defence industries entire history is prefaced on new and innovative technologies that push the boundaries of engineering and materials. "***I find out what the world needs. Then I go ahead and try to invent it.***" Thomas Edison

Today's Nuclear industry has become ultra conservative it its approach to the implementation of new technologies and this seems at odds with the origins of nuclear energy which required an incredible leap of engineering and materials technology. But with increased focus in safety, security and limited funds new technologies need to be able to show the level of maturity that meets all the criteria before implementation.

This chapter seeks to follow a systematic and considered approach in determining the suitability of technologies for the treatment of the identified wastes in chapter one. It is important to understand that no single methodology will necessarily determine the right technology and it should be considered with other factors that are site or region specific. However we do seek to use methodology that allows for a down selection of feasible technologies that could meet a wide range of criterion that could be weighted according to local priorities, for example to one region or country, volume reduction may be a highly weighted criterion due to limited storage space.

The US National Aeronautics and Space Administration (NASA) and US Department of Defense (DoD) technology readiness assessment (TRA) model have been used for decades to assess the maturity of technologies for implementation and to identify the critical technology elements/gaps.

The US Department of Energy (DOE) developed a guide that sort to tailor a version of the methodology used by NASA and DoD specifically for their major projects. This was as a result of an assessment by the US Government Accountability Office (GAO) that found that a root cause for cost overruns on major projects was due to the fact of the low level of maturity of new technologies prior to implementation. Since 2008 the USDOE has been working on a corrective action plan and has been encouraging the use of the TRA guide across all the DOE, the current version of the document is ***DOE G 413.3-4A, 9-15-2011***. The aim of the adoption of use of the guide is to provide a common framework to assess technical maturity to ensure that new technology projects can be implemented successfully. In the words of DoD "a successful project is a project that satisfies its intended purpose in a safe, timely, and cost-effective manner that would reduce life-cycle costs and produce results that are defensible to expert reviewers".

2. Methodology

Relevant parts of the TRA guide will be used to assess the maturity of technologies that have been proposed in Chapter 5. Then should the recommended technologies at the end of the study be selected to progress to a more detailed assessment then the basis of selection is defensible and able to be further progressed through a series of critical design reviews (conceptual and detailed design). The life cycle of a project is shown in Figure 2-1.

A TRA evaluates technology maturity using the Technology Readiness Level (TRL) scale that was pioneered by the NASA in the 1980s. The TRL scale ranges from 1 (basic principles observed) through 9 (total system used successfully in project operations). Note the technology readiness level does not apply if the objective of the project is to research scientific principles.

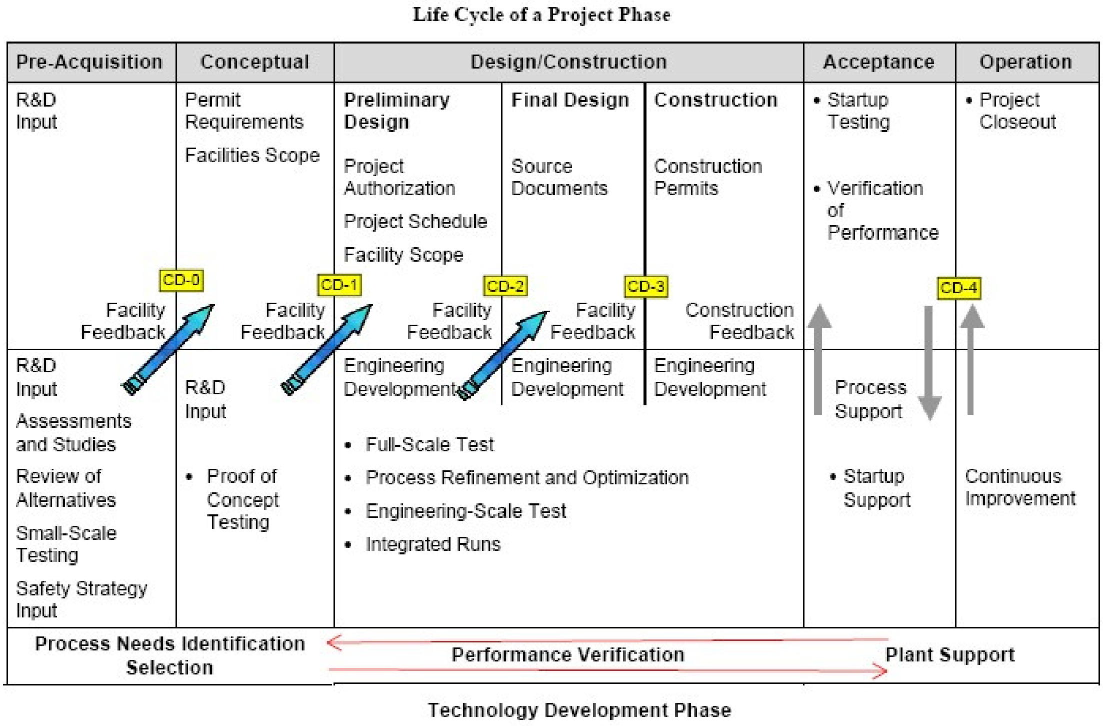

Figure 2-1 Technology Development Integration with Project Management.

The TRA should be done at key project critical design (CD) review points such as preliminary design review or detailed design review (CD-0, CD-1, CD-2, and CD-3 etc). Therefore for this phase of the work proposed it is appropriate we use the methodology to apply to the preliminary design review (CD-0) as part of the next proposed program of work (work order 2).

The following three sequential steps are taken from the DOE guidance document and it is our intention to follow this sequence as part of our evaluation. More details are given in the document and are not being repeated in this chapter.

The TRA process model consists of three sequential steps:

(1) **Identifying the Critical Technology Elements (CTEs)**. CTEs are the at-risk technologies that are essential to the successful operation of the facility, and are new or are being applied in new or novel ways or environment.

(2) **Assessing the Technology Readiness Level (TRL)**. TRL indicates the maturity level of a given technology, as defined in Table 2-1 primarily for hardware items. Figure 2-2 provides a schematic of the meaning of the TRL's in the context of DOE/EM waste processing projects. The TRL scale ranges from 1 (basic principle observed) through 9 (total system used successfully in project operations).

(3) **Developing a Technology Maturation Plan (TMP).** If the TRL level for a CTE does not meet the expectation level at each critical decision level (especially for CD-2 and later), then a maturity level gap exists that requires further evaluation testing or engineering work in order to bring the immature technology to the appropriate maturity level. The development or revision of a Technology Maturation Plan (TMP) identifies the activities required to bring immature CTEs up to the desired TRL

Table 2-1 Technology Readiness Levels.

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
System Operations	**TRL 9**	Actual system operated over the full range of expected mission conditions.	The technology is in its final form and operated under the full range of operating mission conditions. Examples include using the actual system with the full range of wastes in hot operations.
System Commissioning	**TRL 8**	Actual system completed and qualified through test and demonstration.	The technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental testing and evaluation of the system with actual waste in hot commissioning. Supporting information includes operational procedures that are virtually complete. An Operational Readiness Review (ORR) has been successfully completed prior to the start of hot testing.
System Commissioning	**TRL 7**	Full-scale, similar (prototypical) system demonstrated in relevant environment	This represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Examples include testing full-scale prototype in the field with a range of simulants in cold commissioning1. Supporting information includes results from the full-scale testing and analysis of the differences between the test environment, and analysis of what the experimental results mean for the eventual operating system/environment. Final design is virtually complete.

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
Technology Demonstration	**TRL 6**	Engineering/pilot-scale, similar (prototypical) system validation in relevant environment	Engineering-scale models or prototypes are tested in a relevant environment. This represents a major step up in a technology's demonstrated readiness. Examples include testing an engineering scale prototypical system with a range of simulants.1 Supporting information includes results from the engineering scale testing and analysis of the differences between the engineering scale, prototypical system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. TRL 6 begins true engineering development of the technology as an operational system. The major difference between TRL 5 and 6 is the step up from laboratory scale to engineering scale and the determination of scaling factors that will enable design of the operating system. The prototype should be capable of performing all the functions that will be required of the operational system. The operating environment for the testing should closely represent the actual operating environment.
Technology Development	**TRL 5**	Laboratory scale, similar system validation in relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Examples include testing a high-fidelity, laboratory scale system in a simulated environment with a range of simulants1 and actual waste2. Supporting information includes results from the laboratory scale testing, analysis of the differences between the laboratory and eventual operating system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. The major difference between TRL 4 and 5 is the increase in the fidelity of the system and environment to the actual application. The system tested is almost prototypical.
Technology Development	**TRL 4**	Component and/or system validation in laboratory environment	The basic technological components are integrated to establish that the pieces will work together. This is relatively "low fidelity" compared with the eventual system. Examples include integration of ad hoc hardware in a laboratory and testing with a range of simulants and small scale tests on actual waste2. Supporting information includes the results of the integrated experiments and estimates of how the experimental components and experimental test results differ from the expected system performance goals. TRL 4-6 represent the bridge from scientific research to engineering. TRL 4 is the first step in determining whether the individual components will work together as a system. The laboratory system will probably be a mix of on hand equipment and a few special purpose components that may require special handling, calibration, or alignment to get them to function.

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
Research to Prove Feasibility	**TRL 3**	Analytical and experimental critical function and/or characteristic proof of concept	Active research and development (R&D) is initiated. This includes analytical studies and laboratory-scale studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative tested with simulants.1 Supporting information includes results of laboratory tests performed to measure parameters of interest and comparison to analytical predictions for critical subsystems. At TRL 3 the work has moved beyond the paper phase to experimental work that verifies that the concept works as expected on simulants. Components of the technology are validated, but there is no attempt to integrate the components into a complete system. Modeling and simulation may be used to complement physical experiments.
Basic Technology Research	**TRL 2**	Technology concept and/or application formulated	Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytic studies. Supporting information includes publications or other references that outline the application being considered and that provide analysis to support the concept. The step up from TRL 1 to TRL 2 moves the ideas from pure to applied research. Most of the work is analytical or paper studies with the emphasis on understanding the science better. Experimental work is designed to corroborate the basic scientific observations made during TRL 1 work.
Basic Technology Research	**TRL 1**	Basic principles observed and reported	This is the lowest level of technology readiness. Scientific research begins to be translated into applied R&D. Examples might include paper studies of a technology's basic properties or experimental work that consists mainly of observations of the physical world. Supporting Information includes published research or other references that identify the principles that underlie the technology.

[1] Simulants should match relevant chemical and physical properties.

[2] Testing with as wide a range of actual waste as practicable and consistent with waste availability, safety, ALARA, cost and project risk is highly

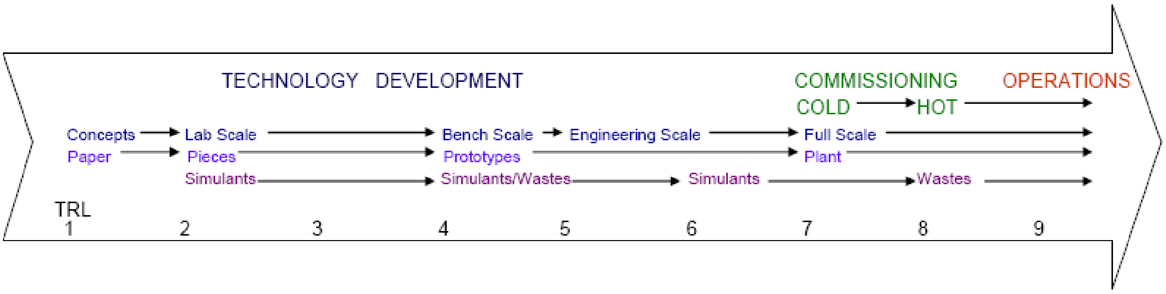

Figure 2-2 Schematic of DOE/EM Technology Readiness Levels.

The project will adapt the templates and check lists from the TRA guide DOE G 413.3-4A, 9-15-201, for use in evaluating technology maturity to aid in the assessment of feasibility. An example of template is shown in Table 2-2. In addition to assist with specific criteria around the waste form durablity or other aspects that may not be covered by the TRA methodology:

Identify FOAK Processes and Equipment. We will identify first of a kind (FOAK) technologies or applications. Environmental differences between the new facility and past experience could include differences in factors such as temperature, process chemicals, pressures or fabrication methods. The product of this initial step is a list of processes, equipment or materials that do not have prior operational experience in the relevant environment (FOAK items) and a description of why the item is FOAK.

Development Feasibility Assessment. The TRL assessment only defines where a technology is in the spectrum of development maturity. The TRL assessment does not determine if a particular technology could be developed further to meet project requirements. A key factor in the feasibility assessment is how closely development work to date duplicates the actual operating environment and the actual scale. Independent engineering judgment, based on relevant experience, is used to assess the feasibility of a new technology being developed successfully to meet project performance requirements in a commercial production environment. The feasibility assessment may be supported by a literature search. For each FOAK item, a statement will be provided of the feasibility of achieving satisfactory operation in the facility environment. The statement will include the rationale for the conclusion.

Table 2-2 Top Level Questions for Determining Anticipated TRL.

TRL	Yes/No	Top-Level Question	If Yes, Then Basis and Supporting Documentation
TRL 9		Has the actual equipment/process successfully operated in the full operational environment (hot operations)?	
TRL 8		Has the actual equipment/process successfully operated in a limited operational environment (hot commissioning)?	
TRL 7		Has the actual equipment/process successfully operated in the relevant operational environment (cold commissioning)?	
TRL 6		Has prototypical engineering scale equipment/process testing been demonstrated in a relevant environment; to include testing of the safety function?	
TRL 5		Has bench-scale equipment/process testing been demonstrated in a relevant environment?	
TRL 4		Has laboratory-scale testing of similar equipment systems been completed in a simulated environment?	
TRL 3		Has equipment and process analysis and proof of concept been demonstrated in a simulated environment?	
TRL 2		Has an equipment and process concept been formulated?	
TRL 1		Have the basic process technology process principles been observed and reported?	

2.1 Waste form Assessment Criteria and Evaluation

The table below will be further developed specifically with criteria that the team believe is most relevant for determining suitable matrices or method for waste encapsulation or immobilization. At this early stage, the table will serve as a method of technology and waste form down selection for progression to the next phase of work. A red indicator will eliminate the technology or waste form.

Table 2-3 Relevant criteria for determining suitable matrices or methods for waste encapsulation or immobilization.

Criteria	Weighting Factor	Waste Stream 1		
		Matrix A	**Matrix B**	**Matrix C**
Pass relevant Waste Acceptance Criteria	**PASS** **FAIL**			
Accepted technology that has been examined previously for the final waste disposal of relevant radionuclides	**Yes** **No**			
Waste loading	**< 5 wt%** **> 5 wt%** **> 50 wt%**			
Additional waste generation-secondary wastes	**No additional waste** **Additional waste generated**			
Flexibility of the matrix to variations in waste composition	**Flexible** **Not flexible**			
Flexibility to Incorporate other waste streams in project scope	**Flexible** **Not flexible**			
Leach resistance/Durabilty	**Pass Result for MCC-1** **Pass result for cement using ANSI/ANS-16.1** **Fail above**			
Selected for this project		**yes**	**yes**	**yes**

The cost of a plant would include full life cycle costs. This would depend on the country in control of the waste. While we have referred throughout the document to relative costs, these would depend somewhat on the technical maturity of a given process. But as a general statement, it is well known that the costs for producing waste forms requiring heating to temperatures of the order of 1000℃ are roughly equal for equal waste loadings and are considerably in excess of those to produce cementitious materials. More detailed cost evaluations will emerge following laboratory work and this will allow easier down selection of a particular waste form. For example, if two waste forms have the same loading, durability, leachability, etc., but one would require twice the capital and/or operating costs, the down select would be easy for a commercial entity.

Information from Table 2-3 will be combined with information from the Technology Readiness Assessment (DOE G 413.3-4A, 9-15-2011) to allow for a complete evaluation of proposed technologies together with waste form performance. These will serve to be the driving factors for the final recommendations for this project.

3. Conclusion

We have proposed the use of applicable parts of US-DOE guidance document Technology Readiness Assessment (DOE G 413.3-4A, 9-15-2011) in order to establish the maturity of a given process and to allow comparison of various technologies that will be assessed in this project. A table outlining the relevant criteria for determining suitable matrices or methods for waste encapsulation has also been generated in order to evaluate the suitability of a given waste form matrix. Both of these methods will be used as guides for the downselection of technologies and waste forms, and ultimately to final immobilization strategy recommendations.

CHAPTER 5: RECOMMENDED WASTE FORM SELECTIONS FOR WASTE STREAMS RESULTING FROM FISSION MO-99 PRODUCTION

1. Waste streams from processing of Mo-99

There is a variety of waste streams that result from fission Mo-99 production. Chapter 1 of this report (Identification and description of all waste streams resulting from fission Mo-99 production) has provided a detailed overview of the waste streams that arise from Mo-99 production using both alkaline and acidic target processing routes. These descriptive and quantitative results were based on Necsa and ANSTO's combined experience in the characterization of waste streams from both types of processes. The results of this analysis will be used to design surrogate matrixes for the development of immobilization technologies. The specific waste streams that will be considered for treatment in this work package result from the alkaline process and include:

1. ***Unprocessed residue***: In case of final disposal of the uranium residue without processing for recovery of uranium
2. Processed residue: In case of processing of the irradiated residue to recover and purify uranium for re-use, the following waste streams are generated
    a. ***Undissolved residue*** after the carbonate leaching process
    b. ***Alumina ion exchangers*** used for retention of fission products in the initial purification step of the uranium
    c. ***Nitric acid solutions*** after the final purification of uranium

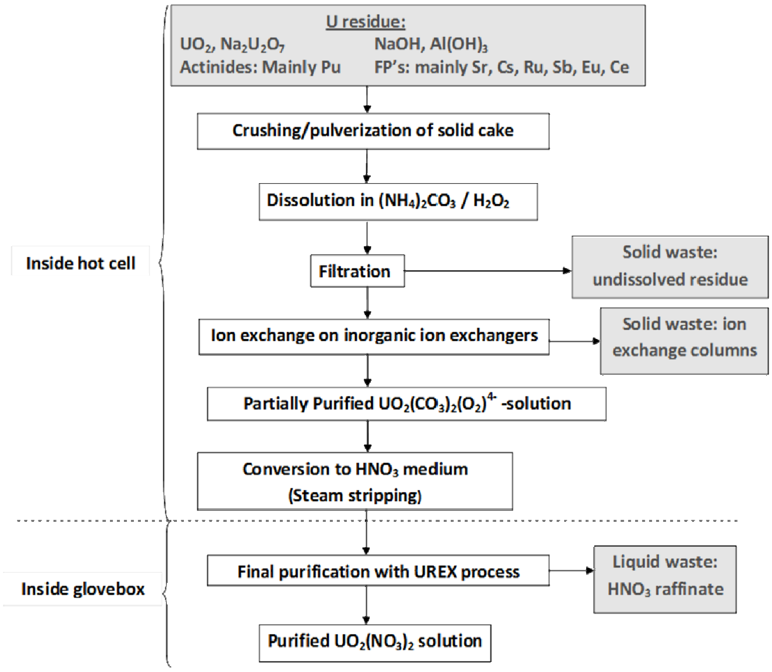

Figure 1-1 *Schematic representation of the process for recovery of uranium from Mo-99 production process solid residue. Shaded boxes indicate the waste streams of interest in this work.*

Figure 1-1 from Chapter 1 describes the process for the recovery of uranium from the Mo-99 alkaline production process solid residue and is repeated here for reference. The waste streams to be addressed are indicated in the figure by the shaded boxes, and described in further detail below.

1.1 Unprocessed residue

This waste consists of approximately 74 wt% UO_{3-x}, 10 wt % NaOH, 10 wt% Fe_2O_3, 3 wt% of $Al(OH)_3$, 2 wt% of Cr_2O_3 and ~ 1 wt% fission products (oxide equivalents). In order to prevent volatile loss of products, neutral or reducing conditions are required during sintering or vitrification. Under reducing conditions the U(IV) oxidation state would be expected to dominate. This influences the choice of host crystalline phase for candidate ceramic and glass-ceramic waste forms and may also result in a lower uranium solubility in glass (as higher uranium valences are more soluble).

Several possible ceramic and glass-ceramic waste forms can be envisaged. For the glass-ceramic candidates, the glass is incorporated to assist in sodium waste loading, which can be limited in ceramic only systems. Both HIPing or melting processes in reducing or neutral conditions would be feasible. Under these conditions uranium can be incorporated into brannerite (UTi_2O_6) or pyrochlore ($CaUTi_2O_7$), both well-known waste form candidate phases for uranium. Sodium could be included in perovskite ($Na_{0.5}Gd_{0.5}TiO_3$) or freudenbergite ($Na_2(Al,Fe,Cr,Ti)_2Ti_6O_{16}$) or a borosilicate glass in the case of a glass ceramic. Iron, chromium and aluminium oxides form spinels ($(Fe,Cr,Al)O_3$) in a multiphase ceramic or are encapsulated in the borosilicate glass in the glass-ceramic waste form. The addition of gadolinium for incorporation into the waste form design is included for neutron absorption in order to defuse criticality issues. Waste loading is expected to be of the order of 30-50 wt%.

As the unprocessed residue contains mainly uranium, lanthanide glasses are most attractive. The lanthanide glasses are known to accommodate Cs, Y, lanthanides and actinides in relatively high concentrations [1]. Loffler's glass is unique in that it combines lanthanide oxides as fluxes in an aluminosilicate type glass in place of the usual alkali metal oxides. The glasses melt at conventional melting temperatures ($\geq$ 1350°C) but have an extraordinarily low viscosity. The Loffler glasses typically contain 10-70 wt% of some lanthanide oxides, 9-20 wt% Al_2O_3 and the remainder is SiO_2 (21.5-46 wt %). Appendix B gives compositions of those glasses.

OPC based cements are not feasible for this waste stream due to the high uranium and sodium content. HEU U-rich wastes bring criticality implications due to the presence of water in the cement process. As a result, very low waste loadings would be required. Radiolytic hydrogen gas build-up during storage and disposal is also of concern for regular cement due to its water content. Further, this waste stream is relatively rich in sodium which is problematic for cement waste forms. The high sodium content is likely to give rise to high leachability unless the waste loading is kept very low. As a consequence, the waste volume would be correspondingly high.

ANL's research programme has centred on the encapsulation of volatile low level radioactive and transuranic mixed waste streams using Ceramicrete [2,3]. ANL has principally tested Ceramicrete to encapsulate plutonium contaminated ashes that reside at the Rocky Flats site. Wagh et al. [3] showed through bench-scale feasibility studies that powdered oxidised cerium (a surrogate which is chemically similar to plutonium and uranium) could be readily incorporated into Ceramicrete. The samples were found to be leach resistant, have low porosity and the radiolytic gas evolution yields were comparable to conventional cement systems. Studies have indicated that samples which incorporated actinide species appeared stable, suggesting that the system is stable to alpha radiation [4].

Sintered SiC coated phosphate cements are worthy of consideration for this waste stream, especially in case of volatile radionuclides. This technology has been demonstrated at Necsa on surrogate residue material. The methodology is the encapsulation of waste into phosphate cement (at room temperature), sintering the monolith up to 800^0C to form a ceramic type structure (remove water and increase physical properties) and finally plasma sputtering a SiC layer onto sintered waste form.

Geopolymers do not rely on hydrous material for strength, thus suppressing radiolytic gas production concerns and they also have advantages over cement with respect to leachability (in addition to the absence of the alkali reaction problem with possible aggregate). Metakaolin-based geopolymer waste form materials are envisaged for this waste stream.

Some thermoplastic polymers like high and low density polyethylene have been applied in the immobilization of low-level and intermediate-level waste by encapsulation. It must be noted that all polymers degrade or crosslink when exposed to radiation. The extent of the degradation depends on the polymer and the total dose of radiation emitted from the specific radionuclide. Further, the incorporation of certain inorganic fillers like carbon fiber [5] and glass fibre [6] can improve the radiation resistance of polymers [7]. Currently studied at Necsa is the use of SSA 602N a thermosetting phenolic novolak resin manufactured by SI Group – South Africa (Pty) Ltd. The resin contains hexamethylene tetramine (hexa) as a crosslinking agent and will be investigated for this purpose.

In unpublished Necsa documents, the use of EKOR 93-500, CV 2510 and RTV 566 white silicon polymer coatings were successfully demonstrated as a coating barrier for radioactive phosphate cement and aluminium and was demonstrated to be radiation resistant. This polymer is also recommended for further studies.

1.2 Undissolved residue

This waste stream consists of approximately 34 wt% Fe_2O_3, 35 wt% of UO_{3-x}, 25 wt% $Al(OH)_3$, 6 wt% Cr_2O_3, 3 wt% of Na_2O + ~1 wt% fission products (oxide equivalents). It is similar to the waste stream discussed above (Section 1.1) however there is significantly more iron and aluminum and less uranium and sodium. Again the presence of fission products may require neutral or reducing conditions during sintering or vitrification, or consideration of of-gas recycling.

The waste form candidates for this waste stream would be similar to those found in Section 1.1 of this chapter. Multiphase ceramics incorporating brannerite or pyrochlore with spinel and perovskite are possible options. Ilmenite ($FeTiO_3$) could also be considered as part of the formulation to assist in the immobilization of the large quantities of iron. A similar glass-ceramic to that described in Section 1.1 could also be viable. The waste loading for these candidates (50-60 wt%) are expected to be higher than those found in Section 1.1 due to the lower uranium content in the waste.

Due to the higher iron content, lanthanide glasses, borosilicate and iron phosphate glasses are candidates for this waste stream (see appendix B). The waste loading is expected to be around 20 wt% and these could be formed via either HIPing or melting processes in neutral to slightly oxidising conditions. Again, potential volatilization of the fission products during the melting process needs to be considered.

OPC based cements are not feasible for those reasons discussed above in Section 1.1, however chemically bonded phosphate cements are again worthy of consideration for this waste stream however. A previous Necsa research programme has centred on the encapsulation of volatile low level radioactive waste containing iron and other radionuclides such as Cs, Sr and Ba by modifying the composition of the phosphate cement. The samples were found to be leach resistant, have low porosity and indicated no radiation damage when irradiated. The proposal is therefore to encapsulate this waste stream into a modified phosphate cement (at room temperature), sintering the monolith up to 800^0C to form a ceramic type structure (remove water and increase physical properties) and finally plasma sputtering a SiC layer onto sintered waste form.

Geopolymers do not rely on hydrous material for strength thus suppressing radiolytic gas production concerns and they also have advantages over cement with respect to leachability (in addition to the absence of the alkali reaction problem). Metakaolin-based geopolymer waste form materials are therefore envisaged for this waste stream.

As mentioned in the previous section Necsa is studying the use of SSA 602N a thermosetting phenolic novolak as well as EKOR 93-500, CV 2510 and RTV 566 white silicon polymer resin. Due to the high Fe content the use of Ciba-Geigy (now Huntsman) Araldite LY 5082 (resin consists of a type of bisphenol-F epoxy) and Araldite HY 5083 (hardener consists of isophorone diamine) purchased from Hi-Tech Polymers could be considered as Necsa [8] report indicated that these polymers with the addition of glass has excellent gas diffusion properties.

1.3 Alumina ion exchangers

The alumina ion exchanger waste consists predominantly of Al_2O_3 (~99.8 wt%) together with trace fission products (~0.2 wt%) (oxide equivalents). High-alumina tailored nuclear waste ceramics have been suggested previously, such as the four phase waste form of alumina, spinel, magnetoplumbite (e.g. $CaAl_{12}O_{19}$), and uraninite developed in the U.S [9]. The magnetoplumbite phase can reportedly incorporate the elements Cs, Sr, Si, Na, Ca, Ba, La, Nd, Mn, Fe, Ce, K, and Ni in its crystal structure [9], whereas the uraninite phase hosts the elements U, Th, and Zr. An alumina glass-ceramic similar to that proposed for Idaho Calcine (~90% alumina) [10] is another potential candidate. Both these candidates would have waste loadings of approximately 80 wt%. Other potential waste forms for this stream could include aluminoborosilicate glasses with a waste loading of around 40 wt% (see Appendix B).

Necsa has demonstrated the encapsulation of the radioactive alumina column generated during the purification of Enriched Uranium in hot cell [11]. The developed glass composition can tolerate 25 wt% alumina resin, 2 wt% Fe_2O_3 and 6 wt% radionuclides. Current leaching experiments indicate that the radioactive alumina column was effectively immobilized as no leaching was observed.

Ordinary cements could potentially be used to encapsulate the waste, however they are not considered here due to the potential for radiolytic hydrogen gas build-up and fission product leachability. However, Necsa has demonstrated the encapsulation of the radioactive alumina column generated during the purification of Enriched Uranium in hot cell [11] into phosphate cement. Unpublished Necsa reports demonstrate that it is possible to sinter a phosphate cement monolith with alumina resin at 800^0C to form a ceramic type structure (remove water and increase physical properties). This will be investigated further using this waste stream composition

As mentioned in the previous section Necsa is studying the use of SSA 602N a thermosetting phenolic novolak as well as EKOR 93-500, CV 2510 and RTV 566 white silicon polymer resin. Radioactive alumina oxide (generated during the recovery of enriched uranium in a hot cell from Mo-99 residue) was successfully encapsulated at Necsa [11] using Ciba-Geigy (now Huntsman) Araldite LY 5082 (resin consists of a type of bisphenol-F epoxy) and Araldite HY 5083 (hardener consists of isophorone diamine) purchased from Hi-Tech Polymers. This project will be extended to include waste loadings and extensive radiation stability studies.

1.4 Nitric acid solutions

This liquid waste will be 0.7 M HNO_3, containing ~0.1 M acidic acid), fission products and plutonium. The organic compound acidic acid will be easily removed during calcination. A Synroc-type pyrochlore or zirconolite-rich multiphase ceramic, glass ceramic, or a borosilicate glass formulation, processed by HIPing or melting under reducing conditions could readily be developed with a waste loading of ~10-20 wt%.

Nitrate waste streams can be problematic for cementitious waste form production and require front end treatment. The acid needs to be neutralized and the precipitate separated and calcined, or other denitration method applied, prior to cementation. Although this may complicate the process Portland cement could be considered for this waste stream. Similarly, for chemically bonded phosphate cements the pH should be adjusted to pH ~ 4 before waste form processing. A metakaolin-based geopolymer could also be considered with a reduced waste loading or ~5 wt%.

As mentioned in the previous section Necsa is studying the use of SSA 602N a thermosetting phenolic novolak, as well as EKOR 93-500, CV 2510 and RTV 566 white silicon polymer resin. Necsa have also demonstrated encapsulation of radioactive alumina oxide (generated during the recovery of enriched uranium in a hot cell from Mo-99 residue) using Ciba-Geigy (now Huntsman) Araldite LY 5082 (resin consists of a type of bisphenol-F epoxy) and Araldite HY 5083 (hardener consists of isophorone diamine) purchased from Hi-Tech Polymers. These polymers could therefore be considered for the encapsulation of AHA, TBP and other organics.

Another polymer absorbent, called Nochar, was used at Necsa to remove the generated radioactive liquid. Nochar's Petrobond is a polymer designed to solidify organics, sludge, acids, alkaline and aqueous radioactive waste into a solid matrix. The possibility of encapsulation radioactive Nochar absorbent into MKP and epoxy resin was investigated and loadings between 5-20% [11] were achieved.

Necsa have also studied the encapsulation of polymer absorbent, Nochar, into OPC cement to investigate compatibility. The results of the small-scale experimental program illustrate that a Nochar polymer loading of 30% forms an effective cement monolith, with no observable leaching. The results also indicate that possible negative environmental conditions (temperature, standing water) will have no adverse effect on the performance of the polymers regarding stability and radionuclide leaching.

2. Technologies and waste forms suggested for different waste streams

2.1 Overview of various technologies

Table 2-1 summarizes the possible waste forms and waste form production technologies available for the various waste streams from alkaline route processing of Mo-99. The options have been ranked according to their viability. In addition, potential concerns or problems that eliminate a technology's candidacy have been highlighted.

The ILLW from target dissolution using either acidic or alkaline processing is out of the scope of this work package; however current technologies considered or being considered for this waste have been included in the table. This provides a useful reference point as it would be beneficial to consider the possibility of utilizing a single plant or technology to process all waste streams from fission based Mo-99 production.

Table 2-1 Potential conditioning matrix and processing technology for the various waste streams from alkaline route processing of Mo-99.

Candidate	**Unprocessed residue**	**Undissolved residue**	**Alumina ion exchanger**	**Nitric acid solution**	***Out of scope***	***Out of scope***
					Target dissolution waste (alkaline)	**Target dissolution waste (acid)**
Glass	**Feasible** - Consider volatilization of FPs. - U(IV) has limited solubility	**Feasible** - Consider volatilization of FPs. - U(IV) has limited solubility	**Feasible**	**Feasible**	ANSTO (Process under investigation)	
Glass-ceramic	**Feasible** - HIP'd to prevent FP loss. - Controlled cooling to reduce segregation	**Feasible** - U in ceramic - TCLP may be required for Cr(III)	**Feasible**	**Feasible**	Feasible – ANSTO	Feasible – ANSTO
Ceramic	**Feasible** - HIP'd to prevent FP loss.	**Feasible**	**Feasible**	**Feasible**	ANSTO (Process under investigation)	Feasible – ANSTO

Table 2-1 Potential conditioning matrix and processing technology for the various waste streams from alkaline route processing of Mo-99.

					Out of scope	***Out of scope***
Candidate	**Unprocessed residue**	**Undissolved residue**	**Alumina ion exchanger**	**Nitric acid solution**	**Target dissolution waste (alkaline)**	**Target dissolution waste (acid)**
Cement	🟥 **Not feasible** - Problematic due to high U/Na content. - Criticality concern. - Radiolytic H_2 gas buildup concern.*	🟥 **Not feasible** - Problematic due to high U/Na content. - Criticality concern. - Radiolytic H_2 gas buildup concern.	🟥 **Not Feasible** - Encapsulation possible but potential for radiolytic H_2 gas buildup and FP leachability.	🟩 **Feasible**	🟩 Feasible NTP process (Portland cement based) COVRA	
MKP	🟨 **Feasible** - Water content may result in radiolytic H_2 gas buildup. - Potential for U incorporation unknown. - Ceramic coat (SiC).	🟩 **Feasible**	🟩 **Feasible**	🟩 **Feasible**	🟨 NECSA (Process under investigation)	
Geopolymers	🟨 **Feasible** - Possible low waste loading for U.	🟩 **Feasible**	🟩 **Feasible** - Dissolve alumina beads. - FPs?	🟩 **Feasible**		
Polymers (imides)	🟨 **Feasible** - Unknown radiation tolerance. - Possible low waste loading.	🟩 **Feasible** - Unknown radiation tolerance.	🟨 **Feasible** - Unknown radiation tolerance.	🟨 **Feasible** - Unknown radiation tolerance.		

The potential waste forms are ranked according to: green – demonstrated technology, yellow – feasible but not demonstrated for this type of waste, and red - not demonstrated. FPs = fission products.

* Radiolysis effects leading to gas generation will occur whenever the waste form contains hydrous material, for example in cementitious material but not ceramics or glasses. The magnitude of gas generation in a cementitious material will depend on the waste loading and the content of hydrous material. Numerical evaluation would be carried out during the course of the first stage of Work Order 2 to quantify the effect.

2.2 Specific Waste Form Candidates to be investigated

Table 2-2 summarizes the various candidate waste forms that will be targeted for each of the four waste streams to be encapsulated in this work package. Ceramics, glass-ceramics, geopolymers, and some glasses will be pursued at ANSTO. Heat treatment will be carried out by HIPing, melting and sintering. Glasses, cements, MKP-chemically bonded phosphate cements, polymers, and some glass-ceramics will be investigated at Necsa using melting and sintering processing. A series of replicate glass and glass-ceramic waste forms are to be fabricated at both organizations in order to assess the benefits of different technology (HIP vs melting for example) and reproducibility.

Table 2-2 Recommended candidate conditioning matrices and processing technology for the various waste streams from alkaline route processing of Mo-99.

	WASTE STREAMS			
Candidate waste form	**Unprocessed residue**	**Undissolved residue**	**Alumina ion exchanger**	**Nitric acid solution**
Glass	*Formed via (a) HIPing or (b) melting or (c)sintering* :* 1. Borosilicate glass in neutral to slightly oxidising conditions with volatile recycle for (b) (expected waste loading of ~20 wt%). 2. Iron phosphate glass with volatile recycle for (b) (expected waste loading of ~20 wt%). 3. The Loffler glasses	*Formed via (a) HIPing or (b) melting or (c)sintering** 1. Borosilicate glass in neutral to slightly oxidising conditions with volatile recycle for (b) (expected waste loading of ~30 wt%). 2. Iron phosphate glass with volatile recycle for (b) (expected waste loading of ~40 wt%). 3. The Loffler glasses	*Formed via (a) HIPing or (b) melting or (c)sintering*:* Aluminoborosilicate glass with volatile recycle for (b) (expected waste loading of ~40 wt%). 3. The Loffler glasses	*Formed via (a) HIPing or (b) melting or (c)sintering*:* Borosilicate glass processed under reducing conditions (expected waste loading ~10-20 wt%).
Glass-ceramic	*Formed via (a) HIPing or (b) melting or (c)sintering*:* 1. (Ca,Gd)UTi_2O_7-type pyrochlore + borosilicate glass. (expected waste loading of ~50 wt%). 2. Perovskite + Zirconolite + borosilicate glass.for (b) (expected waste loading of ~50 wt%). 3. Perovskite + Zirconolite + Iron phosphate glass.for (b) (expected waste loading of ~50 wt%).	*Formed via (a) HIPing or (b) melting or (c)sintering *:* 1. Pyrochlore glass-ceramic: Similarly to that already suggested (expected waste loading of ~60 wt%). 2. Perovskite + Zirconolite + borosilicate glass.for (b) (expected waste loading of ~50 wt%). 3. Perovskite + Zirconolite + Iron phosphate glass.for (b) (expected waste loading of ~50 wt%).	*Formed via (a) HIPing or (b) melting or (c)sintering*:* 1. Alumina glass ceramic as proposed for Idaho Calcine which had 90% alumina 2. Zirconolite + borosilicate glass.for (b) (expected waste loading of ~50 wt%). 3. Perovskite + Zirconolite + phosphate glass. for (b) (expected waste loading of ~50 wt%).	*Formed via (a) HIPing or (b) melting or (c)sintering *:* 1. Titanate glass ceramic expected waste loading ~10-20 wt.%). 2. Zirconolite + borosilicate glass.for (b) (expected waste loading of ~50 wt%). 3. Perovskite + Zirconolite + Iron phosphate glass for (b) (expected waste loading of ~50 wt%).
Multiphase ceramic	*Formed via (a) HIPing or (b) melting:* 1.UTi_2O_6 (brannerite) + $Na_{0.5}Gd_{0.5}TiO_3$ (perovskite) + $(Fe,Cr,Al)O_3$ (spinel) (expected waste loading of ~40 wt%). *2.*UTi_2O_6 (brannerite) + $Na_2(Al,Fe,Cr,Ti)_2Ti_6O_{16}$ (Freudenbergite) + $(Fe,Cr,Al)O_3$ (spinel) (expected waste loading of ~40 wt%). *3.* $CaUTi_2O_7$ (pyrochlore) + spinel + perovskite + rutile (expected waste loading of ~30 wt%).	*Formed via (a) HIPing or (b) melting:* 1. Brannerite + spinel + Gd-bearing perovskite. (expected waste loading of ~60 wt%). 2. $CaUTi_2O_7$ + spinel + ilmenite ($FeTiO_3$) + perovskite + rutile. (expected waste loading of ~50 wt%).	*Formed via HIPing*: Alumina + spinel + magnetoplumbite (expected waste loading ~80%). Estimated melting point 1900®C.	*Formed via (a) HIPing or (b) melting:* A pyrochlore or zirconolite-rich multiphase ceramic having an oxide waste loading of ~10-20 wt%.
Cement (with SiC or polymer coating)	Not applicable	Not applicable	Not applicable	The acid needs to be neutralised and the precipitate separated and calcined prior to cementation. Portland cement.
MKP	MgO, $KH_2P0_4.H_20$, Al_2O_3, ZnP, SiO_2, reducing conditions (e.g. $SnCl_2$), (expected waste loading of ~30 wt%).*	MgO, Fe_2O_3, Al_2O_3, ZnP, SiO_2, $KH_2P0_4.H_20$, reducing conditions (e.g. $SnCl_2$), (expected waste loading of	MgO, $KH_2P0_4.H_20$, ZnP, SiO_2, reducing conditions (e.g. $SnCl_2$), (expected waste loading	Neutralise with MgO to pH ~ 4 MgO, $KH_2P0_4.H_20$, Al_2O_3,

Table 2-2 Recommended candidate conditioning matrices and processing technology for the various waste streams from alkaline route processing of Mo-99.

		~40 wt%).*	of ~40 wt%).*	ZnP, SiO_2, reducing conditions (e.g. $SnCl_2$), Nochar Inc.(N-series) required (expected waste loading of ~40 wt%).*
Geopolymers	Metakaolin-based geopolymer (expected waste loading of ~10 wt%).	Metakaolin-based geopolymer (expected waste loading of ~10 wt%).	Metakaolin-based geopolymer (expected waste loading of ~10 wt%).	CaO +Calcine to remove HNO_3 Metakaolin-based geopolymer (expected waste loading of ~5 wt%).
Polymers (developing technology) NB: Waste loading will depend on radiation level.	1. Phenol formaldehyde resins (Siigroup) 2. Si-Al-Polymers (DC 93-500, CV 2510 and RTV 566 (from Advanced Materials Technology)	1. Phenol formaldehyde resins (Siigroup) 2. Araldite LY 5082 (resin) and Araldite HY 5083 (hardener), glass nanoplatelets 3. Si-Al-Polymers (DC 93-500, CV 2510 and RTV 566 from Advanced Materials Technology) 4. Silicone polyester resin (Evonik Coating systems	1. Phenol formaldehyde resins (Siigroup) 2. Araldite LY 5082 (resin) and Araldite HY 5083 (hardener), glass nanoplatelets 3. Si-Polymers (DC 93-500, CV 2510 and RTV 566 from Advanced Materials Technology)	*Absorb onto Nochar followed by encapsulation with:* 1. Phenol formaldehyde resins (Siigroup) 2. Araldite LY 5082 (resin) and Araldite HY 5083 (hardener), glass nanoplatelets 3. Silicone polyester resin (Evonik Coating systems) 4. Si-Polymers (DC 93-500, CV 2510 and RTV 566 from Advanced Materials Technology) 5. OPC cement

* Necsa to consider if their SiC plasma coating technology has any benefit of being applied to sintered waste forms

2.3 Co-processing of waste streams

Significant economic benefits can be realised if a single process technology platform is capable of treating multiple waste streams. Separate waste forms are proposed above for the four different waste streams identified for this project (unprocessed residue, undissolved residue, alumina ion exchangers and nitric acid solutions), however there would be an economic incentive if a multi-mission technology could be deployed. Co-processing of waste streams does not mean the mixing of different waste streams for processing, rather the ability to treat a range of waste streams in separate campaigns using common waste treatment technology.

Currently ANSTO is constructing a plant to treat its legacy acidic route ILLW and current and future alkaline route ILLW. The acidic route waste is mainly uranyl nitrate plus some fission products and this is to be mixed with additives, dried and calcined, then HIPed to produce a dense pyrochlore-rich waste form. The alkaline route waste is mainly NaOH plus $NaAlO_2$ plus fission products and it will be treated in the same plant to produce a glass-ceramic waste form. In addition other wastes from ANSTO’s current Mo-99 production process such as the low activity liquid waste streams and the uranium filter cake have also been shown to be capable of being treated via the HIP process (unpublished proprietary work) and could therefore use the same plant with minor adaptions.

Although the focus of this report is not on the development of encapsulation technologies for this intermediate-level liquid waste stream, it is prudent that the current proposed encapsulation technologies be investigated for possible co-treatment with this important waste stream. As such, the potential for co-processing the four waste streams in this work package along with the main operational ILLWs from acidic or alkaline route Mo-99 production will be assessed.

3. Recommendations for Work Package 2

The following is an 18-month plan in which a variety of waste forms and processing technologies will be assessed for down selection and progression to the next phase of work. All samples will incorporate where appropriate uranium and inactive representative fission products, for example Cs, Sr, Ba, Ru, La, Mo, Sb, according to waste streams of Chapter 1.

3.1 Phase 1 – Small Scale Testing (first 6 months)

Objective

1. Technology variables identified for manufacturing of small waste forms (~80 samples on 40 gram scale) proposed in Work Order 1.
2. Characterization of the small generated waste forms.
3. Down-selection for the manufacturing of larger waste forms based on measured performance.

Demonstrations proposed:

Manufacturing: Ceramics, glass-ceramics, glass and cement (OPC, MKP, geopolymers) of average size of 40 g lab scale samples with possible compositions as indicated in Table 2-2, will be prepared by various technologies. The emphasis will be on maximizing waste loading within the constraints of producing acceptable solid waste forms. Polymers sourced from international companies will be subjected to radiation at SAFARI to determine possible application.

3.2 Phase 2 - Larger scale demonstration (months 7-12)

Objective

1. Technology variables identified for manufacturing of large waste forms proposed in phase 1.
2. Characterization of generated waste forms.
3. Identification of potential options for the co-processing of waste streams.

Demonstrations proposed

Manufacturing: Down selected compositions (~10-15 samples) identified in Phase 1 will be used to manufacture large waste forms (2 and 10L-sized cans for ceramics, glass-ceramics and glasses and 2 L size waste forms for cement (OPC, MKP and geopolymer compositions) and possible identified polymers. The emphasis will be on maximizing waste loading within the constraints of producing acceptable solid waste forms.

Co-processing selection: Identification of potential waste forms suitable for co-processing of waste streams. Co-processing is defined here as the potential for using the same waste form, plant or processing technology to process a variety of different waste streams.

3.3 Phase 3 – Potential for co-processing of waste streams (months 12-18)

Objective

1. Technology variables identified for manufacturing of large waste forms proposed in phase 2 for possible co-processing of waste streams.

2. Characterization of generated waste forms.

3. Demonstration of hot cell compatibility for future work order 4 (where applicable).

4. Consolidated report.

Demonstrations proposed

Manufacturing: Down selected ceramics, glass-ceramics, glass compositions as indentified in Phase 2 will be used to manufacture large waste forms (2 and 10L-sized cans) and 2 L size waste forms for cement (OPC, MKP, geopolymers compositions) and possible identified polymers. Emphasis here will be on investigating potential co-processing options.

4. Proposed encapsulation program

The proposed encapsulation program recommended for Work order 2 is based on the collective and extensive expertise as well as existing waste treatment technologies available at Necsa and ANSTO. To maximize the effort regarding the encapsulation of the waste streams the following were proposed:

Ansto-Studies: encapsulation into ceramics. glass-ceramics, geopolymers and glasses using HIPing, melting and sintering technology while,

Necsa-studies: encapsulation into glasses, cements, MKP, polymers and glass-ceramics using melting, and sintering technology.

A more detailed proposal is as follows:

4.1 Work to be carried out at ANSTO

Phase 1 (6 months)

Approximately 20 ceramics and glass-ceramics (~40 g lab scale samples) will be processed by HIPing with targeted waste loadings of > 20 wt% for the individual wastes detailed in Chapter 1. Emphasis is given to maximizing waste loading within the constraints of producing solid waste forms which will pass PCT leach tests at 40 and 90℃, plus yield respectable values in periodic analysis in MCC-1 leach tests of up to 90 days at 40 and 90℃. Detailed optical, XRD, and SEM will be carried out as well as other characterization techniques as necessary. Acid digestion and PCT analysis will also be undertaken.

In most cases, parallel tests will be done on melts and Ar- sintered (~1000℃) lab scale samples for comparison.

Approximately 20 metakaolin lab scale geopolymers will also be made using waste loadings of up to ~10 wt%. Here compressive strength, “cure/settability” measurements, LOI, thermal water removal testing and 40℃ PCT leach testing will be carried out.

Phase 2 (6 months)

The best waste forms (~5-8) found from the results in Phase 1 will be scaled up for melts (where appropriate) and sub-solidus HIPing in 2 and 10L-sized cans, on which approximately 10 samples will be selected from different sections of each HIP can and detailed examination pursued as above.

Approximately 2L samples will be made of selected geopolymers and in addition to standard characterization (see above), ANS 16.1 durability measurements will be made.

Phase 3 (6 months)

Approximately 10 ceramics or glass-ceramics and 10 geopolymers will be made to examine candidacy of co-processing of various wastes (including operational wastes from acidic and alkaline route Mo-99 production) to generate good waste forms. A final consolidated report will be written detailing the results of the above.

4.2 Work to be carried out at Necsa

Phase 1 (6 months)

Glass, glass-ceramics and phosphate cement (~40 g lab scale samples) will be processed by melting and sintering with targeted waste loadings of > 20 wt% for the individual wastes detailed in Chapter 1. These waste forms will also be subjected to possible SiC layer coating using plasma sputtering or microwave technology

Emphasis is given to maximizing waste loading within the constraints of producing solid waste forms which will pass PCT leach tests at 40 and 90°C, plus yield respectable values in periodic analysis in MCC-1 leach tests of up to 90 days at 40 and 90°C. Detailed optical, XRD, and SEM will be carried out as well as other characterization techniques as necessary. Acid digestion and PCT analysis will also be undertaken.

Polymers sourced from international companies will be subjected to radiation at SAFARI to determine possible application.

Phase 2 (6 months)

The best waste forms found from the results in Phase 1 will be scaled up. Encapsulation of the waste streams in polymers with glass plates will be processed with targeted waste loadings of > 20 wt% for the individual wastes detailed in Chapter 1. These waste forms will also be subjected to possible SiC layer coating using plasma sputtering or microwave technology. Detailed characterization will be performed as previously mentioned.

Phase 3 (6 months)

Approximately 10 glasses or glass-ceramics and 10 phosphate cement or polymers waste forms will be made to examine candidacy of co-processing of various wastes (including operational wastes from acidic and alkaline route Mo-99 production) to generate good waste forms. A final consolidated report will be written detailing all the results.

5. Conclusion

There are four waste streams that will be considered for encapsulation in this work package; (i) uranium filter cake from the alkaline processing, (ii) undissolved residue after uranium recovery dissolution, (iii) alumina ion exchangers from uranium recovery process and (iv) nitric acid solutions. From the established waste compositions for each of these waste streams, literature surveys and in house experience, recommendations have been made in this chapter for the deployment of encapsulation technologies. Several technologies have been considered and down-selected to what are believed to be the most feasible waste form options. Immobilization matrices for the wastes must demonstrate proliferation resistance and will be assessed against the generic Waste Acceptance Criteria developed as part of this project. Possible waste loading within the constraints of producing suitable solid waste forms are indicated. The possibility of co-processing various waste streams, including operational ILW from acidic or alkaline route Mo-99 production by using the same plant and equipment will also be considered. Recommendations for encapsulation technologies have been made in this chapter and these will form the basis of "Work Order 2". The collective and extensive expertise developed at Necsa and ANSTO in commercial-scale Mo-99 production and in the encapsulation of similar waste streams will ensure a positive outcome for the proposed program.

6. References

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APPENDIX A

Neutron Radiography/tomography and X-Ray tomography can also be considered as possible techniques to contribute to this study as unique tests or to validate results from existing techniques. These types of techniques are very promising, and they may change the way we obtain design parameters in geotechnical and structural engineering. A short description of these alternative technologies are given below.

1.1 Radiography/Tomography techniques

Radiography is a non-destructive examination (NDE) technique based using penetrating radiation to produce 2-D images, called radiographs. Being a non-destructive analytical tool, radiography enables the visualisation of interior features of objects without any physical modification of the object under investigation. When radiation passes through an object, they can be scattered, absorbed and transmitted.

The transmitted portion / component of the initial radiation through a sample of the interaction is detected using flat panel detectors and the consequent radiographs provides information about materials that constitute the object under investigation according to the Beer-Lambert law:

$$I = I_0 e^{-\Sigma d} \qquad (1)$$

where I_0 and I are the intensities of the beam before and after interaction with the sample respectively, and Σ and d are the linear attenuation coefficient (cm^{-1}) and the thickness (cm) of the sample respectively. The linear attenuation coefficient is a function of the type of radiation used in the investigations (Neutrons, X-rays or gamma rays), the energy of the specific radiation used s well as the elemental composition of the sample under investigation.

Tomography is a 3-D non-destructive examination (NDE) technique based on reconstruction of a virtual 3-D image of the object under investigation using multiple 2-D radiographs obtained at different angles of rotation as the object under investigation is rotated through at least 180°.

A 3-D image (tomogram) is composed of slice images. The slice images are reconstructed from a series of radiographs (projections) taken at different angles of rotation of the sample. The reconstruction of slice images was performed using OCTOPUS software which reconstructs cross-sectional images (slices) of the sample using a filter-back projection reconstruction algorithm. Image correction (background, electronic, beam hardening and beam fluctuation corrections) is carried out before the reconstruction. The result of reconstruction is a stack of slice images numbered according to their position on the sample from top to bottom.

VGStudio Max visualisation software provides a 3-D visualisation and analysis of the stack of slice images. The stack is analysed as a 3-D image representation of the sample. Each region of the volume is represented by voxels (volume elements).

Necsa has currently 2 x radiography/tomography facilities available for the purpose of this project:

1.1.1 Neutron radiography/Tomography (NRAD)

At 20 MW reactor power at the SAFARI-1 nuclear research reactor, at beam port no-2, using a 21 mm interior pinhole diameter neutron passage in the collimator, a 93% thermal neutron flux of 1.2 x 10^7 n.cm^{-2}.s^{-1} is delivered at the object position in the centre of the beam at the radiography facility. Radiographs are captured via a lithium-based zinc-sulphate scintillator screen using a Peltier-cooled Charged Coupled Device (CCD) camera with a 1024 x 1024 pixel array and 16-bit image output device. The system has a 2 µs/image readout capability. Using a 100 mm x 100 mm field of view (FOV), a resolution of 0.098 mm/pixel size is achieved. This means that 2-D images (NR) have a 0.0096 mm^2, and 3-D images (NCT) a 0.0009 mm^3, spatial resolution limitation respectively at the 1 horizontal binning and 1 vertical binning of pixels. Binning of pixels horizontally and vertically on the CCD is the concept of grouping a number of pixels into one pixel, thereby affecting the intensity and the spatial resolution but allows for dynamic processes to be studied. Neutron radiography/tomography is carried out at ANSTO at the Bragg Institute on a beamline instrument called “Dingo”.

1.1.2 Micro-Focus X-ray Tomography

Micro-focus X-ray Computed Tomography technology becomes a very attractive radiation based research technique since high quality micron-level information of the interior as well as composition of samples can be obtained non-invasively and non-destructively. The South African Nuclear Energy Corporation (Necsa) perform X-ray investigations in previous research projects using a 100kV X-ray source. There is however a big limitation to this particular system since the focal spot is relatively large (3 mm) and as a result, the spatial resolution obtained, even with small samples, is in the order of 0.08 mm.

In 2012 Necsa installed a Nikon XTH 225 ST micro-focus X-ray tomography systems that consists of 4 separate functional units; a lead-lined cabinet, an external control module, an external chiller and PC’s with software for acquisition, reconstruction into a 3D virtual image and for visualisation and analysis (See Figure A-1). The lead-lined cabinet houses the X-ray tube, sample manipulator and flat panel detector. The lead-lined cabinet meets international radiation standards and is completely shielded so that the total hourly dose rate measures less than 1 micro Sievert on the cabinet surface. The system voltage setting ranges between 30 and 225 kV whilst the beam current ranges from 0 to 1 mA . With a maximum power rating of 30W it ensures that a wide variety of samples can be investigated, even when the density of the sample is relatively high.

A multi-metal reflection target enables the researcher to utilize a specific X-ray energy spectrum depending on the specific sample characteristics that is being investigated. The multi-metal target comprises 4 targets on one rod and consists of molybdenum, copper, silver and tungsten (which are mostly used in X-ray sources).

The Perkin Elmer detector is a flat panel detector with a 16 bit dynamic range. This detector is state of the art and uses a scintillator material in conjunction with a direct output digital panel. The physical active size of the detector is 400 mm x 400 mm with a pixel size of 200micron x 200micron. For tomography applications the Inspect-X dedicated software, developed by Nikon, manage simultaneously the projections for the CT scan that are acquired, the vacuum , and sample manipulation. The Inspect-X software incorporate these images in real-time during the scanning process so that the projections obtained from a CT scan are already normalized.

With a 2048 x 2048 pixel array and 16-bit image output, geometric enlargement of samples onto the detector, a resolution of 0.005 mm/pixel size is achieved.

Figure A-1 Micro-focus X-ray machine at the MIXRAD facility

1.2 Applications of radiography

1.2.1 Water sorptivity measurements

The thermal neutron imaging facility at the SAFARI-1 reactor was used to map water transport through the cement applying radiography and tomography as analytical tools.

For sorptivity measurements by neutron radiography on dried waste form specimens, samples were tightly enclosed in aluminium tape with only the circular bottom faces of the samples exposed, facilitating water transport in one direction only (upwards). The exposed base of each sample was continuously immersed in water to a depth of approximately 2 mm and adsorption measured over periods of 1, 2, 4, 6, 9, 12, 16, 20 and 25 minutes, and for longer time periods (up to a month) where possible. At the end of each time interval the samples were removed from the water, weighed and then transferred to the NR facility to collect 2-D radiographic data and chart water ingress. A rig was specially designed for the radiography facility so that the uncovered face of the samples remained immersed during data acquisition. The 2-D images were obtained over a 3 second exposure time each with horizontal and vertical pixel binning settings of 4 and 1 respectively, resulting in spatial resolution limits of 0.391 mm/pixel and 0.098 mm/pixel respectively. The water could be visualised within each sample after each water absorption period, and a thick line profile was used to obtain intensity data from the sample image (Figure A-2). From the curve of intensity as a function of the length of the sample, the water front could be determined as shown by the dotted marker on Figure A-2b. The defect detection tool of VGStudio was used to detect pores and to provide their size and location inside the volume of the sample, as shown in Figure A-3. The minimum pore volume that can be detected is a voxel resolution and is equal to the product of x, y and z where x, y and z are the dimensional size of the voxel.

1.2.2 Macro pore distribution determination from NCT (3-D investigation)

The 3-D neutron tomography investigation was performed on completely dried specimens to determine macro-pore distributions. These 3-D images were obtained from the reconstruction of 360 x 2-D images acquired over a 20 second exposure period for each of the 2-D images.

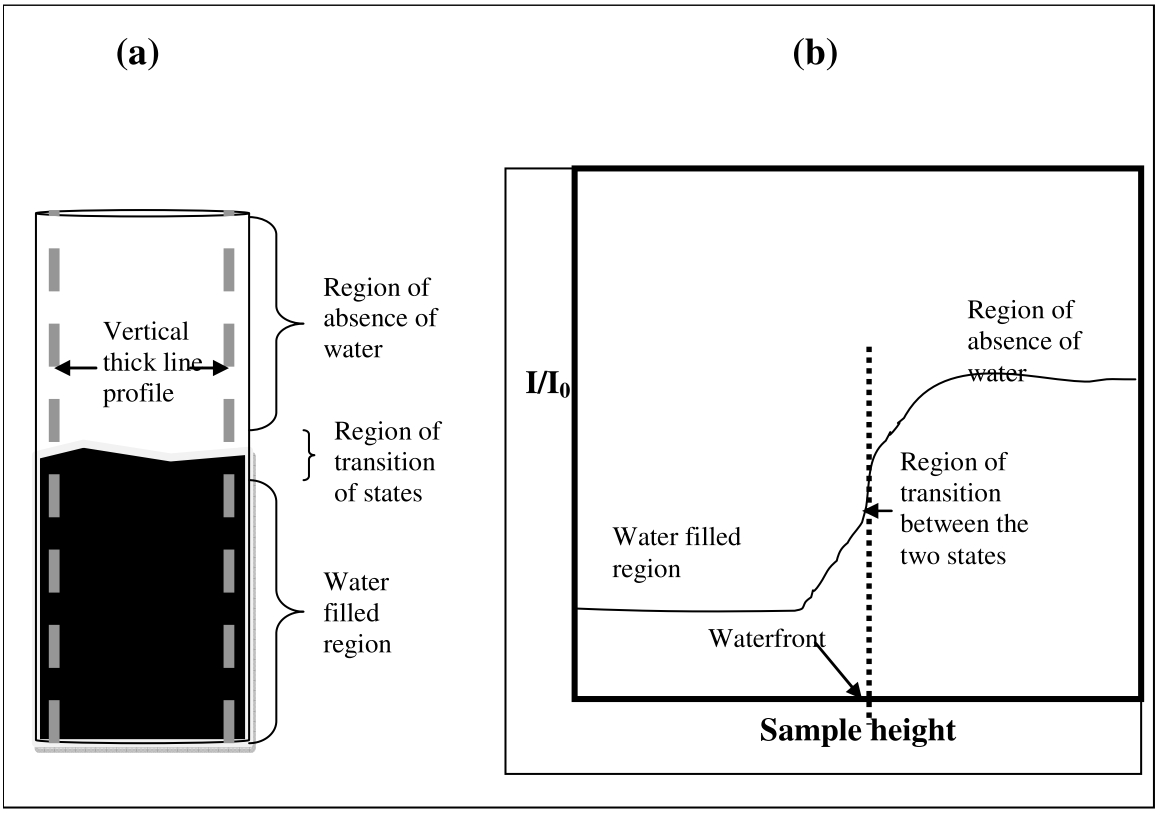

Figure A-2 Examples of pore distribution determinations

- ***(a)*** *Schematic diagram of a radiograph showing a water front within a cylindrical mortar sample and*
- ***(b)*** *Determination of the water front height from the resulting curve of intensity as a function of sample height.*

The defect detection tool of VGStudio was used to detect pores and to provide their size and location inside the volume of the sample, as shown in Figure A-3.

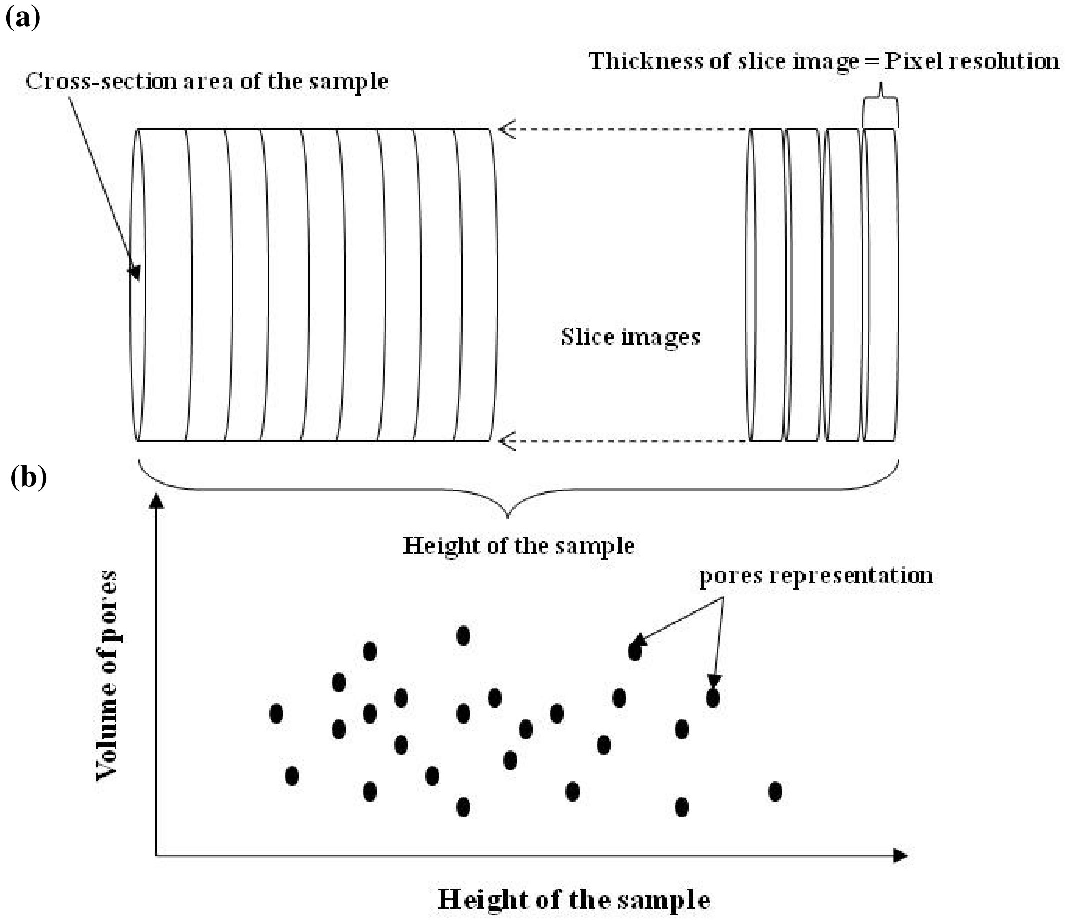

Figure A-3 Reconstruction of cross-sectional images to determine pore size distribution.
(a) Schematic diagram showing the constitution of sample height from slice images
(b) Presentation of pore size distribution as a function of sample height.

1.2.3 Porosity measurements

The porosity and sorptivity tests may be defined as techniques that measure the early age resistance of concrete to the transport of fluids through concrete. The purpose of the NRAD tests is not to determine absolute or intrinsic material characteristics, but to produce reliable values to be used for comparative purposes. Neutron radiography (NRAD) is a useful, non-destructive visualizing method for determining hydrogen content in various materials. Hydrogen content in samples is determined by quantitative analysis of measured profiles of neutron attenuation in the samples. Thermal neutrons are attenuated (mostly scattered) to a significant degree by hydrogen, and substances that contain hydrogen. Thus, neutron radiographs of porous media containing water can provide an accurate indication of the pore structure of the media e.g. pore size distributions.

Preparation of the sample for the porosity test was the same as for the NRAD sorptivity tests. The samples were initially dried in an oven, measured and weighed to obtain their density and then subjected to a vacuum for 1 h to ensure that all the air was removed. After this treatment a neutron radiography image was captured (I_{Dry}). After this initial image of the dry waste forms was captured, the waste forms were subjected to a vacuum for 1 h to ensure that all the air was removed and then saturated with water under the vacuum for another hour. The saturated waste forms were removed and put into the neutron beam at exactly the same geometry as before to capture the saturated neutron image (I_{Wet}). The porosity and thus the distribution of porosity within the sample is being calculated using equation 2:

$$\text{Porosity } (\%) = \frac{\ln(I_{Sat}/I_{Dry})}{h\rho_w\mu_w} \qquad (2)$$

where h is the thickness of the specimen in cm, μ_w is the thermal neutron attenuation of water obtained for the specific specimen geometry in cm^2/g and ρ_w is the density of water in g/cm^3.

1.2.4 Micro-focus X-ray tomographic investigations at MIXRAD

Example of the analysis that can be obtained for HLW matrixes using micro x-ray analysis is indicated in Figure A-4. Figure A-4 shows some micro x-ray slides of a manufactured cold ceramic monolith (MKP) containing Nochar (organic polymer). The 3-dimensional renderings of each sample were obtained by a software package called VG Studio. For correlation purposes, another software package called Image J was used to calculate the % porosity for each slice (different sections of sample).

Figure A-5 shows a representation of the calculated % porosity of the MKP monolith with each individual slice of the scan expressed in % area of the pores against sample length.

Each data point on the graph represents the % porosity of the volume of a single slice of the micro x-ray scan. The scan takes millions of slices of the sample and stores the data in its library. Then with the use of software packages such as Image J, the data can be used to calculate many properties such as porosity

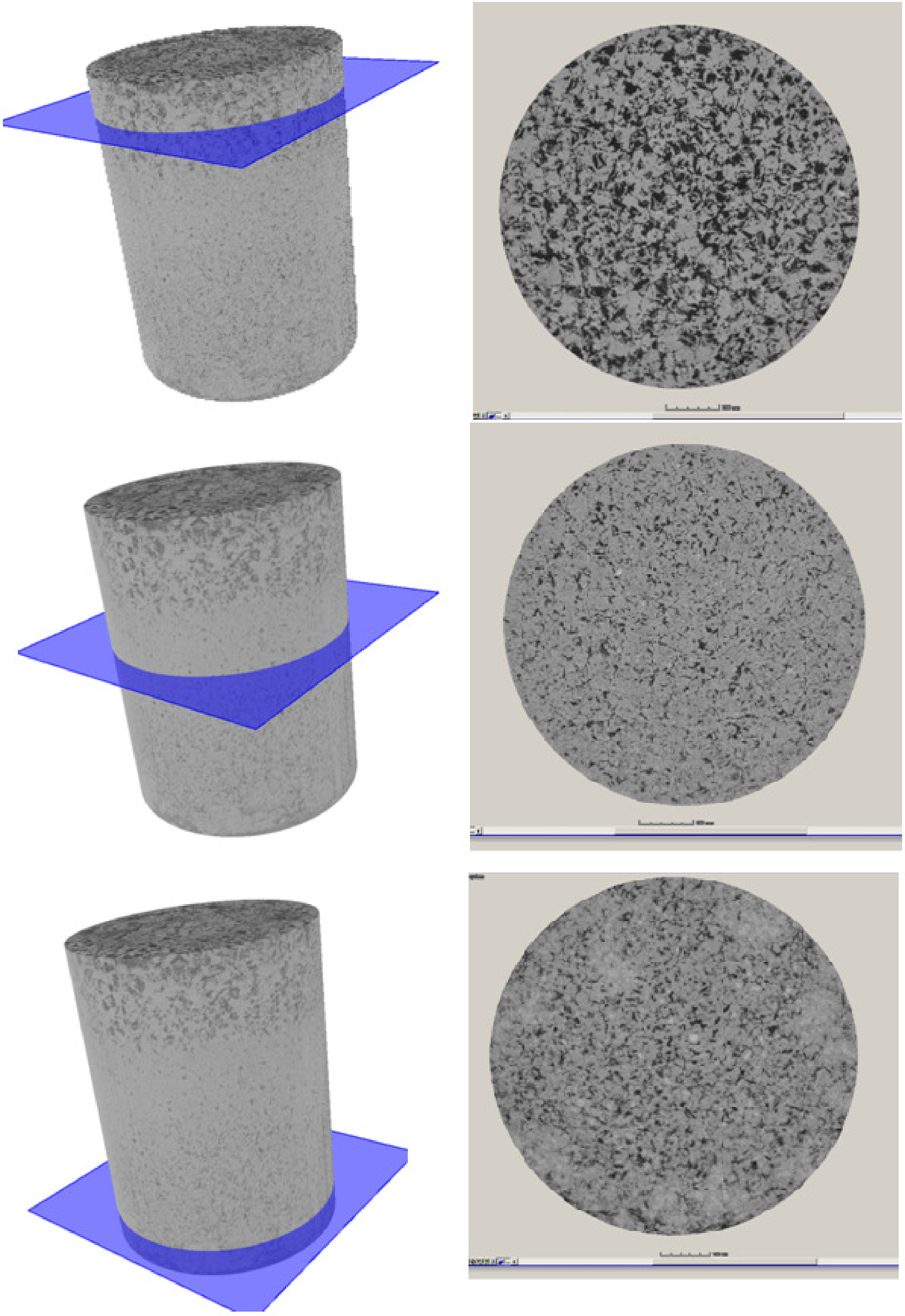

Figure A-4 Micro x-ray slides at different positions of the MKP sample.

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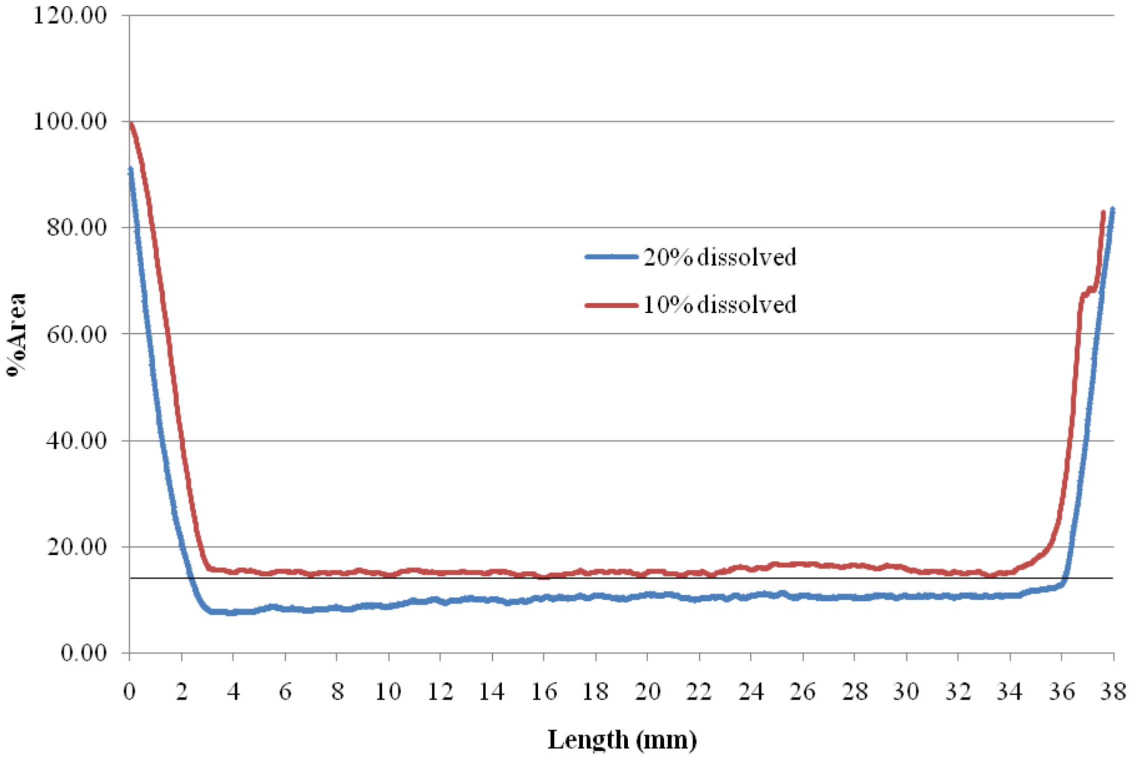

Figure A-5 *% Porosity for each scan slice of the MKP matrices with 10% and 20%* Nochar

The results illustrated that micro X-ray analysis technique can be used to determine porosity, density and possible voids or cracks inside a monolith.

APPENDIX B

Table B-1 Compositions (wt%) of Lanthanide Borosilicate Glasses for immobilisation of actinides [1].

Oxide	**Loffler Glass**[1]	**Ramsey Loffler ThO_2-1**	**Ramsey Loffler ThO_2-2**	**Meaker Loffler ThO_2**	**LaBS PNNL PuO_2**	**LaBS Frit A PuO_2**	**LaBS Frit B PuO_2**	**LaBS Frit X PuO_2**	**LaBS Frit B ZrO_2**	**LaBS Frit B HfO_2**	**LaBS Frit X HfO_2**
Al_2O_3	9.0	9.08	3.58	16.25	19.04	19.46	19.27	9.05	20.35	19.17	9.00
BaO	2.0	2.02	2.14	-	-	-	-	-	-	-	-
B_2O_3	5.0	5.05	7.88	8.85	10.4	10.59	10.50	11.77	11.07	10.44	11.70
Ce_2O_3 (Pr_2O_3)	(3.2)	18.61	-	-	-	-	-	-	-	-	-
Gd_2O_3	-	-	-	17.16	7.61	7.78	11.58	12.22	12.23	11.52	12.15
HfO_2 (frit component)	-	-	-	-	-	-	5.97	6.34	6.23	5.94	6.30
HfO_2 (PuO_2 surrogate)	-	-	-	-	-	-	-	-	-	10.00	10.00
La_2O_3	18.3	0.91	1.21	3.80	11.01	11.22	7.33	17.20	7.70	7.29	17.10
Nd_2O_3	32.5	32.81	34.76	4.05	11.37	11.58	7.42	13.58	7.80	7.38	13.50
PbO	7.9	7.97	8.44	-	-	-	-	-	-	-	-
PuO_2 (Pu_2O_3)	-	-	-	-	11.39	9.50†	9.50	9.50	-	-	-
SiO_2	21.5	21.7	24.36	22.0	25.80	26.43	26.15	18.10	27.52	26.01	18.00
SrO (CaO+ZnO)	-	-	-	1.9	2.22	2.26	2.26	2.26	2.42	2.25	2.25
ThO_2 (PuO_2 surrogate)	-	1.85	17.62	25	11.39	-	-	-	-	-	-
ZrO_2 (frit component)	-	-	-	1	1.15	1.18	-	-	-	-	-
ZrO_2 (PuO_2 surrogate)	-	-	-	-	-	-	-	-	4.56	-	-
Na_2O and Li_2O	-	-	-	-	-	-	-	-	-	-	-
Melt Temp (℃)	1350	1400	1425	1475	1450-1500	1500	1500	1500	1500	1500	1500

[1] This glass also has 0.1 wt% As_2O_5 as a fining agent

† maximum waste loading determined to be 13.4 wt% PuO_2

Table B-2 Proposed glass compositions (wt%) for immobilisation of undissolved residue [2]

Glass Code	**Composition**														
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	TiO_2	ZrO_2	Fe_2O_3/FeO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Others
Borosilicate compositions (UK)															
189	3.59	7.86	-	6.23	-	-	-	-	2.68	0.40	21.87	5.03	41.51	0.23	9.58 FPO; 0.55 Cr_2O_3; 0.36 NiO; 0.1 SO_4; 0.06 U_3O_8
209 frit	5.4	11.2	-	-	-	-	-	-	-	-	15.0	-	68.5	-	-
209	3.99	8.30	-	6.34	-	-	-	-	2.73	0.40	11.12	5.11	50.88	0.23	9.75 FPO; 0.56 Cr_2O_3; 0.36 NiO; 0.1 SO_4
209	-	8.3	-	6.3	-	0.3	-	1.4	2.7	-	11.1	5.1	50.9	-	0.8 Cs_2O_3
MW frit	5.33	11.0	-	-	-	-	-	-	-	-	21.88	-	61.75	-	-
MW(WVPM)	4.0	8.3	-	5.4	-	-	-	-	2.50	-	16.4	4.9	46.3	-	11.1 FPO; 0.4 Cr_2O_3; 1.03 NiO
MW(WVPT)	4.3	8.8	-	-	-	-	-	-	0.70	-	17.5	-	49.4	-	15.9 FPO; 2.7 Gd_2O_3; 0.3 ActO; 0.2 Cr_2O_3; 0.1 NiO
Simulated Magnox	3.82	8.51	-	5.37	-	0.94	1.92	1.57	3.13	-	17.17	4.9	47.94	0.2	1.03 Cs_2O; 0.19 Y_2O_3; 1.62 MoO_3; 3.61 La_2O_3
MS	3.7	7.7	-	6.2	-	-	-	-	2.7	-	21.9	5.0	41.5	-	9.5 FPO; 0.6 Cr_2O_3; 0.34 NiO; 0.4 ActO
M22	4.0	8.3	-	6.3	-	-	-	-	2.7	-	11.1	5.1	50.9	-	9.8 FPO; 0.6 Cr_2O_3
BNFL HM4	4.24	8.80	-	-	-	0.94/0.4	0.53	2.20	0.33	-	17.52	-	49.44	-	3.00 Nd_2O_3; 2.39 MoO_3; 2.27 Gd_2O_3; 1.41 Ag_2O; 1.33 CeO; 1.31 Cs_2O; 0.71 La_2O_3; 0.44 Sm_2O_3; 0.25 Y_2O_3; 0.16 Rb_2O; 0.12 TeO_2, 0.1 Cr_2O_3
Borosilicate compositions(France)															
F-son	-	9.4	-	-	-	0.66	-	3.12	0.6	-	19.0	0.1	43.6	-	1.79 Cr_2O_3
M7 frit	-	14.1	-	-	4.6	-	-	-	3.3	-	16.0	5.6	52.1	-	-
AVM	-	18.6	-	-	-	-	-	-	-	-	25.3	-	56.1	-	-
AVM	2.0	10.0	-	-	4.1	-	-	1.0	2.90	2.6	14.2	5.0	46.6	0.3	10.0 HLW oxides; 0.5 Cr_2O_3; 0.4 NiO; 0.4 UO_3
SON 58 30 20U2	-	9.40	-	-	-	-	-	-	0.60	-	19.0	0.10	43.60	0.60	22.69 FPO; 3.60 U_3O_8; 0.20 Cr_2O_3; 0.10 NiO
SON 64 19 20 F3	-	11.5	-	0.20	-	-	-	-	5.90	-	17.30	-	44.20	-	13.85 FPO; 5.9 Gd_2O_3; 0.9 U_3O_8; 0.5 Cr_2O_3
SON 68 frit	2.4	11.9	-	-	4.9	-	-	-	-	3.0	16.9	5.9	54.9	-	-
SON 68	2.0	9.9	-	-	4.0	-	-	1.0	2.9	2.5	14.0	4.9	43.5	-	11.3 FPO; 0.8 ActO; 0.7 NiO; 0.5 Cr_2O_3

Table B-2 Proposed glass compositions (wt%) for immobilisation of undissolved residue [2]

Glass Code	**Composition**														
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	TiO_2	ZrO_2	Fe_2O_3/FeO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Others
SON 68	1.96	9.86	-	-	4.04	-	-	2.65	-	2.5	14.0	4.91	45.48	-	1.7 MoO_3; 1.59 Nd_2O_3; 1.42 Cr_2O_3; Misc.
SON 68 FR	2.4	11.9	-	-	4.9	-	-	-	-	3.0	16.9	5.9	54.9	-	-
SM 513 FR	4.7	6.5	-	2.3	5.1	-	5.1	-	-	-	14.7	3.0	58.6	-	-
SM 527 FR	4.0	11.0	-	-	5.0	-	2.0	-	-	-	28.0	-	50.0	-	-
R 717 frit	2.4	11.9	-	-	4.9	-	-	-	-	3.0	18.9	5.9	54.9	-	-
CEA SUMo2-12c	-	8.79	-	-	5.67	-	-	7.14	-	5.62	12.96	6.18	35.99	3.68	12.00 MoO_3; 1.96 'others'
Borosilicate compositions (USA)															
PNL 72-68	-	4.0	4.0	1.5	1.5	1.5/ 1.5	-	-	1.0	21.3	11.1	-	27.3	0.2	23.1 FPO; 1.5 ActO; 0.2 Cr_2O_3; 0.1 NiO
PNL 76-68 frit	-	11.3	-	-	2.9	-	4.5	-	-	7.6	14.3	-	59.4	-	-
PNL 76-68	-	12.8	-	-	2.0	0.59/ 0.40	2.97	1.88	10.34	4.97	9.47	-	39.80	0.51	4.67 Nd_2O_3; 2.42 MoO_3; 1.26 CeO_2; 1.13 RuO_2; 1.09 Cs_2O; 0.56 PdO; 0.56 Pr_6O_{11}; 0.56 La_2O_3; 0.44 Cr_2O_3; 0.35 Sm_2O_3; 0.28 TeO_2; 0.23 Y_2O_3; 0.21 NiO; 0.18 Ru_2O_3; 0.13 Rb_2O_3
PNL HW 39-4	3.75	11.25	-	0.84	0.83	0.11/ 0.11	-	3.85	7.19	-	10.53	2.31	53.53	0.11	0.80 CdO; 0.66 La_2O_3; 0.61 NiO; 0.32 F, 0.32 MoO_3; 0.31 Nd_2O_3; 0.16 RuO_2
SRL 131	5.7	17.7	-	2.0	-	-	1.0	0.5	-	-	14.7	-	59.7	-	0.5 La_2O_3
SRL 131	4.1	13.3	-	1.4	1.0	-	0.7	0.4	13.9	-	10.6	3.0	41.7	-	3.7 MnO_2; 2.7 zeolite; 1.6 NiO; 0.4 La_2O_3;0.4Na_2SO_4
SRL 165 frit	7.0	13.0	-	1.0	-	-	-	1.0	-	-	10.0	-	68.0	-	UO_2
SRL 165	4.18	10.85	-	0.70	1.62	0.17	0.14	0.66	11.74	-	6.76	4.08	52.86	0.02	2.79 MnO_2; 0.92 UO_2; 0.85 NiO
SRL 202	4.69	6.75	-	1.47	0.79	0.13	1.32	-	12.05	-	8.06	4.76	51.22	-	3.47 MnO_2; 1.08 UO_2
SRL 202	4.53	7.91	2.01	1.51	1.11	-	0.24	1.19	12.55	0.09	6.99	4.77	51.53	-	3.27 MnO; 1.06 NiO; 0.35 Nd_2O_3
SRL 202 U/A	4.4	7.8	3.7	1.4	1.3	0.21	0.93	0.06	11.9	0.29	8.0	3.9	50.2	-	2.2 MnO_2; 2.0 UO_2; 0.85 NiO; 0.41 CuO; 0.28 ThO_2; 0.12 Cr_2O_3; 0.11 La_2O_3;
SRL 503 frit	8.0	4.0	-	-	-	-	-	-	-	-	14.0	-	74.0	-	-
DWPF 'Slend'	4.40	8.73	3.86	1.35	0.97	-	0.90	-	6.95/ 3.11	-	8.01	3.98	50.20	-	2.14 U_3O_8; 2.03 MnO; 0.89 NiO; 0.44 CuO; 0.27 $BaSO_4$; 0.19

Table B-2 Proposed glass compositions (wt%) for immobilisation of undissolved residue [2]

Glass Code	**Composition**														
															ThO$_2$; 0.19 NaCl; 0.12 Cr$_2$O$_3$; 0.10 Na$_2$SO$_4$
	Li$_2$O	Na$_2$O	K$_2$O	MgO	CaO	BaO/SrO	TiO$_2$	ZrO$_2$	Fe$_2$O$_3$/FeO	ZnO	B$_2$O$_3$	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	Others
DWPF	4.4	8.58	3.47	1.36	1.16	0.22	0.65	-	12.47	-	7.79	3.84	49.61	-	2.05 MnO; 0.53 U$_3$O$_8$; 0.40 CuO; 0.36 ThO$_2$; 0.31 NaCl; 0.22 BaSO$_4$; 0.12 CaSO$_4$; 0.1 Na$_2$SO$_4$; 0.1 Cr$_2$O$_3$;
DWPF Purex	3.12	12.14	3.58	1.33	1.02	-	0.65	-	12.74	-	10.21	2.89	44.56	-	2.89 U$_3$O$_8$; 21.99 MnO; 1.21 NiO; 0.42 CuO; 0.29 BaSO$_4$; 0.26 NaCl; 0.14 Cr$_2$O$_3$; 0.12 CaSO$_4$; 0.12 Na$_2$SO$_4$
DWPF frit 165	7.0	13.0	-	1.0	-	-	-	1.0	-	-	10.0	-	68.0	-	-
DWPF frit 200	5.0	11.0	-	2.0	-	-	-	-	-	-	12.0	-	70.0	-	-
DWPF frit 202	7.0	6.0	-	2.0	-	-	-	-	-	-	8.0	-	77.0	-	-
Borosilicate compositions (Japan)															
Tokai frit (Japan)	-	1.4	-	-	2.8	-	-	-	-	-	19.8	5.0	61.0	-	-
PNC Tokai	3.0	9.6	-	-	3.0	-	-	-	-	3.0	14.3	5.0	46.7	-	9.8 FPO; 3.2 'other oxides'; 2.4 ActO
J-10	-	9.19	1.23	1.60	7.10	-	0.07	-	2.02	-	14.02	3.81	41.22	1.17	18.5 waste oxides
JAERI	2.00	9.78	-	-	4.00	0.62/ 0.34	-	2.64	2.90	2.47	13.90	4.89	45.15	0.30	3.04 Cm oxides; 1.73 MoO$_3$; 0.96 Pu oxides; 0.87 Cs$_2$O; 0.8 RuO$_2$; 0.5 Cr$_2$O$_3$; 0.4 NiO; 0.45 Nd$_2$O$_3$; 0.28 CeO$_2$; 0.26 MnO; 0.23 TeO$_2$; 0.14 La$_2$O$_3$; 0.14 Pr$_6$O$_{11}$
PNC 0422	3.2	0.9	2.0	-	2.0	-	-	-	-	2.5	14.7	4.0	43.9	-	30 waste (includes 9.91 Na$_2$O; 2.67 ZrO$_2$; 1.79 Fe$_2$O$_3$; 0.91 BaO)
PNC 0545	3.0	1.0	2.0	-	2.0	-	-	-	-	2.0	14.2	3.5	43.4	-	30 waste (includes 8.03 Fe$_2$O$_3$; 7.41 Na$_2$O; 2.0 ZrO$_2$; 0.68 BaO)
PNC 0577	2.0	2.0	1.0	-	1.0	1.0	-	-	-	1.0	13.6	2.4	47.5	-	30 waste (includes 7.41 Fe$_2$O$_3$; 7.41 Na$_2$O; 2.00 ZrO$_2$; 0.68 BaO)
PNC 0631	3.6	1.0	2.3	-	2.3	-	-	-	-	2.5	16.4	4.0	48.8	-	20 waste (includes 5.35 Fe$_2$O$_3$; 4.94 Na$_2$O; 1.33 ZrO$_2$; 0.45 BaO)

Table B-2 Proposed glass compositions (wt%) for immobilisation of undissolved residue [2]

Glass Code	**Composition**														
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	TiO_2	ZrO_2	Fe_2O_3/FeO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Others
PNC 0632	2.7	0.8	1.7	-	1.8	-	-	-	-	1.9	12.5	3.1	37.2	-	40 waste (includes 10.7 Fe_2O_3; 79.89 Na_2O; 2.67 ZrO_2; 0.691 BaO)
PNC PO968	2.86	10.0	-	-	2.86	0.66/ 0.38	-	0.90	3.26	2.86	13.59	4.80	44.56	0.37	3.58 La_2O_3; 1.71 Nd_2O_3; 1.06 CeO_2; 0.96 Cs_2O; 0.93 RuO_2; 0.90 MoO_2; 0.57 NiO; 0.53 Cr_2O_3; 0.49 Pr_6O_{11}; 0.47 MnO_2; 0.44 PdO; 0.35 Sm_2O_3; 0.23 Y_2O_3; 0.20 Rh_2O_3; 0.19 TeO_2; 014 Rb_2O
Borosilicate compositions (Miscellaneous)															
'Borosilicate'	-	6.98	5.78	-	3.18	-	5.26	-	-	7.59	18.92	-	53.60	-	-
VG 98/3 (Germany)	-	22.25	-	0.40	2.32	-	3.52	-	0.70	-	10.48	1.20	41.84	-	15.54 FPO_2; 1.21 U_3O_8; 0.24 Cr_2O_3; 0.21 NiO
GPWAKI (Germany)	2.9	6.0	-	1.8	4.5	-	1.0	-	-	-	14.8	2.6	50.4	-	11.7 HLW oxides including 4.3 Na_2O
GGWAW 15 (Germany)	4.0	8.0	-	3.5	6.0	-	1.5	-	-	-	19.0	3.0	55.0	-	-
GGWAKI (Germany)	3.5	7.1	-	2.2	5.3	-	1.2	-	-	-	17.6	3.1	60.0	-	-
LRR-ECM (Italy)	-	12.7	-	-	-	0.1	-	0.6	12.5	-	11.2	2.1	50.9	-	0,2 Cs_2O_3; 0.2 MnO
ABS41 (Sweden)	-	9.4	-	-	-	0.3	-	1.3	3.6	-	15.9	2.5	52.0	-	0.9 Cs_2O_3; 0.8 MnO
204 (Canada)	-	11.7	-	-	-	0.4	-	1.7	9.6	-	7.6	-	52.6	-	1.0 Cs_2O_3
SM58 LW11 (Belgium)	3.7	8.3	-	2.0	3.8	-	4.5	-	1.2	-	12.3	1.2	56.9	-	6.1 FPO; 0.1 NiO
R-111 (India)	-	0.2	-	-	-	-	6.2	-	-	-	6.4	-	34.1	-	9.3 MnO; 43.8 waste oxides
WTR-62 (India)	-	5.0	-	-	-	-	-	-	-	-	20.0	-	30.0	-	25.0 PbO; 20.0 waste oxides
K-26 (Russia)	-	17.9	0.5	-	15.5	-	1.9	-	1.70	-	7.49	2.5	48.12	0.95	0.62 SO_3; 0.73 Cl; 0.95 MnO; 0.95 PbO
K-26 (Russia)	-	23.9	-	-	13.7	-	-	-	1.70	-	6.6	3.1	43.0	-	0.95 MnO
WV-205	4.7	14.2	5.3	1.8	-	-	1.5	-	-	-	15.3	-	57.3	-	-
SM 413 LW11	4.19	9.12	-	2.05	4.54	-	4.54	-	1.70	-	13.08	3.61	52.15	-	-

Table B-2 Proposed glass compositions (wt%) for immobilisation of undissolved residue [2]

Glass Code	**Composition**														
503 R4	8.0	-	-	-	-	-	-	-	-	-	16.0	-	74.0	-	-
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	TiO_2	ZrO_2	Fe_2O_3/FeO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Others
517	10.0	3.0	-	-	-	-	-	-	-	-	17.0	-	70.0	-	-
520	10.0	4.0	-	-	1.0	-	-	-	-	-	8.0	-	77.0	-	-
GP 98/12 frit	-	17.5	-	3.3	4.5	-	3.6	-	-	-	11.0	1.6	58.5	-	-
GP 98/12	-	14.9	-	1.8	3.5	-	4.0	-	0.3	-	10.7	2.3	48.3	-	14.2 HLW
GP 98/12.2	-	15.8	-	1.9	3.8	-	3.7	-	-	-	12.6	2.1	45.2	-	15.0 HLW oxides
PO 422 frit	4.3	1.4	2.8	-	2.8	-	-	-	-	2.8	19.9	5.0	61.0	-	-
Sint VG98/12	-	17.5	-	2.1	4.1	-	4.6	-	-	-	12.4	2.6	56.7	-	-
Na BSil	-	17.5	-	2.1	4.1	-	4.6	-	-	-	12.4	2.6	56.1	-	-
HAL-17	7.4	4.3	5.0	-	12.0	-	-	-	-	-	31.0	-	40.3	-	-

Table B-3 Proposed Si based glass compositions (wt%) for immobilisation of alumina resin with actinides [2]

Glass Code	**Composition**														
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	TiO_2	ZrO_2	Fe_2O_3/FeO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Others
Aluminosilicate compositions															
'Aluminosilicate'	-	5.8	1.1	2.8	14.4	-	5.4	3.6	-	-	-	11.9	55.0	-	-
EMS 11	0.8	-	0.7	1.6	0.8	-	-	-	-	17.7	-	27.2	51.3	-	-
SRL BAS-21	-	5.57	1.91	3.98	4.60	0.01	2.79	-	10.56	0.04	-	18.28	51.67	0.94	0.43 NiO; 0.2 MnO
Canadian 1	-	8.53	-	0.02	15.00	-	-	-	0.06	-	-	20.44	51.2	-	-
Canadian 2	-	11.39	-	0.22	13.8	0/ 0.023	-	-	2.30	-	-	19.37	47.40	-	0.96 UO_2; 0.20 NiO; 0.18 Cr_2O_3
Aluminoborosilicateco[positions (arbitrarilytaken as $Al_2O_3 > 6$ mass%)															
131 HiAl	-	13.8	-	1.0	-	-	-	-	3.4	-	10.2	14.1	41.4	-	3.2 MnO; 1.0 Cs_2O_3
Pamela	-	9.43	-	0.1	-	0.2	-	-	1.7	-	6.92	10.4	42.2	-	0.3 MnO
Sint SG7	-	7.4	-	1.0	2.7	-	-	-	-	-	8.3	8.6	72.0	-	-
WVCM 44	2.80	9.10	3.63	1.38	0.99	0.05	0.88	0.29	11.40	-	8.42	6.14	45.80	2.20	3.3 ThO_2; 1.29 MnO_2; 0.70 UO_2; 0.42 NiO
WVCM 50	2.22	9.79	1.60	0.79	0.82	0.21	0.82	0.39	11.93	-	12.27	9.86	39.60	2.47	3.52 ThO_2; 1.21 MnO_2; 0.70

Table B-3 Proposed Si based glass compositions (wt%) for immobilisation of alumina resin with actinides [2]

Glass Code	**Composition**														
															CeO; 0.61 UO_2; 0.30 NiO; 0.14 Cr_2O_3
PF798	4.0	-	-	-	4.0	-	-	-	-	4.0	19.0	6.7	62.3	-	-
SRL 200R	3.1	14.1	3.4	1.4	0.92	0.02	0.08	0.04	9.1	0.02	10.7	6.3	45.7	-	1.7 MnO_2; 1.7 UO_2; 1.0 NiO; 0.30 Cr_2O_3 0.10 CuO
SRL 131/11R	3.1	15.8	0.18	1.3	3.8	0.02/ 0.02	1.5	0.07	5.9	0.03	10.5	9.9	44.3	-	1.8 MnO_2; 0.51 NiO; 0.40 ThO_2 ; 0.34 Cr_2O_3; 0.21 UO_2; 0.10 La_2O_3
DWPF S00194	4.46	10.18	2.75	1.48	0.69	-	0.36	0.91	9.71	-	7.89	6.25	51.98	-	2.12 MnO; 1.37 Nd_2O_3; 0.60 NiO; 0.45 CuO
LANL EVB frit	10.08	5.66	-	-	-	-	-	-	-	-	8.0	6.0	70.26	-	-

Table B-4 Proposed phosphate based glass compositions (wt%) for immobilisation of alumina resin with actinides [3,4]

Glass Code	**Composition**																
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	La_2O_3	TiO_2	ZrO_2	Fe_2O_3	ZnO	B_2O_3	Al_2O_3	SiO	PbO	P_2O_5	Others
Alkali borosilicate compositions																	
BS1	-	10.07	-	-	-	-	-	-	-	-	-	8.49	4.14	29.30	-	-	48.0 Gd_2O_3
BS2	4.7	10.5	5.9	-	-	-	-	2.2	6.2	-	-	13.5	2.7	46.9	-	-	3.8 Gd_2O_3 ; 3.0 SnO; 0.6 Cs_2O
BS3	4.1	8.9	-	-	-	-	-	-	-	-	-	17.9	6.3	50.4	-	-	12.5 Gd_2O_3
Lanthanum aluminoborosilicate compositions																	
Lan-14 (mol%)	-	-	-	-	-	2.6	9.9	-	-	-	-	7.8	16.9	51.7	5.8	-	5.5 CeO_2
Lan-17 (mol%)	-	-	-	-	-	2.7	5.7	-	-	-	-	6.9	19.9	46.4	4.9	-	7.6 Nd_2O_3 ; 6.0 CeO_2
LaAlBSi	-	-	-	-	-	4.4	23.2	-	0.2	-	-	4.3	9.5	26.3	11.1	-	15.0 PuO_2; 6.1 Sm_2O_3
LaAlBSi	-	-	-	-	-	4.9	5.5	-	-	-	-	3.9	11.8	31.4	13.1	-	10.9 Nd_2O_3; 5.5 Pr_2O_3; 4.9 Ce_2O_3; 2.7 Sm_2O_3; 1.5 Gd_2O_3; 0.6 Eu_2O_3; 0.3 PuO
LaAlBSi	-	-	-	-	-	2.43	8.6	-	1.27	-	-	11.35	20.77	28.16	-	-	11.36 PuO_2; 8.6 Nd_2O_3; 7.45 Cd_2O_3

Table B-4 Proposed phosphate based glass compositions (wt%) for immobilisation of alumina resin with actinides [3,4]

Glass Code	**Composition**																
LaAlBSi	-	-	-	-	-	2.5	12.4	-	1.3	-	-	11.7	21.5	29.1	-	-	12.8 Gd_2O_3 ; 8.6 Nd_2O_3
Loffler based	-	-	-	-	-	2.0	18.3	-	-	-	-	5.0	9.0	21.5	7.9	-	32.5 Nd_2O_3 ; 3.2 Pr_2O_3
LaAlBSi Frit A	-	-	-	-	-	2.5	12.4	-	1.3	-	-	11.7	21.5	29.2	-	-	8.6 Gd_2O_3 ; 12.8 Nd_2O_3
LaAlBSi Frit B	-	-	-	-	-	2.5	8.1	-	-	-	-	11.6	21.3	28.9	-	-	12.8 Gd_2O_3 ; 8.2 HfO_2; 8.2 Nd_2O_3
LaAlBSi Frit X	-	-	-	-	-	2.5	19.0	-	-	-	-	13.0	10.0	20.0	-	-	15.0 Nd_2O_3 ; 13.5 Gd_2O_3 ; 7.0 HfO_2
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO/SrO	La_2O_3	TiO_2	ZrO_2	Fe_2O_3	ZnO	B_2O_3	Al_2O_3	SiO	PbO	P_2O_5	Others
LaAlBSi-X	-	-	-	-	-	2.5	20.3	-	-	-	-	13.0	10.0	20.0	-	-	15.4 Nd_2O_3 ; 11.7Gd_2O_3 ; 7.1 HfO_2
LaAlBSi-E	-	-	-	-	-	2.4	29.5	-	-	-	-	10.4	18.2	26.5	-	-	12.2 Gd_2O_3
LaAlBSi-G	-	-	-	-	-	2.8	22.22	-	-	-	-	10.0	16.1	22.22	-	-	13.33 Nd_2O_3; 13.33 Gd_2O_3
Lead iron phosphate compositions																	
ORNL 1-C	-	-	-	-	-	-	-	-	-	10.8	-	-	-	-	50.6	32.2	6.4 simulated waste
ORNL 5-C	-	-	-	-	-	-	-	-	-	11.2	-	-	-	-	42.0	40.1	6.7 simulated waste
ORNL 7-C	-	-	-	-	-	-	-	-	-	19.7	-	-	-	-	32.2	41.4	6.6 simulated waste
KfK	-	-	-	-	-	-	-	-	-	11.5	-	-	-	-	54.1	34.4	15.0 simulated waste
PNL	-	-	-	-	-	-	-	-	-	8.9	-	-	1.5	0.6	51.5	31.8	2.1 MnO_2; 0.95 NiO
Iron phosphate compositions																	
FeP1	-	-	-	-	-	-	-	-	-	38.0	-	-	-	-	-	62.0	-
FeP2	-	-	-	-	-	--	-	-	-	15.0	-	-	-	-	-	85.0	-
FeP3	-	6.4	-	-	-	-	-	-	-	14.8	-	-	6.2	5.7	-	60.0	6.9 UO_2
FeP4	-	7.4	-	-	-	-	-	-	-	16.4	-	-	6.1	7.6	-	62.5	

Table B-4 Proposed phosphate based glass compositions (wt%) for immobilisation of alumina resin with actinides [3,4]

Glass Code	Composition																
Sodium aluminiumdhosphate compositions																	
Na AlP1	-	40.0	-	-	-	-	-	-	-	-	-	-	20.0	-	-	40.0	-
NaAlP2(mol%)	-	40.8	-	-	-	-	-	-	-	-	-	-	19.4	-	-	39.8	-
NaAlP3(mol%)	-	40.0	-	-	-	-	-	-	-	-	-	2.0	19.0	-	-	39.0	-
Encapsulating glass compositions																	
EG1	-	-	-	23.3	-	-	-	-	-	-	-	0.5	20.3	50.9	-	5.0	-
EG2	-	6.5	0.8	0.4	13.5	0.1	-	-	0.1	-	-	13.9	9.7	55.0	-	-	-
EG3	-	7.1	0.5	-	-	-	-	-	-	-	-	19.1	6.8	66.5	-	-	-
EG4	-	17.5	-	2.1	4.1	-	-	4.6	-	-	-	12.4	2.6	56.7	-	-	-

Table B-5 Proposed Si based glass compositions (wt%) for immobilisation of alumina resin with actinides [3]

Glass Code	Composition														
	Na_2O	K_2O	MgO	CaO	BaO/SrO	TiO_2	ZrO_2	Fe_2O_3/FeO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	PbO	Others
78/7 Pamela (base glass)	-	-	-	-	-	-	-	22.2	-	-	7.1	-	70.7	-	-
78/7 Pamela	-	-	-	-	-	-	-	15.70	-	-	4.90	-	48.50	-	28.1 FPO; 2.40 U3O8; 0.20 Cr2O3;; 0.20 NiO
Rissian 1	25.0	-	-	-	-	-	-	-	-	-	19.6	-	55.4	-	-
Russian 2	44.0	-	-	-	-	-	-	-	-	-	20.0	-	36.0	-	-
Russian 3	44.0	-	-	-	-	-	-	-	-	-	20.0	-	24.0	-	12.0 SO3
Russian 4	44.0	-	-	5.0	-	-	-	5.0	-	-	10.0	-	29.0	-	7.0 SO3
Russian HLW	23.0	-	-	-	-	-	-	-	-	-	18.0	-	51.0	-	8.0 waste
FeP1	2.5	-	-	5.6	-	-	-	30.0	-	-	1.5	1.0	45.2	0.4	10.7 UO2; 3.3 NiO
FeP2	16.38	-	-	-	-	-	-	24.54	-	-	-	-	45.42	-	7.0 CaF2; 2.01 Bi2O3; 1.86 Nd2O3; 1.32 CeO2
PbFeP/1D	1.12	-	-	0.57	0/0.16	-	-	7.75	-	-	1.55	0.20	32.9	51.6	2.14 MnO2; 0.97 NiO; 0.7 U3O8; 0.2 Na2SO4; 0.16 Cs2O
PbFeP/5D	1.41	-	-	0.72	0/0.20	-	-	9.8	-	-	1.92	0.25	43.5	36.9	2.70 MnO2; 1.23 NiO; 0.88 U3O8; 0.25 Na2SO4; 0.20 Cs2O
PbFeP/6D	1.04	-	-	0.53	0/0.14	-	-	7.2	-	-	1.41	0.19	29.3	56.3	1.99 MnO2; 0.91 NiO;

Table B-5 Proposed Si based glass compositions (wt%) for immobilisation of alumina resin with actinides [3]

Glass Code	**Composition**														
															0.65 U3O8; 0.19Na2SO4; 0.14 Cs2O
FeP5 (mol%)	-	-	-	14.0	-	-	-	21.25	-	-	-	-	63.75	-	0.887 HfO2; 0.111 Sm2O3
PbFeP	1.2	-	-	0.58	0/0.13	-	-	8.9	-	-	1.5	0.6	31.8	51.5	2.1 MnO2; 0.95 NiO; 0.19 CeO2; 0.4 Nd2O3; 0.2 SO3
PbFeP/1C	-	-	-	-	-	-	-	10.8	-	-	-	-	32.2	50.6	6.4 simulated waste
PbFeP/4C	-	-	-	-	-	-	-	13.1	-	-	-	-	39.2	41.1	6.5 simulated waste
PbFeP/9C	-	-	-	-	-	-	-	19.7	-	-	-	-	41.4	32.2	6.6 simulated waste
PbFeP/KfK	-	-	-	-	-	-	-	9.0	-	-	-	-	50.0	41.0	

1. References

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