

SYNROC AND GLASS COMPOSITE WASTEFORMS FOR SIMULATED RADIOACTIVE WASTE FROM ADVANCED REPROCESSING

A thesis submitted in partial fulfillment for the degree of Doctor of
Philosophy
in the Department of Materials.

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Declaration

I hereby declare that all the work presented in this thesis is my own and other published works have been referenced and acknowledged appropriately.

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Publications

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ABSTRACT

A novel advanced reprocessing method, EURO-GANEX, has been developed to further separate wastes, in comparison to the PUREX route, and to enhance the proliferation resistance of reprocessing. It produces a waste-stream that contains fission products only, free of traceable actinides. A Synroc derivative wasteform, Synroc-Z, has been developed to contain minimal host phases for actinides and could immobilise up to 35 wt.% EURO-GANEX waste. Synroc-Z was prepared via hot uniaxial pressing and hot isostatic pressing to compare the phase composition and microstructure. Consolidation of the Synroc-Z by hot pressing techniques resulted in a dense microstructure with low porosity (< 0.5 vol%). Processing temperature was the most important factor in controlling density and phase composition. The suggested hot uniaxial pressing conditions determined from this study are a temperature of 1150-1200°C with pressure of >10 MPa for dwell time of 3 h. Another potential matrix is French borosilicate glass, R7T7, which was prepared via melting vitrification and hot isostatic pressing. However, the applied pressure did not enhance the solubility of Ru, Pd, Te and Mo compared to melting vitrification.

The processing conditions, waste loading and surface roughness were varied, and their effects on Synroc-Z durability and microstructure were examined. Synroc-Z samples with dense microstructures displayed similar leach resistance performance and behaviour. Leached samples formed Ti-oxide films and crystals on their surfaces that act as a barrier to mitigate elemental loss. Synroc-Z with low (< 20 wt.%) waste loadings showed slightly poorer durability than Synroc-C while at high (> 20 wt.%) waste loadings, Synroc-Z displayed less degradation in performance compared to Synroc-C. In contrast, the secondary phases formed on the R7T7 glass offer little protection during durability testing as the leach rates of R7T7 displayed only a 1.4 times decrease compared to the 14 times reduction for Synroc-Z between 3 and 28 days.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
AHA	acetohydroxamic acid
ANSTO	Australian Nuclear Science and Technology Organisation
ASTM	American Society for Testing and Materials
BSE	backscattered electron
BTBP	bis-triazine-bipyridine
DIAMEX	Diamide Extraction
DI water	Deionised water
DMDOHEMA	N,N'-(dimethyl-N,N'-dioctylhexylethoxymalonamide)
DTA	Differential Thermal Analysis
EDX	Energy-dispersive X-ray spectroscopy
EW	Exempt waste
FIB	focused ion beam
FP	fission products
GANEX	Group Actinide Extraction
GIXRD	Grazing Incidence X-ray Diffraction
HIP	Hot isostatic pressing
HLW	High-Level Waste
HUP	Hot uniaxial pressing
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ILW	Intermediate-level waste
JRC-ITU	Joint Research Centre- Institute for Transuranium Elements
LLW	Low-level waste
M	molarity
MA	minor actinides
MCC	Materials Characterization Centre
MOX	mixed oxide fuel
NNL	National Nuclear Laboratory, UK
PCT	Product consistency test
PNNL	Pacific Northwest National Laboratory, USA
PTFE	Polytetrafluoroethylene, Teflon

PUREX	Plutonium Uranium Redox Extraction
SA	Surface area
SANEX	Selective Actinide Extraction
SE	Secondary electrons
SEM	Scanning Electron Microscopy
SNF	Spent Nuclear Fuel
SPFT	Single pass flow through test
Synroc	Synthetic rock
T_m	Melting temperature
TBP	tri-butylphosphate
TEM	Transmission Electron Microscopy
TGA	Thermo Gravimetric Analysis
TODGA	N,N,N',N'-tetraoctyl diglyclamide
UoS	The University of Sheffield
V	volume
VHT	Vapor hydration test
VLLW	Very low-level waste
VSLW	Very short-lived waste
XRD	X-ray Diffraction

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Introduction

Commercial nuclear power is a well-established option for electricity generation that can help reduce our reliance on fossil fuels whilst still achieving the general energy policy goal of affordability. Nuclear power can help address the issues of global warming and climate change as it is a technology that has almost zero greenhouse gas via direct emission and a low overall lifecycle impact¹. However, after nuclear fuel has reached the end of its useful life, spent fuel poses a problem as it contains long-lived and highly radiotoxic species. Some countries such as the United Kingdom and France use the standard Plutonium Uranium Redox EXtraction (PUREX) reprocessing method to recover reusable parts of the fuel (U and Pu) from the spent fuel thus greatly reducing the volume and radioactivity of waste that requires disposal^{2, 3}. In recent years, more advanced reprocessing schemes have been designed and developed to further separate the waste and meet the need of environmentally acceptable and economic semi-closed fuel cycles. A promising route, EURO-GANEX (Group ActiNide EXtraction), aims to separate both the major (U, Pu) and minor actinides (Np, Am, Cm) as a group from spent nuclear fuel. Unlike the commonly deployed PUREX process, which has potential proliferation risk associated with the handling of pure fissile materials, EURO-GANEX increases the proliferation resistance of nuclear reprocessing as the waste stream resulting from EURO-GANEX only consists of fission products (FP)⁴. This waste, however is still highly radioactive and should be immobilised to allow its safe management, storage and ultimate disposal.

Many wasteforms have been proposed as candidates to host the waste from PUREX⁵ but little work has been conducted to investigate and develop wasteforms for EURO-GANEX. A possible matrix is Synroc (Synthetic Rock), which is a polyphasic ceramic that can be adapted to host different waste compositions by adjusting the ratio of its constituent phases. Another potential host is borosilicate glass which is the most widely used wasteform for PUREX waste.

The aim of the work described in this thesis was to develop and fabricate a Synroc derivative, Synroc-Z, and explore R7T7 type glass to host

EURO-GANEX wastes and to further our understanding of their microstructures, phase compositions and durability. This thesis is structured as follows:

Chapter 1 provides background knowledge of nuclear waste management, current and advanced reprocessing routes and immobilisation options.

Chapter 2 summarises the materials, experimental methods and basic knowledge of principles for each instrument used in this project.

Chapter 3 describes the results of the fabrication of Synroc-Z with simulated EURO GANEX wastes via hot uniaxial pressing and hot isostatic pressing.

Chapter 4 presents the results of production of R7T7-type glass with simulated EURO GANEX wastes via melting vitrification and hot isostatic pressing.

Chapter 5 gives the results obtained from MCC-1 leach testing performed on selected Synroc-Z and R7T7 glass samples.

Chapter 6 reports the simulations of generated heat with decay time from Synroc-Z and R7T7 glass with real EURO-GANEX waste.

Chapter 7 discusses all the results obtained and compares them with other published work.

Chapter 8 concludes the major findings of this work and makes recommendations for future work.

Chapter 1: Background and Literature Review

The nuclear fuel cycle is introduced briefly in this chapter. Here, emphasis will be placed on the back-end of the cycle namely the stages between reprocessing and final waste disposal⁶. Due to the need to reduce greenhouse gas emissions, there is renewed interest in nuclear energy, which has brought with it a push to deploy more advanced reactors and reprocessing routes. In particular, several countries such as China and India have announced a significant expansion of nuclear power to solve their increasing energy demand in spite of public concerns surrounding waste management and the safety of nuclear power, especially after the Fukushima accident³.

The so-called nuclear fuel cycle (Figure 1.1) is a set of industrial processes that are involved in producing electricity from fissionable materials in nuclear power reactors⁶. The most regularly used fuel source, uranium, is mined in a number of countries⁶. From mining to fuel fabrication, the uranium ore must be processed before it can be used as fuel in a nuclear reactor. The nuclear fuel manufacturer normally enriches uranium to increase the proportion of ^{235}U level in natural uranium to 3 - 5 %. A fuel element is composed of the fuel (usually stacked UO_2 pellets) clad in a metallic sheath (usually zircalloy) to form a fuel pin and these are combined with a structure that holds several tens of pins together. The fuel is generally used in the reactor for 3 - 6 years and 25 - 30 % of the fuel is unloaded and replaced with fresh fuel once a year. The used fuel is stored in ponds for several years to allow most of short-life radioactivity to naturally decay. Used fuel still contains ~96 wt.% U (most of the original ^{238}U and < 1 wt.% unburned ^{235}U and ^{236}U), ~1 wt.% Pu (with about one third non-fissile isotopes) and 3 wt.% fission products (FPs) and actinides, which are wastes. The FPs act as neutron poisons to remove neutrons from the multiplication chain and thus it has to be compensated by more fissile material^{6, 7}. Then, depending on the country's policies, the whole fuel element is either considered as a final waste and therefore directly disposed of (open cycle) or reprocessed to separate the final waste constituents (closed cycle). At the time of writing only a relatively small number of countries are still pursuing reprocessing in their civilian power programmes, namely UK and France.

Countries such as the USA favour the open cycle. The UK currently has a reprocessing capability at the Magnox and THORP facilities at Sellafield. However, THORP operations are expected to end in 2018 with Magnox reprocessing ending soon after in 2020⁸.

Spent nuclear fuel (SNF) still contains a significant amount of fissile material (~97 wt.%) that can be used to generate energy. In the closed cycle option, reprocessing uses chemical and physical processes to separate the required materials from SNF. The current closed cycle is semi-closed as the actinides still cannot be completely recycled and returned to the reactor while the fully closed cycle should ideally separate FPs only from SNF and all actinides should be returned to the reactor. The different separated streams (e.g. cladding, generated FP) can then either be immobilised as waste in durable matrices or used to produce new fuels, in order to reuse the remaining fissile and fertile elements (U and Pu) and/or to transmute the so-called “minor actinides” (MA e.g. Np, Am and Cm). Reprocessing not only uses uranium and plutonium resources more effectively but also greatly reduces the volume of the radiotoxic waste requiring disposal and the time for which the waste needs to be separated from the environment^{3, 6, 7, 9}.

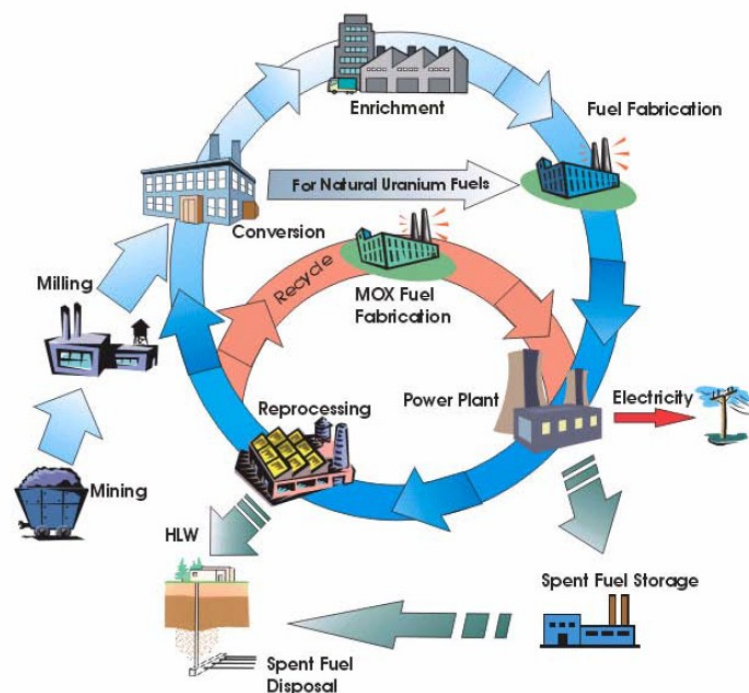


Figure 1.1 The flowsheet of a nuclear fuel cycle⁶. Adapted from IAEA report⁶

1.1 Nuclear waste management

During the fission process in a reactor, the fuel undergoes a number of changes such as the transmutation of part of the ^{238}U to ^{239}Pu and build-up of fission (and decay) products. Unlike fossil fuel power, the vast majority of waste products in nuclear fuel are retained within the fuel pellets in a reactor. Importantly, this results in the fuel becoming intensely radioactive. Materials considered as waste in SNF may simply be disposed of as waste, or undergo another process to recover unused fuel to improve waste management. Both methods require an accepted geological repository engineered to retain the radiotoxic elements for an adequate time to protect the surrounding environment^{3, 7}.

1.1.1 Radioactivity and radiotoxicity of waste

Radioactive decay is a spontaneous breakdown of an unstable atomic nucleus resulting in the release of energy and matter such as an alpha particle, beta particle with neutrino and accompanied by a gamma ray. A material containing such unstable nuclei is considered radioactive. The radioactive forms of elements are called radionuclides. The main source of radioactivity in SNF is the FPs (and their radioactive decay products). The rate of decay is fixed by the half-life. The half-life of a radioisotope describes how long it takes for half of its atoms to decay. Some isotopes decay fast and hence have a high specific activity while others decay at a much slower rate (up to billions of years). Figure 1.2 shows when an actinide element undergoes fission, it splits into two lighter atoms (and 2 to 3 neutrons) that are predominantly radioactive with a short (< 30 years) half-life. ^{235}U generally splits asymmetrically into two large fragments with mass numbers in ranges centred at about 95 and 135 respectively (Figure 1.3). The chemistry of the most challenging elements must be studied in order to manage the recycling and disposal of the SNF effectively. Two of the most problematic short-lived FP elements, ^{90}Sr and ^{137}Cs , and two long-lived FP elements, ^{99}Tc and ^{129}I , are briefly described hereafter^{3, 10}.

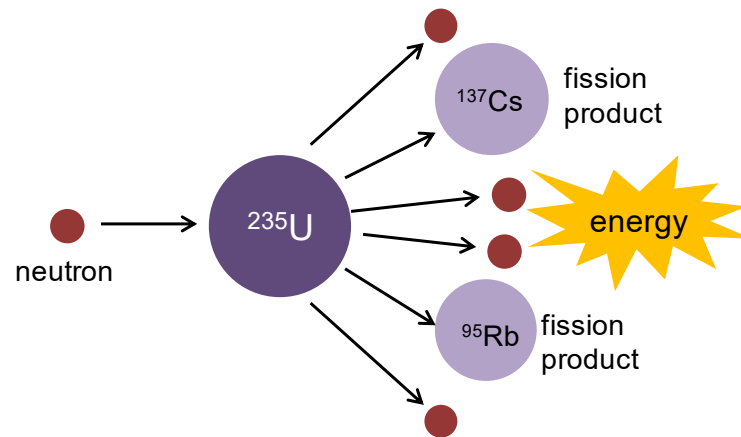


Figure 1.2 Schematic representation of a typical nuclear fission reaction.

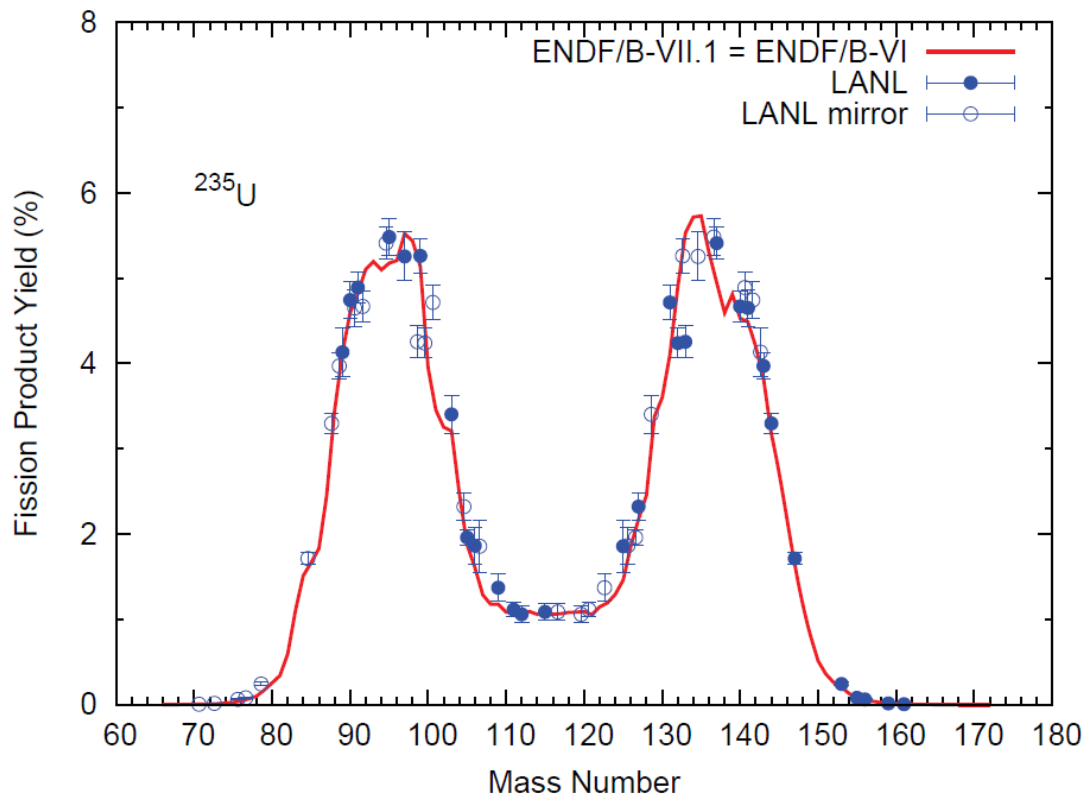


Figure 1.3 Fission products yields for 14 MeV neutrons on U-235. Adapted from Innes *et al.*¹¹

a). Strontium-90

The main source of ^{90}Sr is from the fission of ^{235}U . ^{90}Sr is one of such FP (yields ~4.5 % of overall fission) and thus a major radionuclide in SNF, high-level wastes (HLW) from reprocessing and radioactive wastes associated with the operation of reactors and fuel reprocessing plants. The decay of ^{90}Sr , which has a half-life of ~29.1 years, emits a high-energy beta particle with a maximum energy of 546 keV¹⁰. Sr with chemical forms in oxides, carbonates and nitrates is highly water-soluble and hence is easily transported with rain and ground water, adhering to soil particles. Sr shows similar behaviour to Ca and it concentrates in bone tissues for a long time as the biological half-life of Sr in the body is ~30 years. This means that Sr needs to be monitored carefully as it is one of the most mobile FPs.

b). Caesium-137

Eleven major radioactive isotopes of caesium exist but only three of them (^{134}Cs , ^{135}Cs and ^{137}Cs) have half-lives over a year. ^{134}Cs , ^{135}Cs and ^{137}Cs are produced by nuclear fission and ^{137}Cs , in particular, has a relatively high yield rate of ~6.2 % of overall fission. ~95 % of ^{137}Cs decays with a half-life of ~30 years and undergoes beta emission to a metastable nuclear isomer of $^{137\text{m}}\text{Ba}$ while ~85% of $^{137\text{m}}\text{Ba}$ releases 662 keV gamma rays to populate the ground state. The effect of ^{137}Cs is similar to ^{90}Sr and as such both are major contributors to radioactivity in 10 to ~100 years after fuel unloading in SNF and HLW. Cs is a highly electropositive and is the heaviest alkaline element meaning that it easily gives away its single valence electron to form ionic and electrovalent bonds with anions. Cs with chemical forms in oxides, carbonates and nitrates is therefore water-soluble and is easily transported by ground water.

c). Technetium-99 and Iodine-129

^{99}Tc and ^{129}I which have long half-lives (2.13×10^5 and 15.7 million years respectively) with relatively high fission yield of 6% and 1% are mainly produced by U and Pu fission. ^{99}Tc in liquid wastes as TcO_4^- and ^{129}I as halide anion are highly mobile and soluble in ground water. Both ^{99}Tc and ^{129}I decays by emitting

a beta particle with a maximum energy of 293 and 150 keV respectively. Currently, no suitable wasteform has been found to immobilize TcO_4^- and ^{129}I . Both elements have low solubility in glass wasteforms and are easily volatilised at high processing temperatures used to produce wasteforms.

The other sources of radioactivity are the actinide isotopes classified as MA, i.e. Np, Am, Cm, and major actinides, i.e. U and Pu. Contrary to FPs, the actinides generally have long half-lives and as such are still radiotoxic for a few orders of magnitude more than FP¹⁰. The actinides composition in the spent nuclear fuel depends on the level of uranium enrichment, the type of reactor and the time of fuel burn-up. ^{237}Np , ^{247}Cm and ^{248}Cm are important long-lived minor actinides as their half-lives are longer than 10^5 years¹². Especially, ^{237}Np , it is reactive with many other elements such as halides and oxygen and its ions are also soluble in ground water¹².

The main sources of nuclear wastes are nuclear power plant (NPP) operations and decommissioning, reprocessing facilities, research reactors and facilities, medical and industrial applications and nuclear weapons programmes^{10, 13, 14}. For HLW, more than 90% of inventories are SNF or wastes produced after reprocessing. Figure 1.4 shows the evolution of relative radiotoxicity as compared to mined uranium ore's usual radiotoxicity for three types of waste under a fuel cycle – i.e. direct disposal; reprocessing (of Pu); and advanced reprocessing (of Pu and MA), or so-called Partitioning and Transmutation (P&T). In all closed fuel cycles, the recovery factor is assumed to be 99.9%^{7, 14}. This factor rate can be achieved on an industrial scale^{7, 14} in the case of major actinides, but is presently limited to laboratory scale in the case of MA^{7, 15, 16}. The bottom curve in Figure 1.4 belongs to a SNF that has undergone advanced reprocessing (major and minor actinides recycled), so only FPs and traces of actinides are sent for geological disposal. The radiotoxicity of the disposed wastes from advanced reprocessing may meet the uranium ore's radiotoxicity level after only a few hundred years. On the other hand, the wastes from the open fuel cycle (i.e. direct disposal) take more than 300,000 years^{3, 7}. The intermediate solution, Pu (+U) recycling, as already applied by some countries such as France and UK, allows a radiological safety level to be reached after

around 10,000 years^{3, 7}

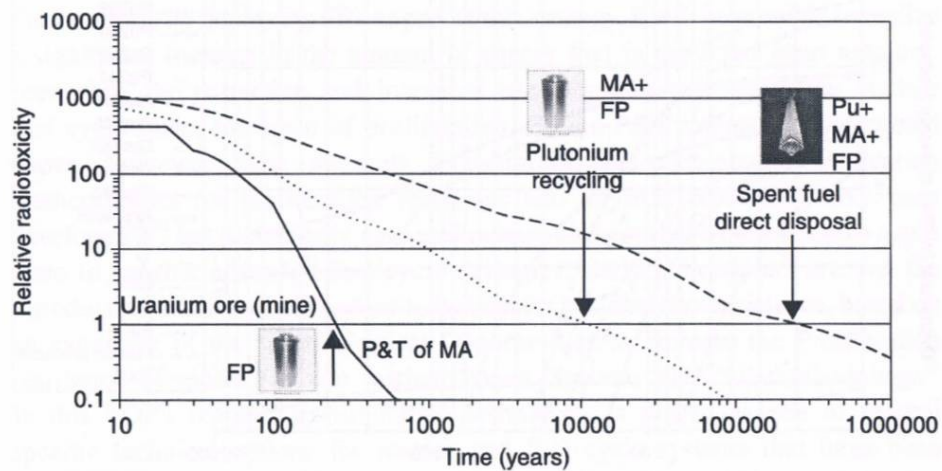


Figure 1.4 Radiotoxicity decay of spent fuel vs. time as a function of reprocessing choices⁷. Adapted from I. Crossland⁷

1.1.2 Waste classification and disposal route

The system of waste classification may improve the efficiency of radioactive waste management. Different radioactive wastes require different lengths of time before they become non-hazardous in terms of radioactivity. Radioactive wastes are typically classified based on their decay time to an acceptable level and radioactivity content. The International Atomic Energy Agency (IAEA) recommends a classification scheme with six different categories¹⁷ which is followed by most countries:

- (a) Exempt waste (EW): The waste meets the necessary criteria for clearance. It can be treated as non-radioactive waste.
- (b) Very short-lived waste (VSLW): The waste can be stored naturally to decay over up to a couple of years and then be treated as EW. This class of waste is usually used in nuclear medicine rather than in the nuclear industry and research.
- (c) Very low-level waste (VLLW): The waste does not meet the EW criteria, but does not need a high level of containment or isolation. It just contains up to a few tens of Bq/g and is suitable for disposal in sealed containers in a low surface landfill facility.

- (d) Low-level waste (LLW): The waste is above clearance level since it contains a few thousand Bq/g and small amounts of long-lived radionuclides. It requires up to a few hundred years to decay and is suitable for disposal in an engineered near-surface facility.
- (e) Intermediate-level waste (ILW): The radioactivity of this waste is above LLW and below HLW. ILW may contain long-lived radionuclides that will not decay to an acceptable level of specific activity during the time period assumed for near surface disposal. It therefore requires disposal at greater depths, tens to hundreds of metres below the surface and immobilisation in a durable waste matrix if the waste itself is not durable against leaching. ILW comprises principally of SNF assemblies and fuel hulls (without the fuel itself). This category is completed by research and defence wastes.
- (f) High-level waste (HLW): The waste contains large concentrations of radioactivity (more than 10^4 TBq/m³) that produce significant quantities of heat and radiation. It requires disposal in deep and stable geological formations for long-term storage.

1.2 Reprocessing

Current reprocessing can mainly recover and separate uranium (U) and plutonium (Pu) from MA and FP in the discharged fuel elements. This allows valuable resources to be reused as new fuel elements, thus reducing the demand for new natural uranium while reducing the volume of waste to about one-fifth as well as the radioactive inventory of the waste requiring disposal. Reprocessing can also lead to separation of the unusable components so they can go into a number of dedicated and adapted waste streams. The progress of current reprocessing involves cutting the fuel elements, separating the cladding components by dissolving the fuel in hot concentrated nitric acid and using solvent extraction steps for the phase separation of desired waste elements^{7, 14}.

1.2.1 Current reprocessing techniques-PUREX

Plutonium Uranium Redox Extraction (PUREX) is the current commercial standard reprocessing method used by the nuclear power industry. The PUREX

process was first reported by Anderson and Asprey in their patent “Solvent Extraction Process for Plutonium” in 1947, describing tri-butylphosphate (TBP) as the main reactant¹⁸. It was developed to purify Pu for military weapons but later was adapted on an industrial scale for SNF to separate U and Pu from FPs and MA and then to purify and separate U and Pu from each other^{3, 19}.

The reprocessing begins with the SNF elements being chopped up and dissolved in a concentrated aqueous nitric solution. The key step relies on TBP, which is used as an extractant in an organic phase that is in contact with the aqueous nitric acid solution containing the dissolved fuel. Actinide elements at oxidation states 6+ and 4+ are selectively extracted by TBP. U^{6+} and Pu^{4+} then migrate to the organic phase while other actinides and most of the FP stay in the aqueous phase (Figure 1.5). This is followed by several steps to further perfect the separation and elimination of impurities from the U + Pu stream (notably Tc and Zr). The final U and Pu products are typically oxides obtained by calcination. The waste stream coming out is neutralized and classified as HLW containing FP and MA with some traceable U and Pu isotopes (up to 1 % of their initial respective content). The next generation of used fuel reprocessing will be based on liquid-liquid extraction PUREX process chemistry technologies to achieve similar results^{3, 7, 20}.

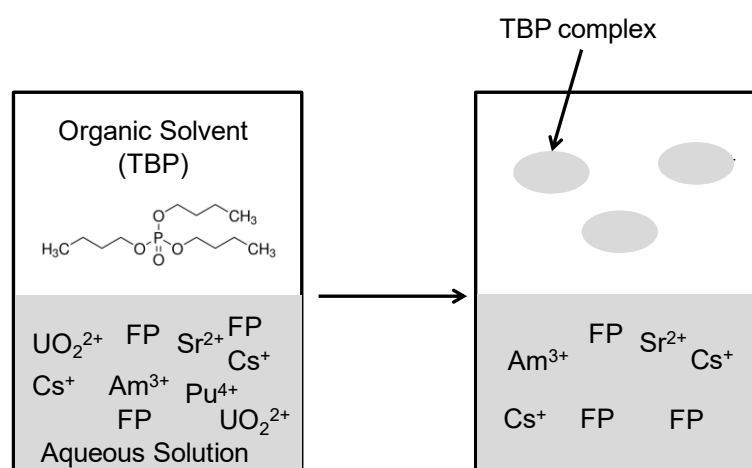


Figure 1.5 Basic principles of the key step of U and Pu extraction in the PUREX process³. Adapted from K. L. Nash *et al.*³

1.2.2 Advanced reprocessing

Although the principal characteristics of PUREX have remained unchanged for decades, a number of countries (e.g. France and Japan) are seeking to further improve the PUREX process. Sustainability is a major consideration in developing advanced nuclear fuel cycle technologies. The development of advanced reprocessing aims to: reduce the cost in comparison to PUREX and direct disposal, recover all actinides and long-lived FP and hence increase the safety while greatly diminishing proliferation risks^{3, 7, 21}. A number of advanced reprocessing routes, involving heterogeneous recycling in the extension of PUREX such as Diamide Extraction (DIAMEX)^{22, 23, 24, 25, 26}, Selective Actinide Extraction (SANEX)^{27, 28, 29, 30}, the combination of DIAMEX and SANEX^{31, 32, 33, 34}, and the homogeneous recycling in Group Actinide Extraction (GANEX)³⁵ are nowadays being developed to meet the requirements of environmentally acceptable and economic closed fuel cycles and aim to further separate the remaining wastes⁴. The heterogeneous reprocessing mode involves recovering MA and major actinides via different streams and placing them in dedicated targets while homogeneous mode separates mixed major and minor actinides.

The GANEX process, in particular, aims to homogeneously recycle U and also Pu plus MA as a group from SNF of Generation IV fast reactors to avoid having a stage where a stream of fissile Pu exists alone, therefore avoiding diversion for military grade Pu production. This aim can improve the process safety and proliferation resistance compared to other strategies³⁶. The GANEX separation process is expected to involve two extraction stages: 1) bulk uranium removal (that can thus be reused to produce new fuels)^{36, 37} and 2) recovery of all the other actinide elements (Pu + MA + remaining U)^{38, 39, 40, 41}. In the first stage, Prabhu *et al.*³⁷ reported that the di(2-ethylhexyl)isobutyramide (DEBIBA) solvent has good extracting properties towards U^{6+} and the extraction ratios of Pu^{4+} from nitric acid are negligibly small. More than 99.99 % of uranium was recovered in this stage. In the next step, the actinides should be extracted as a group from the fission and activation products. This technique uses a combination of extractants, bis-triazine-bipyridine (BTBP) and TBP, which are mixed in cyclohexanone. The BTBP molecule has a well-documented ability to separate trivalent and pentavalent actinides from trivalent lanthanides (and

other FPs as well)²⁷, while the TBP performs the same function as in the PUREX process, i.e. U^{6+} and Pu^{4+} extraction. The objective is to extract not only the 4+ and +6 actinides but also the 3+ and +5 species (Np^{5+} , Am^{3+} , Cm^{3+}) from the dissolved spent fuel. The GANEX process can be performed either directly from the dissolved spent fuel or from dissolved fuel where a large fraction of the uranium had already been removed^{35, 36, 38, 39}.

A novel development of GANEX process, called EURO-GANEX, was designed to improve the 2nd stage of GANEX and tested at NNL (National Nuclear Laboratory, UK) and JRC-ITU (Joint Research Centre- Institute for Transuranium Elements, Germany, European Commission lab)^{42, 43}. The EURO-GANEX process was based on the mixed solvent system of N,N,N',N'-tetraoctyl diglyclamide (TODGA) and N,N'-dimethyl-N,N'-dioctyl-2-(2-hexyloxyethyl) malonamide (DMDOHEMA) in kerosene diluent to co-extract transuranium and lanthanide elements and then use acetohydroxamic acid (AHA) to strip back the transuranium elements to a new aqueous phase^{42, 43, 44}. It is able to achieve > 99 % recovery of the transuranic actinides (Np, Pu, Am) with < 0.1 % contamination by rare earth in the actinide stream^{43, 44}.

With this process, one of the waste streams from EURO-GANEX is therefore likely to be just FP, free of substantial traces of actinides. Although significantly different in composition compared to PUREX it still contains high radioactivity and new advanced immobilisation matrices that are capable of accommodating actinide-free waste streams have to be sought and investigated.

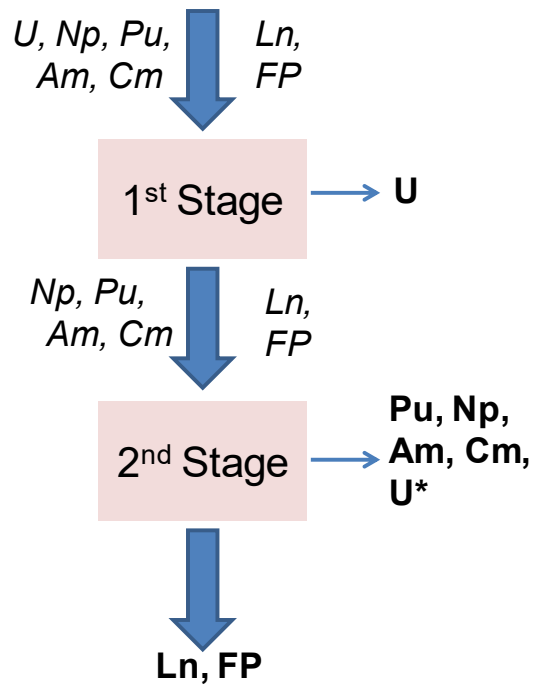
Dissolved Spent Nuclear Fuel

Figure 1.6 The brief flowsheet of GANEX process. The recovery of U can achieve more than 99.999% in the first stage. The rest of U will be separated with other actinides in the second stage.

1.3 General immobilisation options

Treatment of HLW and ILW includes all operations before disposal that are intended to improve safety and/or costs by altering the waste's characteristics. The aim in all countries is to convert raw waste into a solid and stable form termed "wasteform" by radioactive waste immobilisation such as solidification, embedding and encapsulation. There are many different types of wasteforms such as cement^{45, 46}, glass^{47, 48} and ceramic^{49, 50} that may be used to immobilise radioactive wastes¹⁰. The first barrier for disposing HLW and ILW is the wasteform itself so the key properties of wasteforms are physical and chemical stability and resistance to leaching and to self-irradiation damage. The immobilisation of HLW is achieved by chemical incorporation into a glass network or the crystalline structure of a suitable matrix. The general requirements for HLW wasteforms include high waste loading (typically 20 - 35 wt.%), easy processing (by remote handling) and good durability as mentioned above^{10, 51, 52}. This PhD project considers potential wasteforms for HLW and more precisely the immobilisation of EURO-GANEX FP waste streams. The current widely used glass wasteform, borosilicate glass, and a potential ceramic wasteform, Synroc, which can be tailored to immobilise HLW by decreasing or even omitting host phases, were studied and compared in this project.

1.3.1 Ceramic wasteform- Synthetic Rock (Synroc)

The multiphase ceramic Synroc (Synthetic rock) was first developed in Australia by Ringwood in 1979 who reported its suitability as a potential wasteform⁴⁹. Synroc is composed of a family of advanced crystalline phases identical to those of natural minerals, which are known to have existed in geological environments at elevated pressure and temperature and in possible contact with groundwater for up to millions of years, while showing the ability to lock up most of the elements constituting the FPs^{5, 49, 53, 54, 55}. Synroc is composed of titanate phases namely hollandite, perovskite, zirconolite and rutile. These four phases are independently described in the following four sub-sections. Synroc immobilises radionuclides by incorporating them into appropriate phases and forming solid solutions. Each phase is able to contain, and therefore immobilise, a range of radioactive waste elements into a stable

and durable solid solution. This is because of their crystal structure, sharing the common ability to accept substitution into some of their crystalline sites, while preventing precipitation of a secondary phase. Figure 1.7 lists the elements that can be immobilised in each phase^{5, 53, 54, 56}. It is possible to tailor the matrices of Synroc to particular radionuclides by adjusting the ratio of the different titanate components^{5, 56} and several kinds of Synroc have therefore been developed for particular usages: the first formulations, Synroc-A and -B, were developed by Ringwood⁴⁹, the typical form, Synroc-C, has been developed specifically to immobilise HLW occurring from the common reprocessing of light water reactor SNF^{5, 54}; Synroc-D was compositionally modified to deal with wastes from defence weapon production in the U.S.^{57, 58}; Synroc-E was especially designed to suit for geological disposal purpose in salt or deep sea conditions and has a similar composition to Synroc-C but with a large excess (~80 wt.%) of rutile⁵⁹; and Synroc-F, unlike other Synroc-type wasteforms, was developed for SNF that does not undergo a reprocessing stage and contains mainly pyrochlore (host for U) with minor hollandite and rutile^{60, 61}.

Hollandite $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$	Cs, Ba, Rb, K, Cr
Zirconolite $\text{CaZrTi}_2\text{O}_7$	Th, U, Pu, tetravalent actinides, Zr
Perovskite CaTiO_3	Sr, Na, trivalent actinides, lanthanides
Rutile TiO_2	Buffer
Alloys	Tc, Mo, Ru, Pd, Te, Rh

Figure 1.7 Each Synroc phase is the primary host for a number of HLW elements⁵. The rutile phase does not host substantial amounts of radionuclides but acts as a chemical buffer. The phase composition shown here is the nominal chemical formula; the details of formula are described in the following sections.

The main aim of the Synroc strategy for HLW management is to provide a wasteform that has higher density and better resistance to leaching by groundwater than borosilicate glass, which is the most common wasteform used worldwide for HLW^{51, 62}. Synroc can accommodate the same waste loadings in a

smaller volume (~60 % of glass volume based on larger density, 4.35 vs. 2.6 g/cm³) than glass. Synroc also has the advantage that its durability is less affected by compositional changes of the waste⁶².

1.3.1.1 Hollandite

The Synroc-type hollandite minerals have the general formula $(\text{Ba}_x\text{Cs}_y)(\text{M}_{2x+y}^{3+}\text{Ti}_{8-2x-y}^{4+})\text{O}_{16}$, $1.08 \leq x+y \leq 1.51$. The general structure is shown in Figure 1.8. The large yellow (Ba,Cs) cations are monovalent or divalent whilst small blue (M, Ti) atoms represent various di-, tri-, tetra-, and penta- valent cations. The blue cations are octahedrally coordinated by oxygen (red). The (M,Ti)O₆ octahedra are linked together by sharing two edges to form double chains running parallel to the c-axis. These chains are corner-linked to neighbouring paired chains to form a 3-dimensional framework with tunnels running along the c-axis as viewed in Figure 1.8(b). The Ba and Cs cations are located in these cage-like tunnels, typically in an irregular eightfold coordination to oxygen^{63, 64, 65}. Cs radionuclides constitute the principal FPs and are also one of the most difficult elements to immobilise because of its volatility at high temperature, its unstable 1+ oxidation state in solids and its tendency to form water soluble compounds^{5, 64, 66}.

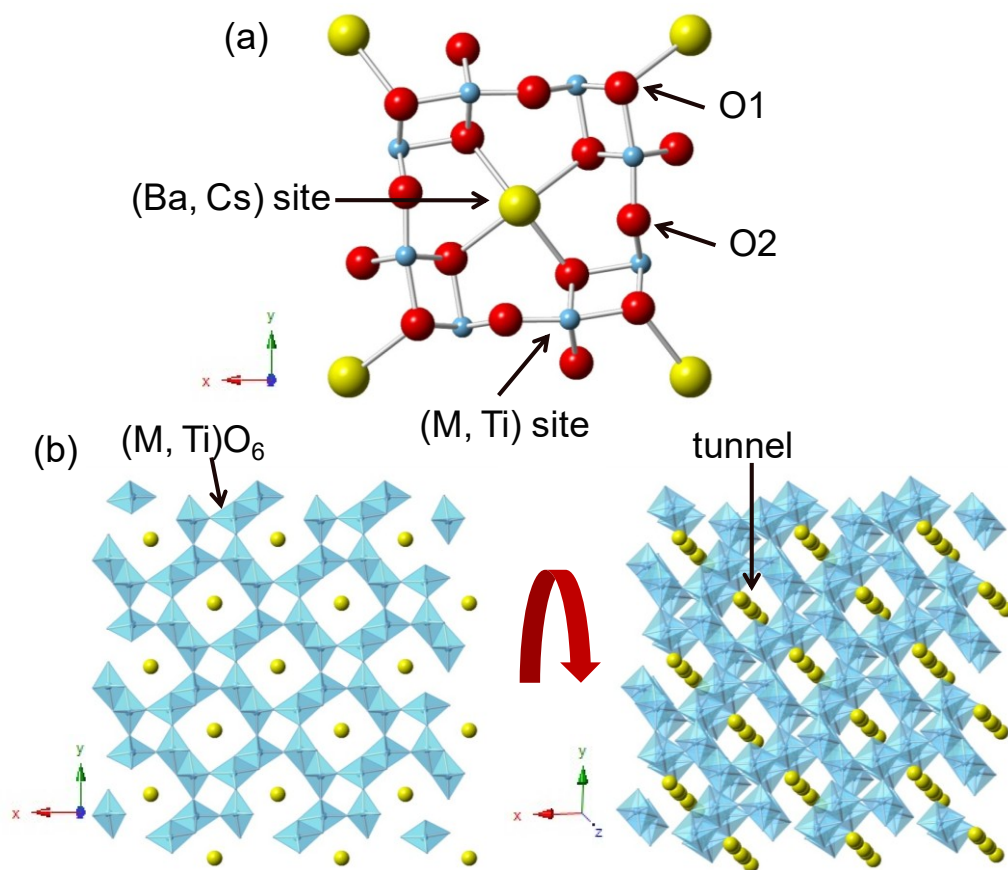


Figure 1.8 The (a) representation of $(\text{Ba}_x\text{Cs}_y)(\text{M}_{2x+y}^{3+}\text{Ti}_{8-2x-y}^{4+})\text{O}_{16}$ hollandite structure viewed along the c axis and (b) structure along the c axis and with 20° rotation to show the tunnels⁶³. The two kinds of oxygen sites which are shown in red, O1 and O2, represent oxygen bonds bonded and not bonded to the (Ba, Cs) site, respectively. The large Ba and Cs cations (yellow) are incorporated in tunnels in the framework of (M, Ti) O_6 (light blue) octahedra⁶³.

1.3.1.2 Zirconolite

The most durable phase in Synroc-C is zirconolite whose formula is $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$, $0.8 < x < 1.37$, where x usually equals one^{5, 67, 68}. Figure 1.9 shows the structure of zirconolite which has a lamellar monoclinic structure with space interlayer. The layered structure is comprised of TiO_6 octahedra, which are corner-linked in rings of alternating three and six to form continuous sheets. There are three different Ti sites. Two of the Ti sites are six-fold coordinated and the third is a half-occupied site which is five-fold coordinated. Ca and Zr atoms enter the large interstices between interlayers. The Ca^{2+} is eight-fold coordinated while the Zr^{4+} is bonded to seven oxygen atoms^{5, 69, 70, 71}.

The sites of Ca and Zr in zirconolite are normally capable of incorporating the trivalent and tetravalent species, specifically rare-earths, FP, major actinides,

Am and Cm, whilst the Ti sites can be substituted by transition metal (e.g. Fe)^{5, 72}. Pyrochlore, which is a cubic structure and may be represented as $A_2B_2O_7$, has a structure closely related to zirconolite. When the sevenfold sites are occupied by a cation such as U^{4+} or Cm^{3+} whose ionic radius is significantly larger than Zr^{4+} , a pyrochlore structure forms^{5, 54}.

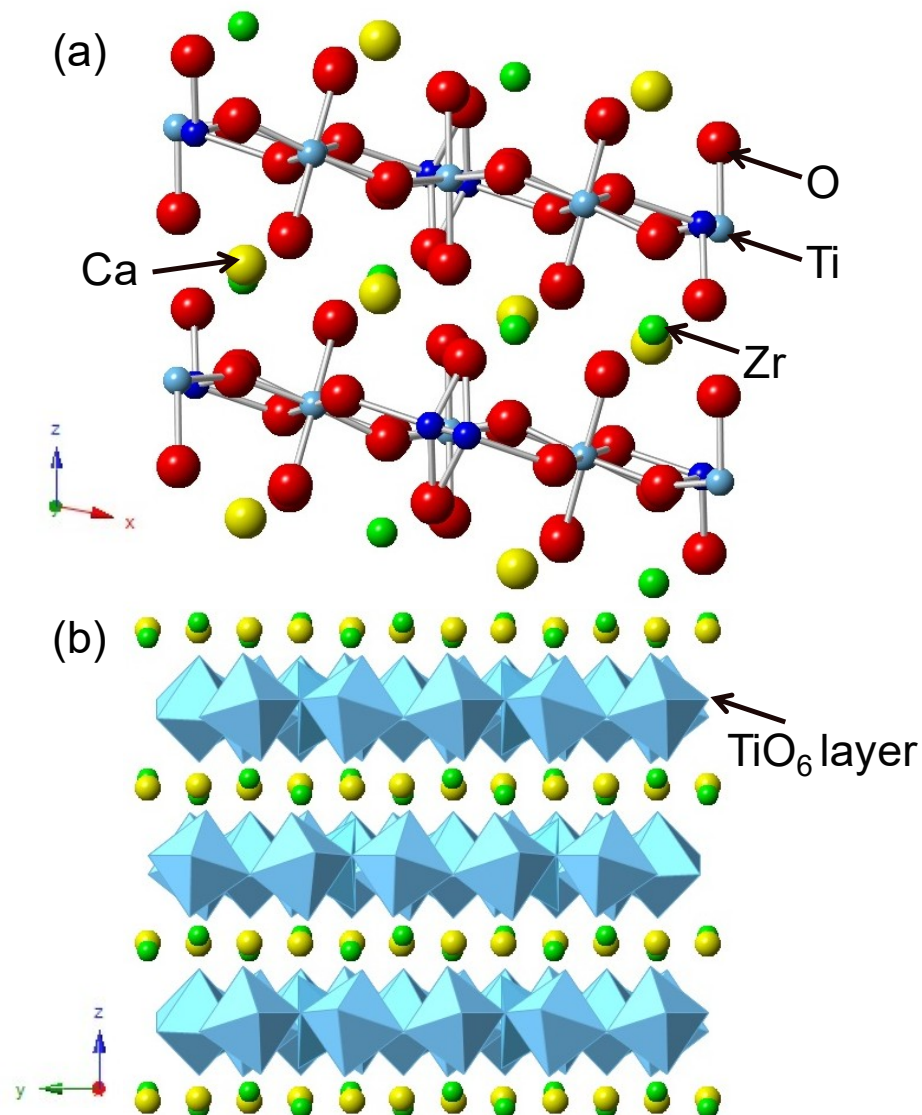


Figure 1.9 (a) Representation of zirconolite structure viewed along the b axis. (b) The layers formed by polyhedra of Ca (yellow) and Zr (green) ions alternate with layers of hexa-coordinated Ti ions (light blue) and penta-coordinated Ti with 50% occupancy (dark blue) viewed along the a axis⁶⁹. O ions are shown in red.

1.3.1.3 Perovskite

The perovskite-type structure can be described by the general formula ABO_3 with the ionic radius of the A cation being substantially larger than B. In perovskite, BO_6 octahedra share corners to form a 3D framework with large central cavities. The A cations are centrally located in these cavities, typically in twelvefold coordination which consist of eight near- and four second nearest-neighbour oxygen atoms⁷³. The perovskites of $(A^{2+}B^{4+})O_3$ are of cubic or orthorhombic symmetry⁷⁴ while $(A^{3+}B^{3+})O_3$ perovskites are rhombohedral or orthorhombic^{5, 75, 76}.

In Synroc-C, the perovskite phase is normally $CaTiO_3$ which mainly hosts Sr, the light and intermediate rare earths, trivalent actinides and Na. It is particularly easy to incorporate Sr in the perovskite structure due to similar ionic radii and the similar chemistry of Ca and Sr. The ability of Sr to incorporate within the structure can be demonstrated by the existence of a $CaTiO_3$ - $SrTiO_3$ solid solution^{74, 77, 78}. Rare earths are easier to incorporate in perovskite as compared to zirconolite as the volume of Ca site for rare earths in perovskite ($56.2 \text{ \AA}^3$) is larger than that for zirconolite ($21.3 \text{ \AA}^3$)^{5, 76}.

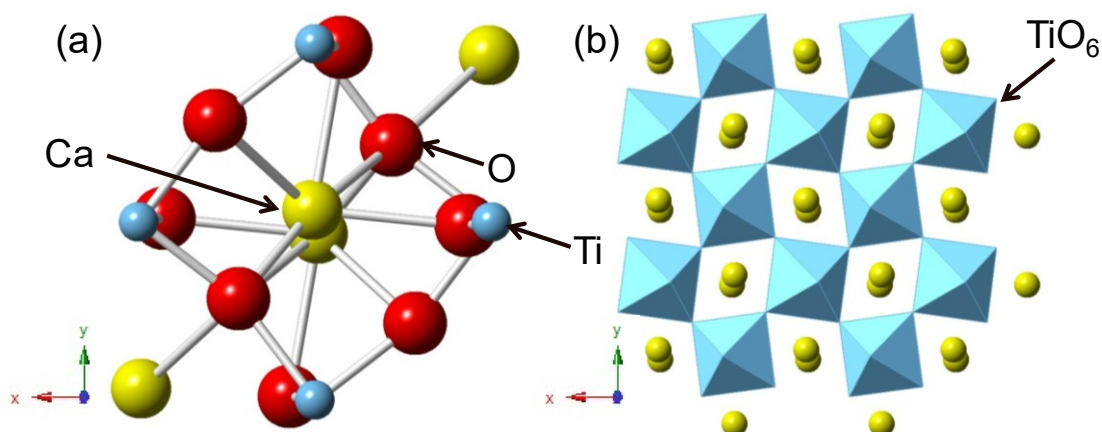


Figure 1.10 (a) The unit cell structure of perovskite viewed along the c axis. (b) The TiO_6 network in perovskite forms large cavities while the Ca (yellow) cations are located at the central cavities viewed along the c axis⁷³.

1.3.1.4 Rutile and related phases

The titanium oxide phase in Synroc may be rutile and/or one or more of the Magnéli phases $\text{Ti}_n\text{O}_{2n-1}$, $7 < n < 9$. Although the titanium oxides merely participate in waste incorporation, they provide a chemical buffer which allows the relative proportion of Synroc phases to vary to accommodate changes in proportions of each radionuclide^{5, 53}. Rutile not only provides such processing flexibility but can also be utilised to incorporate radionuclide host phases for enhancing chemical performance such as Synroc-E⁵⁹. Use of TiO_2 to incorporate Ru and Tc isotopes via occupation of the Ti site as a substitutional defect has been suggested⁷⁹.

1.3.2 Glass wasteform- vitrification technology

Vitrification is currently the most widely used waste immobilisation technology for aqueous radioactive wastes that should be solidified for stable storage and disposal. Vitrification involves melting of nuclear waste elements with glass forming additives so that the final vitreous product incorporates the waste contaminants in its macro- and microstructure. The nuclear waste elements are immobilised either by direct chemical incorporation into the glass structure or by physical encapsulation. Waste vitrification has the following advantages^{13, 80}:

- (a) High capability: the amorphous glass can reliably immobilise a range of nuclear waste elements into its network structure.
- (b) Simple production technology: industrial glass manufacture has already been developed for many decades worldwide, even in highly radioactive environments hence the production process is mature and is more economical, while meeting the need for efficiency, compared to other HLW wasteform candidates such as ceramics.
- (c) High waste volume compaction (relatively high-density and high waste loading capacity).
- (d) High tolerance to radiation damage owing to being amorphous.
- (e) High chemical durability: the glass selected for nuclear waste immobilisation is highly resistant to contact with ground waters for a long

period even with the combined effect of radiation.

Borosilicate glass has become the primary choice of material for nuclear waste immobilisation worldwide via melting vitrification technology. Many countries have their own formulations, their experience and processing conditions and facilities to tailor their type of waste⁵¹. For example, a typical borosilicate glass, PNL 76-68 glass, was designed and developed by Pacific Northwest Laboratories (PNL) in U.S. since 1970s. PNL 76-68 glass was shown to be thermally stable, insensitive to compositional variations and have slower devitrification kinetics compared to other U.S. glass compositions^{5, 81, 82, 83}. Another typical borosilicate glass from France, R7-T7 glass, has been studied and used for current PUREX HLW immobilisation for over 20 years at La Hague^{5, 84, 85}. The vitrification technology has thus been proven as suitable for FP immobilisation and also produces a stable matrix^{84, 85, 86, 87}. The PNL 76-68 and R7T7 glass became one of the typical reference glass wasteforms. Table 1.1 gives the composition of PNL 76-68 and R7T7 glass.

Table 1.1 Composition of PNL 76-68 and R7T7 borosilicate glass^{5, 81, 84}.

Composition	PNL 76-68 (wt.%)	R7T7 (wt.%)
SiO ₂	59.4	54.3
B ₂ O ₃	14.3	16.7
Na ₂ O	11.3	11.8
ZnO	7.6	3.0
CaO	2.9	4.8
TiO ₂	4.5	-
Li ₂ O	-	2.4
ZrO ₂	-	1.2
Al ₂ O ₃	-	5.8

Ideally, the most durable glass wasteform would be vitreous silica, but this material requires high processing temperatures (> 1500°C) that would provoke volatilisation of species such as Cs. Boric oxide is most commonly used to modify the behaviour of silica as this additive lowers the processing temperatures (< 1200°C). Borosilicate glass generally contains SiO₂ as the major component, relatively high B₂O₃, CaO, MgO, Na₂O and Al₂O₃ contents and minor amounts of other oxides. SiO₂, B₂O₃ and Al₂O₃ as network formers generally form strong covalent bonds involving SiO₄, AlO₄ and BO₄ tetrahedra and BO₃ triangles. For low valence ions (i.e. Na⁺, Ca²⁺, Sr²⁺, Cs⁺), they act as a

modifier and are bonded into the network by sharing various nonbridging oxygen bonds. Borosilicate glass and its melts contain an open and random network structure possessing short range order (SRO) around a central atom such as tetrahedral and octahedral structure units and medium range order (MRO) which surrounds second and third neighbour environments around a central atom. The polymerization of the SRO and MRO allows glass to become more flexible in atomically bonding with waste species than crystalline wasteforms¹³. Figure 1.11 illustrates borosilicate glass structure with dissolved wastes. Borosilicate glass (as amorphous material) has an internal structure made of a well-developed, topologically disordered, 3-dimensional (3D) network of interconnected microscopic structural blocks^{10, 80}. The radionuclides enter and become part of the random 3D glass network. Encapsulation is applied to elements and compounds that are insoluble in the glass melt which do not fit into the glass structure, notably RuO_2 . Vitrification avoids excess volatilisation of radionuclides such as Cs and Ru because it can be performed efficiently at temperatures below 1200°C ^{10, 51}.

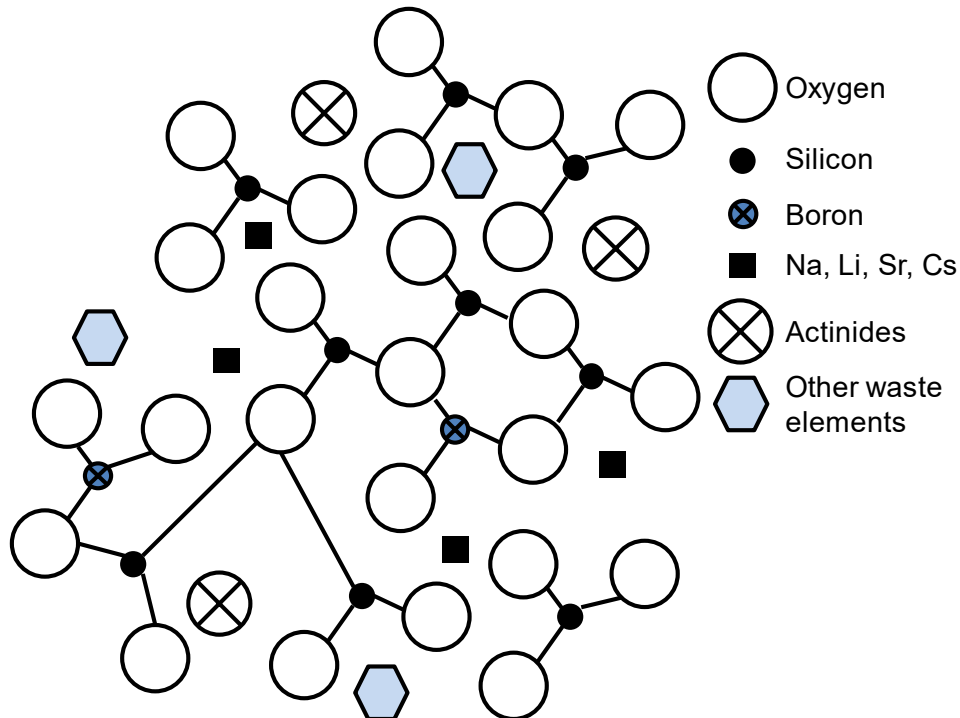


Figure 1.11 Borosilicate glass structure containing dissolved wastes.

1.3.3 General comparison of Synroc and glass wasteforms

Borosilicate glass is the current wasteform employed commercially worldwide for the immobilisation of HLW arising from reprocessing. It therefore occupies a special position as the reference wasteform against which the properties of alternative wasteforms should be compared. Crystalline ceramic wasteforms such as Synroc were developed and investigated as alternative wasteforms. Two important physical and thermal properties of borosilicate glass and Synroc are listed in Table 1.2 for comparison^{5, 88, 89}.

Table 1.2 The key differences of physical and thermal properties of borosilicate glass and Synroc^{88, 89}.

	Borosilicate glass	Synroc-C
Density (g/cm ³)	2.6	4.35
Thermal conductivity (W/mK)	1.1	2.1

The most notable difference between borosilicate glass and Synroc is their densities. The density of Synroc (~4.35 g/cm³) is higher than that of borosilicate glass (~2.6 g/cm³) therefore Synroc has a smaller volume than borosilicate glass when containing the same amount of HLW. Both Synroc and borosilicate glass have been reported to have maximum simulated waste loadings of up to 35 wt.% but most of the loading settings in the studies were usually set at 10-20 wt.% as high waste loading may result in the formation of additional less durable phases and thus impair the durability^{52, 90}. In general, for conventional HLW, Synroc can usually accommodate higher waste loadings than borosilicate glass due to its higher capacity for actinides. The solubility of actinide elements in borosilicate glass is relatively low, i.e. < 5 wt.%. Synroc can immobilise more actinides via increasing the amount of host phases⁵². Higher density and waste loading benefit the waste storage process due to a reduced number of canisters required or size of the repository. Another difference is the thermal conductivity of borosilicate glass and Synroc. Synroc has higher thermal conductivity (2.1 vs. 1.1 W/mK) that results in the reduction of thermal gradients in Synroc, and in turn, reduces the chance of thermal stress cracking. Whereas for borosilicate glass, it is difficult to cast large bulk glass forms without cracks when cooling due to the thermal stresses caused by a relatively low thermal conductivity^{88, 89}.

A drawback associated with Synroc is the greater processing complexity,

which involves hot pressing techniques. The high melting points of major Synroc phases require melting process temperature as high as 1500°C which causes the same problem as vitreous silica which melts at 1600°C. An alternative method is to sinter Synroc at 1250 - 1350°C for longer than 12 h to obtain a dense ceramic (> 85 % of theoretical density, TD)^{52, 91, 92}. However, these processing temperatures are still higher than those of borosilicate glass (1050 - 1200°C) and may cause volatilisation from the waste. The current synthesis route for Synroc at the Australian Nuclear Science and Technology Organisation (ANSTO), which has developed Synroc for over 30 years, is hot isostatic pressing (HIPing)⁹⁰. HIPing can lower the processing temperature (1100 - 1300°C) and achieve >95 % TD for a few hours with negligible off-gas⁹⁰. More details about hot-pressing techniques will be described in Chapter 2.

1.3.4 Leaching durability

Many countries are planning a disposal system for HLW disposal including an engineered wasteform, and multi-engineered barriers in a 300 - 1000 m deep underground geological repository (a natural barrier). The wasteform should be as durable as reasonably possible since multiple barriers might be corroded and the wasteform would then be exposed to groundwater^{14, 93, 94}. The leaching durability of the wasteform is thus a key for avoiding radionuclides escaping back to the biosphere.

A standard series of leach tests has been developed to measure and understand the leach behaviour of wasteforms under the auspices of the International Standards Organization's Materials Characterization Centre (MCC) located at Pacific Northwest National Laboratory (PNNL)⁹⁵ and the American Society for Testing and Materials (ASTM)^{96, 97, 98, 99}. These MCC tests and some advanced tests can be categorized as static tests and dynamic tests to simulate a variety of conditions. Table 1.3 shows some standard tests used worldwide in determining wasteform durability.

Table 1.3 Standard test of durability testing.

Test	Sample	Conditions	Use	Ref.
MCC-1, ASTM C1220	Monolithic specimen	Static; testing temperature < 100°C, usually 40, 70 and 90°C; sample surface area to leachant volume, SA/V, usually 10 m ⁻¹	For comparison of wasteforms	^{95, 96}
MCC-2	Monolithic specimen	Static; testing temperature > 100°C but <200°C, usually 100, 150 and 190°C; SA/V, usually 10 m ⁻¹	Same as MCC-1, but at elevated temperature in a closed system, Teflon-lined steel capsule	⁹⁵
MCC-3, Product Consisten cy Test (PCT), ASTM C1285	Crushed powder sample	Testing temperature <200 °C, usually at 40, 90, 110, 150, 190°C with stirring; SA/V, usually 1000 m ⁻¹	For durable wasteforms to accelerate leaching	^{95, 97}
MCC-4, SPFT, ASTM C1662	crushed sample/ monolith	Single Pass Flow through Test; testing temperature usually at 90°C and the flow rates are usually 0.001, 0.01 and 0,1 ml/min; monolithic specimen	Most closely simulate repository conditions, giving kinetic parameters	^{95, 98}
Vapour Hydration Test (VHT), ASTM C1663	Monolithic specimen	A monolithic specimen is suspended in a sealed vessel with a small volume of leachant at testing temperature in the range 150 - 300°C	Study the corrosion of sample under conditions of high temperature and contact by water vapour	⁹⁹

In terms of chemical durability, Synroc usually has much higher resistance than glass with respect to leaching by groundwater, both at room and elevated temperatures^{5, 88, 89, 100}. Figure 1.12 shows bulk Cs and Ca leach rates at 95°C for Synroc and borosilicate glass (PNL 76-68). Borosilicate glass typically contains low silica and high alkali contents and, as such, alkali metals and B₂O₃ tend to be selectively leached from the surface layers when glass is attacked by aqueous solutions. The surface layers become enriched in silica which can

protect the underlying glass from further leaching. This further leaching can be caused by slow diffusion of cations through the surface layer^{88, 89}. In aqueous solution, monovalent and divalent cations (mainly Cs^+ , Ca^{2+} , Sr^{2+} and Ba^{2+}) are removed from a near-surface layer in Synroc leaving a surface layer enriched in TiO_2 . The extreme insolubility of titanium dioxides in aqueous solutions is the reason for the good leaching resistance of Synroc. Further leaching can be caused by diffusion of cations through the titania-rich surface combined with slow dissolution of the outer layer^{5, 88, 89}. As shown in Figure 1.12, Synroc has better leaching resistance for Cs and Ca. Moreover, the leach rates of Cs and Ca in borosilicate glass did not decrease significantly with time while for Synroc they decreased by several orders of magnitude owing to the “ TiO_2 skin” formation⁸⁹.

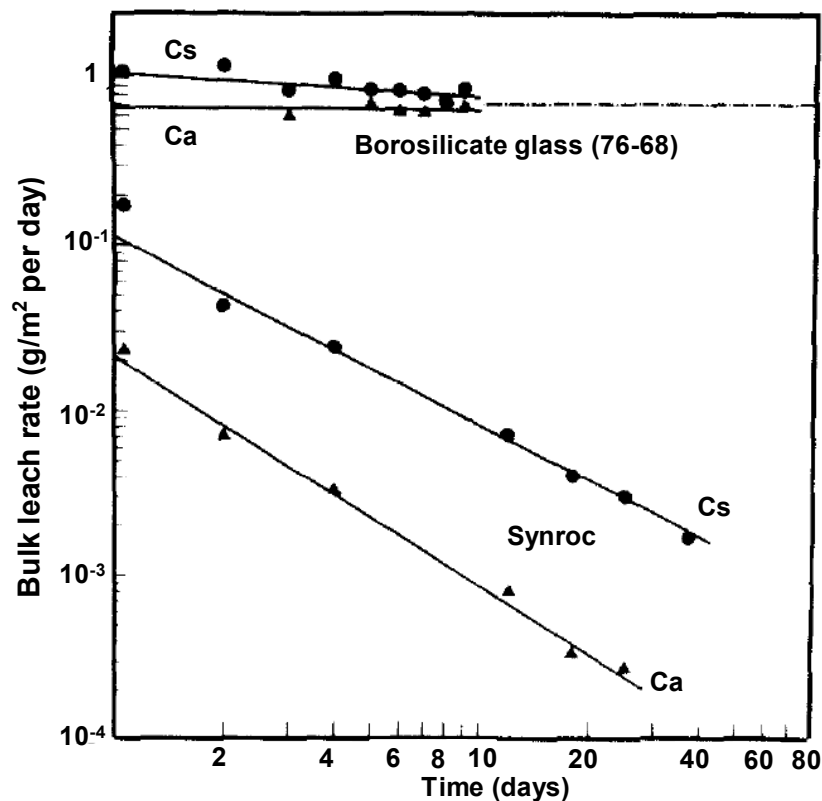
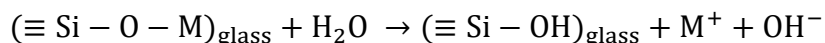


Figure 1.12 Log of leach rates at 95°C in deionized water (based on Cs and Ca losses) vs. log of time for bulk Synroc-C sample (0.36% Cs_2O , 10.8% CaO) hot-pressed at 1150°C and typical PNL 76-68 borosilicate glass⁸⁹. Adapted from A.E. Ringwood *et al.*⁸⁹

The borosilicate glass is the current wasteform for PUREX waste and its leaching behaviour is important to understand and hence avoid the

radionuclides escaping to the biosphere. The glass formed altered layers on its surface during leaching and the mechanisms of alteration of the layers formed during leach testing depend on the composition of glass^{101, 102, 103, 104, 105}. Water leaching of glass wasteforms occurring through several different mechanisms is generally recognized to have three stages:

(1) Initial ion exchange, between mainly light alkali ions (Li, and Na) from the glass and water. The alkali ions act as a modifier in the glass network and are easily removed from the glass. In the beginning of leach testing, the glass wasteform undergoes diffusion with water molecules from the surface of glass matrix. Ion exchange (cation M^+ with a proton from H_2O) is the preferential mechanism of the water-glass reaction for short time periods. The overall chemical reaction is written as^{101, 106}:



Equation 1.1 Ion exchange between cation M^+ and water in glass.

This reaction causes an increase in solution pH.

(2) Hydrolysis where a silica-rich layer forms. Hydrolysis of the silicate network occurs preferentially to ion exchange when the pH of solution increases. Ion exchange and hydrolysis are occurring simultaneously but the rates of each reaction differ across the pH range. The near surface of glass leached out the mobile glass constituents (alkalis and boron) and hence the remained Si formed a hydrated silica rich layer which is termed the gel layer and is always amorphous^{107, 108}. During this time, the dissolution rate of glass becomes dependent on the solution saturation state (concentration of elements in solution) and the overall glass dissolution rate slows down. Eventually, the glass dissolution rate settles at a constant rate^{102, 103, 104, 109}. The ionic species initially present in the leachant may be complex and adsorbed at the solution-gel layer interface and increase saturation^{105, 110}.

(3) Surface precipitation of secondary phases on the surface when leachate saturation occurs^{101, 111}. Secondary phases start to precipitate, mostly at the surface of the altered glass but also in solution^{105, 112, 113}. These precipitates are amorphous or poorly crystallized (i.e. zeolite, and quartz)^{102, 103, 104, 114, 115}.

1.4 Aims and objectives

The aim of this project is the development of advanced wasteforms for EURO-GANEX waste. Efficient routes for the synthesis and durability for advanced matrices were studied.

To achieve the objectives the methods listed below were followed:

- (a) To design a Synroc derivative, Synroc-Z, aimed to immobilise EURO-GANEX wastes
- (b) To fabricate Synroc-Z with simulated waste from EURO-GANEX using hot-pressing techniques.
- (c) To fabricate R7T7-type borosilicate glass with simulated waste from EURO-GANEX using melting vitrification and HIPing.
- (d) To characterise the phase composition and microstructure of the Synroc-Z and R7T7 glass via X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and transmission electron microscopy (TEM).
- (e) To study the durability of both wasteforms using the MCC-1 test and to examine the leached microstructures via SEM, EDX, TEM and atomic force microscopy (AFM).

Chapter 2: Experimental and Instrumental Techniques

2 Experimental techniques

The purpose of this project was to develop suitable wasteforms for the immobilisation of EURO-GANEX waste. Both ceramic (Synroc) and borosilicate glass derived waste hosts were developed and the processing routes and associated techniques are described in this chapter. The aims of experiments described in this chapter were to produce homogeneous Synroc and R7T7 glass powder through an alkoxide and/or oxide route and then fabricate dense samples. The samples were then characterised to examine their bulk density, microstructure, phase composition and durability. The experimental techniques used are described in detail here. The experimental work was mainly performed at Imperial College although some was undertaken at ANSTO, Sydney Australia and the University of Sheffield (UoS). Tables 2.1 - 2.4 list the chemicals, equipment and instruments used at Imperial College and ANSTO.

Table 2.1 List of chemicals used at Imperial College.

	Supplier	Purity or concentration
Synroc Precursors		
Titanium(IV) isopropoxide	Alfa Aesar	>97%
Aluminium sec-butoxide	Alfa Aesar	>97%
Zirconium (IV) propoxide	Sigma-Aldrich	70 wt% in 1-propanol
Calcium hydroxide	Alfa Aesar	>95%
Barium hydroxide	Alfa Aesar	>94%
Glass formers		
Zirconium(IV) oxide	Alfa Aesar	>99.4%
Aluminium oxide, alpha-phase	Alfa Aesar	>99.9%
Calcium oxide	Alfa Aesar	>99%
Lithium carbonate	Strem Chemicals	>99%
Sodium carbonate	Sigma-Aldrich	>99.95%
Zinc oxide	Alfa Aesar	>99%
Boric acid	Alfa Aesar	>99%
Silicon(IV) oxide	Alfa Aesar	>99.5%
Simulated HLW		
Cesium nitrate	Alfa Aesar	>99.8%
Strontium nitrate	Alfa Aesar	>99%
Cerium(III) nitrate hexahydrate	Alfa Aesar	>99.5%
Neodymium(III) nitrate hexahydrate	Alfa Aesar	>99.9%
Samarium(III) nitrate hexahydrate	Alfa Aesar	>99.9%
Gadolinium(III) nitrate hydrate	Alfa Aesar	>99.9%
Zirconium dinitrate oxide hydrate	Alfa Aesar	>99.9%
Silver nitrate	Alfa Aesar	>99.9%
Chromium(III) nitrate nonahydrate	Alfa Aesar	>98.5%
Telluric acid dihydrate	Alfa Aesar	>99%
Barium nitrate	Sigma-Aldrich	>99%
Iron(III) nitrate nonahydrate	Sigma-Aldrich	>98%
Yttrium(III) nitrate hexahydrate	Sigma-Aldrich	>99.9%
Nickel(II) nitrate hexahydrate	Sigma-Aldrich	>98.5%
Ammonium molybdate tetrahydrate	Fluka	>99%
Ruthenium(IV) oxide	Alfa Aesar	>99.9%
Palladium(II) oxide	Alfa Aesar	>99.9%
Cesium carbonate	Alfa Aesar	>99.9%
Strontium oxide	Alfa Aesar	>99.5%
Cerium(IV) oxide	Alfa Aesar	>99.99%
Barium oxide	Alfa Aesar	>90%
Neodymium(III) oxide	Alfa Aesar	>99.99%
Samarium(III) oxide	Alfa Aesar	>99.9%
Yttrium(III) oxide	Alfa Aesar	>99.9%
Zirconium(IV) oxide	Alfa Aesar	>99.4%

Gadolinium(III) oxide	Alfa Aesar	>99.99%
Tellurium dioxide	EMD Millipore	>99.5%
Silver(I) oxide	Alfa Aesar	>99%
Chromium(III) oxide	Alfa Aesar	>99.6%
Phosphorus(V) oxide	Alfa Aesar	>98%
Iron(III) oxide	Sigma-Aldrich	>99%
Nickel(II) oxide	Sigma-Aldrich	>99%
Solvents		
Nitric acid	VWR	70%
DI water	Merck	Milli-Q

Table 2.2 List of equipment and instruments employed at Imperial College.

	Producer	Model
Equipment		
Tube furnace	Lenton, UK	LTF 16/450
Hot uniaxial press machine	FCT Systeme GmbH, Germany	HP W125/1
Instruments		
TGA	Netzsch	STA 449F1
XRD	PANalytical, Netherlands	X'Pert
FEGSEM	Zeiss, Germany	Gemini 1525
FEGSEM	Zeiss, Germany	Sigma 300
EDX	Oxford instruments, UK	INCA
TEM	JEOL, Japan	JEM-2100FX
ICP-MS	Aglient, USA	7700x

Table 2.3 List of chemicals employed at ANSTO.

Chemicals	Supplier	Purity or concentration
Synroc Precursors		
Titanium(IV) isopropoxide	Alfa Aesar	>97%
Aluminium nitrate nonahydrate	unilab	>98%
Calcium nitrate tetrahydrate	Sigma-Aldrich	>99%
Barium nitrate	Chem supply	>99%
Glass formers		
Zirconium (IV) tert-butoxide	Sigma-Aldrich	>98%
Aluminium nitrate nonahydrate	Unilab	>98%
Calcium nitrate tetrahydrate	Sigma-Aldrich	>99%
Lithium nitrate	Unilab	>95%
Sodium hydroxide	Chem supply	>98%
Zinc oxide	Sigma-Aldrich	>99%
Boric acid	BDH	>99%
Ludox (50% colloidal silica)	Chem supply	50%
Simulated HLW		
Cesium nitrate	Aldrich	>99%
Strontium nitrate	Alfa Aesar	>99%
Cerium(III) nitrate hexahydrate	Alfa Aesar	>99.5%
Neodymium(III) nitrate	Aldrich	>99.9%

hexahydrate		
Samarium(III) nitrate hexahydrate	Sigma-Aldrich	>99.9%
Gadolinium(III) nitrate hydrate	Sigma-Aldrich	>99.9%
Zirconium (IV) tert-butoxide	Sigma-Aldrich	>98%
Silver nitrate	Univar	>99.9%
Chromium(III) nitrate nonahydrate	Acros	>99%
Telluric acid dihydrate	BDH	>99%
Barium nitrate	Chem supply	>99%
Iron(III) nitrate nonahydrate	Sigma-Aldrich	>98%
Yttrium(III) nitrate hexahydrate	Alfa Aesar	>99.9%
Nickel(II) nitrate hexahydrate	Fluka	>99%
Ammonium molybdate tetrahydrate	May & Baker	>98.5%
Ruthenium(III) Nitrosol Nitrate Solution	JMC	93 g /L
Palladium (II) nitrate dihydrate	Fluka	>98%
Ammonium phosphate dibasic	Sigma-Aldrich	>98%
Solvents		
DI water	Merck	Milli-Q
Cyclohexane	Univar	>99%

Table 2.4 The list of equipment and instruments used at ANSTO.

	Producer	Model
Equipment		
Furnace	Modutemp, Australia	WW31AN01/SC186EVM01
Rotating furnace	Sandvik, Sweden	Kanthal
Hot isostatic press machine	American Isostatic Presses Inc., USA	AIP6-30H
Instruments		
XRD	PANalytical, Netherlands	X'Pert
GIXRD	Bruker, Germany	D8 advance
FEGSEM	Zeiss, Germany	Gemini 1525
EDX	Oxford instruments, UK	INCA
TEM	JEOL, Japan	JEM-2100FX
AFM	Digital Instruments, USA	Dimension 3000 with Nano Scope IIIa controller
ICP-MS	Aglient, USA	7800x

2.1 Synthesis of potential wasteforms

2.1.1 Composition design of waste from EURO-GANEX

Waste streams from EURO-GANEX advanced reprocessing are different in composition to those from the existing PUREX process. It is therefore important to specify the approximate composition of EURO-GANEX waste before developing advanced immobilisation matrices capable of accommodating such modified waste streams. PW-4b was the U.S. Energy Research and Development Administration shorthand for PUREX process wastes from a light water reactor which was used as the reference waste stream composition in this project^{53, 116}. In principle, the waste stream from EURO-GANEX reprocessing will only contain FPs without traceable major or minor actinides. Consequently, the composition of a commonly used PUREX raffinate may be used to define the reference composition of waste from EURO-GANEX reprocessing but with the actinide components excluded. Although EURO-GANEX is targeted towards the treatment of fast reactor spent fuels, the FP distributions are expected to be similar to those in the suitably altered raffinate composition.

Table 2.5 shows the composition of simulated HLW (PW-4b) which is a nitrate solution based on oxides with and without actinides. The composition without actinides is assumed to be representative of EURO-GANEX waste for the purposes of this work. Simplifications and substitutions for rare-earth and alkali metals are based on accepted crystal chemical considerations of compatible charge and crystal radii.¹¹⁷

Table 2.5 The composition of typical calcined HLW, PW-4b, and wastes from EURO-GANEX (free of actinide and actinide simulant) based on oxides^{53, 116, 117}.

	Constituent (<i>simulated element(s)</i>)	PW-4b (wt. %)	EURO-GANEX (wt. %)
Fission Products	Cs ₂ O (<i>Rb⁺, Cs⁺</i>)	8.0	8.5
	SrO	2.6	2.8
	BaO	3.8	4.0
	Y ₂ O ₃	1.5	1.6
	Ce ₂ O ₃ (<i>La³⁺, Ce³⁺</i>)	11.3	12.0
	Nd ₂ O ₃ (<i>Na³⁺, Pm³⁺</i>)	15.0	16.0
	Sm ₂ O ₃	2.3	2.4
	Gd ₂ O ₃ (<i>Eu³⁺, Gd³⁺</i>)	0.8	0.9
	ZrO ₂	12.1	12.9
	MoO ₃	12.7	13.5
	TeO ₂	1.8	1.9
	Ag ₂ O (<i>Ag⁺, Cd²⁺</i>)	0.4	0.4
	RuO ₂ (<i>Rh³⁺, Ru⁴⁺</i>)	8.6	9.2
	PdO (<i>Tc⁷⁺, Pd²⁺</i>)	6.8	7.2
Actinides	UO ₂ (<i>Np⁴⁺, U₃O₈, Pu⁴⁺</i>)	5.4	-
	Gd ₂ O ₃ (<i>Am³⁺, Cm³⁺</i>)	0.5	-
Processing Contaminants	Fe ₂ O ₃	3.7	3.9
	Cr ₂ O ₃	0.8	0.8
	NiO	0.3	0.3
	P ₂ O ₅	1.6	1.7

2.1.2 Synroc composition design and preparation

The typical formulation developed to immobilise HLW from PUREX is Synroc-C which predominantly contains four different phases and normally hosts 20 wt.% waste⁵. In Synroc, zirconolite is the host phase for most of the actinide component. Consequently, its relative proportions can be reduced or even omitted for immobilising EURO-GANEX wastes.

The composition of Synroc precursors was modified in order to lower the ratio of zirconolite in relation to the other phases. This was achieved by removing ZrO₂ completely and reducing CaO content as these are precursors for zirconolite phase. Hereafter, the modified Synroc composition is referred to as Synroc-Z. Table 2.6 shows how the target phase content relates to precursor composition for Synroc-C and -Z.

Table 2.6 The comparison of the target phase assemblages and precursor composition Synroc-C⁵ and Synroc-Z.

Composition			Synroc Composition		
	Synroc-C (wt.%)	Synroc-Z (wt.%)	Synroc Constituent Phase	Synroc-C (wt.%)	Synroc-Z (wt.%)
TiO ₂	57.0 ^a	61.4	Hollandite	30	35
ZrO ₂	5.4 ^b	-	Perovskite	20	30
Al ₂ O ₃	4.3	5.3	Zirconolite	30	10
CaO	8.9	7.9	Rutile ^c	15	20
BaO	4.4 ^b	5.4	Alloy phases	5	5
HLW	20.0	20.0			

^a does not include 2 wt.% added Ti metal before sintering

^b does not include contribution from HLW

^c includes Ti oxides and Ca-Al-titanates

Powders necessary for the production of Synroc samples containing simulant HLW (Table 2.5) were produced at both Imperial College and ANSTO through an alkoxide route. The scale at which these were produced was quite different at each institution: batch sizes were ~30 g at Imperial College and were considerably larger (~500 g) at ANSTO. As organic solvents are typically removed following reprocessing, through a calcination step, these were not added in the experiments. The chemicals and equipment used for preparing Synroc-Z powder at Imperial College London and ANSTO are listed in Tables 2.1 – 2.4.

At Imperial College, Synroc-Z precursors were prepared by mixing alkoxides of Ti and Al with ethanol to produce a homogeneous mixture and the alkoxide feedstock was then hydrolysed with Ca and Ba hydroxide solution. All simulated wastes are metal oxides and nitrates and are dissolved in 2 M nitric acid, except Mo and Te (ammonium molybdate and telluric acid). The simulated HLW was added to the precursor slurry and mixed. The mixture was stirred on a hot plate at 150°C to vapourize the bulk liquid and then dried at 110°C in the oven to dryness. Calcination was performed with a heating rate of 10 °C/min up to 750°C under reducing conditions (10 v/v % H₂/Ar) for 2.5 h in a tube furnace to prevent the formation of undesirable micropores which may be produced by gases during the subsequent sintering step.

At ANSTO, Synroc-Z with simulated HLW was made by dissolving all metal

nitrate, ammonium molybdate, diammonium phosphate and telluric acid in water to a homogeneous mixture. Then zirconium tert-butoxide and titanium isopropoxide were added to form slurry. The mixture was paddle stir-mixed overnight in a steel container and then poured into a steel bowl to dry at 120°C. The dried mixture was calcined at 750°C under reducing conditions (3.7 v/v % H₂/N₂) for 2.5 h in a rotating furnace which had been placed under a fume hood to capture any NO_x compounds emitted from nitrate decomposition.

2.1.2.1 Hot uniaxial pressing

Hot pressing techniques can be used to densify Synroc samples. There are several different types of hot pressing techniques, however hot uniaxial pressing (HUPing) and hot isostatic pressing (HIPing) were adopted here because they have been used to produce ceramic wasteforms successfully for over 30 years⁵. HUPing is a ceramic synthesis based technique relying on simultaneous heating and die pressing. At a laboratory-scale, a graphite or metallic die is usually used. Here a 30mm diameter cylindrical graphite die was used. This is shown in Figure 2.1 along with its associated punches.

The calcined powder (produced in the manner described above) was ball-milled for 10 h with ethanol or cyclohexane before drying at 110°C. Then, 13 g of the resultant powder was poured into the graphite die and uniaxially pressed at ~10 MPa. The pressed powder was consolidated by HUPing using the processing conditions given in Table 2.7, with a temperature ramp rate of 5 °C/min under Ar (30 mbar above atmospheric pressure) in a cylindrical graphite furnace. The selected HUPing conditions were based on those used to fabricate Synroc previously^{5, 90, 117} and thermo gravimetric analysis (see section 2.2.3) results for volatilisation from volatile waste elements.

Before HUPing, 2 wt.% of fine (<50 µm) titanium metal powder was added to the calcined powder for additional control of the oxygen potential⁵. The Ti metal powder produces reducing condition during HUPing and thus the Mo, Ru, Pd and Te which are supposed to form alloy phases can be reduced to metallic state. The insufficient reducing condition may cause the formation of undesired phases as the Mo may not be reduced to metallic state and thus form other leachable phases^{56, 118}. The graphite dies and the punches were lined with 0.3

mm thick graphite paper to prevent bonding between the sample and graphite tooling.

Table 2.7 The HUP processing conditions and waste loading in this study. Sample ID was presented as processing temperature (°C)- pressure (MPa)- dwell time (h) and waste loading (-wt).

Sample ID	Temperature (°C)	Pressure (MPa)	Dwell time (h)	Waste loading (wt.%)
1250-20-3	1250	20	3	20
1200-20-3	1200	20	3	20
1150-20-3	1150	20	3	20
1100-20-3	1100	20	3	20
1050-20-3	1050	20	3	20
1200-40-3	1200	40	3	20
1200-10-3	1200	10	3	20
1200-20-5	1200	20	5	20
1200-20-1	1200	20	1	20
1200-20-0.5	1200	20	0.5	20
25-wt	1200	20	3	25
30-wt	1200	20	3	30
35-wt	1200	20	3	35

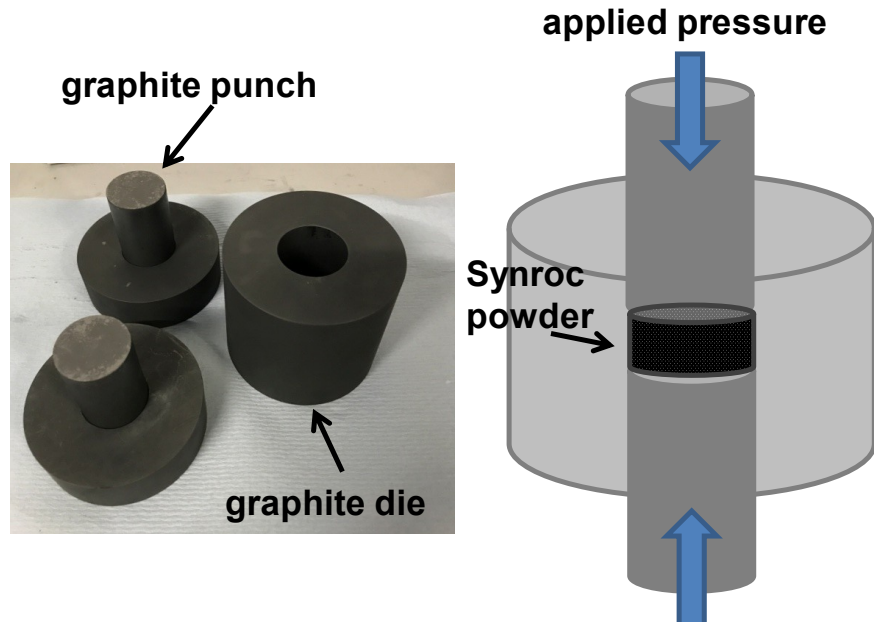


Figure 2.1 The graphite die and punches for HUPing.

2.1.3 Composition and preparation of R7T7 borosilicate glass

Many kinds of glass wasteforms have already been reported with borosilicate glass compositions representing the most commonly used material

type worldwide for immobilising HLW⁸⁴. The R7T7 glass, was selected as the glass wasteforms to immobilise the HLW from EURO-GANEX in this study because it has been studied and used for current HLW PUREX immobilisation for over 20 years^{84, 85, 86}. Table 2.8 gives the compositions of R7T7 glass.

Table 2.8 Compositions of R7T7 borosilicate glass⁸⁴.

Composition	R7T7 (wt.%)
Li ₂ O	2.4
Na ₂ O	11.8
CaO	4.8
ZrO ₂	1.2
ZnO	3.0
B ₂ O ₃	16.7
Al ₂ O ₃	5.8
SiO ₂	54.3

As before, both the glass precursors (Table 2.8) and simulant HLW (Table 2.5) were produced at both Imperial College and ANSTO through oxide and alkoxide routes for ~30 g and ~500 g batch sizes, respectively. The chemicals and equipment used for preparing R7T7 glass powders at Imperial College London and ANSTO are listed in Tables 2.1 – 2.4.

At Imperial College, the R7T7 glass powder with 20 wt.% simulated HLW was prepared by shaking the mixture of metal oxides and carbonates and ammonium molybdate powders for 24 h. The mixture was calcined at 510°C under air for 2.5 h in a furnace to decompose carbonates. The calcined mixture was then loaded into a platinum crucible and then heated at selected temperatures (850, 900, 1000, 1100, 1150, 1200°C) in air and held for 3 h using a ramp rate of 10 °C/min. The selected processing temperatures were based on the results from thermo gravimetric analysis (see section 2.2.3) and melting point of R7T7 glass. The resulting melt was cooled in two steps to room temperature. The first step was to directly cool samples to 500°C via transferring the whole Pt crucible into a pre-heated furnace. The Pt crucible with glass melt was taken out from the furnace which was heated to the desired temperatures and then put into the pre-heated furnace to anneal. In the second step, the pre-heated furnace was switched off after its temperature recovered to 500°C and then the glass was cooled in the furnace to room temperature naturally

(normally 4 - 5 h). By using this two-step approach, a solid glass composite wasteform can be produced without cracks. The R7T7 glass needs to be cooled to below its glass transition point ($\sim 520^{\circ}\text{C}$) as soon as possible to avoid crystal formation. An annealing stage can relieve residual internal stresses. The time necessary for annealing depends on the type of glass and its maximum thickness. However, in this experiment, the annealing stage did not hold for a period (i.e. 1 - 3 h) due to the small batch size (the volume of Pt crucible is 30 mL and the size of glass product is normally about 2.5 cm diameter with 1 cm height). The insufficient annealing time may cause the internal stresses to still be retained in the glass and thus significantly decrease the overall strength of the glass and impair its durability.

At ANSTO, the R7T7 glass with 20 wt.% simulated HLW powder was mainly made for hot isostatic pressing synthesis (see next section). The powder preparation method was similar to Synroc-Z but it was calcined at 510°C instead of the 750°C used for Synroc-Z.

2.1.4 Hot isostatic pressing

Hot isostatic pressing (HIPing) simultaneously applies heat and isostatic pressure to a compact in a sealed canister. HIPing provides more even pressure via a flexible canister than HUPing. The advantages of the HIP technology include negligible off-gas during the high temperature consolidation step and that higher densification can be achieved¹². HIPing is currently being developed for a range of waste immobilisation needs with its processing cycle tailored to a variety of wasteforms¹¹⁹. Here the HIP process was applied to prepare both Synroc-Z and R7T7 glass both at ANSTO and the UoS. As for the HUP method, described above, 4 wt. % of fine titanium metal powder, was added to the Synroc-Z for additional control of oxygen potential. The canister preparation method is a bit different at ANSTO compared to UoS as decided by the team due to their experiences of machine, equipment usage and properties of canister materials.

At ANSTO, the calcined powders were loosely packed into a cleaned thin-wall 316 stainless steel can using the "spoon and tap" method. The lid was then welded onto the HIP canister to seal it. All HIP canisters have an

evacuation tube through which the gas was removed. The evacuation process used at ANSTO was to bake out the canister in steps of 100°C, up to a maximum of 400°C, for > 4 hours until no gases were released. This was to avoid gas evolution during HIPing. At UoS, the calcined powders were pre-pressed using a hydraulic press (up to 2 tonnes) into a cleaned thin-wall 316 stainless steel canister. After the lid was welded, the canisters were evacuated to below 50 mTorr and then were baked out to 600°C and held until the vacuum recovered to < 50 mTorr. In both cases, the evacuation tube was then double-cripped at half of its height and welded to finish.

Following preparation the canisters were HIPed using the conditions stated in Table 2.9 under Ar atmosphere. The HIPing conditions were selected based on the results from HUPed Synroc-Z and molten glass samples. The reason for determining the HIPing conditions will be described in Chapters 3 and 4. The heating and cooling rates were both set at 10 °C/min.

The canister volume displacements of HIPed samples prepared at UoS were measured before and after HIPing using the Archimedes method. This is the preferred method to confirm that the canister has been HIPed successfully (reduced volume) and that the weld was still tight (see Figure 2.2).

Table 2.9 The HIPing conditions for Synroc-Z and R7T7-type glass.

Sample	Bake-out temperature (°C)	Temperature (°C)	Pressure (MPa)	Dwell time (h)	Processed at
Synroc-Z	400	1250	100	2	ANSTO
Synroc-Z	600	1200	20	3	UoS
Synroc-Z	600	1050	100	3	UoS
R7T7	400	1100	100	2	ANSTO
R7T7	600	1100	10	3	UoS
R7T7	600	1200	10	3	UoS



Figure 2.2 Photos of HIP canister before (left) and after (right) HIPing. The unit of calliper is mm. Provided by Dr. Laura Gardner, the University of Sheffield.

2.2 Characterisation techniques

The following characterisation techniques were employed to determine the samples' bulk densities, phase composition, microstructures, and chemical durability.

2.2.1 Standard test method for bulk density measurement

The bulk densities and porosities of samples were measured by the Archimedes method¹²⁰. The samples were first dried at 110°C overnight to determine the dry weight (D) and then were placed into boiling water for 2 h with this process filling the open pores with water. After boiling, the samples were cooled to room temperature and kept immersed in water for another 12 h. A density determination kit (Sartorius mechatronics, YDK01, UK) was used to measure the suspended weight (S) by Archimedes' method by submerging the sample in water to record buoyancy. The value of buoyancy force is the same as that of the weight of the sample displaced by the volume of the sample. After determining the suspended weight, the wet weight (W) was measured by a balance after being wiped with wet tissue to remove any excess water beading on the surface of the sample. The bulk density (B, g/cm³) and apparent porosity (P, vol.%) can be determined by the following equations:

$$B = \frac{D \cdot \rho}{(W - S)}$$

Equation 2.1 The bulk density (B)

and

$$P = \frac{(W - D)}{(W - S)}$$

Equation 2.2 The apparent porosity (P)

where:

ρ = the density of the liquid (in this case water), in g/cm³

D = the dry weight, in g

W = the wet weight, in g

S = the suspended weight, in g

At ANSTO, the boiling water was replaced by a vacuum chamber (at room temperature) in order to obtain a more precise result. The dried samples were placed into the vacuum chamber to suck out any liquids and vapour inside the pores. Water was added while still under vacuum until the water is able to immerse the samples and water will hence enter the pores. After this step, the suspended weight and wet weight were measured using the same method as at Imperial College.

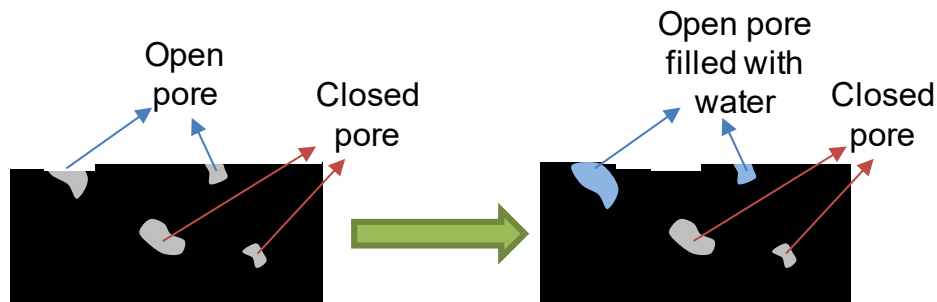
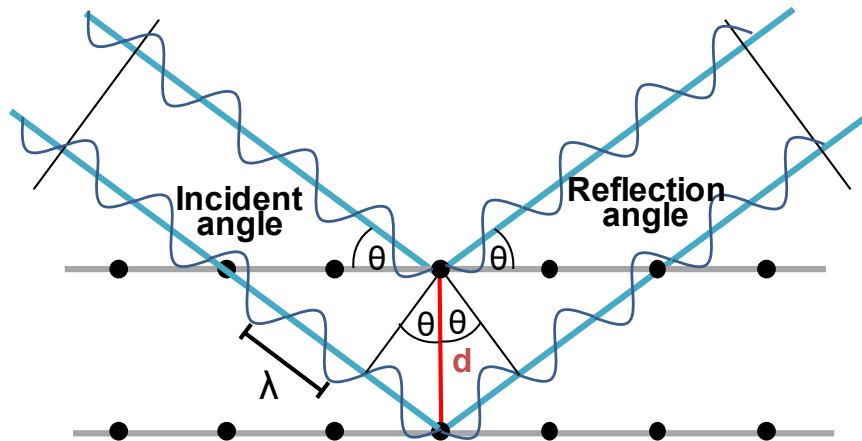


Figure 2.3 Diagrams of sample before and after immersing in the water.

2.2.2 X-ray Diffraction

For crystalline materials, X-ray diffraction (XRD) is used to determine the interatomic spacing and crystal structure by variable diffraction angle, θ , but fixed wavelength, λ . W.L. Bragg noted that the diffraction of X-rays could be thought of as the reflection of the X-rays from the crystal plane but unlike true reflection, only certain orientations of the crystal relative to the source and detector can reflect the X-rays. These orientations can be denoted by the incident angle formed with the X-ray source, and applied to the Bragg's Law, or the conditions for constructive interference (Figure 2.4)^{121, 122}

Figure 2.4 Schematic of Bragg's law¹²¹.

When X-rays are scattered by the atoms in a set of crystal planes of spacing d , a maximum in the scattered amplitude occurs when^{121, 122, 123}.

$$n\lambda = 2d\sin\theta$$

Equation 2.3 Bragg's law

where:

n = the order of corresponding diffracted beam, which is an integer consistent with $\sin\theta$

λ = the wavelength of the incident X-ray beam,

d = the interatomic spacing in the crystal,

θ = the angle of the incident beam

n is equal to the number of wavelengths in the path difference between X-rays scattered by each of the two ions.

This Bragg equation can be used to calculate the spacing between crystal planes d by giving a peak in the diffraction pattern from the angle between the source and detector. The interatomic spacing is called d -spacing which acts as a fingerprint for identifying the crystal structure. The diffraction patterns can be compared and matched with references to determine to crystalline materials^{121, 122, 123}. Cu K radiation source is the most widely used in XRD machine.

An X-ray diffractometer consist of an X-ray generator, a diffractometer assembly and X-ray data collection and processing software. A schematic of a

diffractometer circle is shown in Figure 2.5. A flat sample sits at the centre of the diffractometer circle. The sample plate rotates through a θ angle while the receiving slit and detector rotates through a 2θ angle. After diffracting, the beam from the sample is converted by the detector into electrical pulses in order to measure the intensity of the diffracted beam^{122, 123}. The different Synroc crystalline phases can be determined by matching their characteristic reflections with a database, such as the International Centre for Diffraction Data (ICDD)¹²⁴.

XRD also allows identification of amorphous phases such as glass. Although, these amorphous structures lack long range order, with the result that they do not present any clear diffraction peaks, they do display broad “amorphous humps”, the shape, position and magnitude of which are still characteristic of particular materials. All XRD patterns were obtained using the above method by a PANalytical X’Pert XRD with the settings listed in Table 2.10. The bulk sample was stuck on the sample holder by blue tack and then was pressed to a uniform height with the sample holder. The XRD was set to spin the sample to reduce the preferred orientation effects during measurement. Flat and rod shaped particles tend to lie flat on the surface of bulk sample and hence increase the intensities of some Bragg reflections while reducing the intensities of others. The ICDD cards used for identification of Synroc phases and crystals formed in R7T7 glass samples were listed in Table 2.11 and 2.12 respectively.

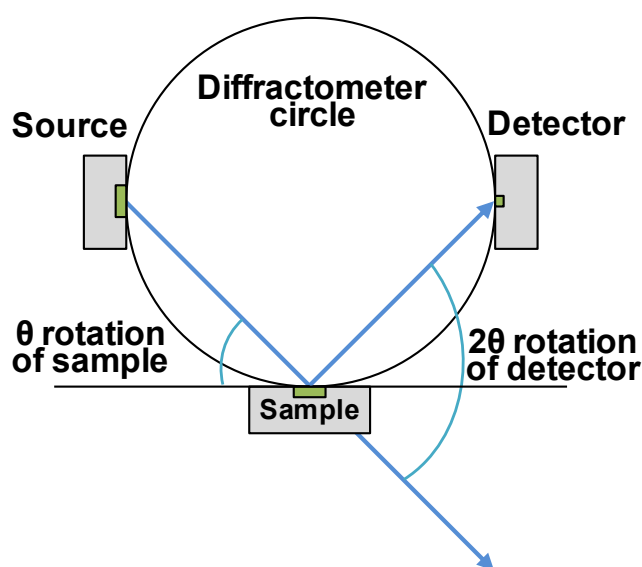


Figure 2.5 X-ray diffractometer¹²².

Table 2.10. Instrument setting for XRD analysis.

Parameters	Value
Scan Range	10 - 100 2 θ ^o
Step Size	0.0170 2 θ ^o
Scan Step Time	65.7701 s
Anode Material	Copper
Generator Settings	40 mA, 40 kV
Spinning	Yes

Table 2.11 ICDD cards used for identification of Synroc phases.

Phases	Composition	ICDD card number	Ref.
Hollandite	$\text{Ba}_{1.07}\text{Ti}_8\text{O}_{16}$	01-080-0908	125
		01-080-0913	
		01-080-0912	
	$\text{Ba}_{1.239}\text{Al}_{0.631}\text{Fe}_{1.847}\text{Ti}_{5.522}\text{O}_{16}$	01-077-2439	126
	$\text{Ba}_{1.17}\text{Ti}_{5.84}\text{Al}_{2.10}\text{O}_{16}$	01-084-0509	127
	$\text{Ba}_{0.965}\text{Cs}_{0.187}(\text{Al}_{2.115}\text{Ti}_{5.885})\text{O}_{16}$	01-078-0018	128
Perovskite	CaTiO_3	01-082-0229	129
		01-082-0228	
		01-081-0561	130
Zirconolite	$\text{Ca}_{0.584}\text{Nd}_{0.249}\text{TiO}_3$	01-088-0082	131
	$\text{CaZrTi}_2\text{O}_7$	01-084-0163	132
		00-034-0167	133
	$(\text{Ca}_{0.645}\text{Nd}_{0.56})\text{Zr}_{0.775}\text{Ti}_{1.975}\text{O}_7$	01-088-0415	134
Rutile	TiO_2	01-076-1939	135
		01-089-0552	136
		01-077-0441	137
		01-076-0318	138
		01-076-0321	
Aluminum oxide	Al_2O_3	00-035-0121	139
		00-046-1131	140
		01-081-2266	141
Zirconium oxide	ZrO_2	00-034-1084	142
Barium Titanium oxide	$\text{Ba}_2\text{Ti}_9\text{O}_{20}$	01-076-1424	143
Titanium oxide	Ti_3O_5	01-072-0519	144

Table 2.12 ICDD cards used for identification of crystals formed in glass before and after leach testing.

Crystals	Composition	ICDD card number	Ref.
Aluminium chromium iron	AlCrFe ₂	00-042-1486	¹⁴⁵
Molybdenum	Mo	00-042-1120	¹⁴⁶
Molybdenum oxide	MoO ₂	01-076-1807	¹⁴⁷
Cerium oxide	CeO ₂	01-075-0076	¹⁴⁸
		01-078-0694	¹⁴⁹
Palladium	Pd	01-087-0639	¹⁵⁰
		01-088-2335	¹⁵¹
		01-087-0641	¹⁵²
Silver	Ag	01-087-0597	¹⁴⁶
Palladium oxide	PdO	01-075-0584	¹⁵³
Palladium Zinc	PdZn ₂	00-031-0942	¹⁵⁴
Ruthenium	Ru	01-088-2333	¹⁵¹
Ruthenium oxide	RuO ₂	01-073-1469	¹⁵⁵
		01-088-0322	¹⁵⁶
		01-088-0323	
		01-088-0286	¹⁵⁷
Powelite	CaMoO ₄	01-085-0546	¹⁵⁸
Scheelite		01-077-2239	¹⁵⁹
Silicates	CaAl ₂ Si ₂ O ₈	00-041-1486	¹⁶⁰
	CaSiO ₃	00-018-0306	¹⁶¹
	BaSiO ₃	01-070-2112	¹⁶²
Silicon oxide	SiO ₂	01-085-0335	¹⁶³
		01-083-0539	¹⁶⁴
		00-050-1708	¹⁶⁵
		01-079-1915	¹⁶⁶

2.2.2.1 Grazing Incidence X-ray Diffraction

Grazing incidence x-ray diffraction (GIXRD) with small incident angle ($< 2^\circ$) can be used to analyze phases present near the surface of a sample as a function of depth. If the incident angle is small enough (typically $0.05 - 2^\circ$), the total external reflection will only come from the surface. However, there are some limitations for this technique. With only a few X-rays falling on to the surface at small incident angles, most of the incoming X-ray beam is wasted and thus the intensity of the diffracted beam is too small to distinguish between signal and noise. The rest of the beam either hits the side of sample or passes over the sample^{167, 168, 169}. Effective penetration depth can be calculated by HighScore Plus software¹⁷⁰ using the following equations. The required inputs are the incident angle, the sample composition and the density of sample.

$$I_L = I_0 \exp^{-(\mu/\rho)\rho L}$$

where:

I_L = the intensity of path length

I_0 = the initial intensity

μ = linear absorption coefficient

ρ = density of sample

L = the path length, the length of material that the X-rays travel through

The penetration depth, x , can be calculated with a given incident angle, θ .

$$x = 0.5 L \sin\theta$$

Within the present work, the GIXRD method was primarily employed to detect any crystallites that formed on the surface of the wasteforms during leaching tests. This was achieved by comparing the GIXRD patterns of leached samples with XRD patterns of unleached samples.

2.2.2.2 Rietveld refinement

The Rietveld refinement method^{171, 172, 173} uses a least squares approach to refine user-selected parameters to minimize the difference between the measured XRD pattern (observed data) and a model based on the theoretical crystal structure and instrumental parameters (calculated pattern). Several details are required prior to refinement, such as an estimate of the phases present and crystallography including their approximate lattice parameters, their space group and crystallographic positions. Furthermore, instrument (diffractometer) parameters such as wavelength and the instrumental contribution to peak broadening are required inputs. A reasonable estimate helps the refinement to obtain the desired results faster in cases where some information is unknown.

The least squares method is illustrated in the following equation:

$$S_y = \sum_j w_i (y_{i,obs} - y_{i,calc})^2$$

Equation 2.4. Crystallographic least-squares refinement which is the most common approach to minimize a function.

where:

S_y = the weighted difference,

w_i = the weighting factor which is equal to $1/y_{i,obs}$,

$y_{i,obs}$ = the observed intensity at step i ,

$y_{i,calc}$ = the calculated intensity at step i .

The calculated pattern of calculated intensity equation:

$$y_{i,calc} = S \sum_k m_k L_k |F_k|^2 G(\Delta\theta_{ik}) P_k A_k + y_{i,b}$$

Equation 2.5 The calculated intensities of simulation patterns.

where:

$y_{i,calc}$ = calculated intensity at a 2θ point i ,

S = the scale factor,

m_k = the multiplicity factor,

L_k = the Lorentz-polarisation coefficient for reflection k ,

F_k = the structure factor,

G = the reflection profile function,

$\Delta\theta_{ik} = 2\theta_i - 2\theta_k$, $2\theta_i$ is the 2θ position of the i^{th} profile point in the diffraction pattern while $2\theta_k$ is the calculated 2θ position of the k^{th} reflection,

P_k = the preferred orientation function,

A_k = the absorption factor,

$y_{i,b}$ = the background intensity.

The fit of the calculated pattern compare to the observed data can be used to judge its quality via calculated R values. The most common ones are so-called weighted profile R-factor (R_{wp}) which is defined by the following equation:

$$R_{wp} = \left\{ \frac{\sum_i w_i [y_{i,obs} - y_{i,calc}]^2}{\sum_i w_i [y_{i,obs}]^2} \right\}^{1/2}$$

Equation 2.6 R_{wp}

and the statistically expected R value, R_{exp} ,

$$R_{exp} = \left[\frac{(N - P - C)}{\sum_i w_i (y_{i,obs})^2} \right]^{1/2}$$

Equation 2.7 R_{exp}

where:

w_i = the weighting factor,

$y_{i,obs}$ = the observed intensity,

$y_{i,calc}$ = the calculated intensity,

N = the number of observations,

P = the number of parameters

C = the number of constrains.

The level of agreement between calculated (R_{wp}) and the observed (R_{exp}) factors is indicated by “Goodness of Fit” which is ideally equal to one in a perfect refinement. However, this is rarely achieved in reality.

$$\text{Goodness of Fit} = \left(\frac{R_{wp}}{R_{exp}} \right)^2$$

Equation 2.8 Goodness of Fit

Many Rietveld refinement programs are free to use such as Rietica¹⁷⁴, GSAS¹⁷⁵, and the commercially available Topas¹⁷⁶, with all these programs having similar capabilities. However, all the Rietveld refinements in this thesis were performed using Rietica v 4.2 software¹⁷⁴ to determine the ratio of phases in Synroc samples. All the XRD patterns were refined to R_{wp} value < 10 %.

2.2.3 Thermo Gravimetric Analysis / Differential Thermal Analysis

Thermo gravimetric analysis (TGA)/ Differential thermal analysis (DTA) was performed to measure the changes in physical and chemical properties and the weight of a sample using a microbalance during a thermal cycle. The measurements via TGA/DTA provide information relating to the physical and chemical phenomena such as crystalline transition, vaporization and decomposition¹⁷⁷. In this work, a Netzsch STA 449F1 TGA/DTA was used under flowing Ar (60 ml/min) for Synroc and flowing air or Ar (60 ml/min) for glass. The particle size of calcined Synroc-Z is ~1 - 10 μm while the particle sizes of calcined R7T7 glass producers via oxide and alkoxide routes are ~5 - 50 μm and ~1 - 20 μm respectively. The sample powder was placed in an alumina crucible and then heated to 1300°C with ramping rate at 5 °C/min. Calcinations were performed with TGA/DTA prior to HUP and HIP to determine the weight loss due to the decomposition of NO_x from nitrates.

2.2.4 Polishing and Scanning Electron Microscopy / Energy Dispersive X-ray Spectroscopy

Scanning electron microscopy (SEM) is a practical technique used in imaging the surface and microstructure of a sample. Samples were cut into a small piece (~ 10 x 10 x 4 mm) from the bulk samples using a 540X surface grinder (Jones and Shipman, UK) and the cut samples were mounted in resin. Mounted samples were then prepared by a 5-step metallographic grinding/polishing process. The details of grinding and polishing process for SEM samples are listed in Table 2.13.

Table 2.13 Grinding/polishing routes for SEM specimens' preparation

Step	Surface	Lubricant	rpm/Force (N)	Time (min)
Plane grinding	MD-Piano P220	Water	300/30	5-10
Plane grinding	MD-Piano P1200	Water	300/30	5
Fine grinding	MD-Largo	DiaPro Allegro/Largo 9 μm	200/20	5
Diamond polishing	MD-Dac	Dia Pro Dac 3 μm	150/10	3
Oxide polishing	MD-Chem	OP-S 0.04 μm	150/10	3

The polished samples are observed and imaged their surface roughness via reflected light optical microscopy and are imaged by SEM to see different phases by contrast from various signals associated with the electron beam/sample interactions (Figure 2.6). The interactions can be divided into two major types: inelastic interactions and elastic interactions. Inelastic scattering occurs through interactions between the incident electrons, the electrons and atoms of the sample within the near surface region. If the energy of the incident electron is high enough, the valence electrons of the surface atoms can be released from the atoms. These electrons are called secondary electrons (SE). Elastic scattering comes from the deflection of the incident electron by the sample atomic nucleus or by outer shell electrons of similar energy. A negligible amount of energy loss is made by this interaction during collision and a wide-angle directional change of the scattered electron. Backscattered electrons (BSE) are incident electrons that are elastically scattered through an angle of greater than 90° and BSE signals penetrate further than SE signals for imaging the sample^{178, 179, 180}.

Energy Dispersive X-ray Spectroscopy (EDX) is an analytical technique that is used to detect X-rays emitted from a sample during electron irradiation. It takes advantage of the focused electron beam which excites electrons to higher-energy levels. As the atom returns to its ground state and the electrons fall back to their initial energy levels, the excess energy is released as X-ray photons. The wavelength of these X-rays is characteristic of the difference in energy between the excited and relaxed states and with knowledge of their electronic structure can be used to identify each element in the periodic table.

This allows for the identification and quantification of the elements present at the surface of the sample^{178, 179, 180}.

All observations were carried out in back scattered imaging mode at 5 keV, as this gives good chemical contrast and resolution, which is because the intensity (and hence the contrast in a micrograph) is a function of the local electron density, hence the higher the electron density the higher is the BSE energy, and the brighter is the pixel in the resultant image. In most cases, local contrast is proportional to the local atomic mass (as heavier elements tend to have more electrons) and is therefore useful for distinguishing the different phases in a polyphasic material. EDX which was set at 15 keV can then be used to perform further phase identification as some Synroc minerals have similar compositions and average atomic numbers e.g. perovskite, zirconolite and hollandite. Table 2.14 shows the comparison of weighted average atomic numbers (Z)¹⁸¹ for typical Synroc precursors and phases¹¹⁷. The low values of Z for perovskite are 16.47 and 17.71 which is similar to rutile (16.39). For perovskite containing rare earths, the values of Z (20.66 to 24.02) is indistinguishable from zirconolite (21.98 to 26.23) and hollandite phases (22.72 to 23.40).

SEM is also useful for the detection of gross structure features such as porosity, microcracking and inhomogeneity. Before imaging, all the samples were Cr or C coated to approximately 10 nm thickness to produce a conductive surface.

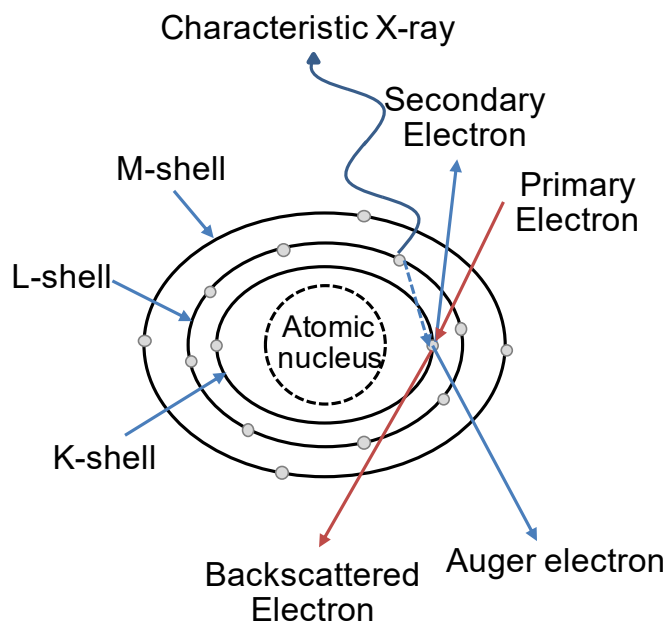


Figure 2.6 Interactions between primary electrons and electrons in atomic shells¹⁸⁰.

Table 2.14 Comparison of weighted average atomic numbers (Z) for typical Synroc precursors, phases and simple radwaste-containing analogues.

Phase	Chemical Formula	Weighted average atomic numbers
Precursors	TiO ₂	16.39
	ZrO ₂	31.69
	Al ₂ O ₃	10.65
	BaO	50.99
	CaO	16.58
Hollandite	BaAl ₂ Ti ₆ O ₁₆	22.82
	Ba _{0.75} Cs _{0.25} Al ₂ Ti ₆ O ₁₆	22.72
	BaTi ₈ O ₁₆	23.40
Perovskite	CaTiO ₃	16.47
	Ca _{0.9} Sr _{0.1} TiO ₃	17.71
	Ca _{0.9} Nd _{0.1} TiO ₃	20.66
	Ca _{0.8} Nd _{0.1} Ce _{0.1} TiO ₃	24.02
Zirconolite	CaZrTi ₂ O ₇	21.98
	Ca _{0.9} Nd _{0.2} Zr _{0.9} Ti ₂ O ₇	24.63
	CaZr _{0.9} U _{0.1} Ti ₂ O ₇	26.23
Rutile	TiO ₂	16.39
Alloy	Pd ₄ Te	47.38
	Mo ₄ Ru ₃	42.88

2.2.5 Focused Ion Beam / Transmission Electron Microscopy

The Synroc-Z samples described in Chapter 3 and leached HIPed Synroc-Z in Chapter 5 for transmission electron microscopy (TEM) imaging were prepared using a Helios Nanolab 600 focused ion beam (FIB). The FIB uses a

liquid-metal ion source at the top of its column to produce ions such as Ga^+ . The ions are pulled out and focused into a beam by an electric field and subsequently passed through apertures. The ions collide with the atoms at the sample surface causing either elastic or inelastic collision. The FIB is able to thin out a region of bulk material by digging as well as the basic techniques of lift-out and micro-pillar sampling¹⁷⁸. Figure 2.7 shows images of TEM sample preparation steps via FIB. A selected area of sample is milled down by making trenches alongside the section of interest. The sample is cut out and welded to the FIB needle using Pt in order to perform the lift-out (Figure 2.7 (a-c)). The sample is attached to a TEM grid and then detached from the needle by cutting the Pt weld (Figure 2.7 (d)). A final thinning step is conducted to achieve a thickness of ~ 100 nm which is thin enough to allow electron transmission through the sample (Figure 2.7 (e,f)). The secondary phase formed on the leached HUPed Synroc-Z in Chapter 5 was prepared via powder TEM preparation method. The secondary phase was removed from the leached sample using an ultrasonic acetone bath for 5 min which dispersed the secondary phase particles in acetone. The acetone with secondary phase was dropped on a copper grid. The copper grid was left in the fume hood for acetone to evaporate for 8 h before analysis.

TEM can show atomic configuration and defects in materials at or close to 0.1 nm resolution, by using correct operating conditions and well-prepared samples. The physical processes fundamental to TEM are different to SEM in the sense that the imaging signal passes through the sample in TEM, collecting information from the entire thickness; while in SEM the imaging signal is reflected, interacting only with the material volume close to the surface of the material (Figure 2.8). As a consequence, the thickness of a TEM sample must be approximately 100 nm or less, but this value depends on the accelerating voltage^{179, 182}. The image formation in TEM occurs in two stages. Incoming or incident electrons that are accelerated by a high voltage produced via a high-voltage generator undergo interactions with atoms of the sample. These involve both elastic and inelastic scattering processes. The electron, which emerges through the exit surface of the sample, is then transmitted through the objective lens and magnifying lenses of the electron microscope to form the final

enlarged image^{179, 180}.

Electron diffraction (ED) is the elastic scattering of electrons (deflection by the Coulomb field of atomic nuclei) in a crystalline material. The arrangement and spacing of the atomic nuclei result in a redistribution of the angular dependence of scattering probability. This angular distribution of scattering can be shown on the TEM screen^{179, 182}. Fast Fourier Transform (FFT) is a software using ImageJ^{183, 184} transformation and gives the corresponding diffraction pattern of the selected region of interest in the high resolution TEM image. FFT can be compared with the Selected Area Electron Diffraction (SAED) and simulated electron diffraction patterns to obtain orientation of localised micro-structures and to confirm the single crystal area¹⁷⁸. Selected samples were observed via TEM to overcome the limitation of SEM resolution.

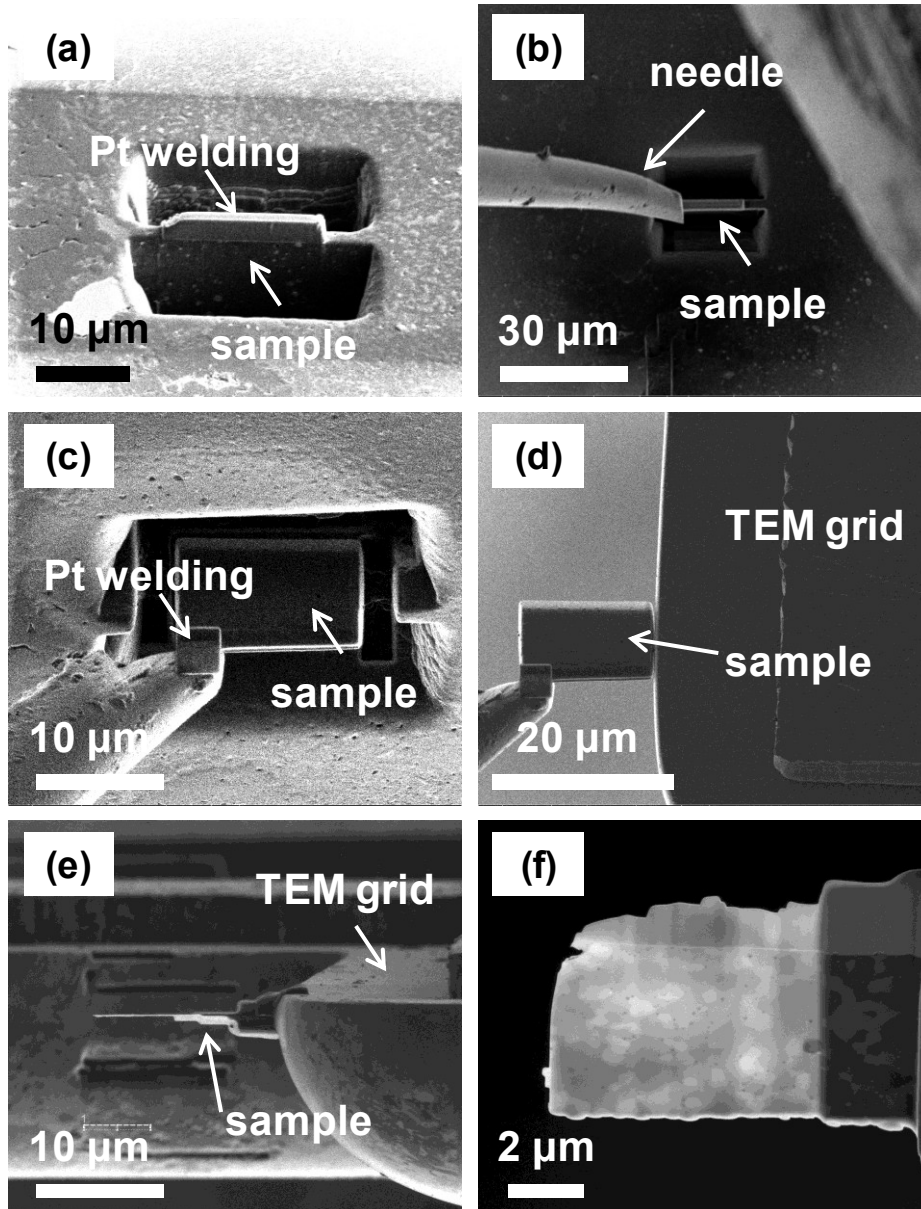


Figure 2.7. SEM images of sample preparation for TEM via FIB. (a) A selected area is deposited with a Pt layer and milled down by making trenches (b, c) The sample is welded to the FIB needle and then cut to enable the lift-out process. (d) The sample is welded to a TEM grid and detached from the needle for final milling. (e, f) The sample is thinned to ~ 100 nm thickness by Ga^+ milling.

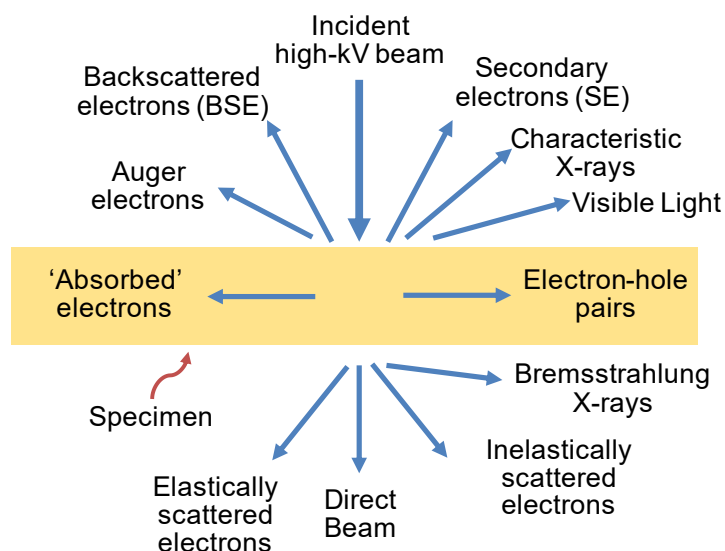


Figure 2.8 Signals generated in SEM and TEM¹⁸².

2.2.6 Atomic Force Microscopy

Atomic force microscopy (AFM) is useful for examining a materials surface relief and can be done on non-conductive samples and in non-high vacuum conditions. The main components are the laser source, scanner, force sensor, controller, sample stages, and optical microscopes (Figure 2.9)¹⁸⁰. AFM images surface topographic features at nano-scale by measuring forces between a sharp probe and sample surface at a short distance (depending on different operation modes, for non-contact mode, normally 1 - 10 nm). The probe is supported on a flexible cantilever which has a sharp tip at its end that acts as the probe of interactions. Cantilevers are commonly either V-shaped or in the style of a rectangular diving board. Further, the tips are generally in the form of a pyramid or a cylindrical cone.

The sharp tip at the free end of the cantilever contacts with the sample and a laser beam is focused on the back of cantilever near its free end. Features on the sample surface cause deflections of the cantilever as the sample moves under the tip. The reflected laser beam is directed through a mirror onto a four-segment photodetector allowing the deflection of the cantilever to be monitored^{180, 185}. A Dimension 3000 AFM with Nano Scope IIIa controller was used to measure the height difference between the surface and any secondary phases that had formed on the surface of the unleached and leached Synroc-Z

samples in Chapter 5.

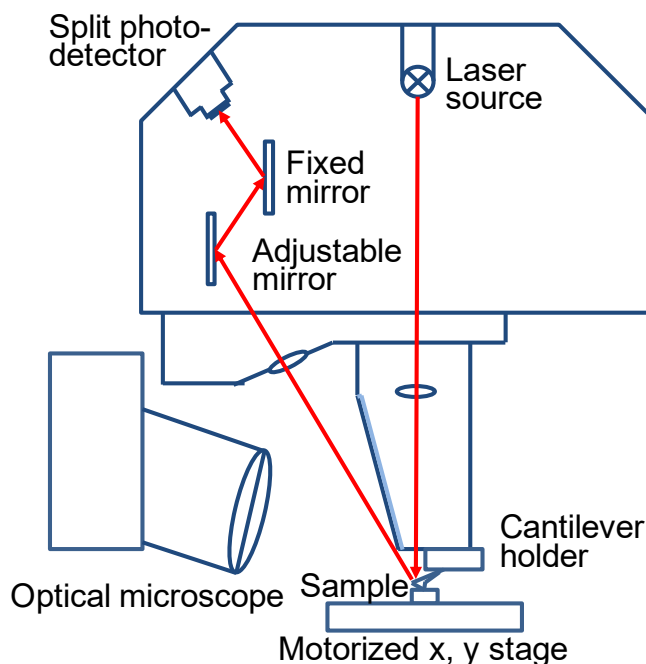


Figure 2.9 Main parts of the AFM¹⁸⁰.

2.2.7 MCC-1 leach testing

For HLW wasteform candidates, it is of prime importance to test chemical durability and leaching resistance under a range of likely repository groundwater conditions. The MCC-1 test is most widely used today to examine the durability and leach ability of wasteforms^{95, 96}.

In this work, the MCC-1 procedure was conducted on selected ground and polished samples under static conditions at 90°C for 3, 7, 14, 28 days in deionized water (DI water) in Teflon vessels. The geometrical specimen surface area to leachant volume ratio, SA/V, was approximately 10 m⁻¹. Tests for each sample were carried out in triplicate to provide estimates of experimental variability. The vessel setup used for MCC-1 leach tests is presented in Figure 2.10. After completion, the total material dissolved was determined by analysing dissolved element concentrations using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which is described in the following section.

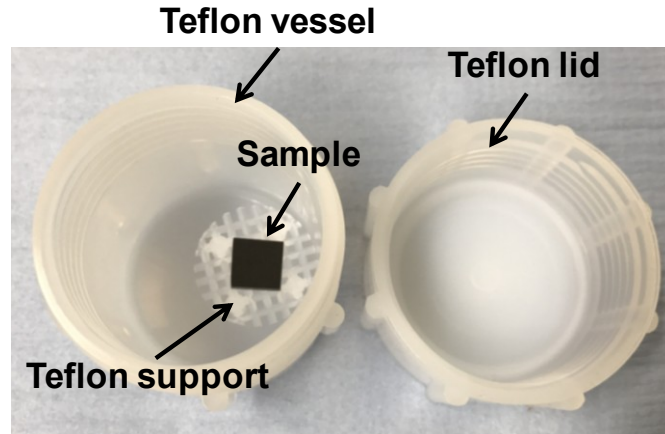


Figure 2.10 The Teflon vessel and support used in this study. The size of test sample is $\sim 10 \times 10 \times 2$ mm.

Test sample preparation

The test samples were cut from as-prepared samples to $\sim 12 \times 12 \times 3$ mm by a 540X surface grinder. The test specimens were ground to $\sim 10.5 \times 10.5 \times 2.5$ mm via P220 ($\sim 60 \mu\text{m}$) diamond abrasive with alcohol based lubricant while the final grinding step involved using P1200 ($\sim 15 \mu\text{m}$) diamond abrasive to reduce the size down to $\sim 10 \times 10 \times 2$ mm. This process can reproduce test samples with uniform size and surface finish. The ground samples were cleaned in an ultrasonic bath with ethanol 3 times for 3 min. The cleaned specimens were dried in the oven at 110°C for 12 h. Triplicate tests were performed to improve the data precision.

At ANSTO, the as-cut test samples were ground via P250 and P1200 SiC paper with oil and then both larger faces were polished with 9, 3, and $1 \mu\text{m}$ alcohol based diamond suspensions. The final size of polished samples was $\sim 10 \times 10 \times 2$ mm. The test samples were cleaned in ultrasonic bath in acetone for 3 min and then in cyclohexane for 5 min. The cleaned specimens were dried in the oven at 110°C for 12 h. The lubricant and cleaning media were water-free to avoid any elements leaching during preparation and enhance the data precision.

The surface roughness of samples prepared for leach testing were observed via reflected light optical microscopy (observation limit: up to $20 \mu\text{m}$ roughness) to ensure no obvious scratches on the surfaces and the surface finish.

Cleaning of PTFE vessels

New PTFE vessels and supports must be cleaned prior to leaching test to reduce the amount of F^- released. The details of the cleaning procedure are described in ASTM standard test method⁹⁶.

The cleaning procedure of used PTFE vessels and supports used the following steps:

1. Rinse vessels, lids and supports with DI water and then soak them in 0.16 M nitric acid at 90°C for 2 h.
2. Rinse vessels, lids and supports with DI water and then soak them in DI water at 90°C for 2 h.
3. Fill the vessels with supports approximately 90 % full with DI water. Close the lids and heat them at 90°C for 16 h.
4. Measure the pH value of the water in each vessel. If the pH value is in the range of 5.0 to 7.0, dry the vessels and supports at 90°C for 16 h and the vessels are ready to use. If the pH value is not in the range, repeat the cleaning steps.

Cleaning of solution bottles

Solution bottles used for analysis leachate need to be cleaned before use. The cleaning method involved the following steps:

1. Fill bottles to 10 % bottle volume with 2 wt. % nitric acid and then shake to rinse all surfaces after closing the caps. Repeat this step for 3 times.
2. Fill bottles to 25 % bottle volume with DI water and then shake to rinse all surfaces after closing the caps. Repeat this step for 3 times.
3. Dry the bottles and caps in an oven at 40°C for 8 h.

Test procedure

Before starting the leach testing, the samples' geometric surface area and weight were measured using a digital calliper and a balance respectively while

the pH value of leachant (fresh DI water) was determined via a pH meter. The test sample was placed on the PTFE support in the vessel to maximize the surface area of monolith in contact with leachant. The volume of leachant used in each test was based on the geometric surface area of each specimen and $SA/V = 10 \text{ m}^{-1}$. Two blank tests (without sample) were also done. Teflon tape was used to tighten the closure to prevent significant leachant loss during the test. The weight of combined vessel, support, lid, Teflon tape and test sample was measured before and after adding the leachant.

All the test vessels were placed in a preheated oven at 90°C and the lids retightened after 1, 3 and 24 h to ensure good sealing. The test vessels were cooled to room temperature by taking them from the oven at the end of the scheduled testing period. The weight of the test vessels was measured to determine the leachant loss. The leachate was removed and filtered through 0.45 µm syringe filter for solution analysis prior to removing the test sample. The leachates were replaced by fresh leachants after each testing period (3, 4, 7, and 14 days). After 28 days' testing, the test sample was rinsed with DI water and then dried at 40°C for 16 h. Before leachate analysis, 2 wt.% nitric acid was added to all leachates to dissolve any test elements that may have adhered to the interior surface of the bottle. Dissolved element concentrations in leachates were determined by ICP-MS. The leached samples were characterised via GIXRD, XRD, SEM, and AFM (the results of this are given in Chapter 5).

Calculations

The normalized elemental mass loss can be calculated by the following equation:

$$NL_{ij} = \frac{(C_{ij} - B_{ik}) \times V_{fj}}{f_i \times SA_j}$$

Equation 2.9 Normalized elemental mass loss

where:

NL_{ij} = normalized elemental mass loss from sample j based on element i, in g/m^2

C_{ij} = concentration of element i measured in leachate from sample j, in g/L

B_{ik} = average concentration of element i measured in blank test k , in g/L

V_{fj} = final volume of leachate in test vessel containing sample j , in L

f_i = mass fraction of element i in sample j

SA_j = surface area of specimen j , in m^2

The normalized elemental leach rate can be obtained by the following equation:

$$NR_{ij} = \frac{NL_{ij}}{t}$$

Equation 2.10 Normalized elemental leach rate

where:

NR_{ij} = normalized elemental leach rate, in g/m^2day

NL_{ij} = normalized elemental mass loss, in g/m^2

t = duration of leach test, in days

2.2.8 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful tool for quantifying dissolved elements in the leachates. It combines a high temperature ICP source for atomizing and ionizing injected samples with the sensitivity and selectivity of mass spectrometry. The leachates are pumped into a nebulizer and then be converted into an aerosol. The aerosol interacts with a high energy Ar plasma generated in the ICP torch and becomes ionized as it passes through the plasma. The newly formed ions can be analyzed by the mass spectrometry (MS), usually a quadrupole. The ions travel to the MS through the sampler, skimmer cones and accelerating voltages. Once the ions enter the MS, they are dispersed in the mass analyser by their mass to charge ratio and produce an amplified ion signal to be detected. The concentration of a sample can then be determined through calibration with reference solution standards^{186, 187}.

An Aglient 7700x ICP-MS at Natural History Museum and 7800x ICP-MS at ANSTO were used to measure the concentration of ions that have been leached

out from the selected Synroc-Z and R7T7 glass samples in Chapter 5. The leachates were added with 2 wt. % nitric acid and diluted 10 times before analysis. The multi-element (all elements in Synroc-Z and R7T7 glass) standard solution for calibration was prepared between 0.1 and 500 ppb and examined alongside the sample solutions to ensure the accuracy of measurements. The measurements were repeated at least three times to obtain a mean and relative standard deviation. All negative concentration values and low concentration values (< 1 ppb) with a relative standard deviation >20 % were assumed to be the detection limit of the instrument (the detection limit depends on the different elements and ranges from 0.02 - 50 ppb).

Chapter 3: Characterisation of Synroc-Z fabricated by HUPing and HIPing

This chapter discusses the fabrication of a Synroc derivative wasteform, Synroc-Z, designed for immobilisation of EURO-GANEX wastes via two hot-pressing techniques, hot uniaxial pressing (HUP) and hot isostatic pressing (HIP). The modified precursor composition from Synroc-C and target phase composition were shown earlier in Table 2.6. All HUPed Synroc-Z samples were prepared at Imperial College London while HIPed samples were produced at ANSTO and the University of Sheffield (UoS). HUPing processing parameters such as temperatures, pressures, and dwell times were varied to develop optimal processing conditions (Table 2.7). HIPing conditions were determined from the HUPing results (Table 2.9).

3.1 Volatile losses from simulated HLW

The mass loss of calcined Synroc-Z precursor with 20, 25, 30, and 35 wt.% simulated EURO-GANEX waste was examined at a high processing temperature of 1300°C (approached from room-temperature using a heating ramp of 5 °C/min) with the TGA method as shown in Figure 3.1. The aim of this was to allow conditions to be chosen that prevent the Synroc-Z powder releasing large volumes of gas during the hot-pressing process. The mass loss should be kept as low as possible (< 2 mass%). TGA was performed on every batch of calcined Synroc-Z to confirm its mass loss before hot-pressing. At temperatures up to 210°C, all calcined Synroc-Z mixtures lost a small amount of mass (< 0.5 mass%) which may be caused by water loss. However, the water loss should be expected at ~100°C, other types of water such as hydrates may be retained in the calcined powders and thus increase the water loss temperature. For Synroc-Z precursor, it kept releasing the adsorbed liquids until 600°C. All Synroc-Z powders stayed at the same level until 1000°C while Synroc-Z with waste loadings started to lose weight from 1000°C and showed a dramatic drop after 1200°C. This mass loss may be caused by volatilisation of some waste elements such as Mo and Cs. By comparison, the Synroc precursor remained unchanged. This indicated that processing temperatures should be

kept below 1200°C to limit mass loss. However, the accurate composition of mass loss can not be confirmed as they were not recycled to be analyzed.

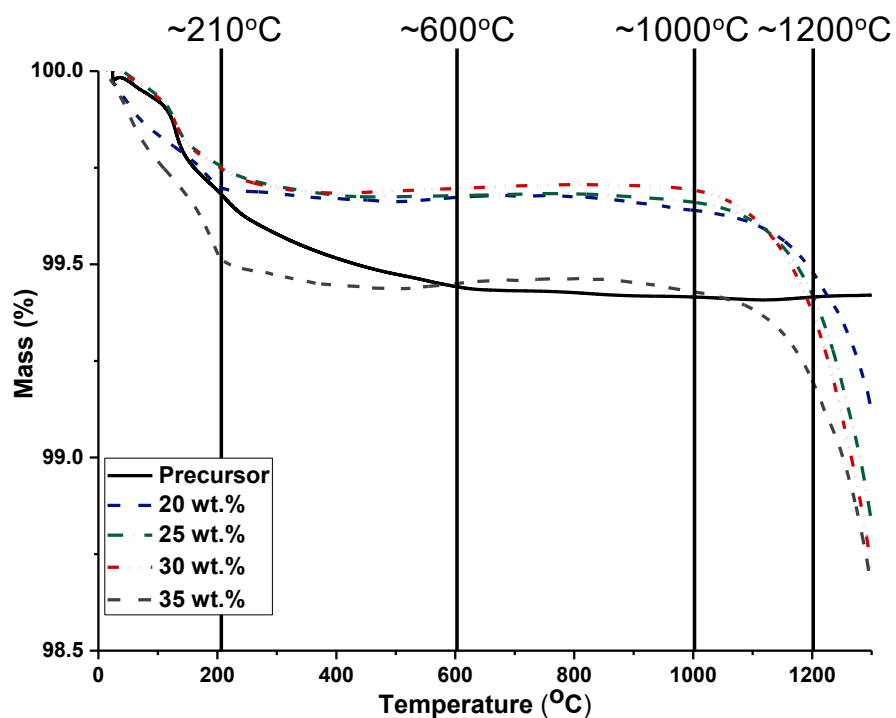


Figure 3.1 TGA (Ar atmosphere) of Synroc-Z precursor with different waste loadings after calcination at 750°C under reducing conditions (10 v/v % H₂/Ar) for 2.5 h.

3.2 Synroc-C vs. Synroc-Z

Synroc-C was created specifically to immobilise HLW from light water reactors following PUREX reprocessing and has been developed for many years and its details are provided in section 1.3.1. As a baseline study, synthesized Synroc-C and Synroc-Z with 20 wt.% simulated waste, which have been HUPed under similar conditions (1200°C and 20 MPa for 3 h), were compared with each other.

3.2.1 XRD- Characteristic phases

XRD (Figure 3.2) shows that Synroc-C contains four main phases which are hollandite, perovskite, zirconolite and rutile with small quantities (~2.4 wt.%) of Al_2O_3 . The weight fraction of phases is described in section 3.2.3. Similarly, Synroc-Z also exhibits these four main characteristic Synroc phases but displays about a factor of 3 or 4 lower peak intensity for the zirconolite phase, indicating a dramatically lower volume fraction, which is as intended. The ICDD reference cards used to identify Synroc phases are listed in Table 2.11. These results can be linked with results from additional analytical techniques (SEM, TEM and EDX) for discussion later in this chapter.

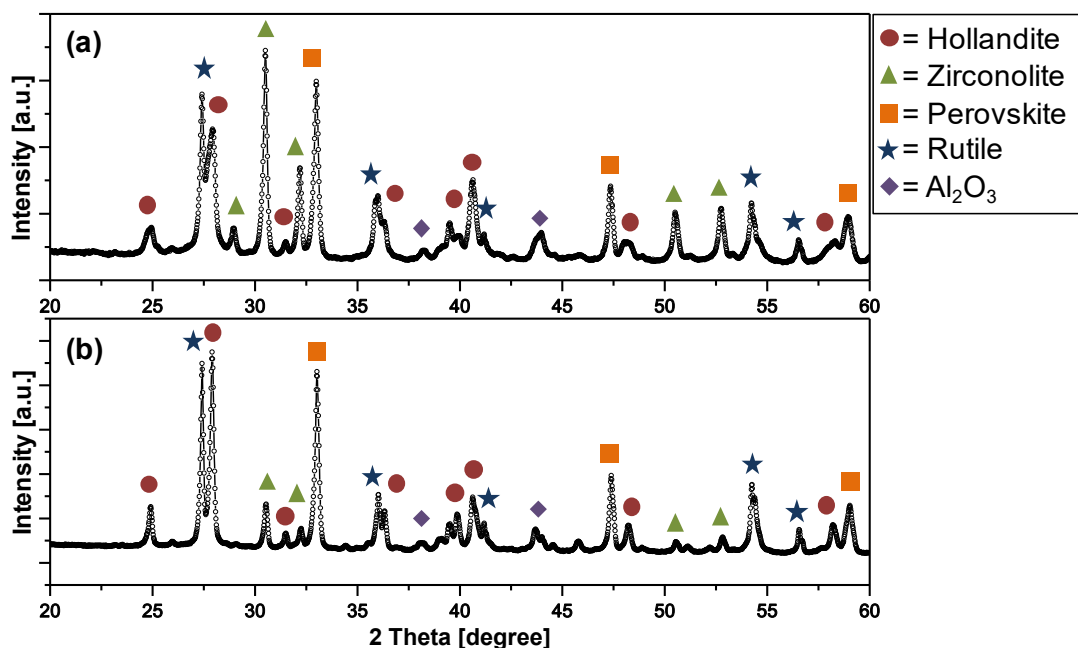


Figure 3.2 XRD of (a) Synroc-C and (b) Synroc-Z with 20 wt.% simulated HLW HUPed at 1200°C and 20 MPa for 3 h. The ICDD cards used for identification: hollandite (H: 01-080-0908)¹²⁵, zirconolite (Z: 01-084-0163, 00-034-0167)^{132, 133}, perovskite (P: 01-082-0229)¹²⁹, rutile (R: 01-077-0441, 01-076-1939)^{135, 137}, alumina (A: 00-046-1131, 00-035-0121)^{139, 140}.

3.2.2 Microstructures

Both Synroc-C and Synroc-Z exhibit a dense microstructure with five distinct contrast levels in BSE images (Figure 3.3). At lower magnification (Figure 3.3a and d), both Synroc-C and -Z consisted of a mixture of dark and light regions. A higher magnification and EDX can allow those phases to be distinguished in those regions. The dark regions were mainly rutile with minor quantities of alumina. The light areas were zirconolite, hollandite and perovskite. At a finer scale, Figure 3.3 (b) and (e) show that the rutile regions were interspersed with domains of alumina, on the order of ~1 μm diameter while the light region co-existed in the dark region. Figure 3.3 (c) and (f) show that the hollandite/perovskite regions contained sub-micron particles of zirconolite. The zirconolite content (by area) could be measured by its contrast threshold range. Synroc-C contained a larger area of zirconolite contrast (~25 area%) than Synroc-Z (~9 area%) which agrees with the XRD results as Synroc-Z contained less zirconolite (Figure 3.2). Figure 3.4 shows the elemental distribution in HUPed Synroc-Z which can be used to distinguish phases. Ca, Ce and Nd are associated with perovskite, Ba and Cs with hollandite distribution, Zr with

zirconolite and Mo and Ru indicate the metallic phases. EDX was used to determine the identities of the phases in different contrast regions. However, it was not definitive because of their similar average atomic numbers (Table 2.14) and small grain sizes (0.5 - 2 μm) compared to the EDX measurement volume (1 μm^3). Generally, the darkest contrast was alumina (A), dark grey phase was rutile (R), intermediate grey contrast was either hollandite or perovskite grains (H/P), bright grey was zirconolite (Z) and white regions were metallic precipitates (M). The method to measure bulk density and apparent porosity is described in section 2.2.1. The measured bulk densities of Synroc-C and Synroc-Z are ~ 4.51 and ~ 4.47 g/cm^3 while the apparent porosities are ~ 0.2 and ~ 0.3 vol.%, respectively. This is in agreement with Figure 3.3, which displays cross-sectional BSE micrographs, showing the absence of any cracks and obvious pores.

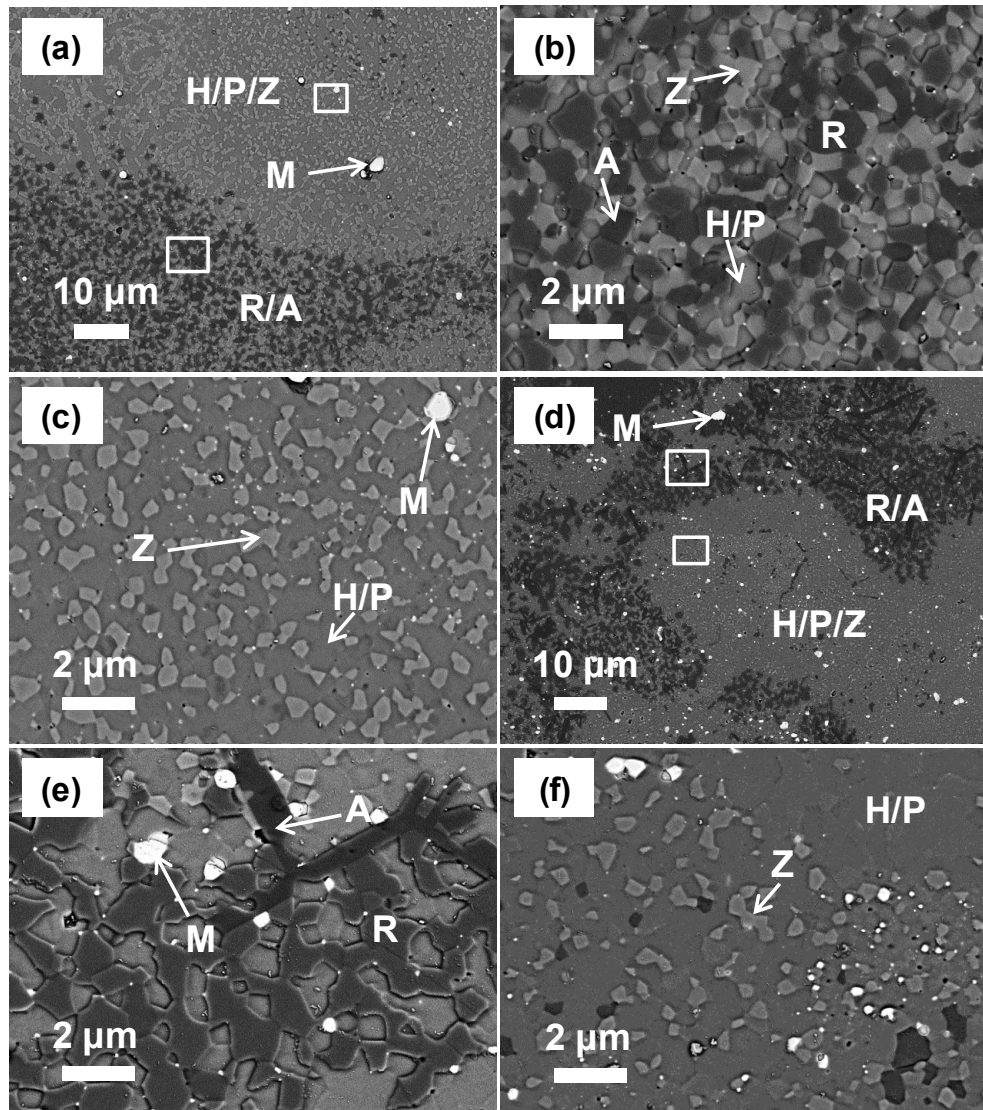


Figure 3.3 BSE images of (a) Synroc-C and (d) Synroc-Z at lower magnification, (b) and (e) the darker region and (c) and (f) the brighter area in Synroc-C and -Z, respectively, at higher magnification. Generally, the darkest contrast was alumina (A), dark grey phase was rutile (R), white regions were metallic precipitates (M) and intermediate grey contrast was either hollandite or perovskite grains (H/P), and bright grey was zirconolite (Z).

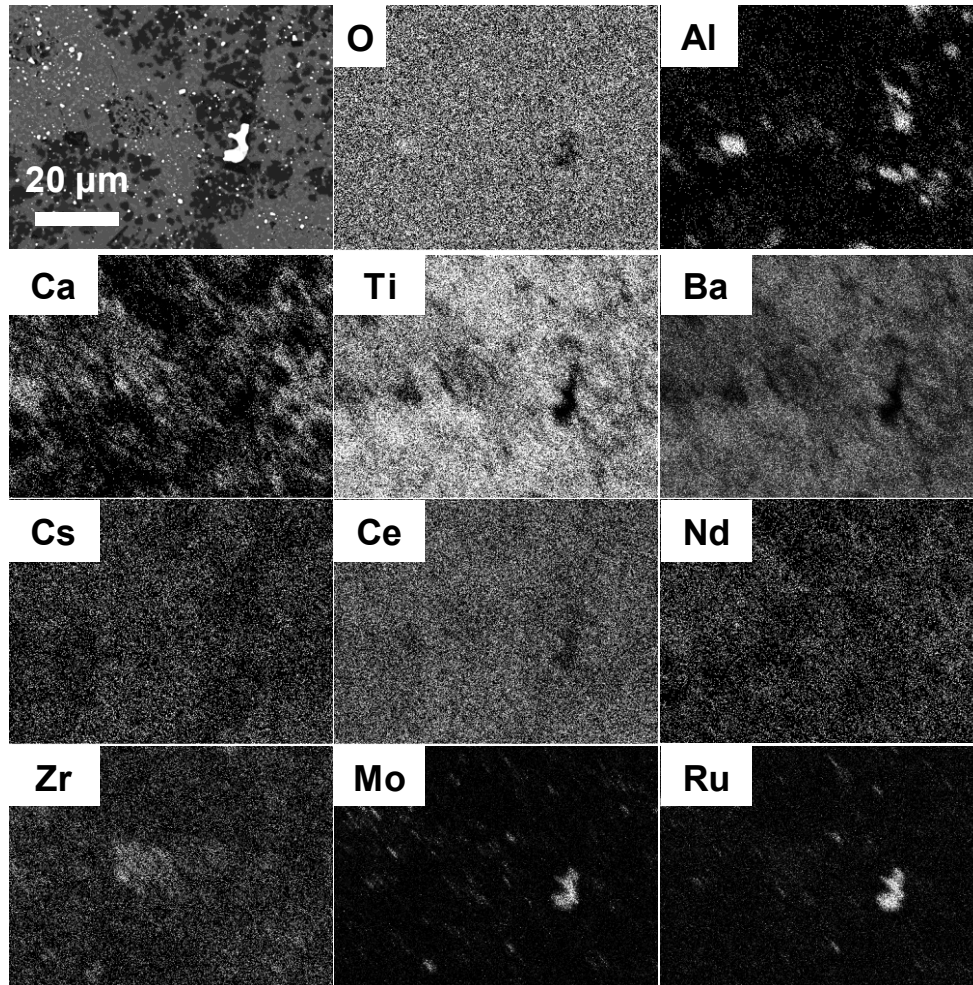


Figure 3.4 Elemental distribution plots of HUPed Synroc-Z by SEM/EDX mapping for 1 h.

Figure 3.5 shows the TEM image and EDX spectra of Synroc-Z sample obtained via FIB milling to give a thickness of ~ 100 nm. The grain size of the major phases in Synroc-Z was $0.5 - 2 \mu\text{m}$ (usually $< 1 \mu\text{m}$) while the minor phases were $10 - 80$ nm. The minor phases were found both at grain boundaries and also embedded in the main crystalline phases as shown in the TEM image (black parts). The predominant chemical element ratios of major crystalline grains can be analyzed to determine the phase (Table 3.1). The minor phases (black spots) were found to contain mainly waste elements (Mo, Pd, and Ru, total > 50 atomic %) as expected, but at the same time, carrying O and minor Ti. This suggests that those black spots in the TEM images were alloy phases, yet due to the volume detection limit of TEM/EDX, some overlapping side grains were analyzed which explains the presence of O and minor Ti.

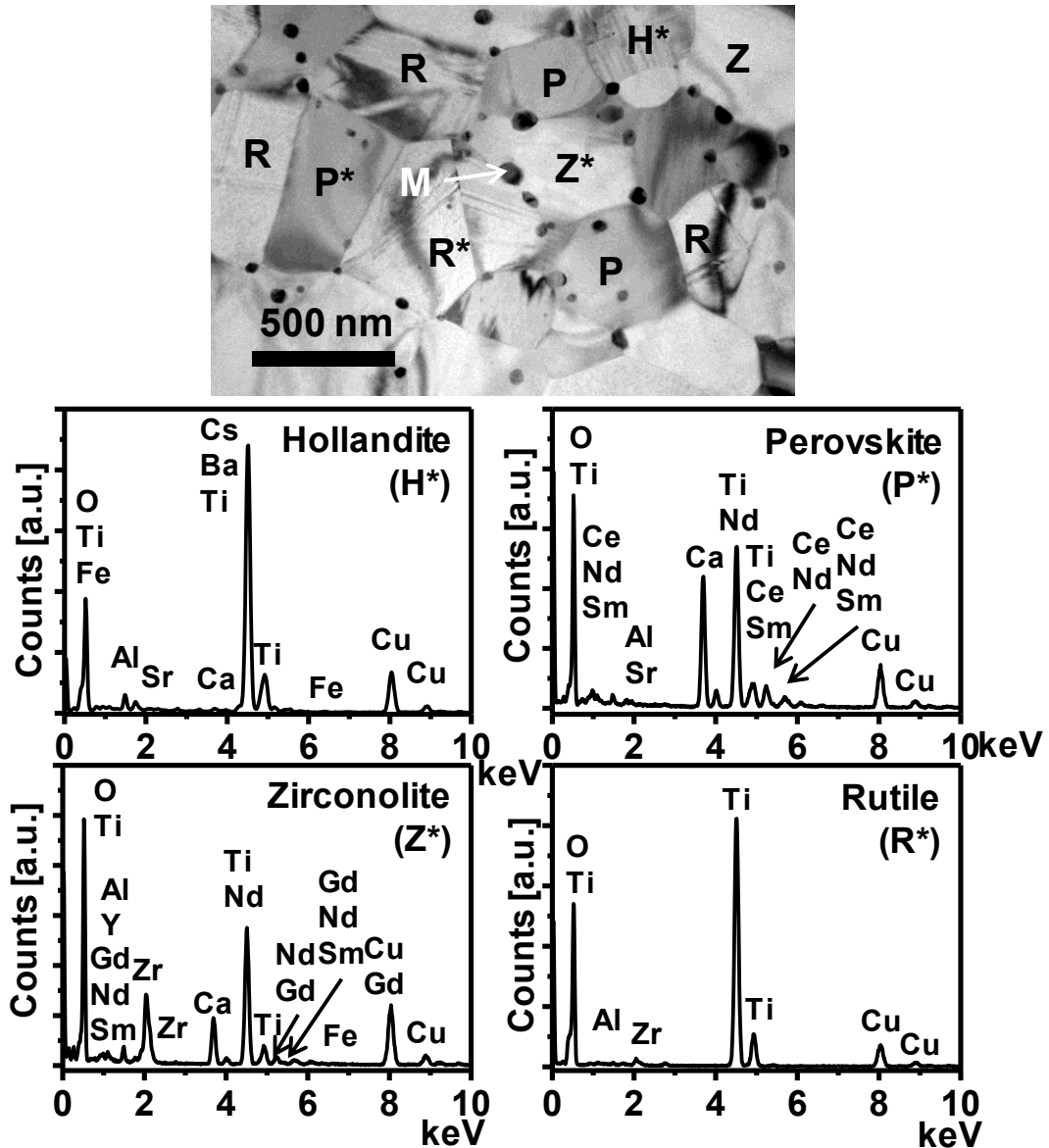


Figure 3.5 TEM image and EDX spectra of Synroc-Z with 20 wt.% HLW prepared via FIB. Parts of grains were determined via EDX (with *) and were labelled as hollandite (H), perovskite (P), zirconolite (Z), rutile (R) and metallic precipitates (M). The metal phases were either located on grain boundaries, in front, behind or embedded in the major crystalline phases. The EDX results were shown in the Table 3.1. The Cu presented in the EDX is from the Cu grid used for TEM preparation.

Table 3.1 EDX results of four main phases in atomic%. Error ranges represent the standard deviation from 3 EDX analyses in the same grain.

	O	Al	Ca	Ti	Fe	Sr	Ba	Cs
Hollandite	79.4 ± 1.0	3.3 ± 0.1	0.2 ± 0.1	12.4 ± 0.3	0.1 ± 0.04	0.2 ± 0.04	3.4 ± 0.5	1.0 ± 0.1

	O	Al	Ca	Ti	Sr	Ce	Nd	Sm
Perovskite	66.4 ± 2.5	0.8 ± 0.04	12.5 ± 0.8	16.5 ± 1.5	0.2 ± 0.04	1.4 ± 0.1	1.9 ± 0.1	0.3 ± 0.03

	O	Al	Ca	Ti	Fe	Y	Zr	Nd	Sm	Gd
Zirconolite	70.5 ± 2.0	1.7 ± 0.2	4.9 ± 0.3	15.1 ± 1.3	0.1 ± 0.01	0.8 ± 0.1	5.5 ± 0.3	0.9 ± 0.04	0.3 ± 0.1	0.2 ± 0.02

	O	Al	Ti	Zr
Rutile	70.9 ± 3.2	0.3 ± 0.1	28.3 ± 3.0	0.5 ± 0.1

3.2.3 Rietveld refinement

The refined patterns and phase weight fraction estimates for Synroc-C and -Z are shown in Figures 3.6 and 3.7 respectively. The raw XRD data (shown as dots) have been fitted with a simulated pattern using Rietveld Refinement (red line) to determine the phase compositions. The starting compositions of major phases for refinement were estimated based on SEM/EDX and TEM/EDX results. Alloy phases that were detected using EDX analysis were not found in XRD patterns, presumably because of excessive peak overlap and low peak intensity, and/or because they had an amorphous nature. Weight fractions of alloy phases are based on the assumption that they were only composed of Mo, Te, Ag, Ru or Pd metals, in accordance with previous observations of analogous Synroc structures⁵. The simulated profile which matched Synroc-C XRD patterns is shown in Figure 3.6(a) yielded $R_{wp} = 8.31\%$, $R_{exp} = 2.22\%$ and Goodness of Fit = 14.01 % while that of Synroc-Z in Figure 3.6(b) obtained $R_{wp} = 8.51\%$, $R_{exp} = 2.27\%$ and Goodness of Fit = 14.05 %. Five main phases were shown: hollandite (H), perovskite (P), zirconolite (Z), rutile (R) and alumina (A), with weight percentages of 31.9 wt.%, 22.5 wt.%, 28.5 wt.%, 14.9 wt.% and 2.0 wt.% respectively in Synroc-C, and 35.6 wt.%, 30.3 wt.%, 6.7 wt.%, 24.8 wt.% and 2.6 wt.% respectively in Synroc-Z. The weight fractions of both Synroc-C and -Z were in fair agreement with the targeted weight percentages (Table 2.6) as Synroc-Z contained less zirconolite

but more hollandite and perovskite than Synroc–C.

Table 3.2 displays the refined unit cell parameters of each phase in Synroc-C and –Z. The error ranges of unit cell parameters in phases are little except zirconolite in Synroc-Z. This may be caused by small amount (~6.4 wt.%) of zirconolite in Synroc-Z and hence more difficult to obtain accurate values. Both hollandite and perovskite showed similar unit cell volumes in Synroc-Z and –C while for zirconolite, Synroc-Z ($\sim 1000.1 \text{ \AA}^3$) yielded a 0.3 vol.% smaller unit cell volume than that of Synroc–C ($\sim 1003.4 \text{ \AA}^3$). This suggests that the waste elements were incorporated in similar sites in the all host phases in both Synrocs.

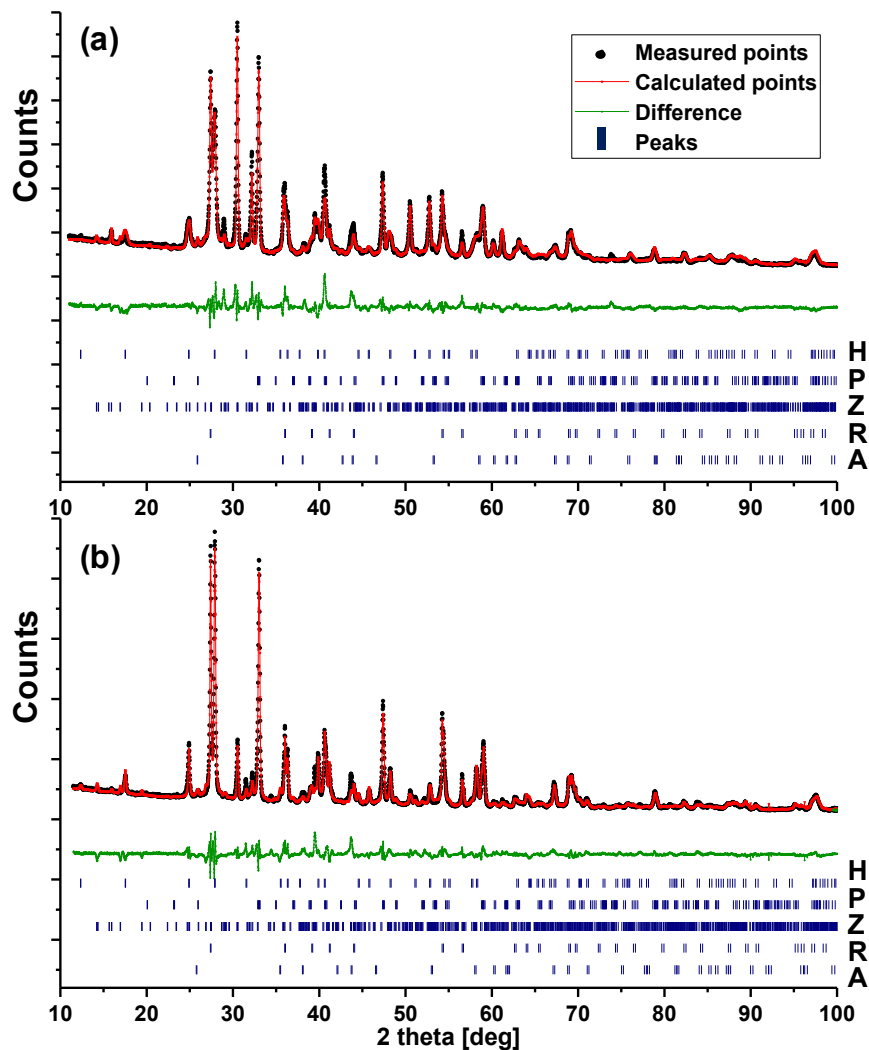


Figure 3.6 Refinement of HUPed (a) Synroc-C and (b) Synroc-Z using Rietica software. Phases 1 - 5 were hollandite (H), perovskite (P), zirconolite (Z), rutile (R), and alumina (A), respectively. The R_{wp} , R_{exp} and Goodness-of-fit for Synroc-C refinement were 8.31, 2.22 and 13.99 respectively while those for

Synroc-Z refinement were 8.51, 2.27 and 14.02 respectively.

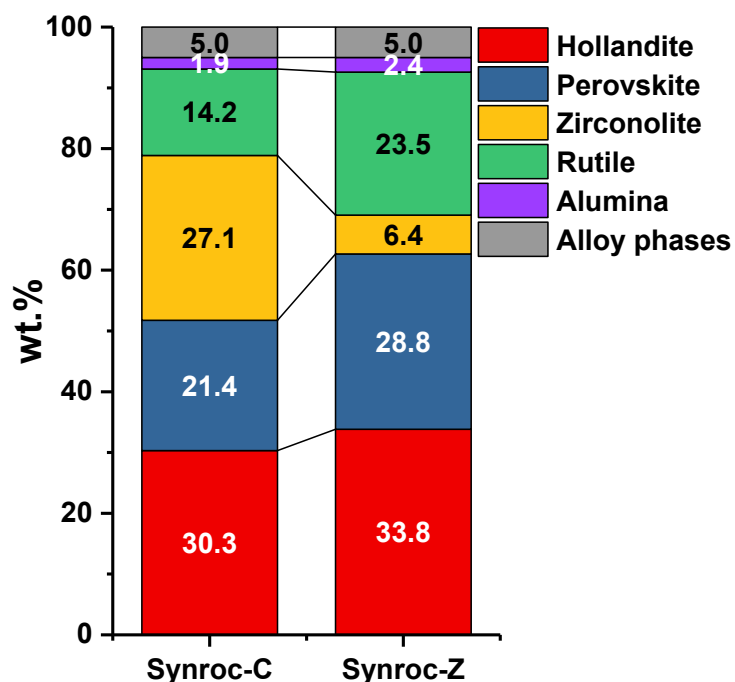


Figure 3.7 Weight fractions of HUPed Synroc-C and -Z with 20 wt.% HLW samples determined by Rietveld refinement for comparison.

Table 3.2 Crystallographic parameters of each phase in refined Synroc-C and Synroc-Z via Rietica programme.

	Synroc-C			Synroc-Z		
	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)
Hollandite	10.11 ± 0.02	10.11 ± 0.02	2.95 ± 0.006	10.10 ± 0.01	10.10 ± 0.01	2.95 ± 0.001
Perovskite	5.45 ± 0.002	7.66 ± 0.003	5.41 ± 0.001	5.44 ± 0.003	7.66 ± 0.003	5.41 ± 0.001
Zirconolite	12.49 ± 0.01	7.23 ± 0.004	11.31 ± 0.001	12.53 ± 0.01	7.20 ± 0.02	11.28 ± 0.08
Rutile	4.60 ± 0.005	4.60 ± 0.005	2.96 ± 0.002	4.60 ± 0.002	4.60 ± 0.002	2.96 ± 0.001

3.3 Effect of HUPing conditions

Calcined Synroc-Z with 20 wt.% simulated HLW from EURO-GANEX samples were HUPed under three distinct conditions of temperature, pressure, and dwell time in order to determine optimal processing conditions. These are summarised in Table 2.7. The ICDD reference cards used to match XRD patterns for this section are given in Table 2.11.

3.3.1 Temperature

The effect of HUPing temperature was studied. Samples were heated to the designed temperature at a heating rate of 5 °C/min, a pressure of 20 MPa which was then applied and the dwell time was 3 h. After the process was finished, the samples were cooled at a rate of 5 °C/min until 750°C and then left in the machine until reaching room temperature. The cooling time from 750°C to room temperature in the machine was normally 3 - 4 h. HUPing temperatures were set at 1250, 1200, 1150, 1100, and 1050°C to test the optimum range of processing temperatures (sample ID: X-20-3, *X is the process temperature*). Figure 3.8 shows the XRD patterns and matched profiles for the refinements of samples HUPed at 1250 and 1050°C that yielded $R_{wp} < 10\%$, and Goodness of Fit $< 15\%$ and they are representative of all others. All of the samples contained the four main characteristic Synroc phases (hollandite, perovskite, zirconolite and rutile) with minor alumina content.

Figure 3.9 shows the weight fractions of HUPed Synroc-Z samples as determined by Rietveld refinement. This allows the effect of HUPing temperature on the material to be compared at the same pressure and holding time. The process temperature was found to have a significant effect on phase ratio: as the consolidation temperature dropped from 1250 to 1050°C, large decreases in zirconolite and hollandite content were observed. This was compensated for by an increase in the rutile and alumina phases. The higher processing temperature it was heated at, the more amount of host phases (hollandite + zirconolite + perovskite) formed. In general, perovskite needs the lowest processing temperature (1050°C) to be produced as its content did not increase when the processing temperature increased. The rates of reaction to develop zirconolite and hollandite were faster when the HUPing temperature

increased as the sample HUPed at 1250°C formed the largest zirconolite and hollandite content. Although the sample prepared at 1250°C was closest to the desired phase composition, this was at the expense of an increased volatilisation rate.

Figure 3.10 shows BSE images of samples HUPed at the different temperatures. The phases present and their morphology are similar to those in Figure 3.3 – the only difference being the relative weight fractions and grain size (Table 3.3). The grain size increased with HUPing temperature: with the sample HUPed at 1250°C giving the largest grain size. It was difficult to calculate the theoretical density of Synroc-Z as the amounts and densities of each minor alloy phases were unknown. However, the Synroc-Z HUPed at 1100°C and above exhibited low porosity (< 0.5 vol.%) which agreed with BSE images as no obvious pores and cracks were displayed (Table 3.3). The sample which was HUPed at the lowest temperature (1050°C) was found to contain a relatively high porosity (~ 2.5 vol.%) and regions showing incomplete densification, as shown in Figure 3.10(d). The grain sizes of different phases in each sample were similar and fall within a narrow range of sizes (Table 3.3) while the alloys were 10 - 500 nm.

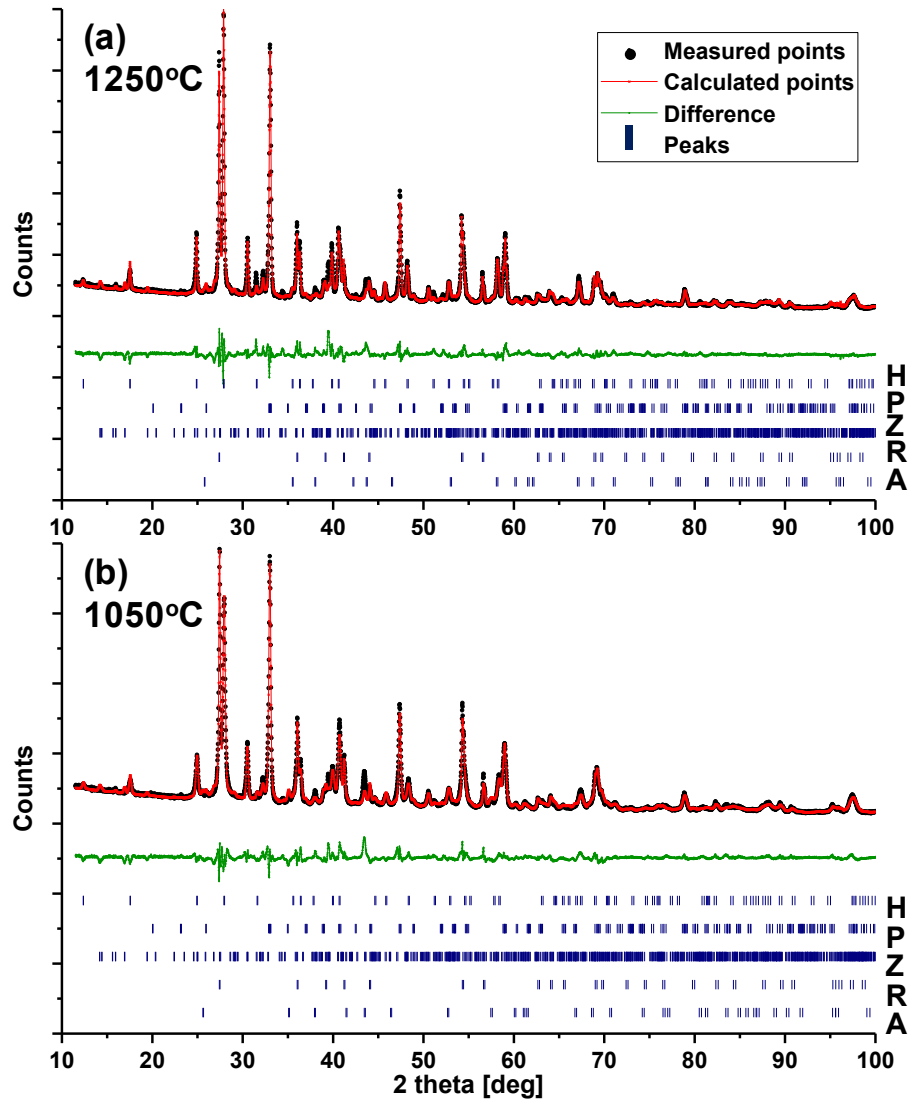


Figure 3.8 Refinement of Synroc-Z HUPed at (a) 1250°C, and (b) 1050°C with 20 MPa for 3 h using Rietica software. Phases 1-5 were hollandite (H), perovskite (P), zirconolite (Z), rutile (R), and alumina (A), respectively. The R_{wp} , R_{exp} and Goodness-of-fit for (a) refinement were 8.61, 2.31 and 13.86 respectively; and (b) refinement were 7.59, 2.28 and 11.08 respectively.

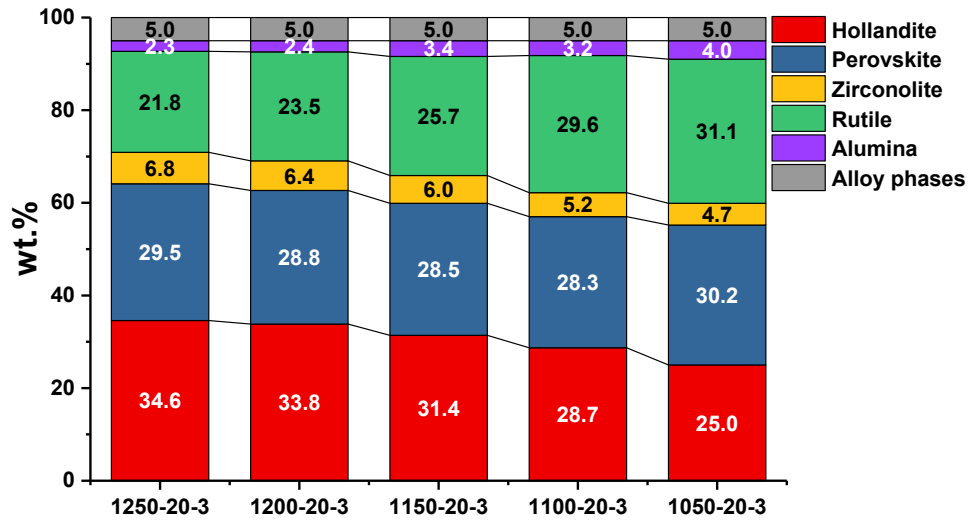


Figure 3.9 Weight fractions of Synroc-Z with 20 wt.% HLW samples HUPed at different temperatures determined by Rietveld refinement.

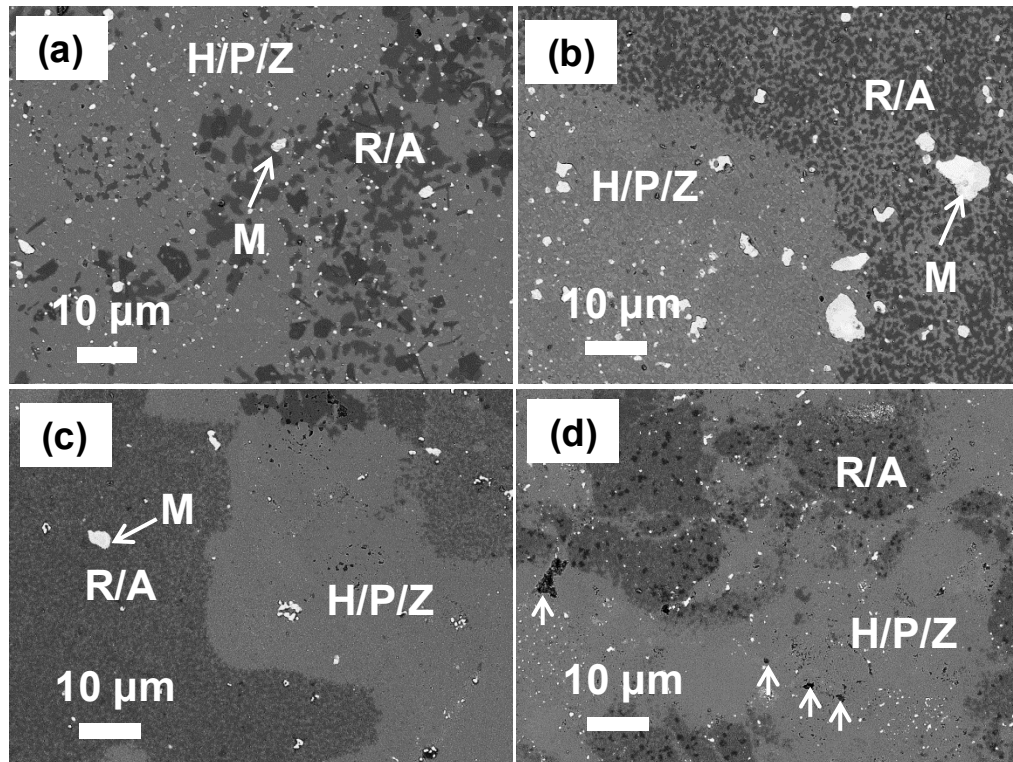


Figure 3.10 BSE images of Synroc-Z HUPed at (a) 1250°C, (b) 1150°C, (c) 1100°C and (d) 1050°C. The grain size decreased when the HUPing temperature decreased. (d) Sample 1050-20-3 contained some pores (indicated by arrows) and was thus incompletely densified. The phases in the images are hollandite (H), perovskite (P), zirconolite (Z), rutile (R), alumina (A) and metallic precipitates (M).

Table 3.3 Measured bulk density, apparent porosity and grain size of Synroc-Z samples HUPed at various temperatures. Error ranges represent the standard deviation in the 3 measurements.

Sample ID	Bulk density (g/cm ³)	Apparent porosity (vol%)	Grain size (μm)
1250-20-3	4.50 ± 0.03	0.2 ± 0.07	0.8 - 4
1200-20-3	4.47 ± 0.01	0.3 ± 0.02	0.5 - 2
1150-20-3	4.51 ± 0.03	0.3 ± 0.06	0.4 - 2
1100-20-3	4.49 ± 0.02	0.2 ± 0.04	0.15 – 0.8
1050-20-3	4.33 ± 0.01	2.5 ± 0.10	0.1 – 0.6

3.3.2 Pressure

The effect of applied load during HUPing was studied. Samples were heated to 1200°C by ramping at 5 °C/min before applying the desired pressure for 3 h. After this, the samples were cooled at a rate of 5 °C/min to 750°C. Samples were then left in the machine until reaching room temperature. HUPing pressures of 40, 20 and 10 MPa were chosen for these tests. These pressures span the range possible with the equipment used: the maximum pressure was limited by die materials (the maximum pressure possible was ~50 MPa), whilst the lower bound was defined by the HUPing machine which had a minimum pressure of ~10 MPa (sample ID: 1200-*X*-3, *X* is the process pressure). Figure 3.6(b) is representative to the XRD patterns obtained at the different pressures alongside the profiles refined using the Rietveld method (for refinements giving $R_{wp} < 10\%$, and Goodness of Fit $< 15\%$). As before, all samples were found to contain the four primary Synroc phases (hollandite, perovskite, zirconolite and rutile) again alongside small amounts (2.1 - 2.7 wt.%) of alumina. Figure 3.11 shows the weight fractions of the HUPed Synroc-Z samples determined via Rietveld method allowing the effect of HUPing pressure to be observed. A similar trend as seen for processing temperature was observed, higher HUPing pressure produced more hollandite and zirconolite and thus less rutile. However, the magnitude of the effect was smaller than that obtained by varying temperature (Figure 3.9), in particular between 10 and 20 MPa as both samples contained similar amounts of rutile.

The phases present, their morphology, and even their relative volume fractions of phases are all similar regardless of the pressure used in BSE image (Figure 3.3d). The applied load during HUPing had a negligible effect on both

density and phase composition as a dense sample, with similar phase composition was obtained even at the lowest pressure of 10 MPa.

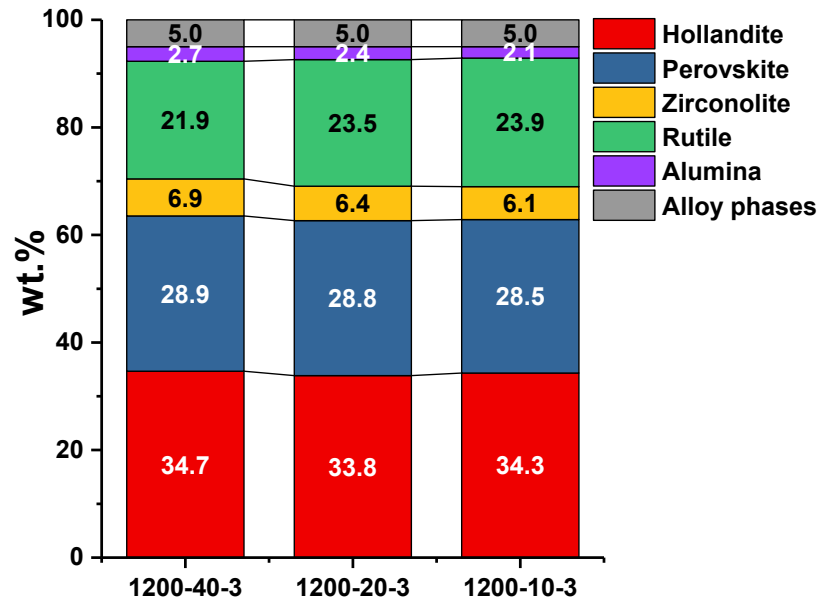


Figure 3.11 Weight fractions of different phases in Synroc-Z with 20 wt.% HLW samples HUPed at different pressures determined by Rietveld refinement.

3.3.3 Dwell time

The effect of dwell time during HUPing was studied by heating samples to 1200°C at a rate of 5 °C/min at an applied pressure of 20 MPa for dwell times of 0.5, 1, 3, and 5 h (sample ID: 1200-20-*X*, where *X* is the dwell time). After this process was completed, samples were cooled at a rate of 5 °C/min to 750°C and left in the machine until they reached room temperature.

XRD patterns and Rietveld refined profiles for the relevant samples are representative to Figure 3.6 (b). All refinements yielded $R_{wp} < 10\%$, and Goodness of Fit $< 15\%$. Once more, it was confirmed that the samples contained the four main characteristic Synroc phases (hollandite, perovskite, zirconolite and rutile) alongside small amounts (< 3.5 wt.%) of alumina. Figure 3.12 shows the weight fractions of the HUPed Synroc-Z samples as determined from the Rietveld refinements. By comparing these results, it can be seen that the dwell time had a significant effect on phase content, particularly between 0.5 h and 3 h, and to lesser extent between 3 and 5 h. Shorter dwell times led to less hollandite and zirconolite and thus more rutile.

Figure 3.13 shows BSE image of samples HUPed at 1200°C and 20 MPa for 0.5 h. The phases present and the morphology were similar: all of Synroc-Z samples HUPed for four different dwell times display a dense microstructure with five different levels of contrast. The holding time during HUPing had a negligible effect on density as dense Synroc-Z was obtained even at the shortest dwell time of 0.5 h.

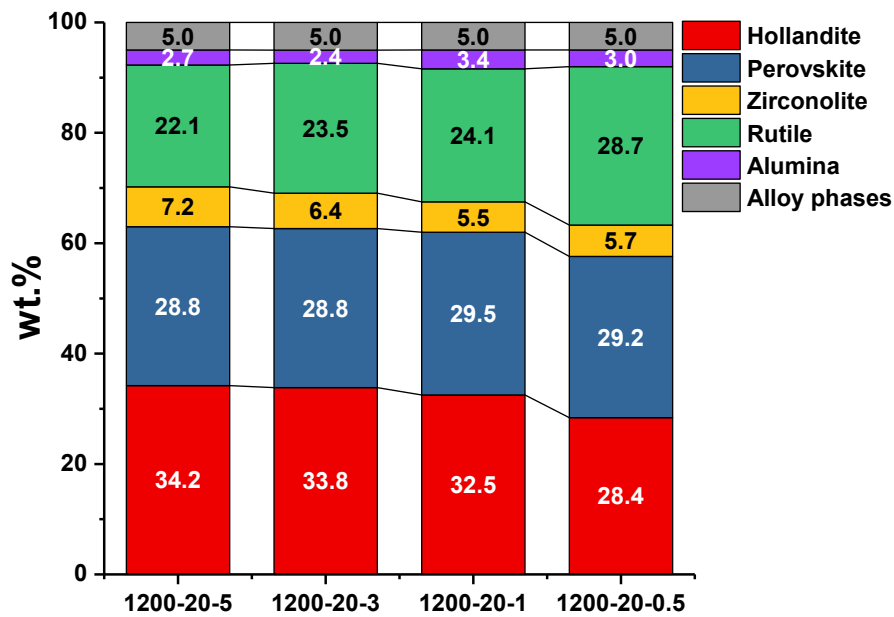


Figure 3.12 Weight fractions of phases in Synroc-Z with 20 wt.% HLW HUPed for different dwell times determined by Rietveld refinement.

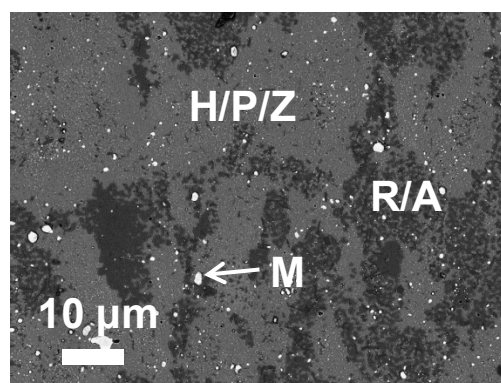


Figure 3.13 BSE image of Synroc-Z sample 1200-20-0.5. The holding time did not make a significant effect on density and grain size. The phases in the image are hollandite (H), perovskite (P), zirconolite (Z), rutile (R), alumina (A) and metallic precipitates (M).

3.4 Effect of waste loading via HUPing

Synroc-Z was HUPed at 1200°C and 20 MPa for 3 h with different waste loadings (20, 25, 30, 35 wt.%) as shown in Table 2.7 to determine the maximum capacity for simulated EURO-GANEX wastes.

Synroc-Z with higher waste loadings (> 20 wt.%) did not form any new crystalline phases. They were all HUPed at 1200°C and 20 MPa for 3 h and contained the four main Synroc phases with minor alumina. Figure 3.14 shows the XRD patterns and matched profiles of HUPed Synroc-Z with 35 wt.% waste loading when the refinements yielded $R_{wp} < 10\%$, and Goodness of Fit < 15 %. Figure 3.15 shows the weight fractions of HUPed Synroc-Z with different waste loadings determined by Rietveld refinement. The Synroc-Z with higher waste loading formed greater amounts of host phases (hollandite, perovskite and zirconolite) and therefore retained less rutile.

Figure 3.16 shows BSE images of Synroc-Z with four different waste loadings HUPed at 1200°C and 20 MPa for 3 h. The phases present and their morphology were similar as all of them displayed five different levels of contrast and a dense microstructure. The higher waste loadings caused a higher quantity of the alloy phases to form and hence the bulk densities increased as shown in Table 3.4.

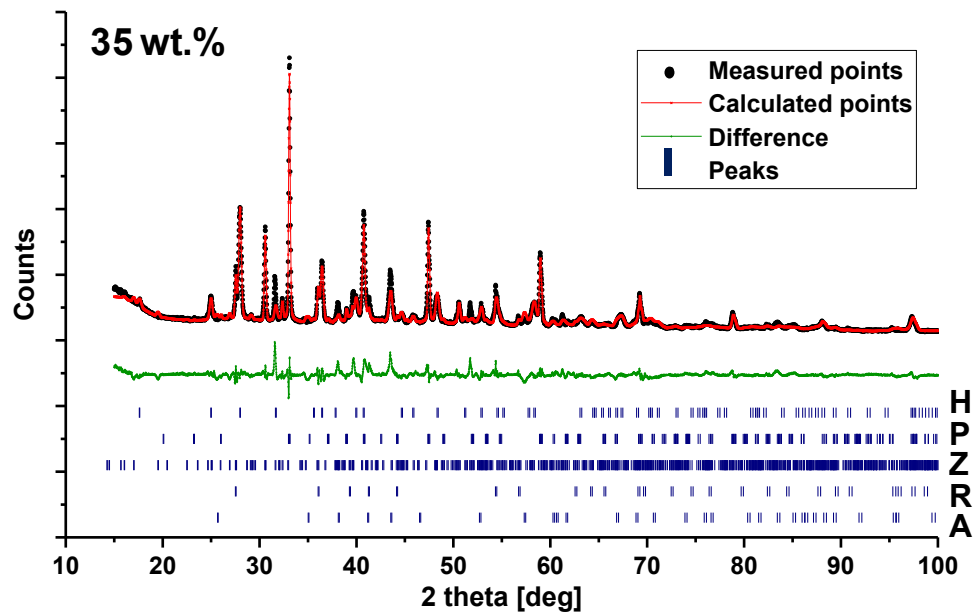


Figure 3.14 Refinement of Synroc-Z HUPed at 1200°C and 20 MPa for 3 h with 35 wt.% waste loading using Rietica software. Phases 1-5 were hollandite (H), perovskite (P), zirconolite (Z), rutile (R), and alumina (A), respectively. The R_{wp} , R_{exp} and Goodness-of-fit for refinement were 9.78, 2.53 and 14.92 respectively.

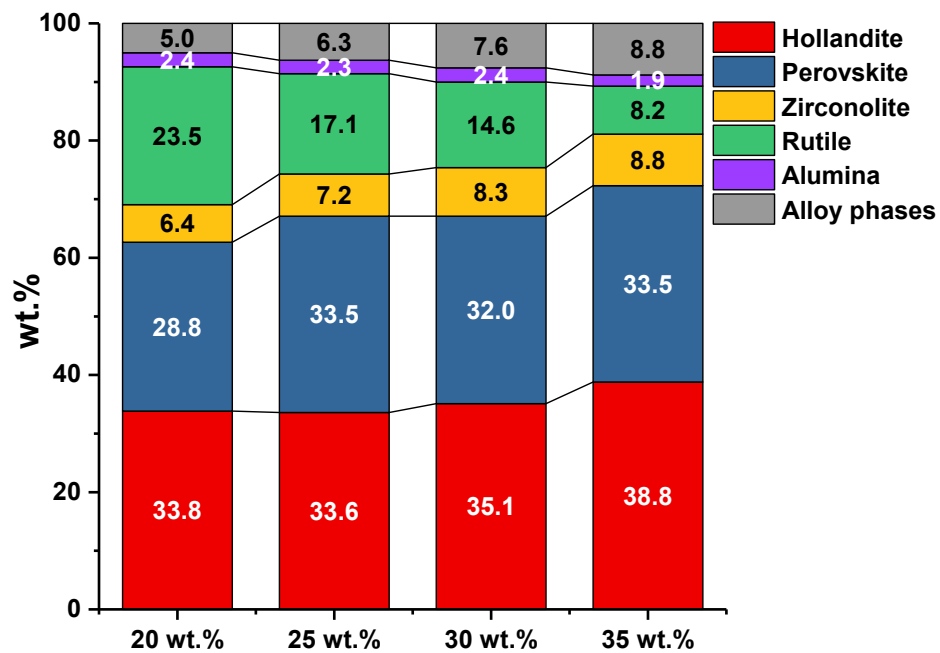


Figure 3.15 Weight fractions of HUPed Synroc-Z with different waste loadings determined by Rietveld refinement.

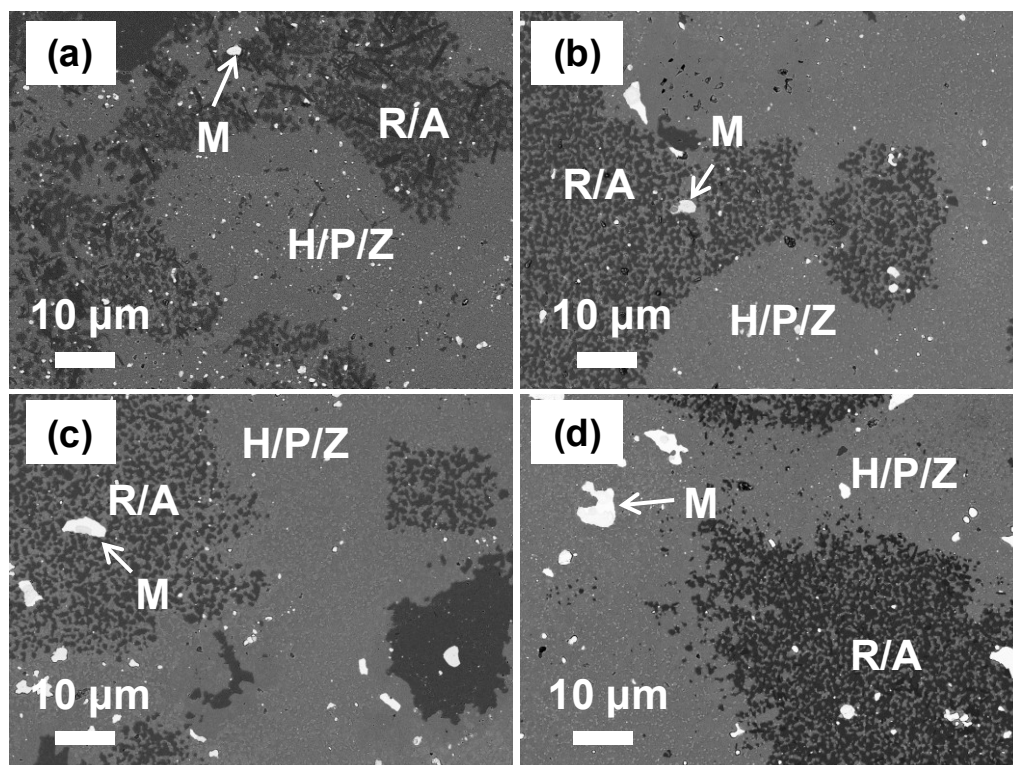


Figure 3.16 BSE images of Synroc-Z samples with (a) 20 wt.%, (b) 25 wt.%, (c) 30 wt.% and (d) 35 wt.% waste loading. The phases in the images are hollandite (H), perovskite (P), zirconolite (Z), rutile (R), alumina (A) and metallic precipitates (M).

Table 3.4 Measured bulk density, apparent porosity and grain size of HUPed Synroc-Z samples with different waste loading. Error ranges represent the standard deviation in the 3 measurements.

Sample ID	Bulk density (g/cm ³)	Apparent porosity (vol.%)	Grain size (μm)
25 wt. %	4.56 ± 0.01	0.3 ± 0.02	0.5 - 2
30 wt. %	4.59 ± 0.02	0.3 ± 0.03	0.5 - 2
35 wt. %	4.56 ± 0.01	0.4 ± 0.03	0.5 - 2

3.5 Effect of HIPing conditions

Another hot-pressing technique, HIPing, has been used to fabricate ceramic and glass composite material (GCM) wasteforms at laboratory scale for many years¹¹⁹. Synroc-Z samples fabricated using both hot-pressing (HUPing and HIPing) methods were compared. To facilitate this, three different sets of HIPing conditions (Table 2.9) were chosen to be either similar to those for the HUPed samples, or to expose the advantages of HIPing (i.e., application of higher pressure and negligible off-gas). All the HIPed Synroc-Z was produced with a 20 wt.% waste loading. One Synroc-Z sample was HIPed at the lowest processing temperature (1050°C) but the higher pressure (100 MPa instead of 20 MPa for the HUPed sample) to investigate the effect of higher pressure. Another was HIPed with exactly the same conditions as HUPing (1200°C and 20 MPa for 3 h) to allow direct comparison of the two techniques. Finally, a sample was HIPed at 1250°C and 100 MPa for 2 h as this was expected to give the closest match to target phase composition (Table 2.6) with conditions being chosen based on ANSTO researchers' experience. HIPing could heat the samples 50 - 100 °C higher than 1200°C without volatile losses due to its negligible off-gas advantage. The HIPed samples were analysed using XRD, SEM, and TEM to determine their phase content and microstructure while the HIPed Samples are labelled using following identifying code: *HIP-HIPing temperature- pressure- dwell time* (i.e sample HIP-1200-20-3 means that the sample was HIPed at 1200°C and 20 MPa for 3 h).

Figure 3.17 shows the photos of HIP canisters before and after HIPing. All canisters have deformed uniformly on the sides, top and bottom without any damage to the welds. This suggested that the HIP process for the Synroc-Z samples had been successful.

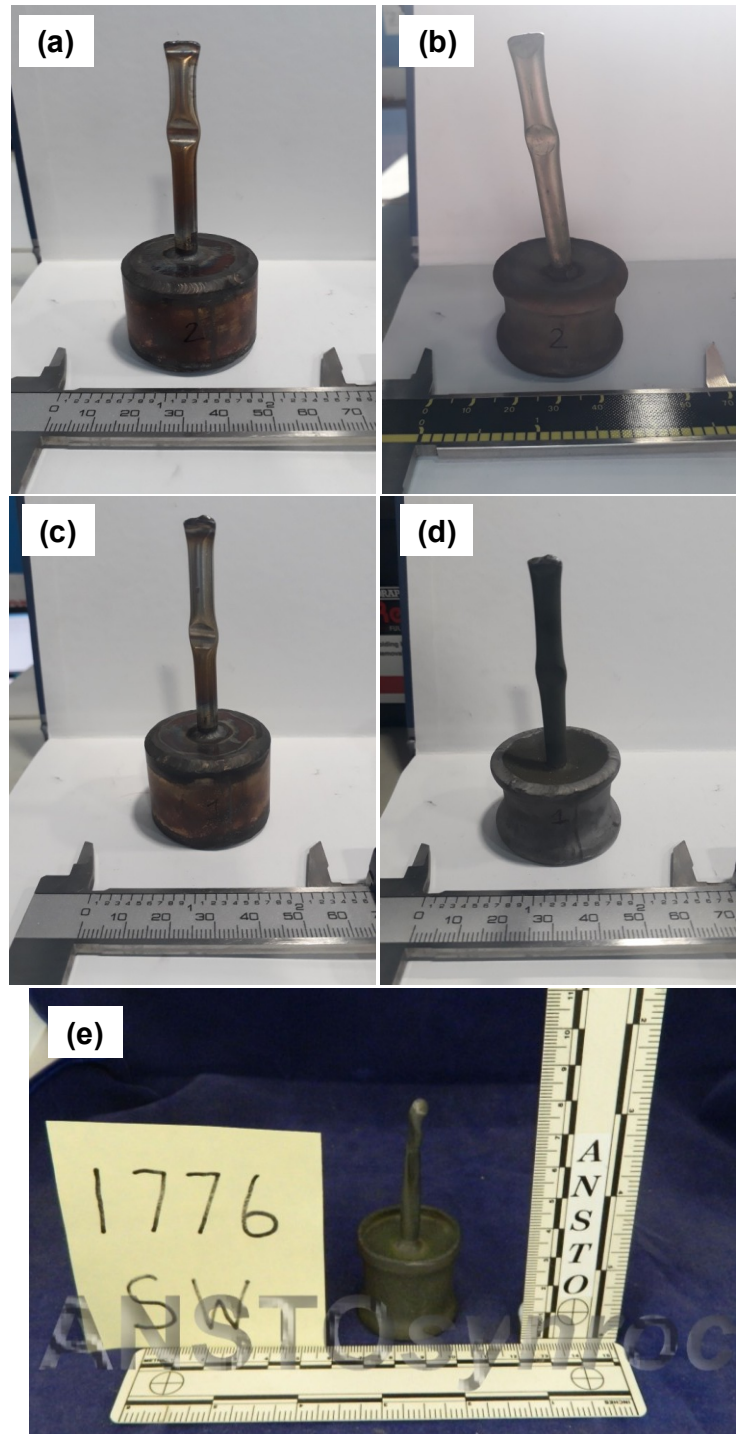
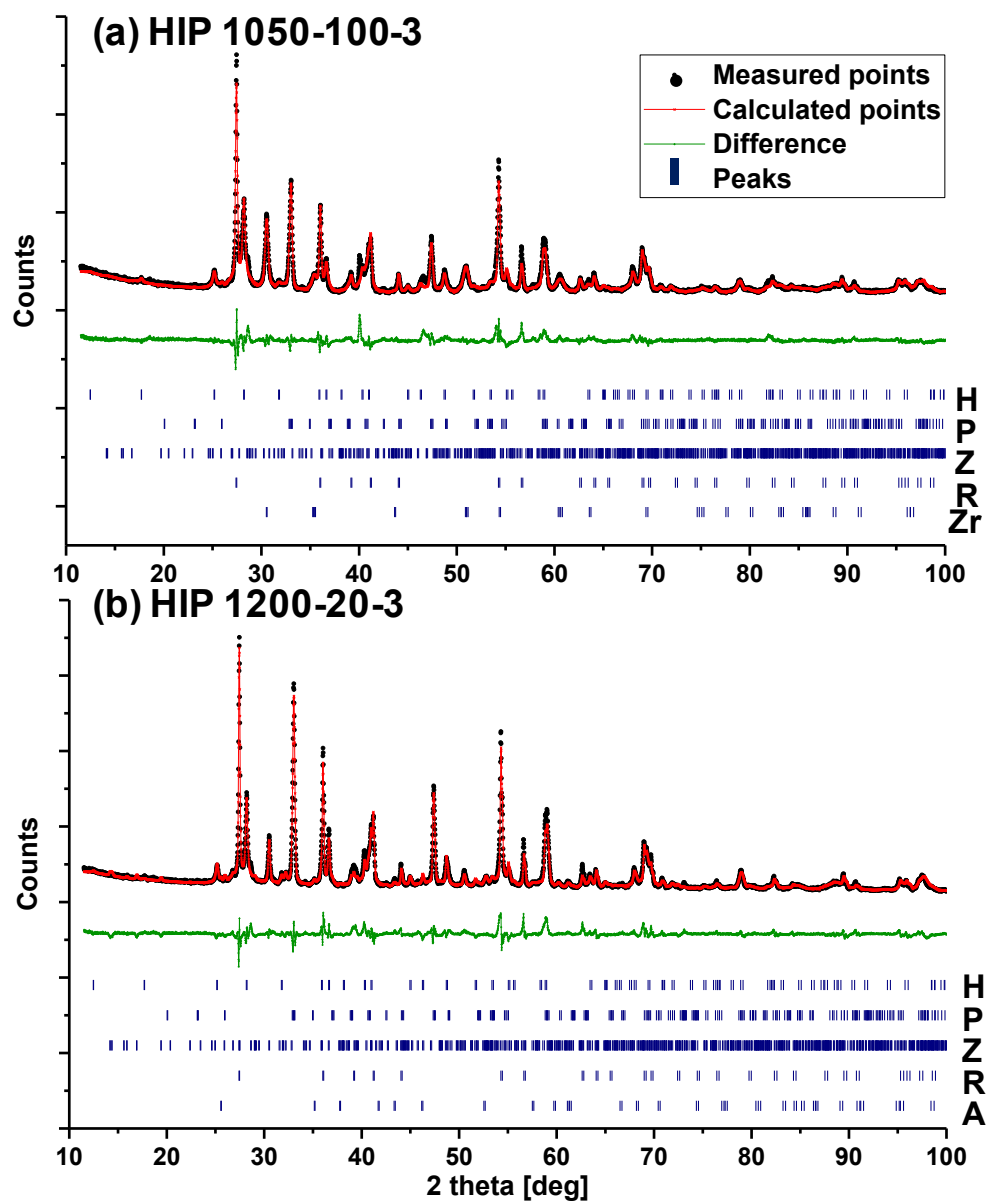


Figure 3.17 Photos of HIP canister (a,c) before HIPing and after HIPed at (b) 1050°C and 100 MPa, (d) 1200°C and 20 MPa and (e) 1250°C and 100 MPa. Provided by Dr. Laura Gardner, the University of Sheffield and Dr. Daniel Gregg, ANSTO.

3.5.1 Phase composition- XRD

XRD was performed on the HIPed Synroc-Z to determine the phase content and Table 2.11 lists their matched ICDD reference cards.

The HIPed Synroc-Z samples contained the four main Synroc phases with minor amounts of alumina and zirconia (1 to 7 wt.%). Figure 3.18 shows their XRD patterns and matched profiles for refinements that yielded $R_{wp} < 10\%$, and Goodness of Fit $< 15\%$. Figure 3.19 displays the weight fractions of HIPed Synroc-Z determined from Rietveld refinements. The sample HIPed at 1050°C and 100 MPa for 3 h did not produce greater amounts of host phases (hollandite, perovskite and zirconolite) compared to the sample which was HUPed at the same temperature but lower applied pressure of 20 MPa (51.2 wt.% vs. 59.9 wt.%). The HIPed sample (1200°C, 20 MPa, 3 h) contained less perovskite (~23 wt.%) than the corresponding HUPed sample (~29 wt.%) and hence retained ~30 wt.% rutile + alumina. However, the sample HIPed at 1250°C and 100 MPa for 2 h achieved the target amount of perovskite and zirconolite (see table 2.6) while containing more hollandite + hollandite related phases ($Ba_2Ti_9O_{20}$) than targeted and thus has lower amounts of rutile/Magnéli (Ti_3O_5). Although $CaMoO_4$ can fit with the XRD patterns of HIPed samples (1200°C, 20 MPa, 3 h and 1050°C, 100 MPa, 3 h), it was difficult to add to the refinement, presumably because of excessive peak overlap with hollandite and/or low peak intensity. Some minor phases were observed by SEM and TEM and described in detail in the next section.



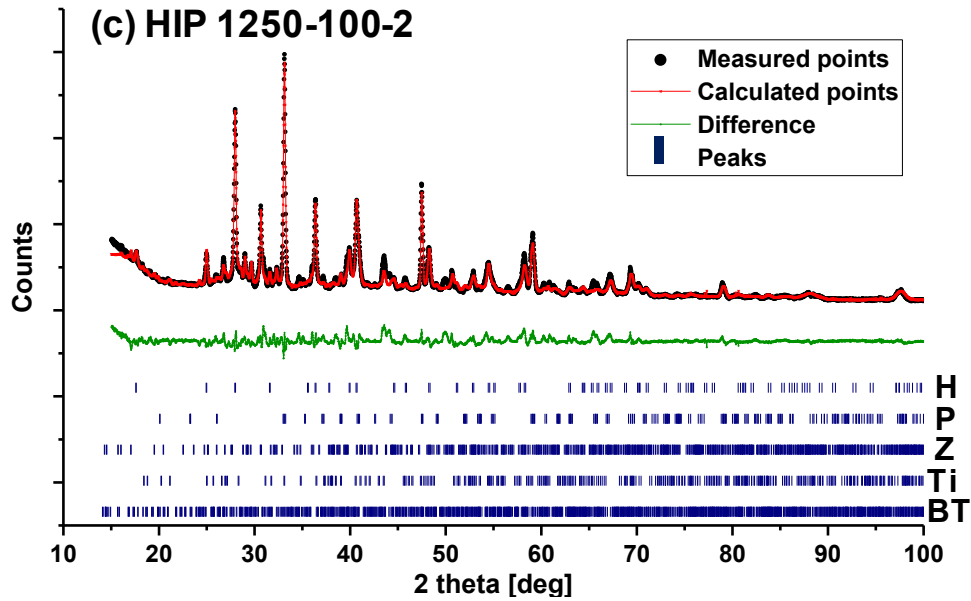


Figure 3.18 Refinement of Synroc-Z HIPed at (a) 1050°C and 100 MPa for 3 h, (b) 1200°C and 20 MPa for 3 h and (c) 1250°C and 100 MPa for 2 h using Rietica software. Phases 1-4 were hollandite (H), perovskite (P), zirconolite (Z), and rutile (R), respectively. The phase 5 in (a) sample HIP-1050-100-3 was zirconia (Zr) while (b) sample HIP-1200-20-3 was alumina (A). The phase 4 and 5 in sample HIP-1250-100-2 were Magnéli (Ti_3O_5 , Ti) and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (BT). The R_{wp} , R_{exp} and Goodness-of-fit for (a) refinement were 7.06, 2.66 and 7.03 respectively, (b) refinement were 7.96, 2.59 and 9.43 respectively and (c) refinement were 9.49, 2.55 and 13.84 respectively.

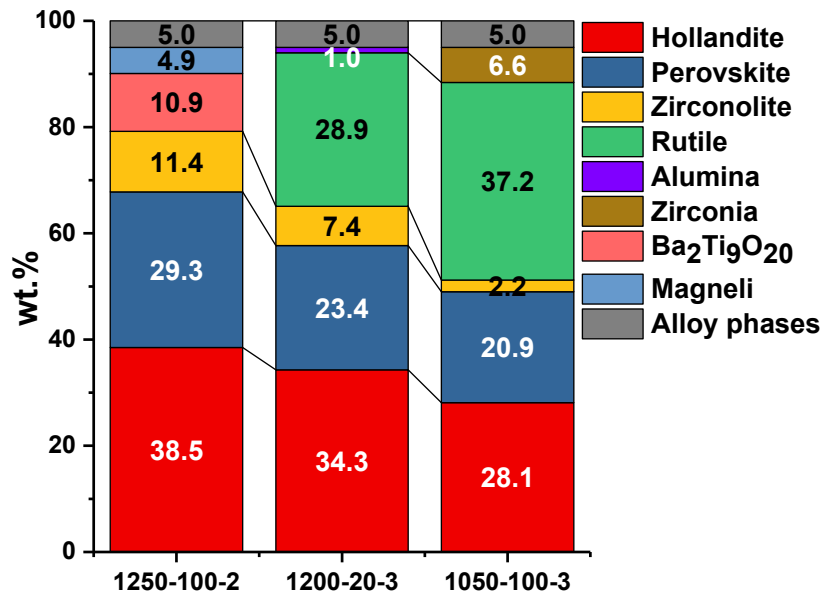


Figure 3.19 Weight fractions of phases in HIPed Synroc-Z determined by Rietveld refinement.

3.5.2 Microstructure

Figure 3.20 displays BSE images of HIPed Synroc-Z samples. The measured densities of HIPed Synroc-Z samples were smaller than those of the HUPed Synroc-Z samples (~ 4.3 vs. ~ 4.5 g/cm³) even though they were fabricated with similar processing conditions (1200°C, 20 MPa, 3h) and obtained higher porosities (~ 0.7 vs. ~ 0.3 vol%). The microstructure of HIPed Synroc-Z was similar to those of the HUPed Synroc-Z ones as they all generally contain three different levels of contrast at low magnification (dark grey, light grey and white). Figure 3.21 and 22 display the elemental distribution mapping of HIPed Synroc-Z samples to distinguish which contrast is which phase. The alumina (A) was black while rutile (R) showed dark grey contrast. For the light grey areas, the three host phases, hollandite, perovskite and zirconolite, were not distinguishable as their average weighted atomic number (Z) was similar. The white areas were alloys.

However, Cs-Mo compounds (white regions) and Ca-Mo phases (light grey) were observed in HIPed samples (1200°C, 20 MPa, 3 h and 1050°C, 100 MPa, 3 h). Figure 3.20(c) reveals the Cs-Mo phases rich regions (~ 23 area%) in the sample HIPed at 1200°C and 20 MPa for 3 h. Those Cs-Mo compounds were $\sim 1 - 50$ μm in size and decreased the measured densities of HIPed Synroc-Z as cracks appeared in these phases (Figure 3.20a). The Cs-Mo compounds may be amorphous nature as they were plenty (~ 23 area%) in the SEM images (Figure 3.20) but were not detected via XRD (Figure 3.18). Figure 3.21 illustrates the Ca-Mo phases in the elemental distribution mapping. Ti was not as rich in some light grey contrast regions but Ca and Mo were. The undesired Cs-Mo compounds and Ca-Mo phases formed will be discussed in section 7.1. However, the sample HIPed at ANSTO researchers' suggestion (1250°C, 100 MPa, 2 h) displayed similar elemental distribution mapping to HUPed Synroc-Z in Figure 3.22.

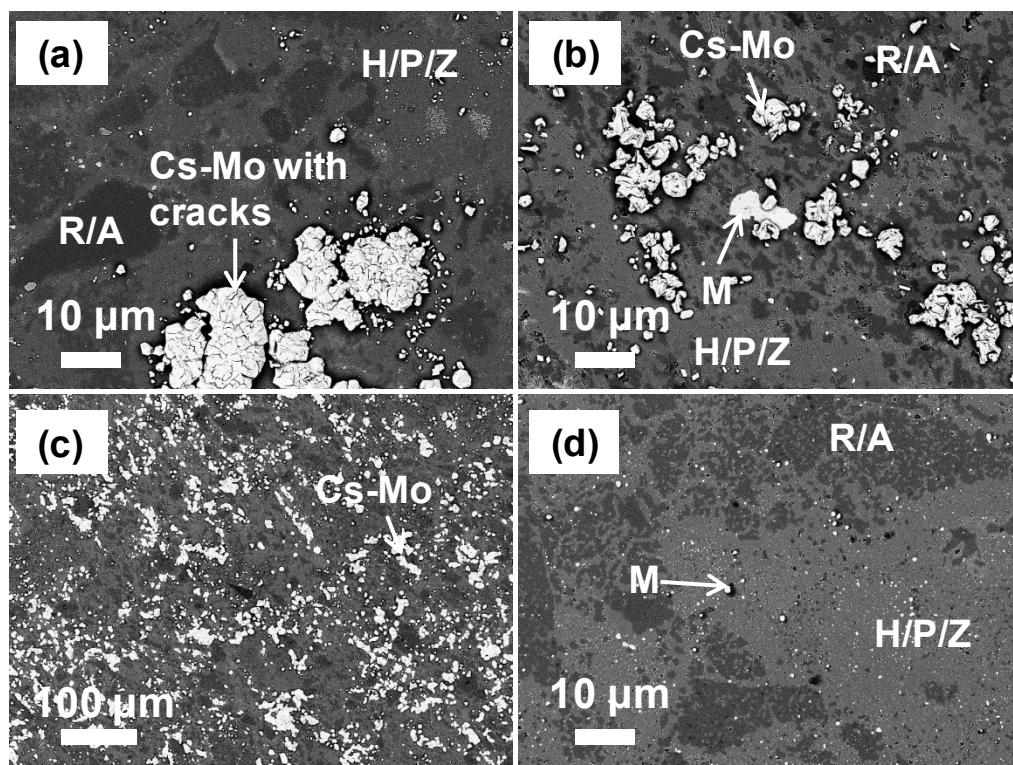


Figure 3.20 BSE images of HIPed Synroc-Z samples (a) HIP 1050-100-3, HIP 1200-20-3 at (b) high magnification and (c) low magnification and (d) HIP 1250-100-2. The HIPed Synroc-Z generally contained 3 different levels of contrast. The rutile (R) and alumina (A) located at the dark grey regions; the host phases (hollandite (H), perovskite (P) and zirconolite (Z)) presented at the light grey areas; the “pop up” Cs-Mo compounds and alloys (M) displayed as the white parts.

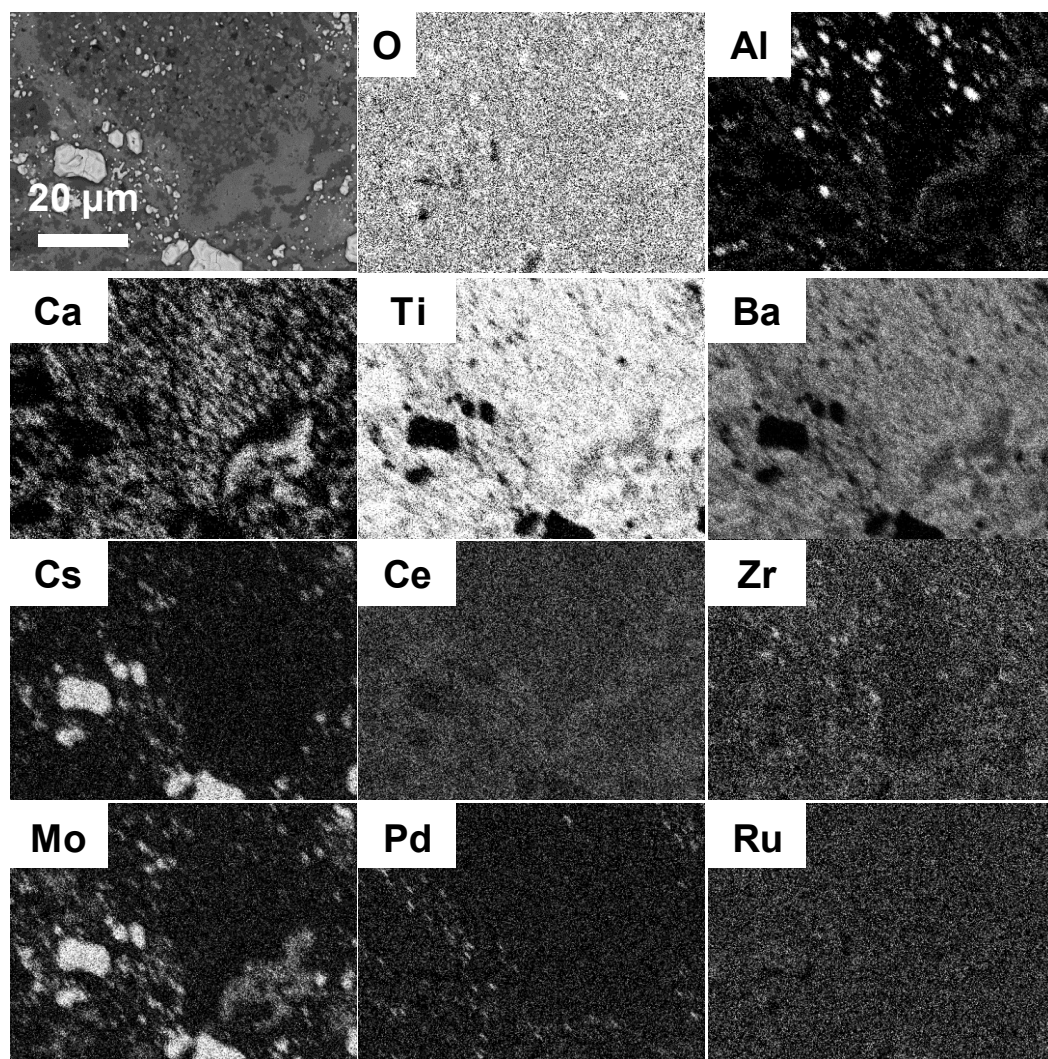


Figure 3.21 Elemental distribution plots of HIPed Synroc-Z sample HIP 1200-20-3 by SEM/EDX mapping for 1 h.

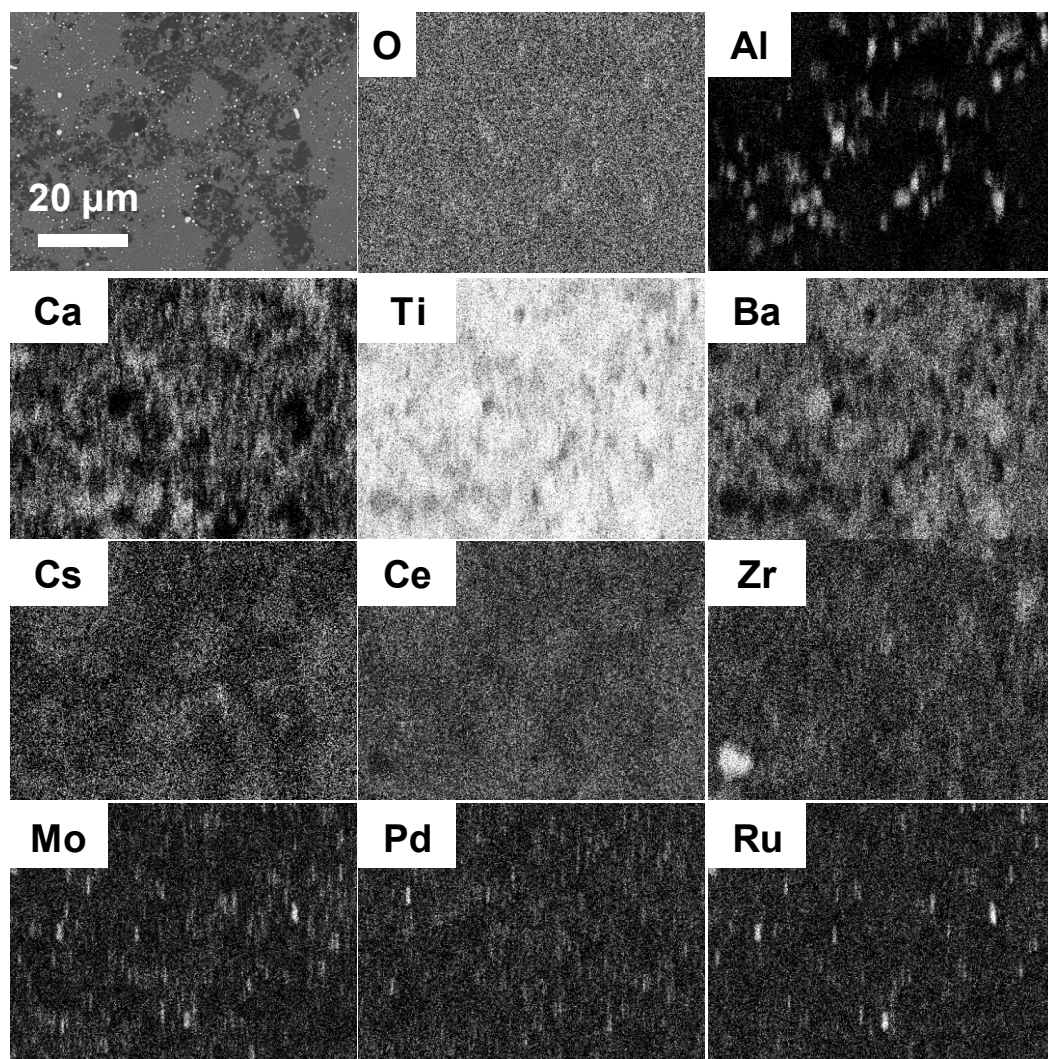


Figure 3.22 Elemental distribution plots of HIPed Synroc-Z sample HIP 1250-100-2 by SEM/EDX mapping for 1 h.

Figures 3.23 and 24 show the TEM images and EDX results for the HIPed Synroc-Z obtained from samples milled to a thickness of ~ 100 nm using the FIB method. The grain size of the major phases in the HIPed Synroc-Z sample for the processing conditions of $T = 1200^\circ\text{C}$, $P = 20$ MPa, and $t_{\text{dwell}} = 3$ h was $\sim 0.5 - 4$ μm (usually > 1 μm , Figure 3.23). The last HIPed Synroc-Z sample was prepared successfully without Cs-Mo compounds at ANSTO. The grain size of sample HIPed at 1250°C and 100 MPa for 2 h was $\sim 0.5 - 2$ μm (usually < 1 μm , Figure 3.24). The grain sizes of minor phases were around ten to a few hundred nm and were generally located at grain boundaries of the major phases and/or embedded in the main crystalline phases as shown as the black contrast regions in TEM images. The minor phases were composed of Mo, Ru, Pd and Te. Some pores were observed in HIPed Synroc-Z (1250°C , 100 MPa, 2 h) located at grain boundaries with minor phases (Figure 3.24). Those pores may come from alloys which were stripped off during grinding as measured porosity was small (0.4 vol%) and these samples did not show obvious pores in SEM images (Figure 3.20). Figure 3.25 shows the TEM sample preparation via FIB in Cs-Mo compound region while the Cs-Mo compound displayed in SEM image (Figure 3.25a) was a layer deposited on the HIPed Synroc-Z. Synroc-Z substrate was clearly observed under the Cs-Mo compound layer. However, the Cs-Mo compound layer detached from the Synroc-Z during transferring the sample from FIB to TEM. A gap with ~ 1.6 μm thickness between Synroc-Z substrate and the Pt weld was discovered in Figure 3.25(b). The Synroc-Z substrate exhibited a flat surface in contact with the Cs-Mo compound layer. This indicated that the Cs-Mo layer was formed after the Synroc-Z substrate.

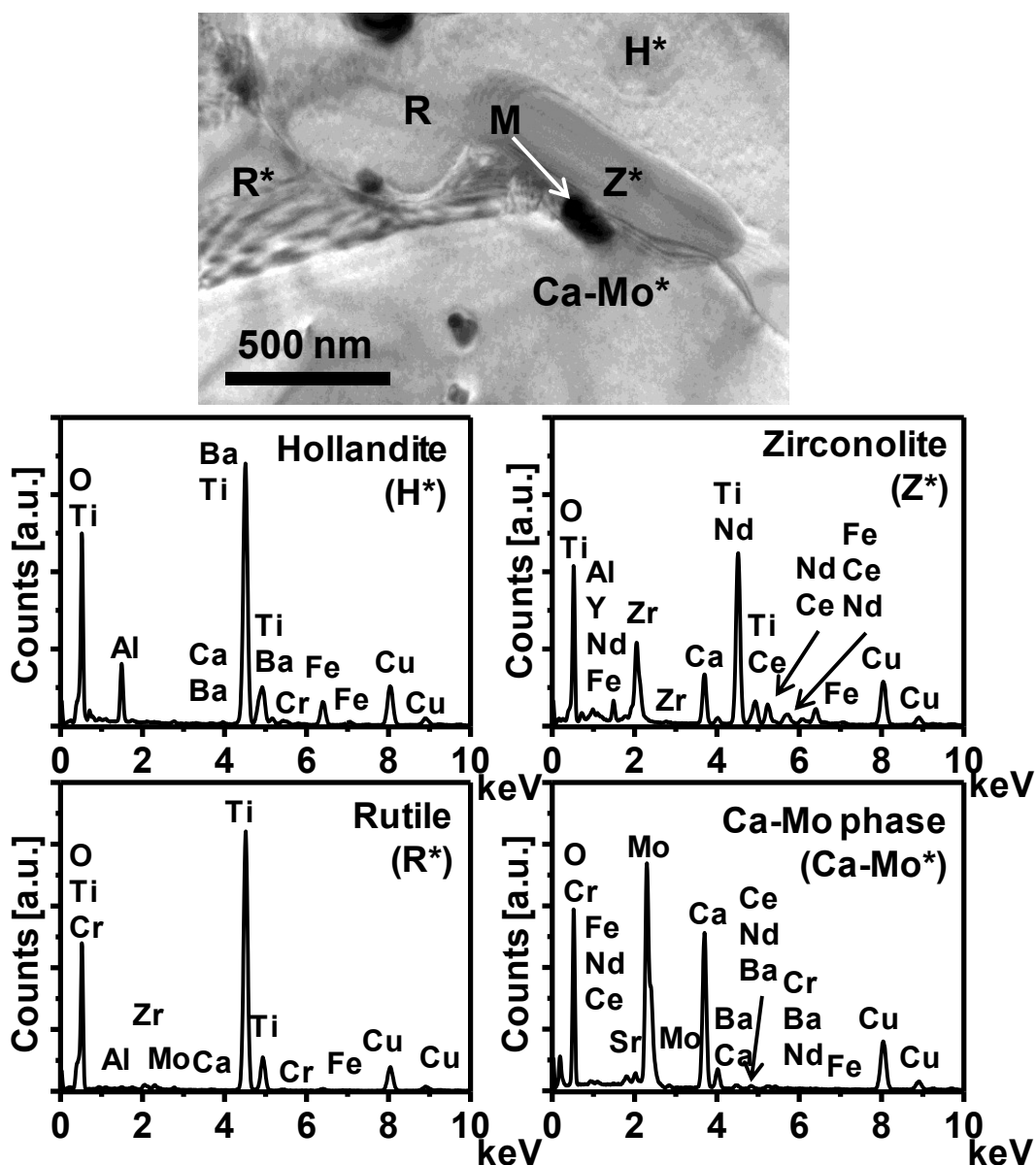


Figure 3.23 TEM image and EDX spectra of HIPed Synroc-Z sample HIP 1200-20-3 prepared via FIB. Some grains were determined via EDX (with *) and were labelled as hollandite (H), zirconolite (Z), rutile (R), metallic precipitates (M) and Ca-Mo phase (Ca-Mo). The metal phases were either located in grain boundaries or embedded in the major crystalline phases. The Cu presented in EDX comes from the Cu grid used for TEM preparation.

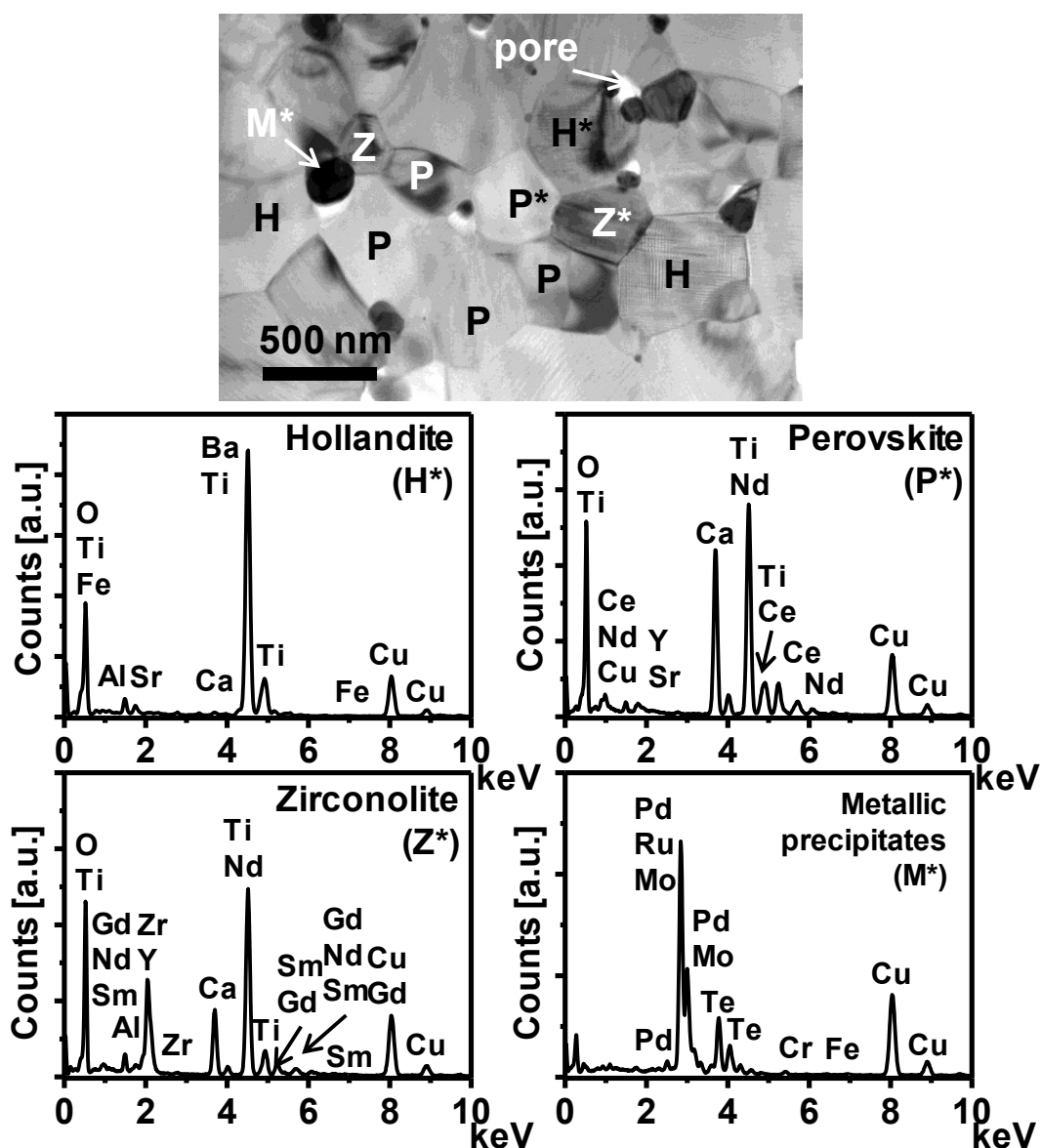


Figure 3.24 TEM image and EDX spectra of HIPed Synroc-Z sample HIP 1250-100-2 prepared via FIB. Some grains were determined via EDX (with *) and were labelled as hollandite (H), perovskite (P), zirconolite (Z), and metallic precipitates (M). The metal phases were either located in grain boundaries or embedded in the major crystalline phases. The Cu presented in EDX is the Cu grid used for TEM preparation.

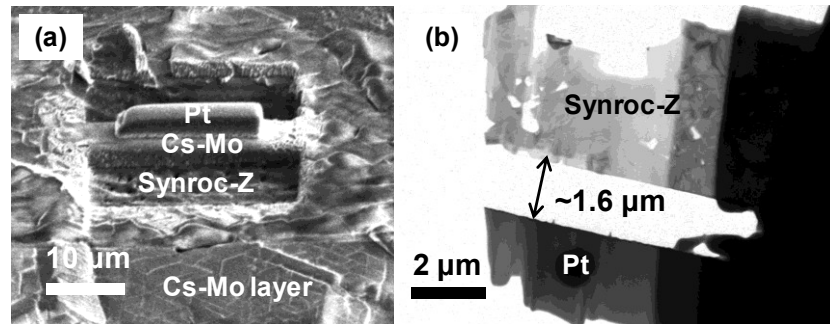


Figure 3.25 (a) SEM image of Cs-Mo compound of TEM sample preparation via FIB and (b) TEM image of the thickness of Cs-Mo compound layer. The Cs-Mo compound came off from the Synroc-Z substrate during transferring sample from FIB to TEM.

3.6 Summary

Table 3.5 summarises the results of this chapter. A novel Synroc composition and HUPing process have been developed to incorporate up to 35 wt.% actinide-free wastes from EURO-GANEX. Both higher processing temperatures and pressures lead to a lower ratio of rutile to the hosting phases. However, above 1200°C, deleterious volatilisation of waste elements occurred which should be avoided. Furthermore, the dwell time had less of an effect when longer than 3 h. The recommended process conditions are therefore a trade-off between improvements in phase content (less rutile), high density and degradation from volatilisation processes. On the basis of this study, the suggested HUPing parameters are temperatures of 1150 - 1200°C together with a pressure >10 MPa for 3 h.

Synroc-Z samples were also produced successfully using HIPing technology. HIPing is a more complex process than HUPing as more parameters such as materials of canisters and baking temperatures need to be considered. Undesired Cs-Mo compounds and Ca-Mo phases were observed in HIPed Synroc-Z samples.

Table 3.5 Summary of Synroc-Z samples in this chapter

Sample ID	Processing conditions	Waste loading (wt.%)	Porosity (vol%)	Present phases*
1250-20-3	HUP: 1250°C; 20 MPa; 3 h	20	0.2 ± 0.07	H, P, Z, R, A , M
1200-20-3	HUP: 1200°C; 20 MPa; 3 h	20	0.3 ± 0.02	H, P, Z, R, A , M
1150-20-3	HUP: 1150°C; 20 MPa; 3 h	20	0.3 ± 0.06	H, P, Z, R, A , M
1100-20-3	HUP: 1100°C; 20 MPa; 3 h	20	0.2 ± 0.04	H, P, Z, R, A , M
1050-20-3	HUP: 1050°C; 20 MPa; 3 h	20	2.5 ± 0.10	H, P, Z, R, A , M
1200-40-3	HUP: 1200°C; 40 MPa; 3 h	20	0.2 ± 0.02	H, P, Z, R, A , M
1200-10-3	HUP: 1200°C; 10 MPa; 3 h	20	0.3 ± 0.01	H, P, Z, R, A , M
1200-20-5	HUP: 1200°C; 20 MPa; 5 h	20	0.2 ± 0.02	H, P, Z, R, A , M
1200-20-1	HUP: 1200°C; 20 MPa; 1 h	20	0.2 ± 0.02	H, P, Z, R, A , M
1200-20-0.5	HUP: 1200°C; 20 MPa; 0.5 h	20	0.2 ± 0.03	H, P, Z, R, A , M
25 wt. %	HUP: 1200°C; 20 MPa; 3 h	25	0.3 ± 0.02	H, P, Z, R, A , M
30 wt. %	HUP: 1200°C; 20 MPa; 3 h	30	0.3 ± 0.03	H, P, Z, R, A , M
35 wt. %	HUP: 1200°C; 20 MPa; 3 h	35	0.4 ± 0.03	H, P, Z, R, A , M
HIP 1050-100-3	HIP: 1050°C; 100 MPa; 3 h	20	0.7 ± 0.04	H, P, Z, R, Zr , M, Cs-Mo , Ca-Mo
HIP 1200-20-3	HIP: 1200°C; 20 MPa; 3 h	20	0.6 ± 0.02	H, P, Z, R, A , M, Cs-Mo , Ca-Mo
HIP 1250-100-2	HIP: 1250°C; 100 MPa; 2 h	20	0.4 ± 0.02	H, P, Z, BT, R, M

*: Hollandite (H), Perovskite (P), Zirconolite (Z), Rutile and Magneli (R), Alumina (A), Zirconia (Zr), Alloy phases (M), Ba₂Ti₉O₂₀ (BT), Cs-Mo and Ca-Mo phases. The undesired phases were shown as bold.

Chapter 4: Characterisation of R7T7 glass fabricated by melting vitrification and HIPing

This chapter discusses the fabrication of R7T7 borosilicate glass wasteforms for the immobilisation of EURO-GANEX wastes via vitrification and HIPing. R7T7 glass has been used as a wasteform to incorporate PUREX waste since the late 1970s and hence was selected to potentially host EURO-GANEX waste. The glass and EURO-GANEX waste compositions are shown in Table 2.5 and 2.8. All R7T7 glass samples fabricated via melting route were prepared at Imperial College London while the HIPed R7T7 samples were produced at ANSTO and the University of Sheffield (UoS).

The glass precursors with 20 wt.% simulated EURO-GANEX wastes were prepared via an oxide route at Imperial College. The mixture was calcined at 510°C using a heating rate of 10 °C/min for 2.5 h in air. At ANSTO, the glass precursors with 20 wt.% waste were produced via an alkoxide method and also calcined at 510°C with a heating rate of 10 °C/min for 2.5 h but under a reducing atmosphere (3.7 v/v% H₂/N₂). These latter calcined powders were used for HIPed R7T7 sample syntheses. The details of preparation were given in section 2.1.3.

4.1 DTA/TGA

The R7T7 glass precursors with 20 wt.% simulated EURO-GANEX waste prepared via oxide and alkoxide routes were examined for their mass loss during high temperature processing (1200°C) by TGA (see section 2.2.3). This was conducted in air for the oxide melting route and in Ar during HIPing. Details of two fabrication routes, vitrification and HIPing, were described in sections 2.1.3 and 2.1.4 respectively. TGA results from both oxide and alkoxide routes of samples weighing ~150 mg are shown in Figure 4.1. The particle sizes of glass precursors with 20 wt.% waste prepared via oxide and alkoxide methods were 10 - 50 µm and 1 - 20 µm respectively. Both powders prepared via oxide and alkoxide routes had lost the adsorbed moisture by ~120°C. However, the glass precursor prepared via the oxide route showed rapid mass loss (~8.8 % mass) above 510°C. The carbonates used in the oxide routes evidently did not decompose completely during calcination as their decomposition temperatures (Na_2CO_3 : ~1000°C and Li_2CO_3 : ~720°C in air based on Figure 4.1) are higher than the calcination temperature used (510°C). The higher calcination temperature was not conducted as the glass transition temperature of R7T7 glass¹⁸⁸ is ~510°C and the powder produced via oxide route reacted with and adhered to the alumina crucible used when the calcination temperature was higher than 520°C. By comparison, the mass loss from the powders produced via the oxide method mainly came from carbonate decomposition while the mixture from the alkoxide route exhibited a further ~1.2 % mass loss above 510°C which may be due to volatilisation of elements such as Na, B, and Li from the glass forming additives in addition to possible losses of Mo, and Cs from the waste¹⁸⁹. However, the volatiles were not recycled to analyze the accurate composition.

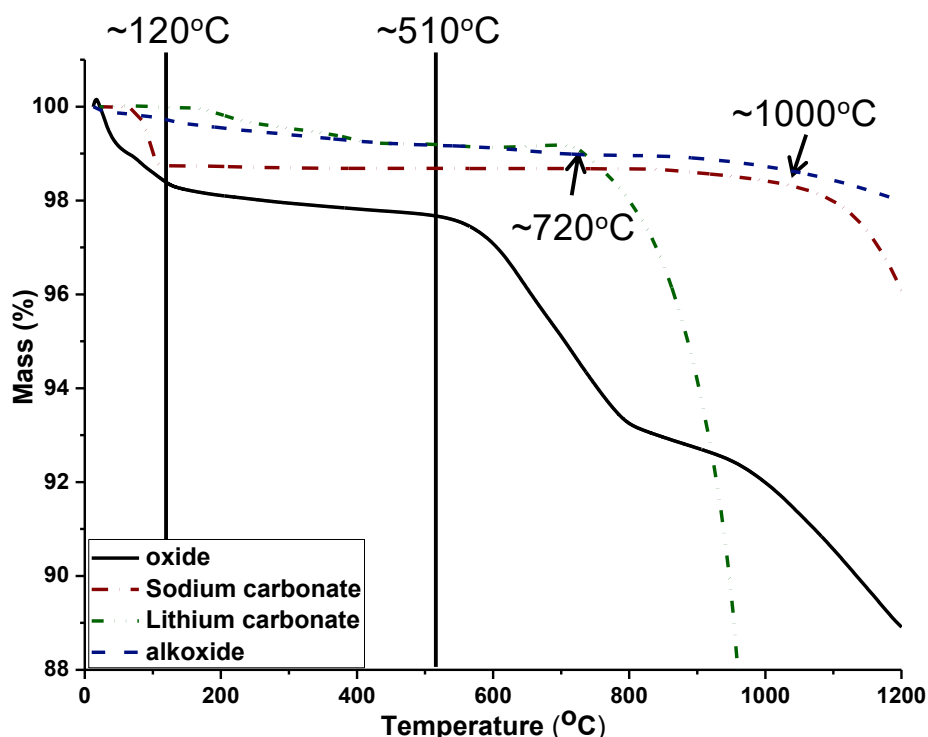


Figure 4.1 TGA analysis of the R7T7 glass precursors with 20 wt.% waste loading prepared via oxide and alkoxide methods, and TGA analysis of sodium and lithium carbonates (decomposition temperatures at 1000 and 720°C respectively).

4.2 Glass prepared via vitrification route

For glass wasteforms, the simulated waste should be chemically immobilised in the R7T7 glass matrix. The calcined R7T7 glass precursors with 20 wt.% simulated waste via the oxide route were heated to 850, 900, 1000, 1100, 1150 and 1200°C for 3 h to determine if any crystalline material was not incorporated in the glass structure at these temperatures. Large ($> 2 \mu\text{m}$) undissolved crystals can be observed by optical microscopy due to the heterogeneity between the glass and the undissolved crystals. The ICDD reference cards used to identify these crystalline phases by XRD were listed in Table 2.12. The glass samples' identification used in figures and tables is presented as R7T7- *processing temperature* (i.e R7T7-1200 means that the sample was heated at 1200°C).

4.2.1 Effect of temperature

4.2.1.1 Melting at 850 and 900°C

The glass heated to 850 and 900°C contained many large (0.5 - 2 mm) closed pores in the glass matrix and broke into flakes and small pieces (< 5 mm diameter) when being taken out of the Pt crucible (Figure 4.2). The glass adhered to the Pt crucible after removal from the furnace. Pacaud *et al.*¹⁸⁸ measured the viscosity of R7T7 glass melt between 950 and 1200°C. The pores were likely formed from gases evolving during carbonate decomposition when glass melt viscosity was high¹⁸⁸ ($> 50 \text{ Nm}^{-2}\text{s}^{-1}$) which meant the gases were trapped (Figure 4.2a). As a result, all the pores are strictly bubbles. Figure 4.2 also displays the heterogeneity of glass samples prepared at 850 and 900°C. The samples contain glass matrix, bubbles (0.5–2 mm) and small ($> 2 \mu\text{m}$) angular features which were later identified by SEM/EDX as Pd and RuO₂ crystals. The crystals show up as a different contrast (bright) to the glass substrate (light grey) in the optical microscopy images.

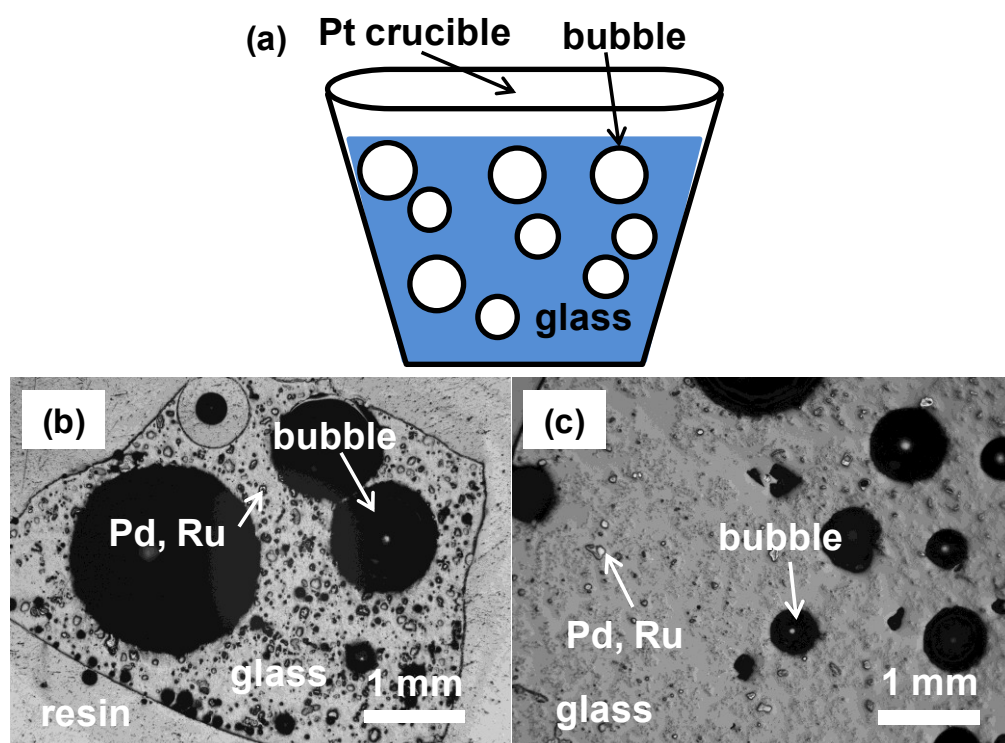


Figure 4.2 (a) Schematic diagram of R7T7 samples prepared at 850 and 900°C after taking out from the furnace and optical microscopy images of R7T7 glass heated at (b) 850 and (c) 900°C which were mounted in resin. Pd alloys (Pd) and RuO₂ crystals (Ru) which were confirmed by SEM/EDX later appeared in the glass.

XRD (Figure 4.3) shows that both glasses made at 850 and 900°C formed crystalline silicates, such as CaSiO_3 , and contained undissolved oxides, powellite and metallic Pd which were distinguishable in BSE images (Figure 4.4). The EDX spectra from the various regions (labelled with * in BSE images) are shown in the bottom of Figure 4.4. The dark grey matrix in this figure was identified as R7T7 glass via EDX as it contained mainly Si and O and did not show many peaks for Si crystals in XRD. The two phases exhibiting intermediate grey contrast were also identified via EDX; the first, with the smaller feature size of $< 0.1 \mu\text{m}$ are RuO_2 crystals (labelled Ru), and the second larger phases ($> 2 \mu\text{m}$) as powellite (labelled Mo in the figure) with atomic ratios of Ca and Mo of 1 : 1.4. RuO_2 was usually found in the form of aggregates up to $500 \mu\text{m}$ in some regions (labelled Ru^a in the figure). White regions were identified as metallic Pd (labelled Pd). It was sometimes difficult to separate the Pd and RuO_2 signals from the glass substrate during EDX due to their small grain size ($< 1 \mu\text{m}$) and the limit of the EDX detection volume ($\sim 1 \mu\text{m}^3$).

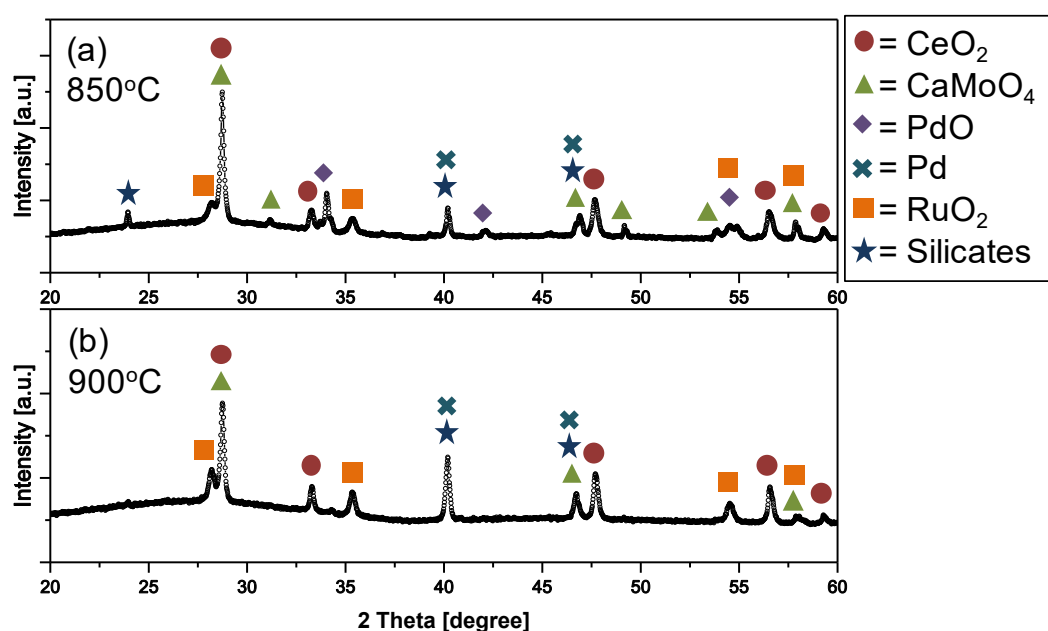


Figure 4.3 XRD of R7T7 glass samples prepared at (a) 850 and (b) 900°C. The ICDD cards used for identification: RuO_2 (01-088-0323)¹⁵⁶, Pd alloys (Pd: 01-087-0639, 01-088-2335)^{150, 151}, PdO (01-075-0584)¹⁵³, silicates - $\text{CaAl}_2\text{Si}_2\text{O}_8$ (00-041-1486)¹⁶⁰, and CaSiO_3 (00-018-0306)¹⁶¹, CaMoO_4 (01-085-0546, 01-077-2239)^{158, 159}, and CeO_2 (01-075-0076)¹⁴⁸.

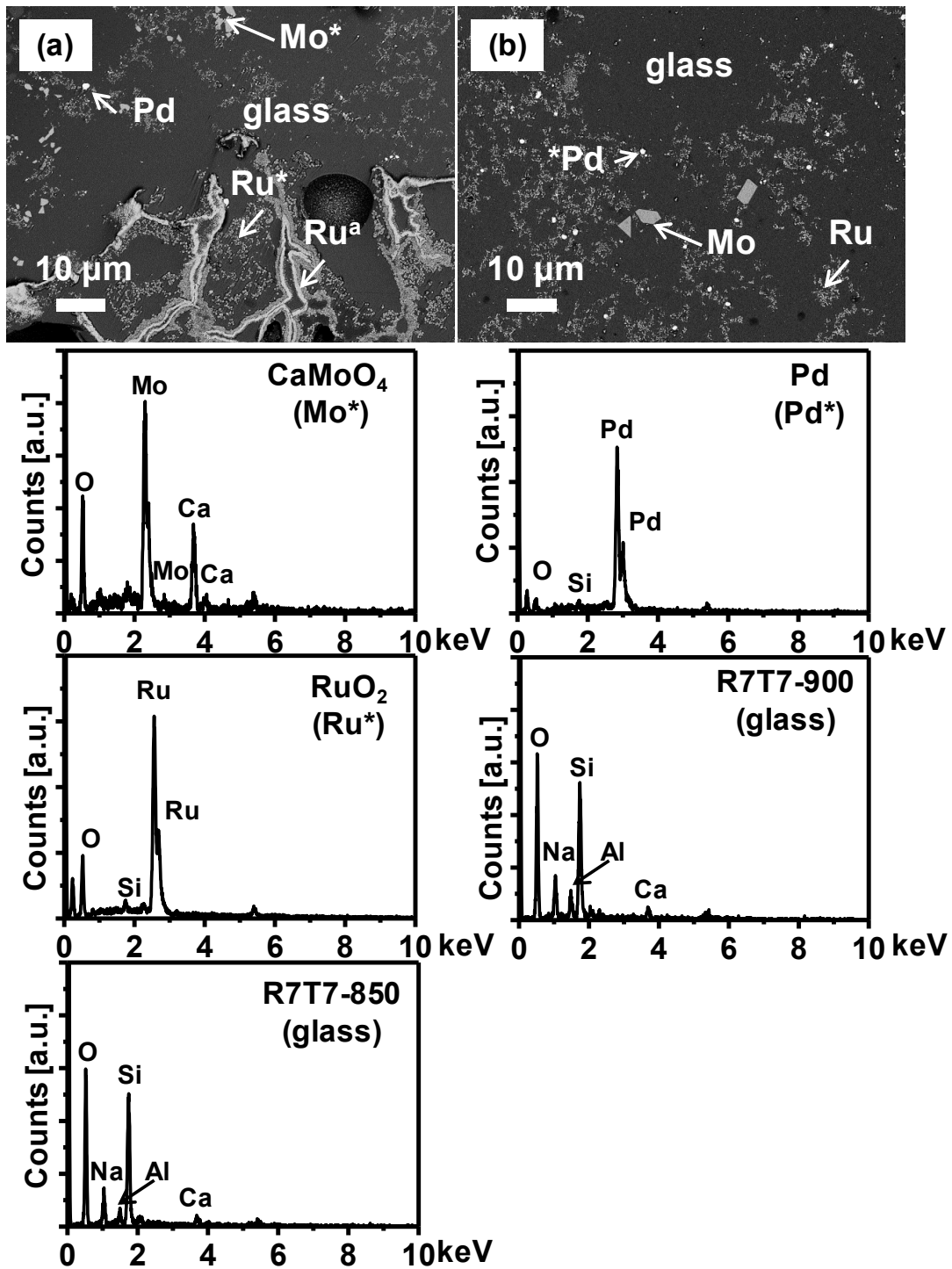


Figure 4.4 BSE images of (a) R7T7-850 and (b) -900. Generally, the dark grey contrast was glass, small ($< 0.1 \mu\text{m}$) intermediate grey phase was RuO_2 (Ru), large ($> 2 \mu\text{m}$) intermediate grey phase was powellite (Mo), and white regions were Pd (Pd). The RuO_2 was also found in the form of aggregates in some regions (Ru^a). *: EDX point analysis.

4.2.1.2 Melting at 1000 and 1100°C

The glass formed a block without visible pores on the bottom of the Pt crucible when the heating temperature was increased to 1000°C and above (Figure 4.5). The viscosity of the glass melt at this temperature was low enough¹⁸⁸ ($< 40 \text{ Nm}^{-2}\text{s}^{-1}$) for the gases decomposed from carbonates to be released. Theoretically, the undissolved Pd and RuO₂ crystals should sink to the bottom of glass as they have higher densities (~ 11 and 7 g/cm^3 respectively) than glass melt ($\sim 2.8 \text{ g/cm}^3$), however, the viscosity of the glass melt was presumably still high, hence the crystals were observed to be dispersed throughout the whole volume of the glass. The higher the processing temperature, the lower the glass melt viscosity and hence the more Pd and RuO₂ crystals should be found at the bottom. Figure 4.6 shows the top (plan view), cross section and bottom (plan view) images of R7T7 glass prepared at 1000 and 1100°C via optical microscopy. Figure 4.6(a) and (d) display the top of sample heated at 1100°C which contained less Pd and RuO₂ (~ 6.4 area %) than the sample produced at 1000°C (~ 20.4 area %), consistent with the lowering of viscosity with increasing processing temperature.

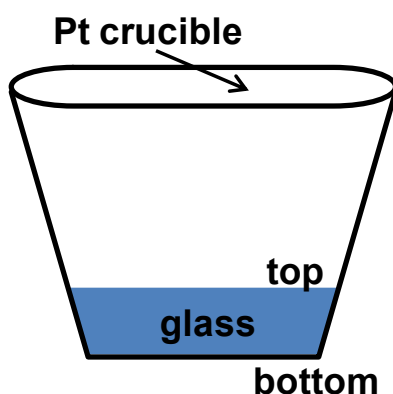


Figure 4.5 Schematic diagram of R7T7 samples prepared at 1000 and 1100°C after taking out from the furnace.

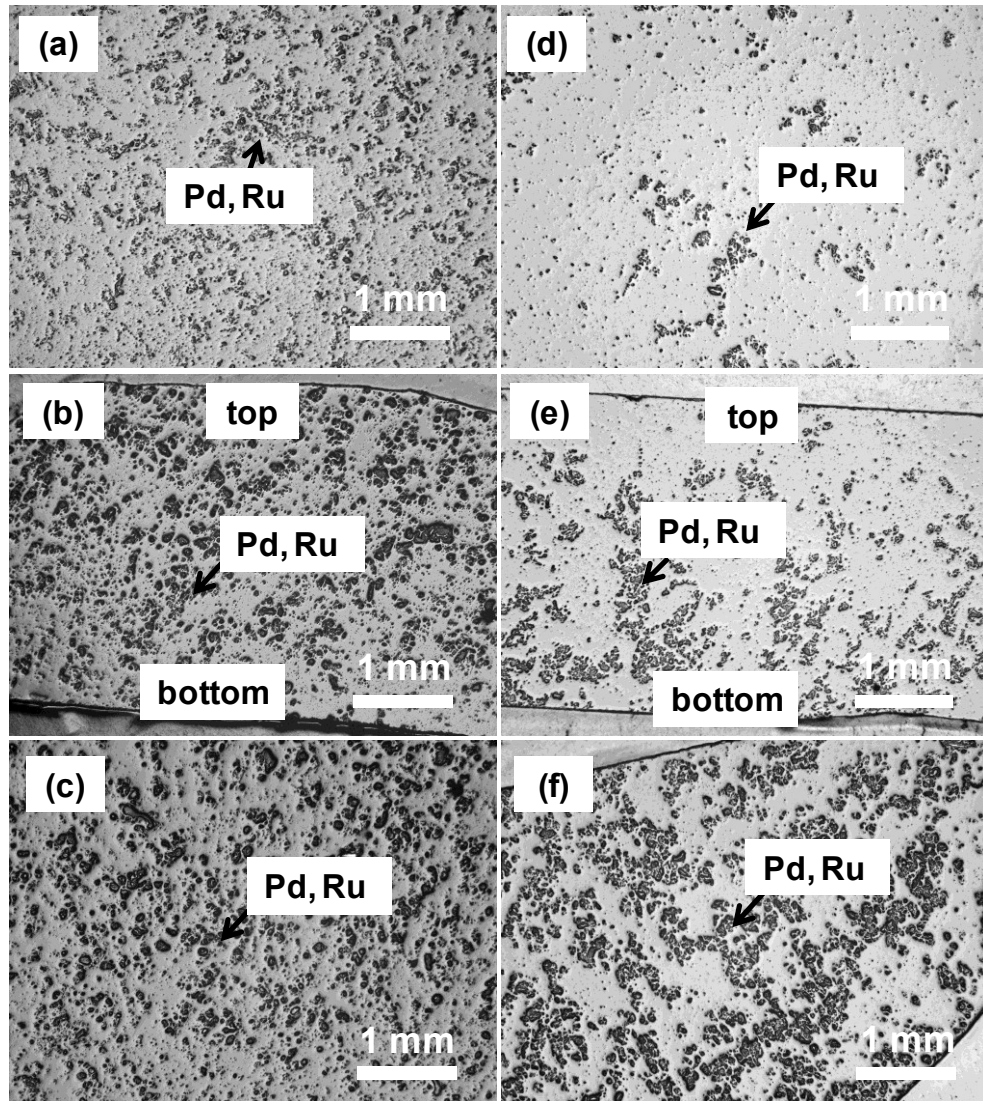


Figure 4.6 Optical microscopy images of plan view top (first row), cross section (middle row) and plan view bottom (last row) of R7T7 type glass heated at (a,b,c) 1000 and (d,e,f) 1100°C respectively. Pd and RuO₂ are the dark regions, a few microns in size.

Figure 4.7 shows the XRD of R7T7 samples heated at 1000 and 1100°C. The higher processing temperature (1100°C) dissolved CeO_2 in the glass while silicates were not present in either glasses prepared at 1000 or 1100°C. Figure 4.8 reveals undissolved Pd-Te alloy (white contrast) and RuO_2 (light grey) regions while the EDX spectra for the points analyzed (labelled with * in BSE images) are shown in the bottom of Figure 4.8. The grains of Pd-Te alloys are 1 - 4 μm in size and are generally larger than the metallic Pd grains found in the glass fabricated at 850 and 900°C (0.5 - 2 μm). The measured bulk density and apparent porosity of both glasses are similar ($2.83 \pm 0.06 \text{ g/cm}^3$ and $0.3 \pm 0.05 \text{ vol\%}$ respectively).

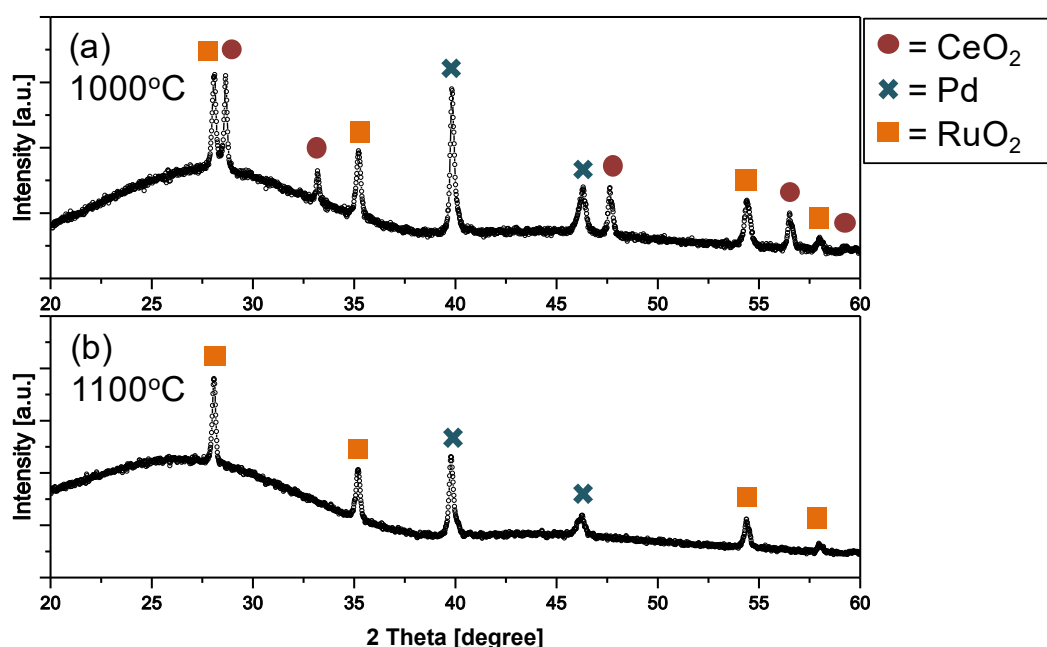


Figure 4.7 XRD of R7T7 glass processed at (a) 1000 and (b) 1100°C. The ICDD cards used for identification: RuO_2 (01-088-0286)¹⁵⁷, Pd alloys (Pd: 01-088-2335, 01-087-0641)^{151, 152}, and CeO_2 (01-078-0694)¹⁴⁹.

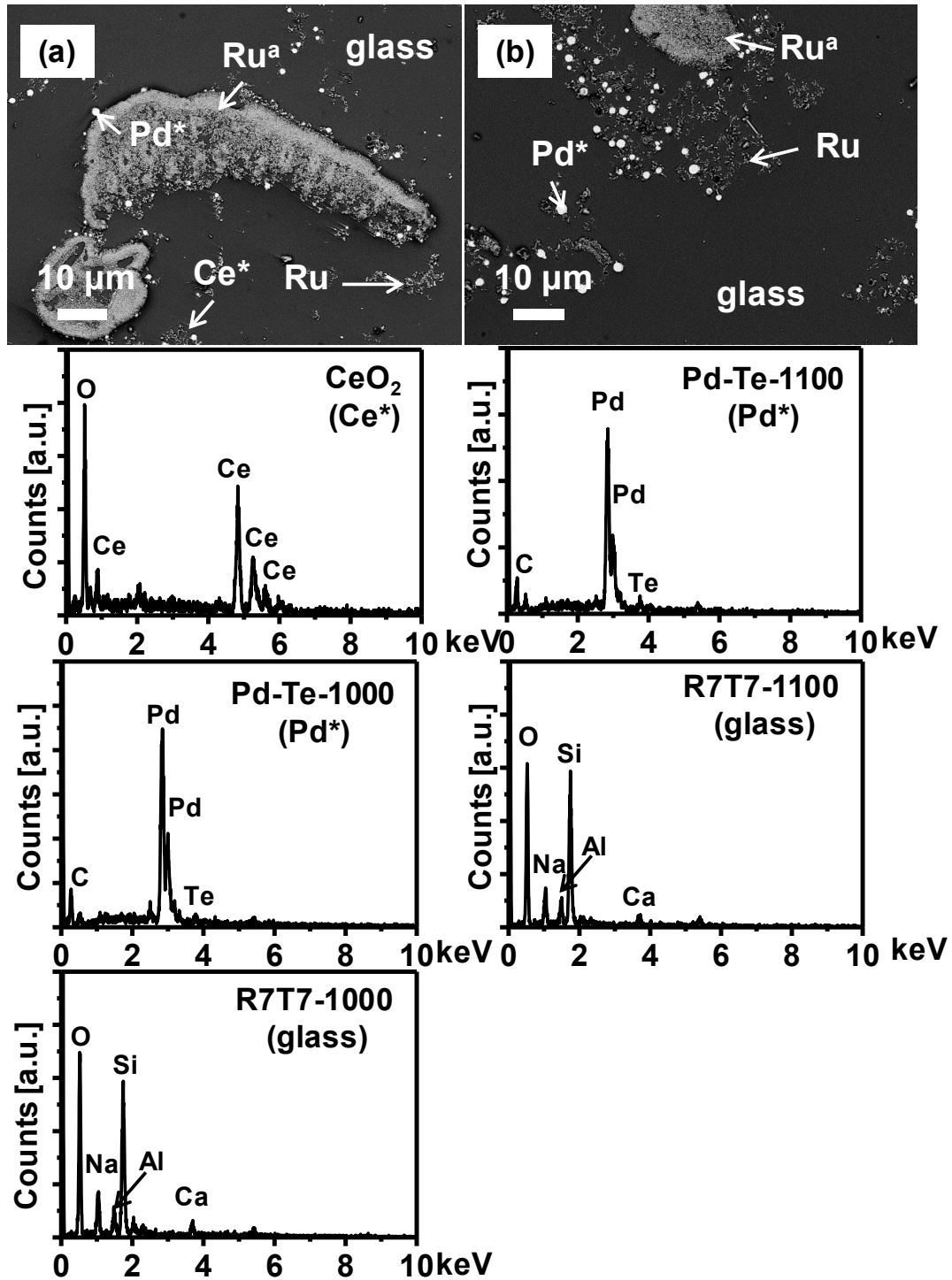


Figure 4.8 BSE images of R7T7 glass prepared at (a) 1000 and (b) 1100°C. The dark grey contrast is glass, small ($< 0.1 \mu\text{m}$) intermediate grey phase is RuO_2 (Ru), large ($> 0.5 \mu\text{m}$) intermediate grey phase was CeO_2 (Ce) and white regions were Pd-Te alloys. The RuO_2 was also found in the form of aggregates in some regions (Ru^a). The carbon present is from the coating required to obtain a conductive surface. *: EDX point analysis.

4.2.1.3 Melting at 1150 and 1200°C

Glass samples heated at 1150 and 1200°C formed similar shapes (Figure 4.5) to the glass prepared at 1000 and 1100°C but fewer Pd-Te alloys and RuO₂ (~2.0 area %) were retained near the top surface of glass samples (Figure 4.9a and d). The viscosity of the glass melt was low¹⁸⁸ ($< 20 \text{ Nm}^{-2}\text{s}^{-1}$) and hence the gases from decomposition of carbonates were able to be released and most of the undissolved Pd alloys and RuO₂ settled to the bottom of the glass (Figure 4.9 c and f).

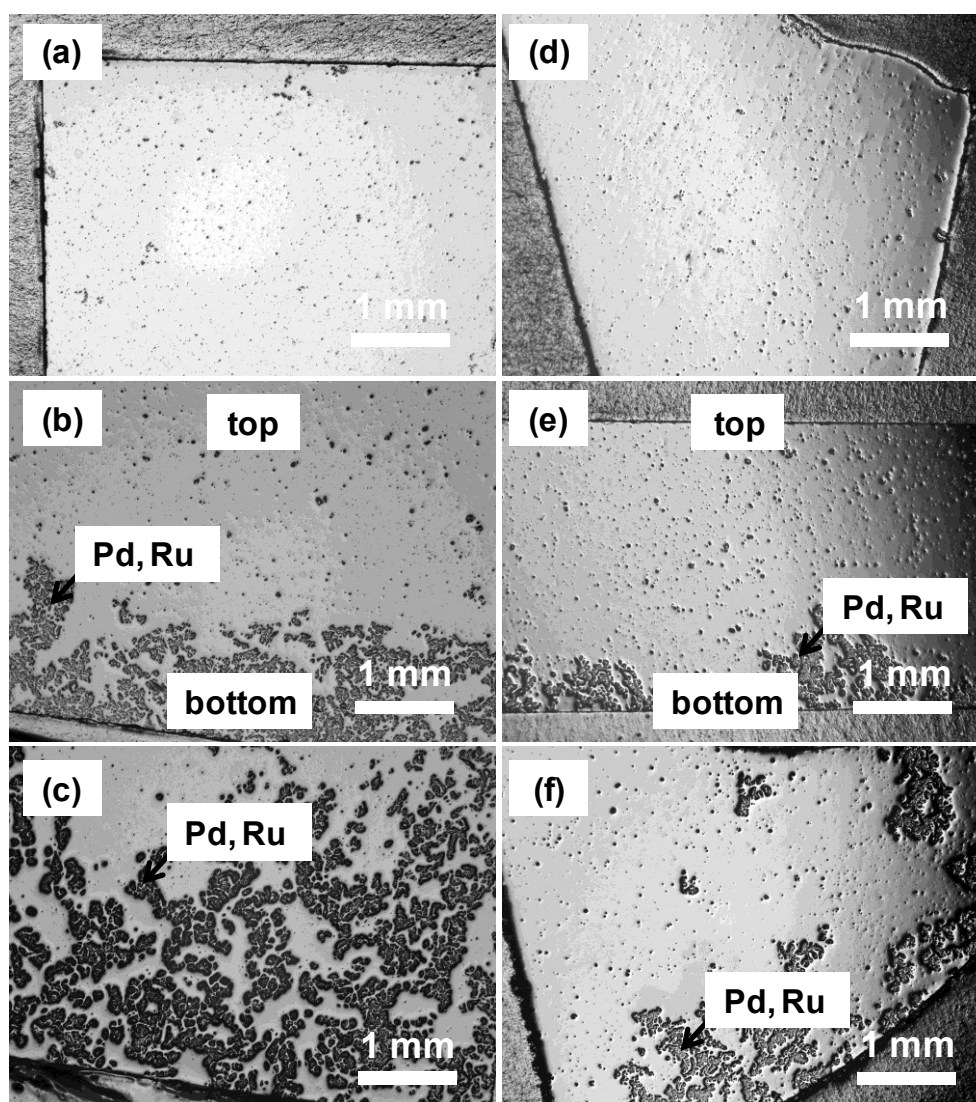


Figure 4.9 Optical microscopy images of top plan view (first row), cross section (middle row) and bottom plan view (last row) of R7T7(a,b,c) -1150 and (d,e,f) -1200°C respectively.

Figure 4.10 shows the XRD of top and bottom of R7T7 glasses prepared at 1150 and 1200°C. The top of both glasses displayed a factor of ~30 times and ~5 times lower peak intensity relative to the bottom, for RuO₂ and metallic Pd respectively, and hence confirmed the observations from optical microscopy (Figure 4.9). The Pd-Te particles with low Te concentration (less than 20 atomic%) were detected to have a similar structure to pure metallic Pd^{190, 191}. For the R7T7 glass prepared here, their Pd-Te composition was in a range of atomic Pd ratio of 80 – 95 and Te ratio of 5 – 20 which was analyzed via SEM/EDX later. The peaks of Pd alloys in Figure 4.10 (b) were different to others. This may be due to various ratio of Pd-Te precipitates in the glass. Chattopadhyay et al.¹⁹⁰ reported that the lattice parameter *a* increases when concentration of Te increases and hence the peaks of XRD patterns detected decrease. The Te concentration of Pd-Te particles in the back of R7T7 glass prepared at 1150°C was lower than R7T7 produced at 1200°C and hence the peaks increased.

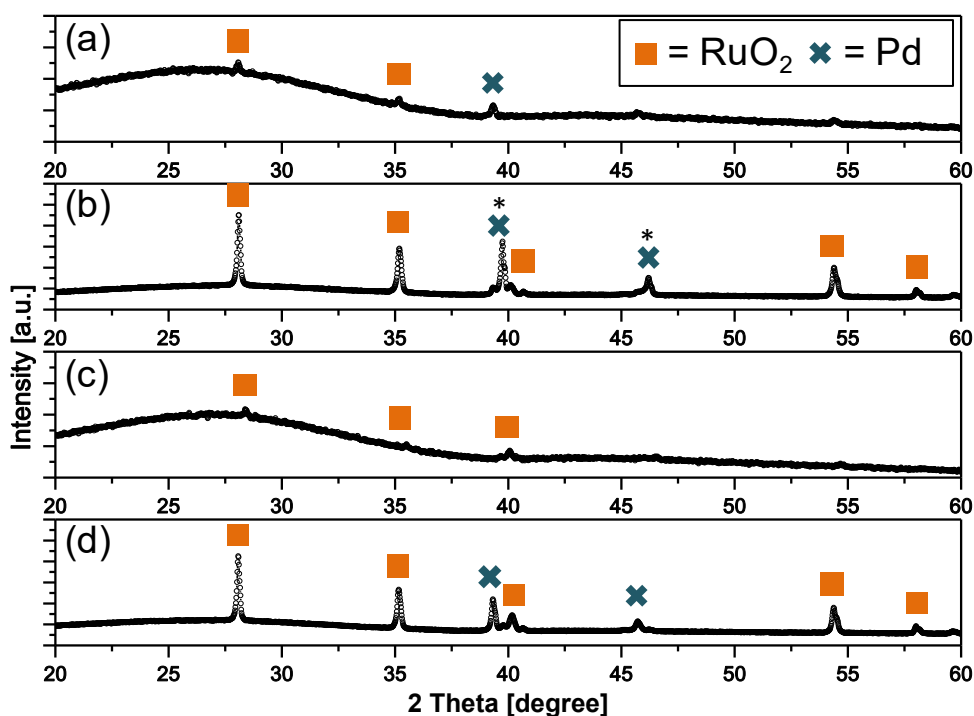


Figure 4.10 XRD of top (a,c) and bottom (b,d) of R7T7 glass prepared at (a,b) 1150 and (c,d) 1200°C respectively. The ICDD cards used for identification: RuO₂ (01-088-0286)¹⁵⁷, and Pd alloys (Pd: 01-087-0641, 01-087-0639*)^{150, 152}. The peaks of Pd alloys in (b) is from ref.¹⁵⁰ labelled with *.

Figure 4.11 shows undissolved Pd-Te alloys (white contrast) and RuO₂

regions (intermediate grey) in the glass matrix while the EDX spectra of analyzed points (labelled with * in the BSE images) are shown at the bottom of Figure 4.11. The main composition of the glass region in all R7T7 glass samples was similar which was in a range of atomic O ratio of 72.0 - 74.5; Na ratio of 6.0 - 8.5; Al ratio of 1.5 - 2.5; Si ratio of 15.5 - 17.0 and Ca ratio of 1.5 - 2.0. The measured bulk density and apparent porosity of both glasses were 2.81 ± 0.04 g/cm³ and 0.2 ± 0.03 vol% respectively.

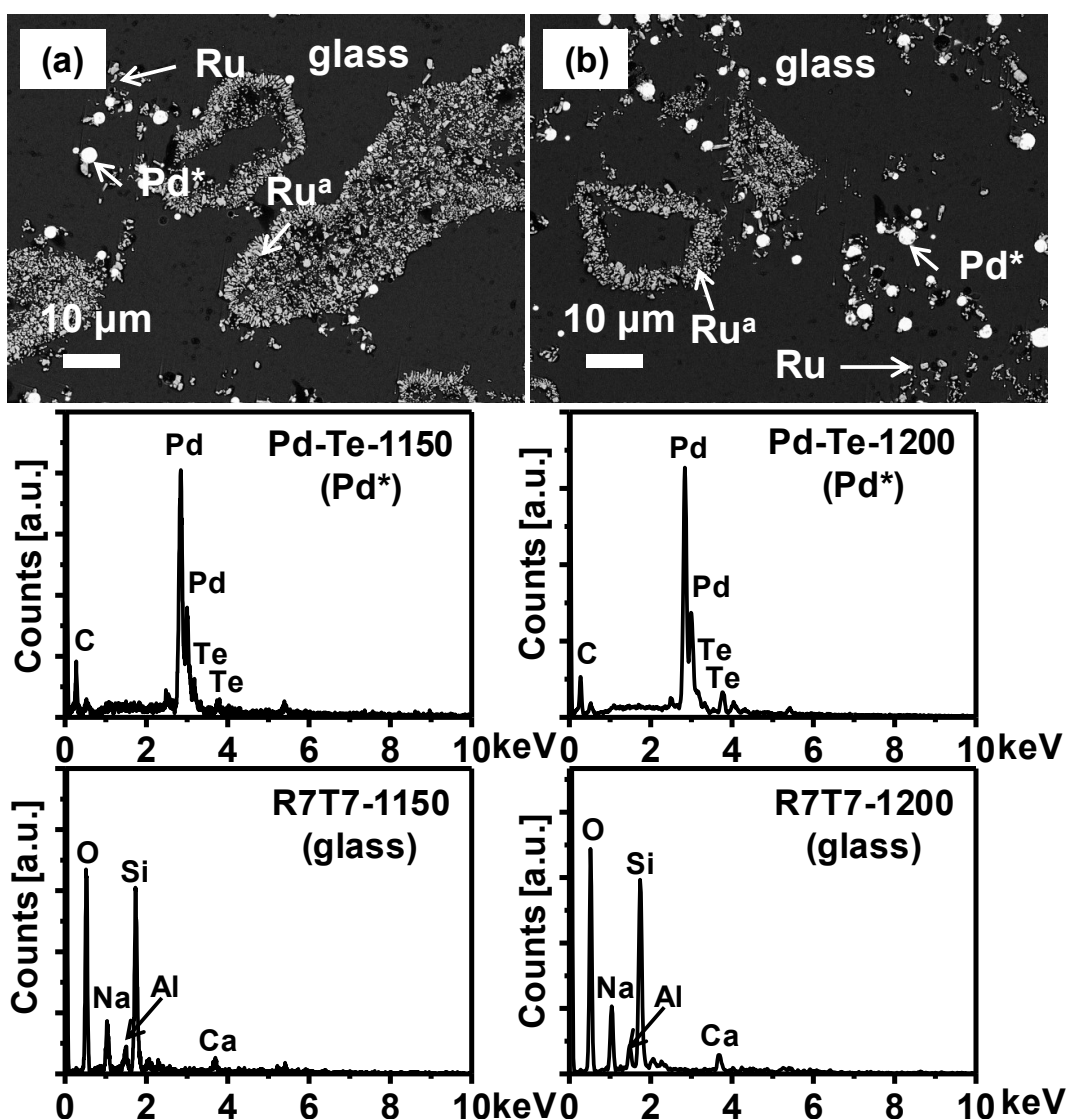


Figure 4.11 BSE images of R7T7 glass prepared at (a) 1150 and (b) 1200°C. Generally, the dark grey contrast was glass, small (< 0.1 μm) intermediate grey phase was RuO₂ (Ru), and white regions were Pd-Te alloys (Pd). The aggregate RuO₂ was labelled as Ru^a. *: EDX point analysis. The carbon present is from the coating required to obtain a conductive surface.

4.3 HIPed glass

R7T7 glass was prepared via HIPing to compare with the melting route in this project. The glass fabricated via the melting route still retained RuO₂ crystals and Pd alloys even when the processing temperature was increased from 1100 to 1200°C. The effect of applied pressure for those undissolved wastes was examined via HIPing technology. The HIPing conditions (Table 2.9) were designed based on the results from glass prepared from melting method. All HIPed glass contained 20 wt.% waste loading. Two R7T7 glasses were HIPed at 1100°C at a low (10 MPa) and a high (100 MPa) pressure. The final R7T7 sample was HIPed at 1200°C at the lower (10 MPa) pressure. Samples are labelled using following identifying code: *HIP-HIPing temperature- pressure-dwell time* (i.e R7T7 HIP-1100-10-3 means that the R7T7 glass sample was HIPed at 1100°C and 10 MPa for 3 h). The HIPed samples were analysed using optical microscopy, XRD and SEM to determine their phase content and microstructure. The ICDD reference cards used to identify X-ray patterns of crystals formed are listed in Table 2.12.

Figure 4.12 shows optical photos of HIP canisters before and after HIPing. All canisters were deformed on the sides, top and bottom but without any damage to the welds. This deformation is suggestive of a successful HIPing. However, the wall of the canisters did not deform as much as the bottom and the top. The HIPed glass coated and adhered to the wall of the canister and hence the glass samples were broken to small pieces (< 10× 10× 2 mm) when opening the canister. Figure 4.13 exhibits the shape of HIPed glass in the HIP canister based on the observation of appearance of HIP canisters and two parts of HIPed glass (edge and central region) characterised in the following sections.

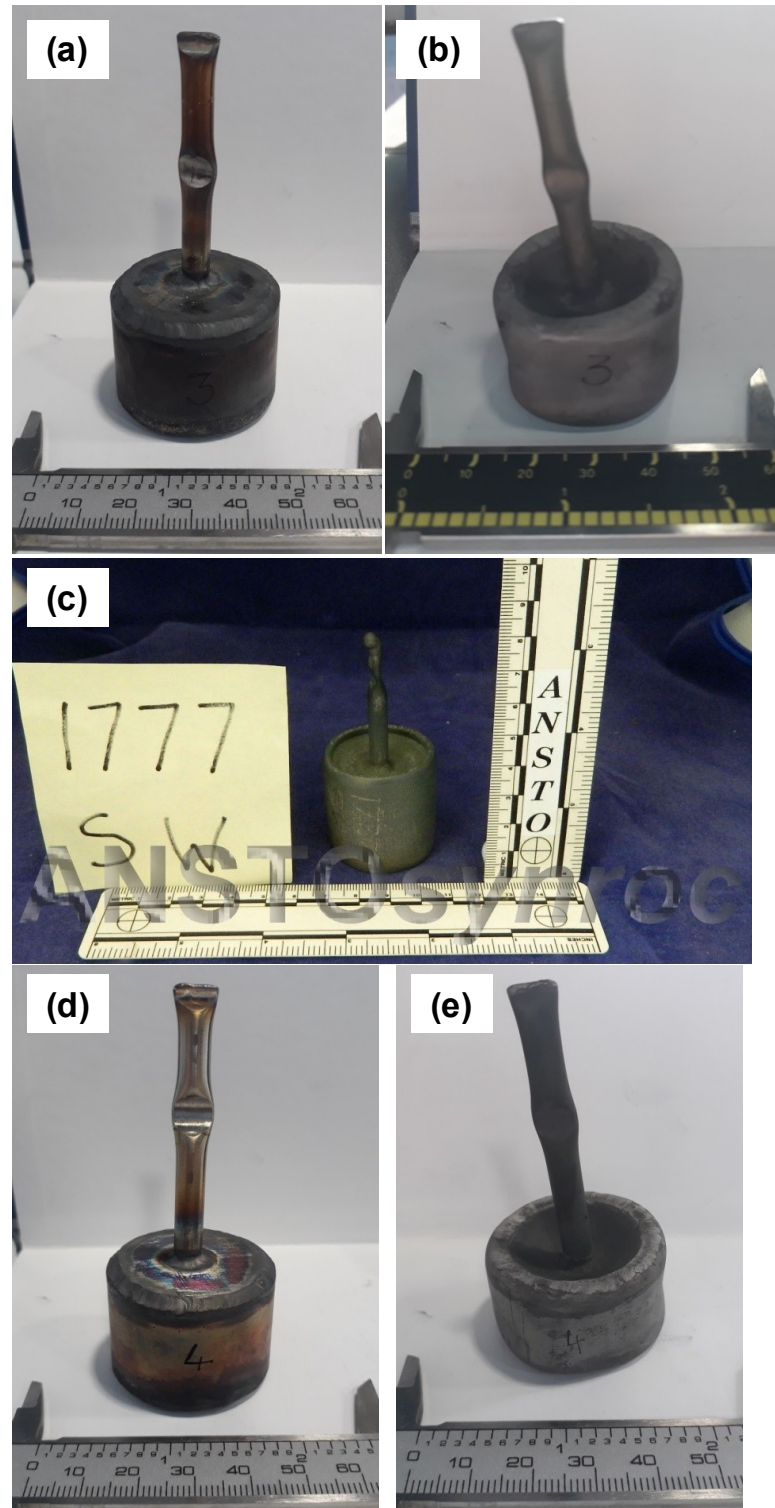


Figure 4.12 Photos of HIP canisters (a,d) before HIPing and after HIPing at (b) 1100°C and 10 MPa, (c) 1100°C and 100 MPa and (e) 1200°C and 10 MPa. The deformation of canisters indicated that the three samples have been HIPed successfully. Provided by Dr. Laura Gardner, the University of Sheffield and Dr. Daniel Gregg, ANSTO.

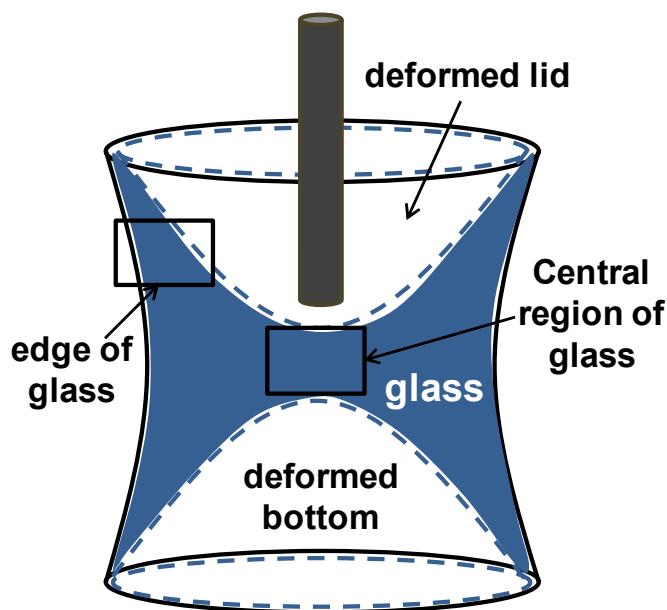


Figure 4.13 Schematic diagram of HIPed R7T7 glass canister and two parts of HIPed glass characterised in this chapter.

4.3.1 Effect of HIPing

The HIPed glass samples were too brittle to obtain a large block ($> 10 \times 10 \times 2$ mm) upon opening the canisters and thus MCC-1 leach testing (which requires a relatively large volume of unbroken sample) described in Chapter 5 could not be conducted for the particular sample. Moreover, some visible metal/alloys appeared on the edges of the samples (Figure 4.14 a,c,e). The R7T7 sample HIPed at 1100°C and 10 MPa for 3 h exhibited some visible metallic regions, which were identified as Fe via EDX later (white regions in Figure 4.14a), on the edges of the glass. The colour of this metallic Fe partly turned to rust colour (brown) which indicated this metallic Fe oxidised to Fe_2O_3 (dark grey contrast) upon polishing. Figure 4.14 (c) and (e) displayed visible alloys (white areas) consisting of Pd, Mo, Ru, Ag, Te, Zn, Fe, and Cr in the HIPed R7T7 (1100°C , 100 MPa, 2 h and 1200°C , 10 MPa, 3 h) samples. The central part of HIPed glass samples contained some bubbles, RuO_2 and alloys as confirmed by SEM/EDX later.

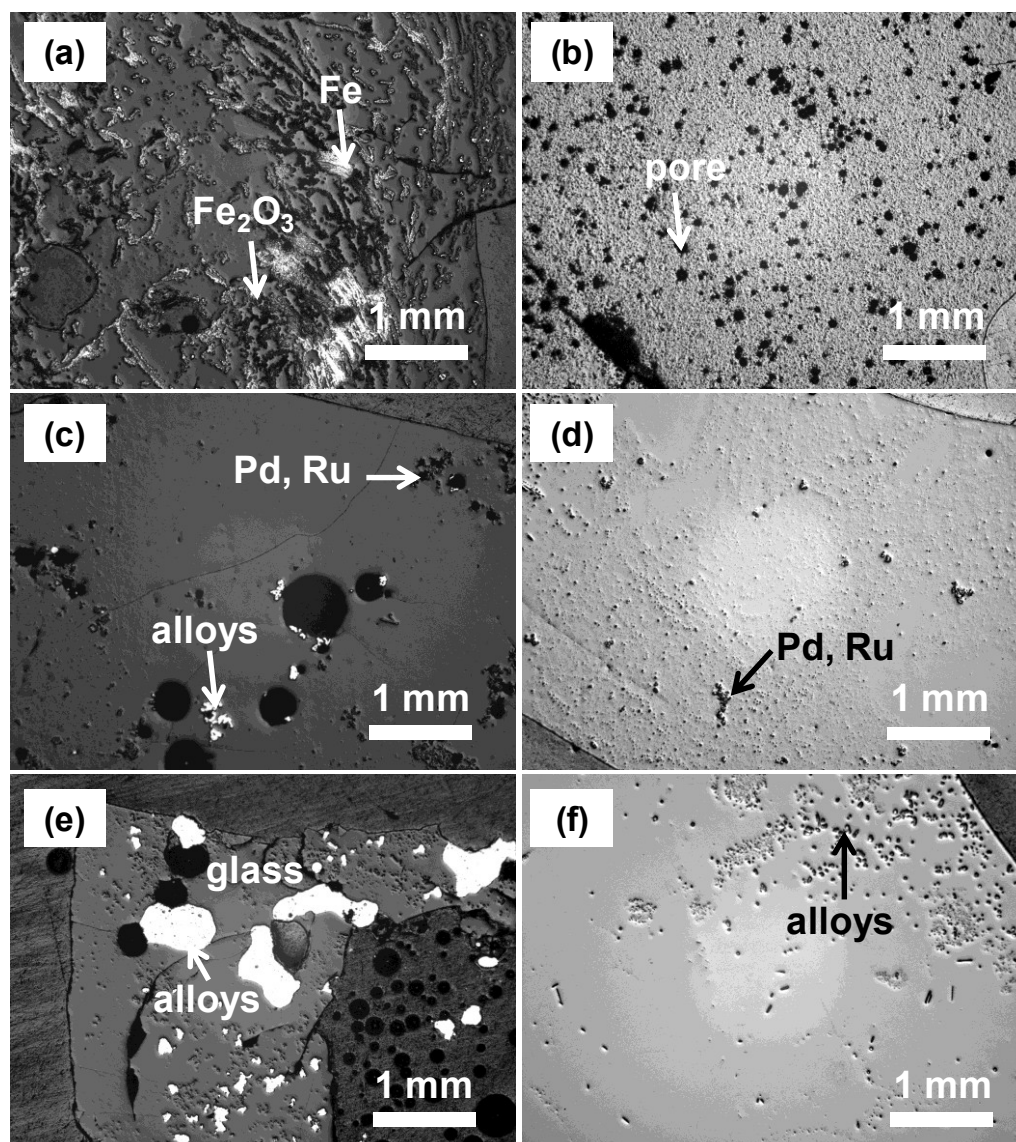


Figure 4.14 Optical microscopy images of the edge (left column) and centre (right column) parts of R7T7(a,b) HIP-1100-10-3, (c,d) HIP-1100-100-2 and (e,f) HIP-1200-10-3 respectively.

XRD (Figure 4.15) showed that the sample HIPed at 1100°C and 10 MPa for 3 h formed silicates, undissolved oxides, and Al-Cr-Fe metal. When the HIPing pressure was increased to 100 MPa, the silicates were not present (having apparently dissolved into the sample) but some undissolved oxides and alloys were retained (Figure 4.16). Furthermore, the HIPed glass (1200°C, 10 MPa, 3 h) incorporated all oxides but still formed alloys (Figure 4.17). All of the HIPed glass contained Al-Cr-Fe alloy which presumably was due to reactions/corrosions between glass and canister (316 grade stainless steel) during HIPing.

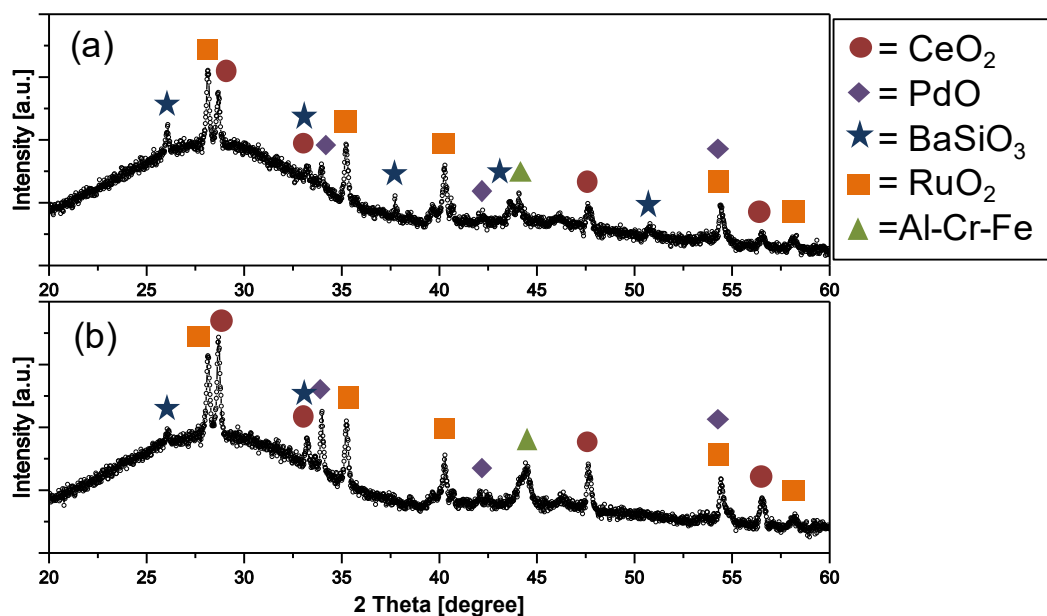


Figure 4.15 XRD of (a) edge and (b) centre of R7T7 HIP-1100-10-3 sample. The ICDD cards used for identification: RuO_2 (01-073-1469)¹⁵⁵, PdO (01-075-0584)¹⁵³, BaSiO_3 (01-070-2112)¹⁶², AlCrFe_2 (00-042-1486)¹⁴⁵ and CeO_2 (01-075-0076)¹⁴⁸.

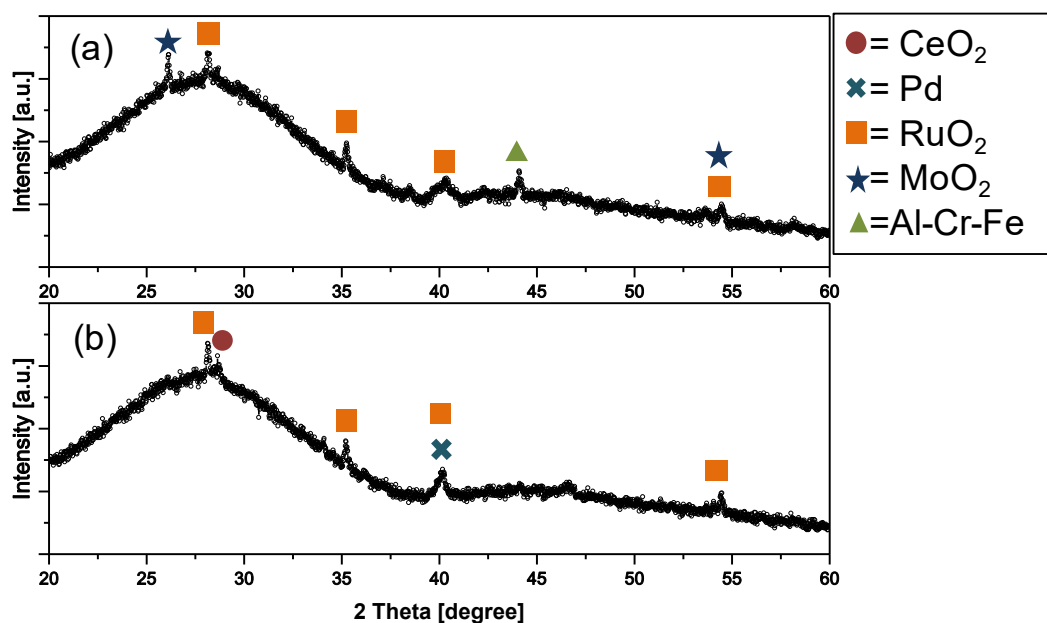


Figure 4.16 XRD of (a) edge and (b) centre of R7T7 HIP-1100-100-2 sample. The ICDD cards used for identification: RuO_2 (01-073-1469)¹⁵⁵, Pd alloys (Pd : 01-087-0639)¹⁵⁰, MoO_2 (01-076-1807)¹⁴⁷, AlCrFe_2 (00-042-1486)¹⁴⁵ and CeO_2 (01-075-0076)¹⁴⁸.

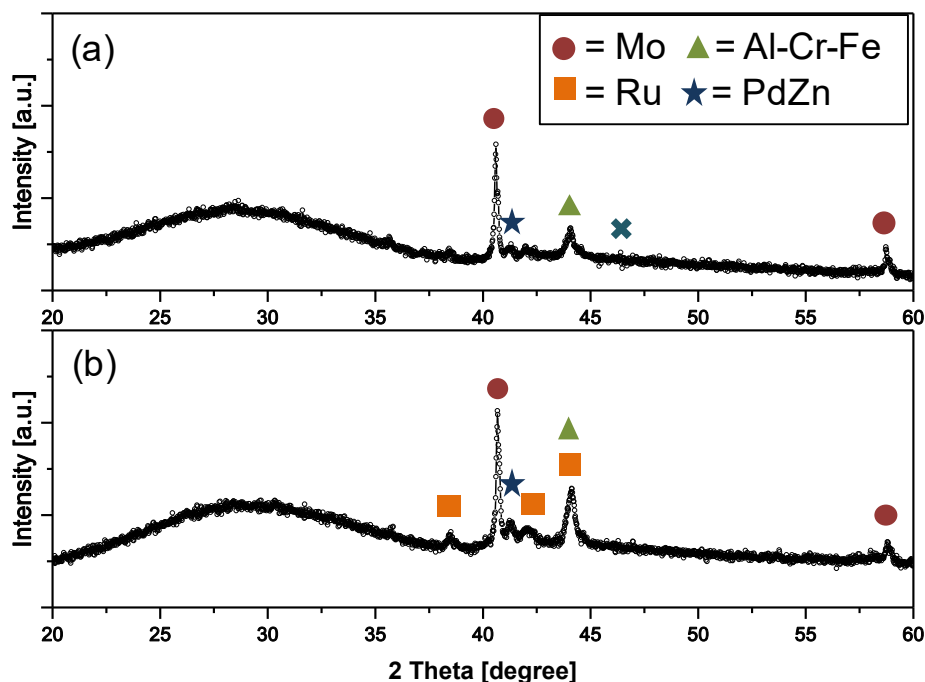


Figure 4.17 XRD of (a) edge and (b) centre of R7T7 HIP-1200-10-3 sample. The ICDD cards used for identification: Ru (01-088-2333)¹⁵¹, PdZn₂ (00-031-0942)¹⁵⁴, AlCrFe₂ (00-042-1486)¹⁴⁵ and Mo (00-042-1120)¹⁴⁶.

Figures 4.18 – 4.20 show Cr-Fe, Fe₂O₃, alloys and oxide regions at the edges and centre of HIPed R7T7 samples. The size of the alloys embedded in the HIPed R7T7 glass matrix were larger (~1 - 1000 μm) than in the samples obtained by the melting route where they were <10 μm . Furthermore, the large alloy inclusions were composed of Pd, Mo, Ru, Ag, Te, Zn, Fe, and Cr. This composition is considerably more complex than of the alloys found in the glass samples prepared via melting which only contained Pd and Te. By comparison, the glass matrix forming the bulk of the material had similar main compositions (O, Na, Al, Si, Ca, total > 95 atomic%) in samples from both the HIPing and melting routes (Figures 4.11 and 4.18 – 4.20). The measured bulk densities and apparent porosities of HIPed glasses were also similar (density of 2.81 ± 0.06 g/cm³ and porosity of 1 ± 0.11 vol%).

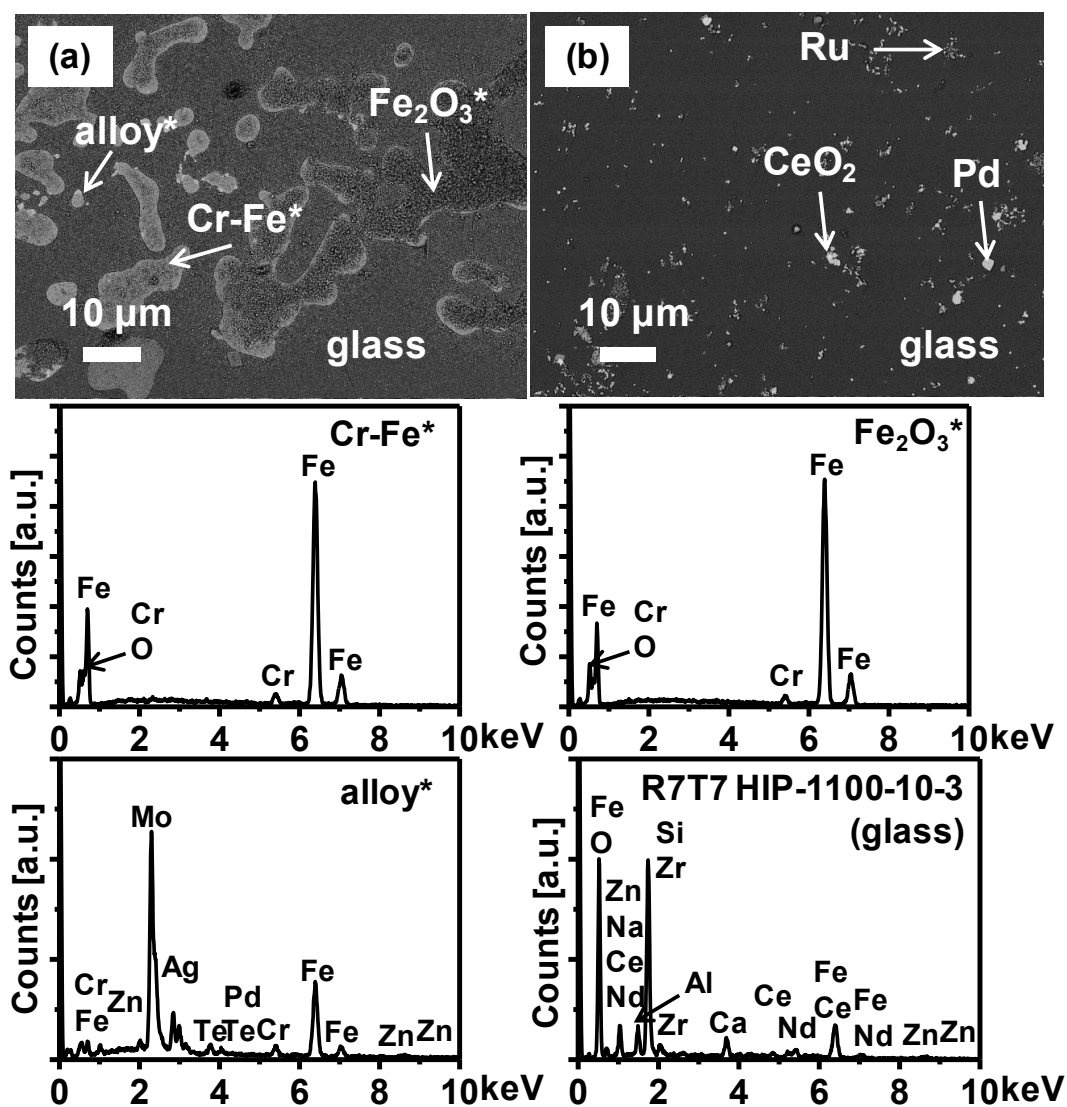


Figure 4.18 BSE images of (a) edge and (b) centre of HIPed sample HIP-1100-10-3. In general, the dark grey background was glass, small ($< 0.1 \mu\text{m}$) intermediate grey phase was RuO_2 (Ru), large ($1\text{--}1000 \mu\text{m}$) intermediate grey phases were Cr-Fe, Fe_2O_3 and complex alloys (more than 3 different metals) and white regions were Pd alloys. *: the EDX points analysis.

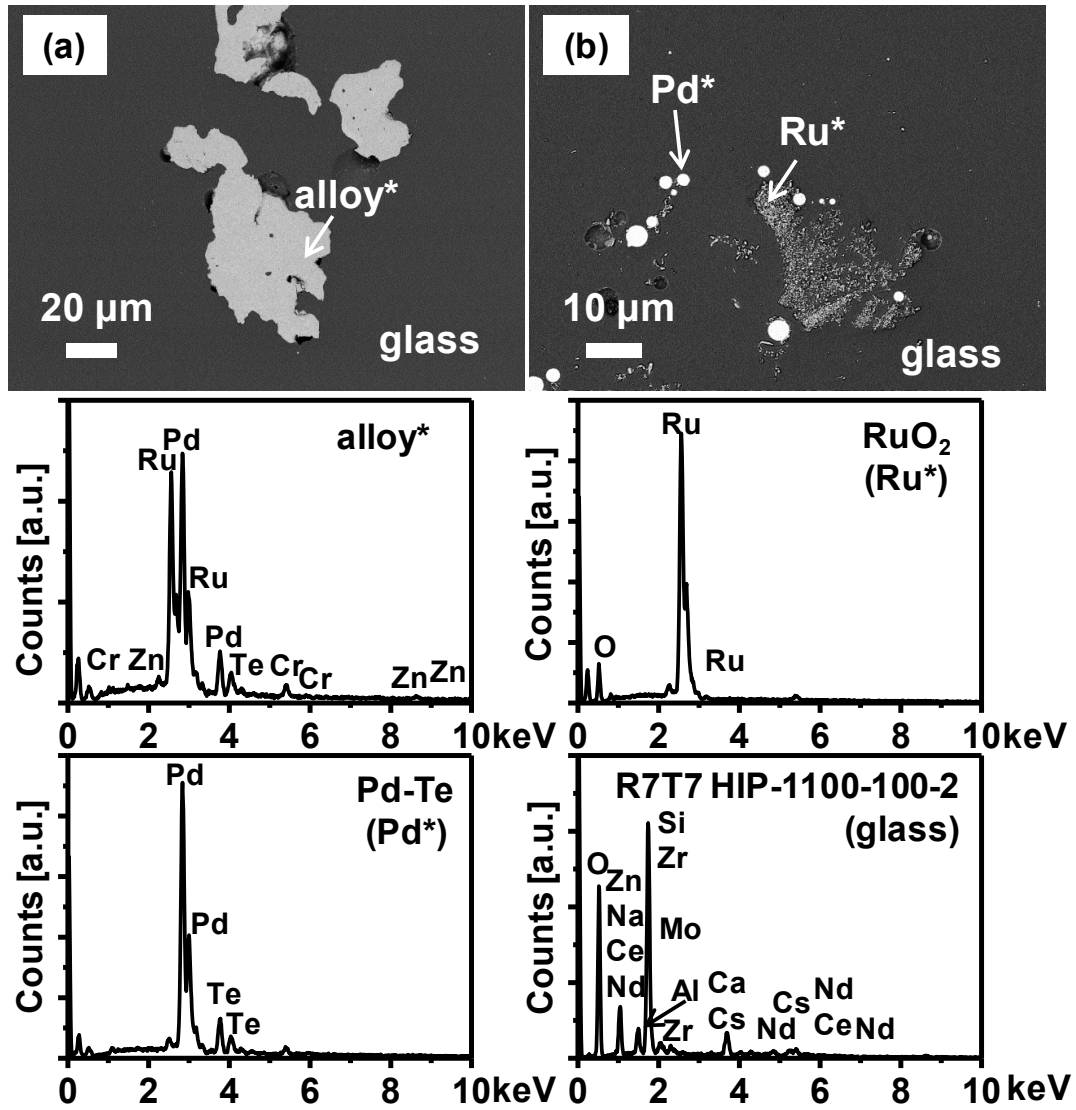


Figure 4.19 BSE images of (a) edge and (b) centre of HIPed sample HIP-1100-100-2. The dark grey background was glass, small ($< 0.1 \mu\text{m}$) intermediate grey phase was RuO_2 (Ru), large ($1\text{--}1000 \mu\text{m}$) intermediate grey phase was complex alloys (more than 3 different metals) and white regions were Pd-Te alloys. *: the EDX points analysis.

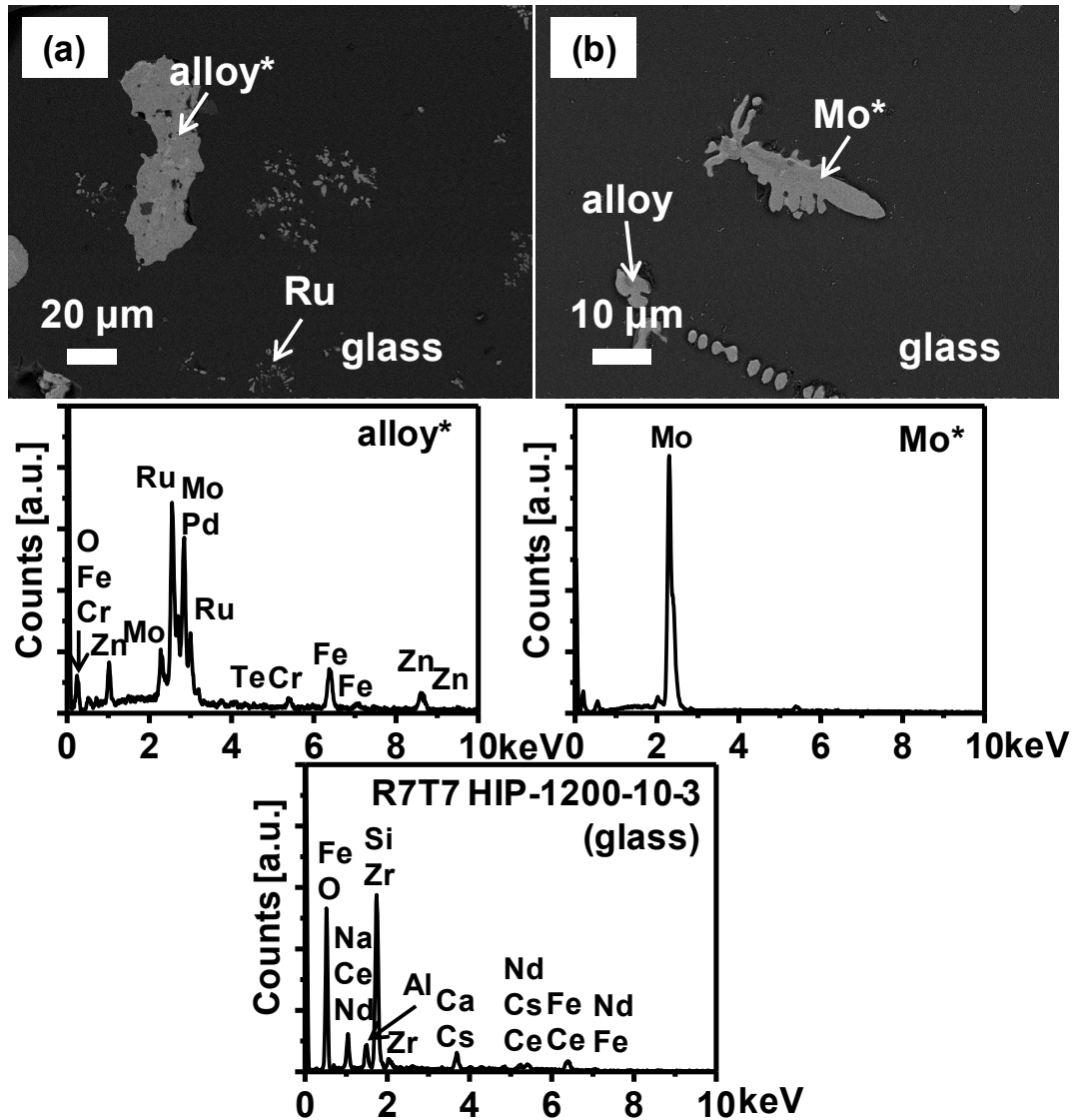


Figure 4.20 BSE images of (a) edge and (b) centre of HIPed sample HIP-1200-10-3. The dark grey background was glass, small ($< 0.1 \mu\text{m}$) intermediate grey phase was RuO_2 (Ru), and large (1-1000 μm) intermediate grey phases were Mo and complex alloys (more than 3 different metals). *: the EDX points analysis.

4.4 Summary

Both melting vitrification and HIPing methods have produced R7T7 glass successfully which incorporated most of the EURO-GANEX waste elements into the glass matrix. Table 4.1 summarises the main characteristics of the glass samples produced in this chapter. However, both glass samples prepared via melting and HIPing still have difficulty in incorporating some elements (i.e. Ru, Pd, Te, Mo) which have low solubility in borosilicate glass. The undissolved crystals may affect the physical behaviour of the glass melt and cause higher viscosity affecting the vitrification process^{192, 193, 194} while they sink to the bottom of the melter and may clog the melter nozzle^{195, 196}. The pressure applied to the glass did not enhance the solubility of those elements. Considering the process complexity, the HIPing procedure is not a good method to produce R7T7 borosilicate glass and to date there has been no large scale demonstration of HIPing of tonne quantities of nuclear waste glass.

Table 4.1 Summary of R7T7 samples in this chapter.

	Processing conditions	Apparent porosity (vol%)	Bulk density (g/cm ³)	Crystals present
R7T7-850	Heat at 850°C			CeO ₂ , CaMoO ₄ , PdO, Pd, RuO ₂ , Silicates
R7T7-900	Heat at 900°C			CeO ₂ , CaMoO ₄ , Pd, RuO ₂ , Silicates
R7T7-1000	Heat at 1000°C	0.3 ± 0.05	2.83 ± 0.07	CeO ₂ , Pd-Te, RuO ₂
R7T7-1100	Heat at 1100°C	0.3 ± 0.04	2.83 ± 0.05	Pd-Te, RuO ₂
R7T7-1150	Heat at 1150°C	0.2 ± 0.03	2.82 ± 0.04	Pd-Te, RuO ₂
R7T7-1200	Heat at 1200°C	0.1 ± 0.02	2.81 ± 0.04	Pd-Te, RuO ₂
R7T7 HIP-1100-10-3	HIP: 1100°C; 10 MPa; 3 h	1.0 ± 0.09	2.82 ± 0.05	CeO ₂ , Al-Cr-Fe, Fe ₂ O ₃ , PdO, RuO ₂ , complex alloys, Silicates
R7T7 HIP-1100-100-2	HIP: 1100°C; 100 MPa; 2 h	0.8 ± 0.11	2.81 ± 0.05	CeO ₂ , Al-Cr-Fe, Pd-Te, RuO ₂ , MoO ₂ , complex alloys,
R7T7 HIP-1200-10-3	HIP: 1200°C; 10 MPa; 3 h	1.1 ± 0.12	2.81 ± 0.07	Mo, Al-Cr-Fe, Ru, complex alloys

Chapter 5: Durability of candidate wasteforms

This chapter discusses the chemical durability of selected HUPed and HIPed Synroc-Z and R7T7 glass wasteforms when tested using the MCC-1 leach test at 90°C for period up to 28 days in deionised (DI) water. In Chapter 3, Synroc-Z was developed as a reformulation of Synroc-C to suit the waste from EURO-GANEX and an appropriate set of HUPing conditions were identified that gave high density (< 0.5 vol% porosity), optimized phase composition and low volatilisation¹⁹⁷. Three factors that may have an effect on durability were considered: (i) HUPing conditions, (ii) waste loading and (iii) surface roughness. The HUPing variables were temperature, pressure and dwell time. HIPed Synroc-Z (1200°C, 20 MPa, 3 h) and R7T7 glass heated at 1200°C for 3 h were chosen to be compared against HUPed Synroc-Z. Samples were prepared by cutting as-synthesized discs and grinding the faces with P1200 (~15 µm) diamond abrasive with alcohol based lubricant to meet the standard test method roughness conditions⁹⁶. HUPed Synroc-Z (1200°C, 20 MPa, 3 h) and R7T7 (prepared by melting route at 1200°C for 3 h) samples were also prepared with a higher quality surface finish to consider the sensitivity of the leach test to roughness. These were additionally polished to a 1 µm finish using an alcohol based diamond suspension. The preparation schedule and leach test parameters are summarised in Table 5.1. The leachates were analyzed by ICP/MS while the leached samples were characterised by GIXRD, XRD, SEM, TEM and AFM to reveal the formation of possible secondary phases during the test.

Table 5.1 Selected HUPed and HIPed Synroc and R7T7 samples and their leach testing period.

Sample ID	Processing conditions	Leach testing period (days)
HUPed Synroc-Z 1200-20-3	HUP: 1200°C; 20 MPa; 3 h	3, 7, 14, 28
HUPed Synroc-Z 1150-20-3	HUP: 1150°C; 20 MPa; 3 h	28
HUPed Synroc-Z 1050-20-3	HUP: 1050°C; 20 MPa; 3 h	28
HUPed Synroc-Z 1200-40-3	HUP: 1200°C; 40 MPa; 3 h	28
HUPed Synroc-Z 1200-10-3	HUP: 1200°C; 10 MPa; 3 h	28
HUPed Synroc-Z 1200-20-5	HUP: 1200°C; 20 MPa; 5 h	28
HUPed Synroc-Z 1200-20-0.5	HUP: 1200°C; 20 MPa; 0.5 h	28
HUPed Synroc-Z 35 wt. %	HUP: 1200°C; 20 MPa; 3 h	3, 7, 14, 28
HIPed Synroc-Z HIP-1200-20-3	HIP: 1200°C; 20 MPa; 3 h	3, 7, 14, 28
R7T7-1200 glass	Melted at 1200°C; 3 h	3, 7, 14, 28

5.1 HUPed Synroc-Z

5.1.1 Effect of HUPing conditions

HUPing conditions were selected to allow the effect of temperature, pressure and dwell time to be related to leach resistance. The pH values of the deionised (DI) water leachant were 5.5 - 6, at the start of the test while the pH values of leachates after testing were 4.5 - 5.5. A small volume (5 ml) of leachants and leachates were collected for pH value measurement using a pH meter. The pH values of DI water used as leachant are supposed to be 7, but they absorb CO₂ in the air and hence values lower than 7 were obtained. 2 wt.% nitric acid was added to leachates to dissolve all elements in solution stably as some elements such as Zr, Ru are not completely soluble in near-neutral solution at room temperature. The leachates were diluted by 10 times and their composition was measured using ICP-MS. Figure 5.1 reveals a decrease in normalized leach rates of precursors (Ba and Ca), and the three most soluble waste elements (Cs, Mo and Sr) against time for Synroc-Z samples HUPed at 1200°C and 20 MPa for 3 h. The concentrations of Ti and Al in leachates were all extremely low (below the detection limit: < 10 ppb) and thus no obvious trend was observed. The leach rates of FPs range from 0.1 to 1 gm⁻²d⁻¹ on average for the first three days of leaching. All values are found to decrease by one order of magnitude when leaching is extended to 28 days.

Table 5.2 and Figure 5.2 show how HUPing conditions affected durability, giving the leachate compositions obtained from Synroc-Z samples prepared under different HUPing conditions after a 28 day test. In most cases, the element losses of Ca, Ba, Cs, Mo and Sr were similar, apart from the sample fabricated at 1050°C and 20 MPa for 3 h which occurred 2 - 60 times faster than from the other samples (Figure 5.2a). This is likely due to its higher porosity (~2.5 vol.% vs. < 0.5 vol%) as it was consolidated at the lowest temperature (1050°C) (more details were given in section 3.3.1). The effects of pressure and dwell time were negligible as the leach rates of Ba, Cs, Mo and Sr largely overlap in Figure 5.2 (b). However, this was not the case for the Ca dissolution rate. The Synroc-Z HUPed at the highest pressure (40 MPa) had the slowest Ca leach rate while the Synroc-Z HUPed at the shortest dwell time displayed the fastest Ca dissolution rate. Reasons for this behaviour will be discussed in

Chapter 7.

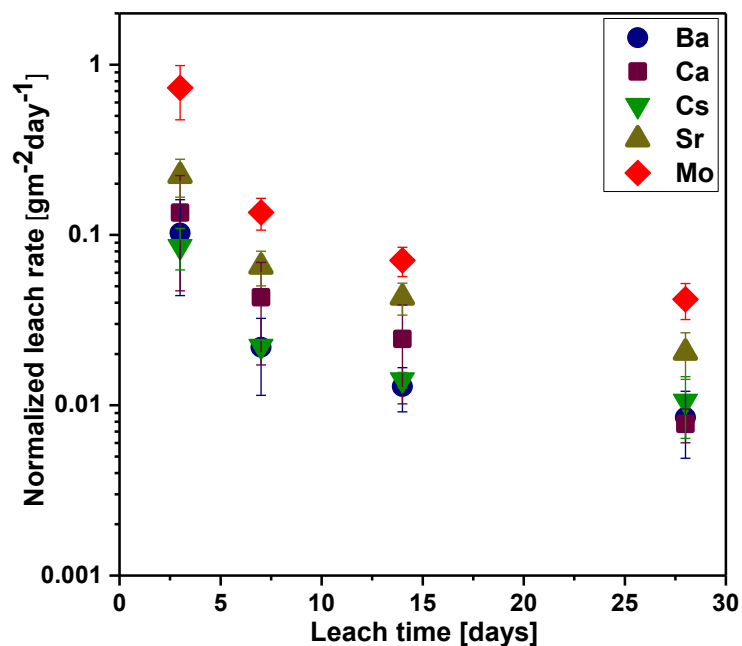


Figure 5.1 Logarithmic representation of normalized leach rates of Synroc-Z sample HUPed at 1200°C and 20 MPa for 3 h under MCC-1 test at 90°C. Error bars represent the standard deviation from triplicates of leach testing measurements.

Table 5.2 Leach rates ($\times 10^{-2} \text{ gm}^{-2}\text{d}^{-1}$) of precursors and Cs, Mo and Sr for Synroc-Z samples HUPed at different conditions via MCC-1 test at 90°C for 28 days. Error ranges represent the standard deviation from triplicates of leach testing measurements.

The effect of temperature (20 MPa, 3 h):

	1200°C	1150°C	1050°C
Al	< 0.1	< 0.1	0.3 ± 0.1
Ba	0.9 ± 0.4	3.5 ± 0.3	49.6 ± 3.3
Ca	0.8 ± 0.2	0.6 ± 0.1	2.4 ± 0.3
Cs	1.1 ± 0.4	1.9 ± 0.2	41.4 ± 2.3
Mo	4.2 ± 0.7	7.5 ± 0.3	36.0 ± 1.5
Sr	2.1 ± 0.6	4.0 ± 0.1	27.3 ± 4.2
Ti	< 0.001	< 0.001	< 0.001

The effect of pressure (1200°C, 3 h):

	40 MPa	20 MPa	10 MPa
Al	< 0.1	< 0.1	< 0.1
Ba	1.5 ± 0.2	0.9 ± 0.4	2.2 ± 0.5
Ca	0.3 ± 0.1	0.8 ± 0.2	0.6 ± 0.1
Cs	1.9 ± 0.1	1.1 ± 0.4	2.5 ± 0.5
Mo	7.7 ± 0.3	4.2 ± 0.7	9.5 ± 0.3
Sr	2.6 ± 0.8	2.1 ± 0.6	5.1 ± 0.5
Ti	< 0.001	< 0.001	< 0.001

The effect of dwell time (1200°C, 20 MPa):

	5 h	3 h	0.5 h
Al	< 0.1	< 0.1	< 0.1
Ba	0.9 ± 0.3	0.9 ± 0.4	1.5 ± 0.01
Ca	0.7 ± 0.2	0.8 ± 0.2	1.6 ± 0.01
Cs	1.7 ± 0.4	1.1 ± 0.4	1.4 ± 0.1
Mo	5.3 ± 1.3	4.2 ± 0.7	6.5 ± 0.4
Sr	2.8 ± 0.5	2.1 ± 0.6	5.2 ± 0.5
Ti	< 0.001	< 0.001	< 0.001

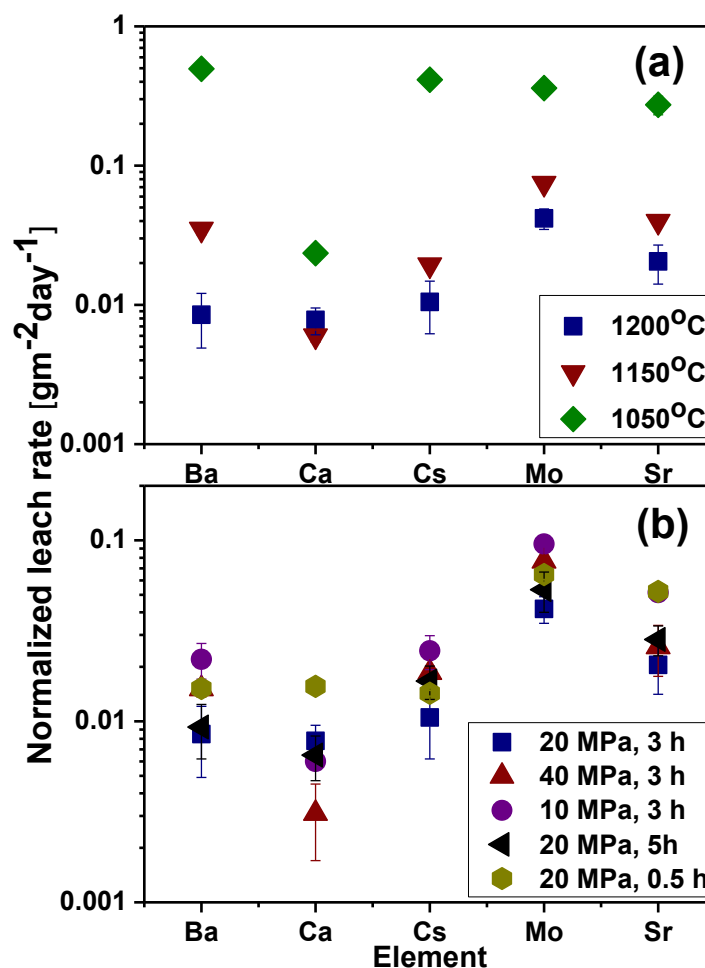


Figure 5.2 Logarithmic representation of normalized leach rates of Synroc-Z sample HUPed at different (a) temperatures (with fixed 20 MPa, 3h) and (b) pressures and dwell times (with fixed 1200°C) via MCC-1 test at 90°C for 28 days. Error bars represent the standard deviation from triplicates of leach testing measurements.

The leached samples were dried at 40°C for 16 h. GIXRD at low incident angle (0.5°) and XRD were performed on the leached samples to analyze phases present on the near-surface (GIXRD: penetration depth: ~0.4 μm and XRD: penetration depth: ~45 μm) and any bulk phase changes respectively. The penetration depth was calculated by X'Pert HighScore Plus software¹⁷⁰. Figure 5.3 shows the GIXRD and XRD of leached and unleached Synroc-Z samples HUPed at 1200°C and 20 MPa for 3 h. The phases detected via GIXRD and XRD after 28 days' leaching of Synroc-Z samples are similar (Figure 5.3a and b) although the intensity of peaks in GIXRD are small and not clearly distinguishable from the noise. The 28-day-leached Synroc-Z samples did not reveal any new crystal peaks in their GIXRD and XRD patterns as their peaks

are seen to overlap with XRD of unleached Synroc-Z sample (Figure 5.3c). The GIXRD and XRD results in Figure 5.3 are representative of all other leached Synroc-Z samples with 20 wt.% waste loading HUPed at various conditions. This indicates good durability of HUPed Synroc-Z as no major phase changes occurred during leach testing.

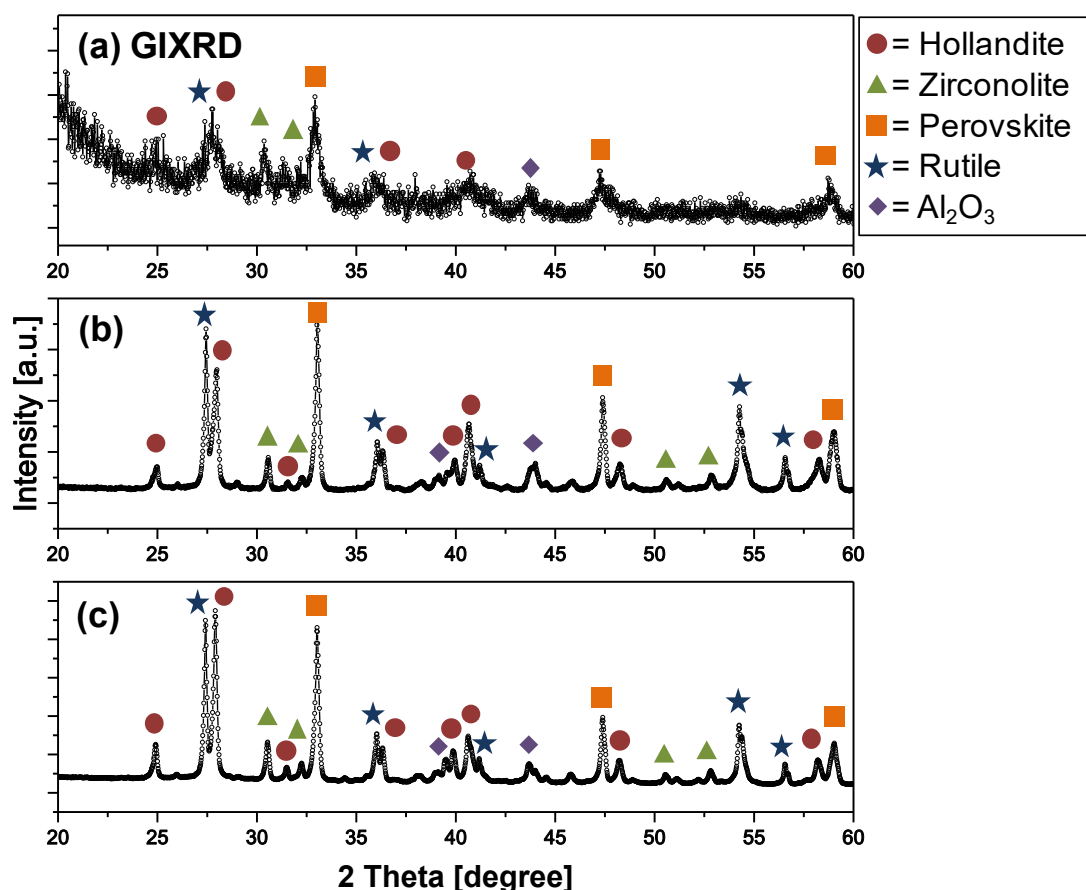


Figure 5.3 (a) Representative GIXRD pattern of leached Synroc-Z samples 1200-20-3 at a fixed 0.5° of incident angle (penetration depth: ~0.4 μm) and XRD of (b) leached and (c) unleached samples. The ICDD cards used for identification: hollandite (H: 01-080-0908)¹²⁵, zirconolite (Z: 00-034-0167)¹³³, perovskite (P: 01-082-0229)¹²⁹, rutile (R: 01-076-1939, 01-076-0321)^{135, 138}, alumina (A: 00-046-1131, 00-035-0121)^{139, 140}.

Figure 5.4 exhibits BSE images of the HUPed Synroc-Z samples before (a) and after (b, c) 28 days of leach testing. In hollandite/perovskite/zirconolite contrast regions (Figure 5.4a), all unleached samples show evidence of mechanical damage by coarse grinding before exposure to aqueous solution. SEM observations revealed that all leached specimens formed a secondary phase on the surface after a 28 days' leach test. All leached samples, except for samples prepared at 1050°C, were covered by spots of secondary phase on the mixed hollandite/perovskite/zirconolite contrast regions (Figure 5.4b) and they were present in greater numbers in the valleys of scratches. The secondary phase that was found in SEM but was not detected via GIXRD (Figure 5.3a) may be due to excessive peak overlap with major phases and low peak intensity and it is difficult to distinguish between signal and noise. The secondary phase displayed a bright contrast in BSE mode. The leached sample HUPed at 1050°C was covered by larger (~1 µm), flake-shaped secondary phase on the hollandite/perovskite/zirconolite areas as shown in Figure 5.4(c). The flake-shaped secondary phase was mainly present in and around damaged regions and hence leads to a ring of particles. More details of secondary phase particles on the surface are described in section 5.1.3 as they are more easily observable in the finely polished (1 µm) Synroc-Z samples after 28 days' leach testing.

The mechanical damage by coarse grinding mainly located at perovskite/hollandite/zirconolite contrast regions (Figure 5.4a). This may be caused by different hardness of phases. The mohs scale of mineral hardness¹⁹⁸ for perovskite, hollandite, zirconolite, and rutile is 5.5, 6, 6.5 and 6-6.5 respectively. This suggests that the mechanical damage may occur primarily in perovskite regions as the hardness of perovskite is the smallest. The hardness of phases is also related to durability as perovskite is the less durable phases and zirconolite is the most durable phase in Synroc^{54, 199}.

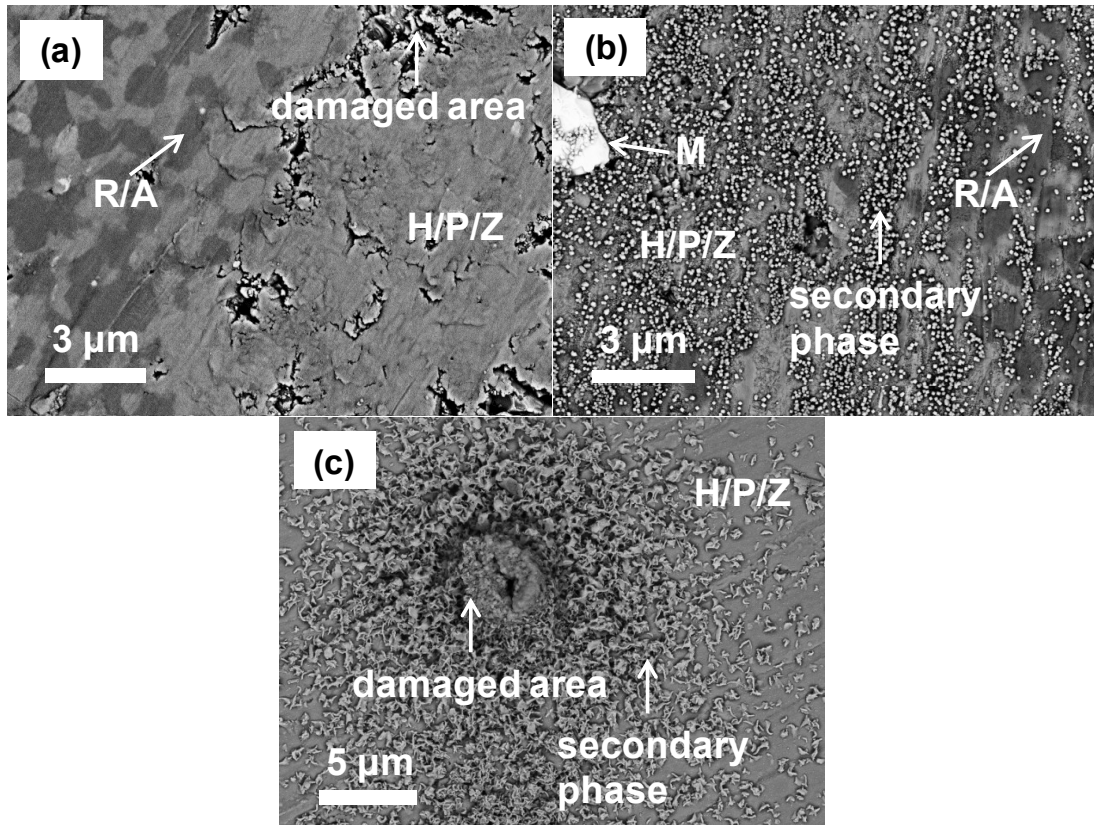


Figure 5.4 BSE images of (a) representative unleached HUPed Synroc-Z samples and 28-day-leached Synroc-Z (b) sample HUPed at $T = 1200^{\circ}\text{C}$, $P = 20$ MPa, $t = 3$ h and (c) sample HUPed at $T = 1050^{\circ}\text{C}$, $P = 20$ MPa, $t = 3$ h. Coarse grinding ($\sim 15\text{ }\mu\text{m}$) caused some damage in hollandite/perovskite/zirconolite-rich regions. The phases of Synroc-Z in the images are rutile (R)/alumina (A) in the dark grey contrast, perovskite (P)/hollandite (H)/zirconolite (Z) in the light grey, and alloys (M) in the white regions. The coarse ground samples were not easy to observe due to their contrast difference. More details for the contrast of phases in the BSE images for the finely polished ($0.04\text{ }\mu\text{m}$) unleached samples were described in section 3.3.2.

5.1.2 Effect of waste loading

HUPed Synroc-Z with higher waste loading (35 wt.%) was selected to determine the effect of waste loading on its durability. In general, the higher waste loading did not affect the durability of Synroc-Z significantly, as shown by the trend of leach rates (Figure 5.5) which reveals that higher waste loaded Synroc-Z maintains its durability performance. The data point for Ca leach rate for 28 days in Synroc-Z with 35 wt.% waste loading was removed from Figure 5.5(a) as its measured leach rate was close to the detection limit ($0.005 \text{ gm}^{-2}\text{d}^{-1}$ vs. $0.005 \pm 0.0003 \text{ gm}^{-2}\text{d}^{-1}$). For HUPed Synroc-Z with lower and higher waste loadings the durability performances were alike, as the leach rates were in similar ranges, especially when considering the Sr loss in perovskite (Figure 5.5a) after 28 days. For hollandite and Mo-alloy phases, the leach rates of Ba and Cs in the 35 wt.% waste loaded sample were about 3 - 6 times faster across the whole testing period while the Mo loss rate in the sample with higher loading was comparable in the first three days but then diverged for longer testing periods (Figure 5.5b).

The GIXRD and XRD results were similar to the samples loaded to lower levels of waste (20 wt.%) in Figure 5.3 as no obvious peaks were observed for new phases after leach testing. BSE images of leached Synroc-Z 35 wt.% (Figure 5.6) were compared to other leached Synroc-Z with 20 wt.% simulated waste. As before, the secondary phase formed on the surface and occurred at the hollandite/perovskite/zirconolite regions of the surface.

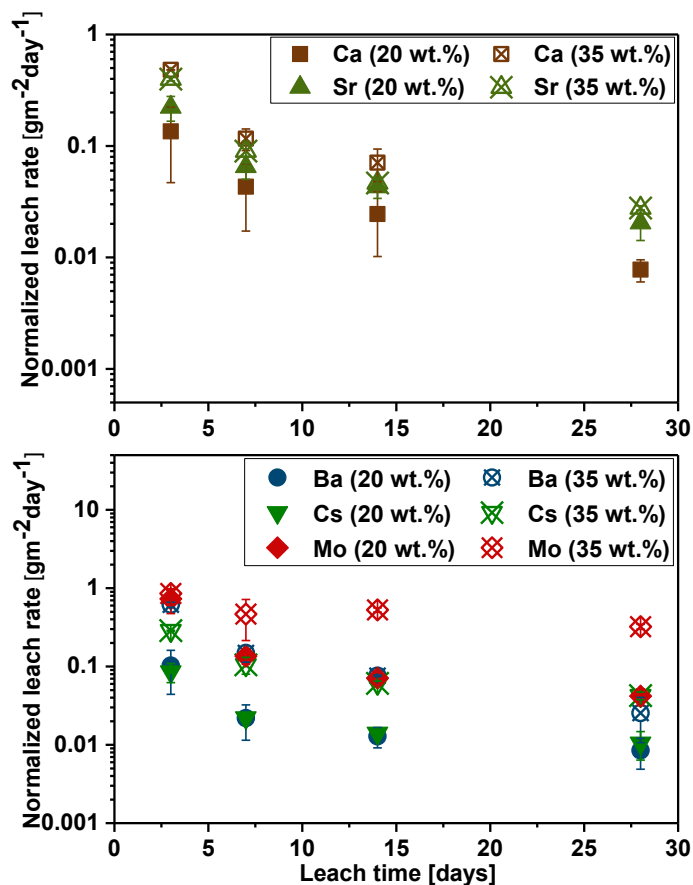


Figure 5.5 Logarithmic representation of normalized leach rates of Synroc-Z with different waste loading indicated in brackets after the relevant element in the boxes from species in (a) perovskite and (b) hollandite and Mo-alloy phases under MCC-1 test at 90°C. Error bars represent the standard deviation from triplicate leach testing measurements.

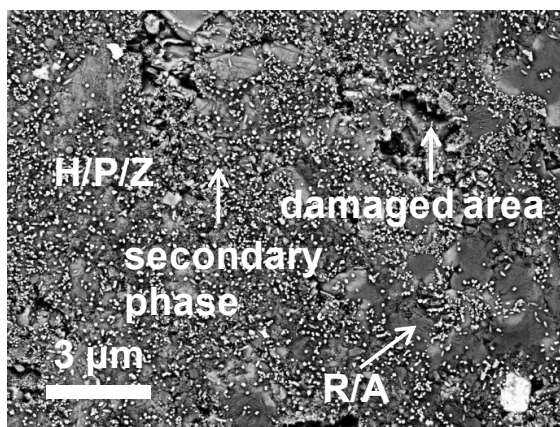


Figure 5.6 BSE image of leached HUPed Synroc-Z sample with 35 wt.% HLW after 28 days' MCC-1 testing. The bright spots are secondary phase particles.

5.1.3 Effect of surface roughness

HUPed Synroc-Z samples (1200°C, 20 MPa, 3 h) were polished to 1 μm to determine the effect of surface roughness on their resistance to aqueous attack. Figure 5.7 shows that the finely polished (1 μm) surface enhanced the durability of Synroc-Z. The finely polished surface only affected Ca and Cs slightly but more significantly for Ba, Sr and Mo. In the first three days, the rates of Ca and Sr loss in the perovskite phase were ~ 3 times lower for the finely polished sample. However, the Ca leach rate became similar after longer leaching times while the rate of Sr loss maintained the initial difference (Figure 5.7a). For the hollandite and Mo-alloys, the flatter surface decreased the Ba and Mo dissolution rates by a factor of 2 - 5 (Figure 5.7b) during the whole test.

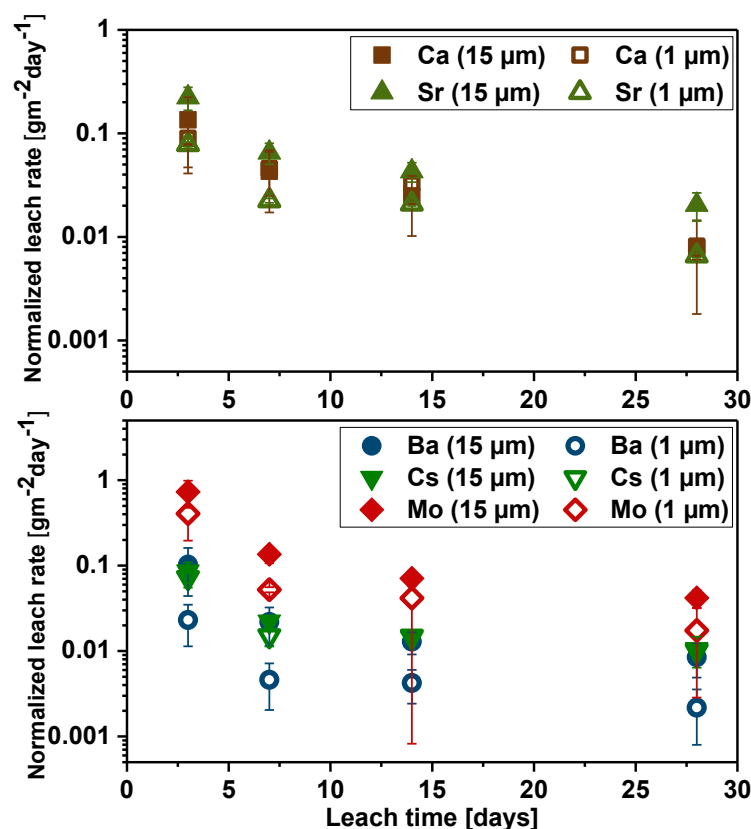


Figure 5.7 Logarithmic representation of normalized leach rates of HUPed Synroc-Z (with different surface finish) indicated by 1 μm and 15 μm in brackets in the boxes in (a) perovskite and (b) hollandite and Mo-alloy phases under MCC-1 test at 90°C. The finer polish finishing generally led to lower Ba, Sr and Mo leach rates. Error bars represent the standard deviation from triplicates of leach testing measurements.

Figure 5.8 reveals that the finely polished sample has similar behaviour as coarse ground sample in microstructure after 28 days' MCC-1 testing. The BSE images of finely polished unleached and leached samples (Figure 5.8a and b, respectively) show no obvious mechanical damage and an array of secondary phase crystals mainly forming with some intermediate grey contrast (perovskite/hollandite). Those grey contrast regions with secondary phase were confirmed by EDX to be the composition which is Ti oxide with minor Ca (< 3 atomic%). The particle-area density of secondary phase was an average of 40 ± 7 particles/ μm^2 . The secondary phase particles were removed by vibrating for 5 min in an ultrasonic acetone bath during TEM sample preparation. This indicated the secondary phase crystals are loosely bound to the surface and suggests the secondary phase crystals found over phases other than perovskite might have simply moved there during SEM sample preparation. Powder TEM samples were prepared as described in section 2.2.5. TEM image reveals that the “washed off” crystals were polyhedral pyramidal-like shaped (Figure 5.9a). They were analyzed via electron diffraction (ED), fast Fourier transform (FFT) of TEM images and TEM/EDX. The secondary phase particles were mostly composed of small crystallites of 5 - 10 nm in diameter (Figure 5.9b). ED patterns showed these crystallites to all be slightly misoriented revealed by streaking in the zone axis [1 0 0] pattern for the particle (Figure 5.9b inset). The spots visible in FFT (Figure 5.9c) of these small crystallites match with the rotated simulations of ED patterns of anatase while its composition from EDX (Figure 5.9d) confirmed that the main content was Ti oxide with minor impurities of Fe and Al. This indicates that the secondary phase formed is anatase. The formation of secondary phases will be discussed further in section 7.3.5.

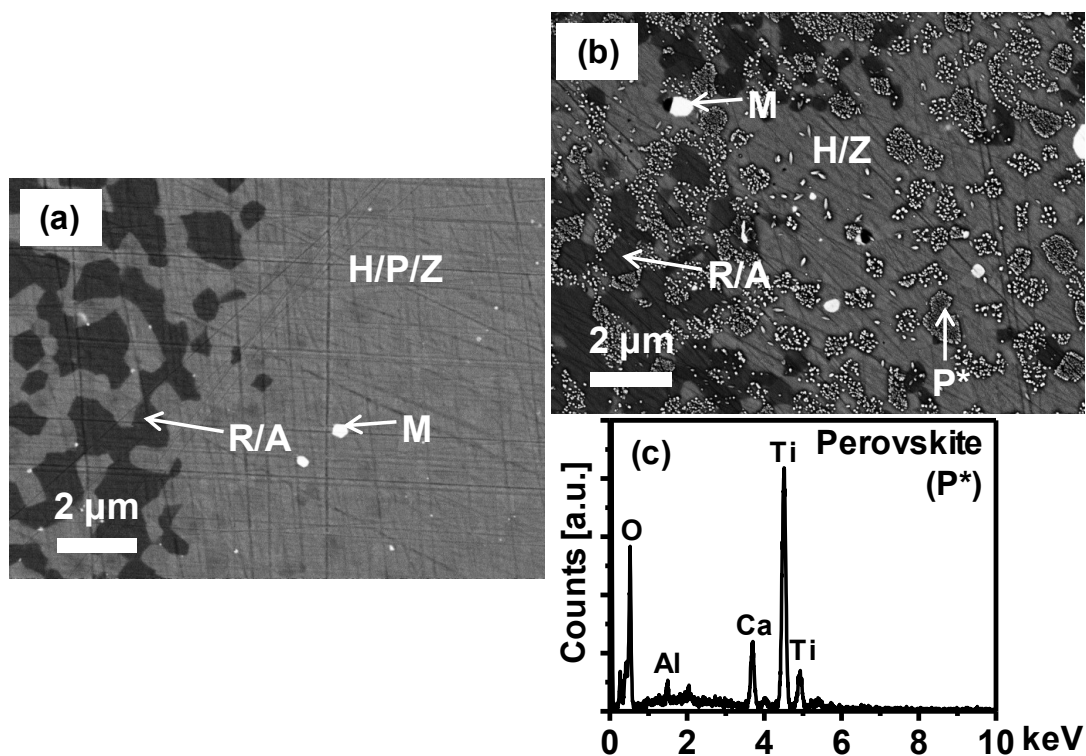


Figure 5.8 BSE images of (a) unleached and (b) leached finely polished Synroc-Z sample HUPed at 1200°C and 20 MPa for 3 h and (c) EDX spectra of perovskite (labelled with *). The surface was covered by a layer of well-aligned individual crystals in perovskite-rich areas. The crystals were confirmed as anatase via TEM later.

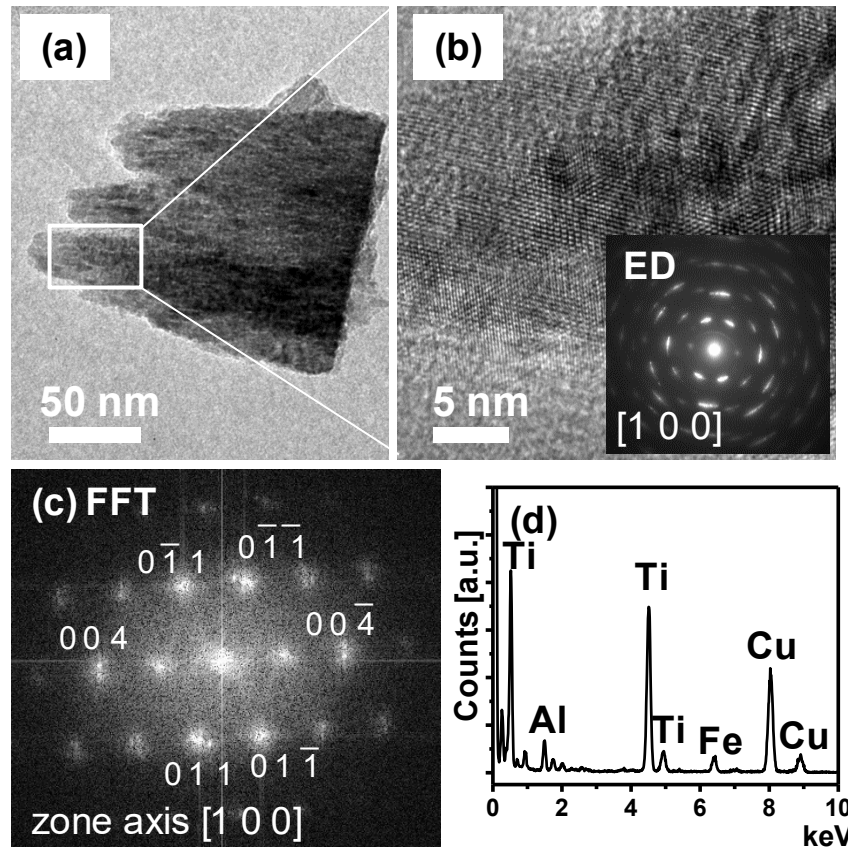


Figure 5.9 Structural characterization via TEM images of secondary phase precipitates on the leached Synroc-Z (HUP: $T=1200^{\circ}\text{C}$, $P=20\text{ MPa}$, $t=3\text{ h}$ for 28 days' MCC-1 test) surface at (a) low and (b) high magnification with ED patterns.

(c) FFT shows the symmetry of crystal and can match with simulations of anatase ED patterns rotated 5° from x axis. (d) TEM/EDX showed that the metal oxides were mainly Ti-based, with minor impurities of Al and Fe. Cu present in EDX comes from the Cu grid used for TEM preparation.

AFM measurements (as described in section 2.2.6) obtained by scanning Synroc-Z sample with polished surfaces before and after leach testing are shown in Figure 5.10(a) and (b) respectively. The anatase particles (Figure 5.10c) were ~ 100 nm tall, and ~ 125 nm wide, consistent with the TEM images shown in Figure 5.9(a). Figure 5.10(d) shows the 3D view from 5.10(b) which clearly revealed the height difference between the polished surface and the anatase particles.

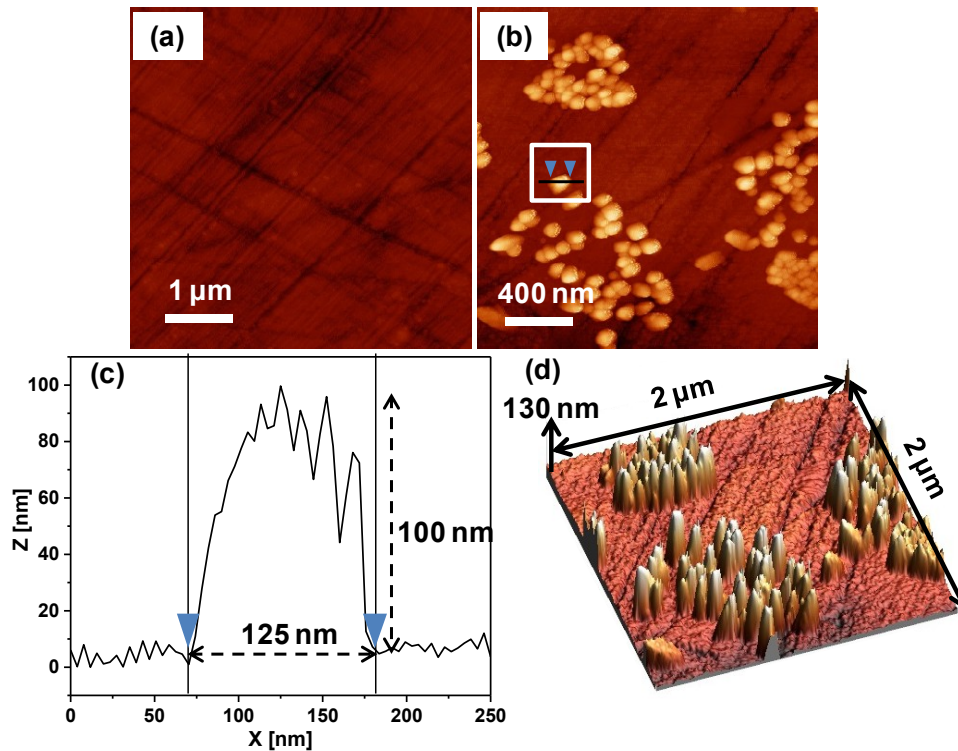


Figure 5.10 2D morphology of (a) unleached and (b) leached Synroc-Z sample (HUP: $T=1200^{\circ}\text{C}$, $P=20$ MPa, $t=3$ h for 28 days' MCC-1 test) with finely polished surface via AFM. The greatest height is 130nm, and is shown by bright regions. (c) The nano particle was up to ~ 100 nm high and ~ 125 nm wide. (d) 3D view of leached sample tilted 45° .

A 5 min acetone ultrasonic bath “washed” the leached finely polished ($1\ \mu\text{m}$) Synroc-Z sample as some anatase crystals were removed from the surface. However, there were no obvious pores under the removed crystals, where they were expected. A thin (up to 10 nm) film was clearly present on the “cleaned” area with some undetached particles as shown in Figure 5.11.

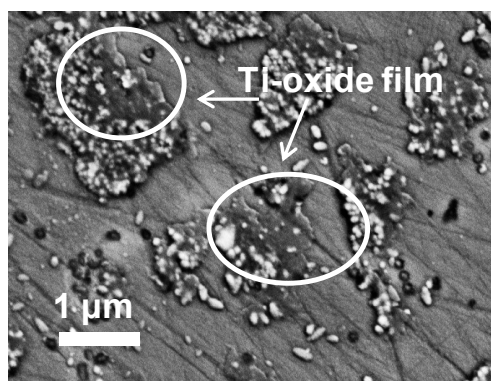


Figure 5.11 BSE image of leached finely polished ($1\ \mu\text{m}$) Synroc-Z sample (HUP: $T=1200^{\circ}\text{C}$, $P=20\ \text{MPa}$, $t=3\ \text{h}$ for 28 days' MCC-1 test) after ultrasonic bath in acetone. No obvious pores can be found in the area from which anatase particles has been removed (circled regions).

5.2 HIPed Synroc-Z

HIPed Synroc-Z samples (1200°C, 20 MPa, 3 h) were selected to perform MCC-1 testing and will be compared with the HUPed Synroc-Z material discussed in section 5.1. The results were somewhat surprising; the HIPed Synroc-Z formed leachable Cs-Mo compounds and thus exhibited high leach rates for Cs and Mo (Figure 5.12). The elemental loss rate for Cs and Mo in the HIPed Synroc-Z was $10^3 - 10^4$ times faster than HUPed Synroc-Z. Ba, Sr and Ca losses in HIPed Synroc-Z displayed similar rates to HUPed Synroc-Z in the first three days but then stayed at the same level for the remainder of the test while the leach rates of HUPed Synroc-Z were found to diminish (see Figure 5.1). High leach rates obviously due to insufficiently reducing conditions prevailing during HIPing and the Cs-Mo compounds formed (Figure 3.20).

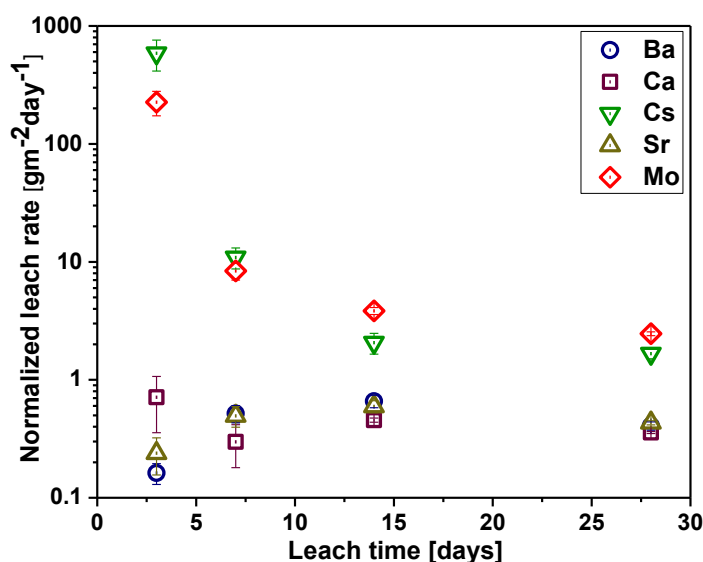


Figure 5.12 Logarithmic representation of normalized leach rates of HIPed Synroc-Z sample HIP-1200-20-3 under MCC-1 test at 90°C. Error bars represent the standard deviation from triplicates of leach testing measurements.

No significant phase changes were observed on leach testing for HIPed samples based on XRD as unleached and leached samples gave similar patterns (Figure 5.13). However, they formed two different secondary phases which were anatase crystals and a dried “alumina” layer determined from SEM/EDX observation. HIPed Synroc-Z displayed similar behaviour to HUPed Synroc-Z as both of them formed anatase crystals on their surface during

MCC-1 test (Figure 5.14a). However, a dried “alumina” layer (Figure 5.14b) was also observed on some regions of the leached HIPed Synroc-Z. TEM sample preparation via FIB was described in section 2.2.5. Figure 5.15 reveals that the thickness of the alumina layer is up to 200 nm in the TEM image while the gap between the alumina layer and leached/damaged layer is up to 50 nm. The EDX of leached/damaged area suggests that these regions were either zirconolite or perovskite as they contained minor amounts of Zr, Ca and rare earths (total < 5 atomic%). The thickness of leached/damaged areas is up to 150 nm. Overall, the leached HIPed Synroc-Z was covered by either anatase crystals (up to 100 nm tall) or alumina layers (up to 200 nm thick).

Moreover, the Cs-Mo compounds which were observed before leach testing were not present. This agrees with the high leach rates of Cs and Mo as those soluble Cs-Mo compounds were dissolved. Precipitation of Cs and Mo on the surface of the sample did not occur during the test period although leach rates of both elements decreased by two orders of magnitude between 3 and 14 days. The leachates were replaced by fresh leachants (DI water) at 3, 7, and 14 days during the leach testing period. The leachate solution was not saturated by the dissolved Cs and Mo thus phase precipitation did not occur in the temperature range of interest. The behaviour of leached HIPed Synroc-Z will be discussed further in section 7.3.5.

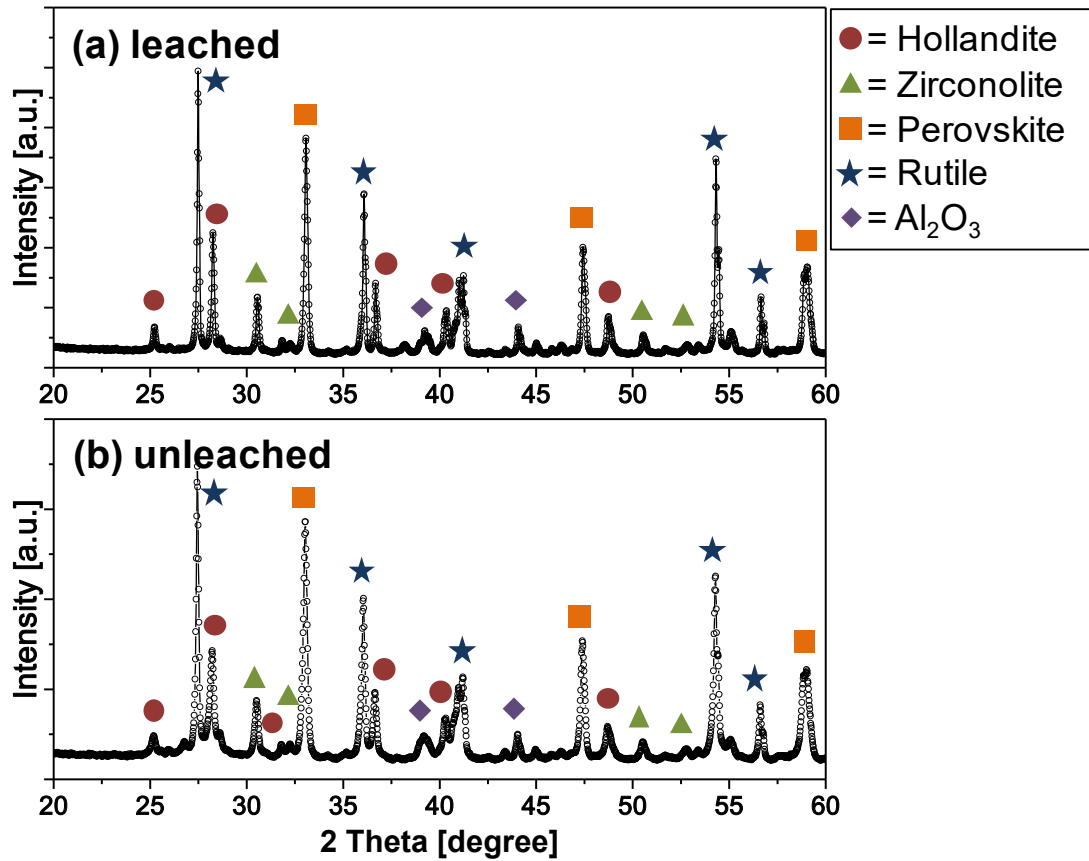


Figure 5.13 XRD patterns of (a) 28 days' leached and (b) unleached Synroc-Z sample HIPed 1200°C and 20 MPa for 3 h. The ICDD cards used for identification: Hollandite (H: 01-077-2439)¹²⁶, zirconolite (Z: 01-088-0415)¹³⁴, perovskite (P: 01-081-0561)¹³⁰, rutile (R: 01-089-0552)¹³⁶, alumina (A: 01-081-2266, 00-035-0121)^{139, 141}.

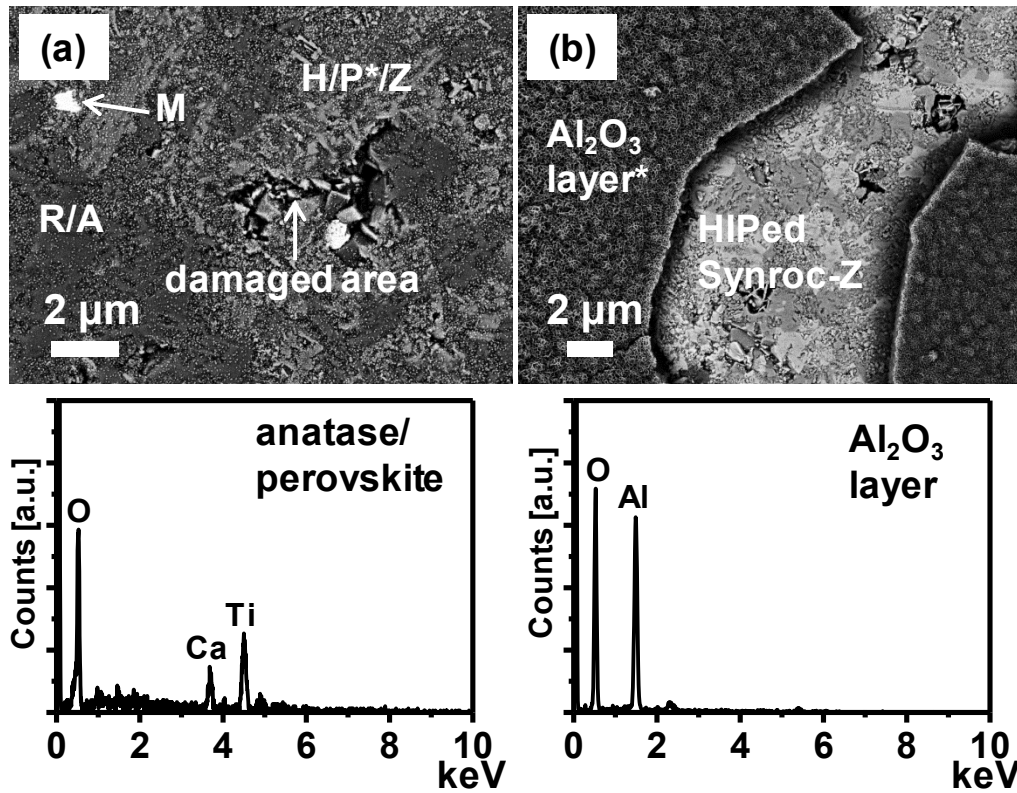


Figure 5.14 BSE images and EDX spectra of 28 days' leached sample HIP-1200-20-3 in (a) anatase crystals rich region and (b) alumina layer area. The EDX analysed regions were labelled with *.

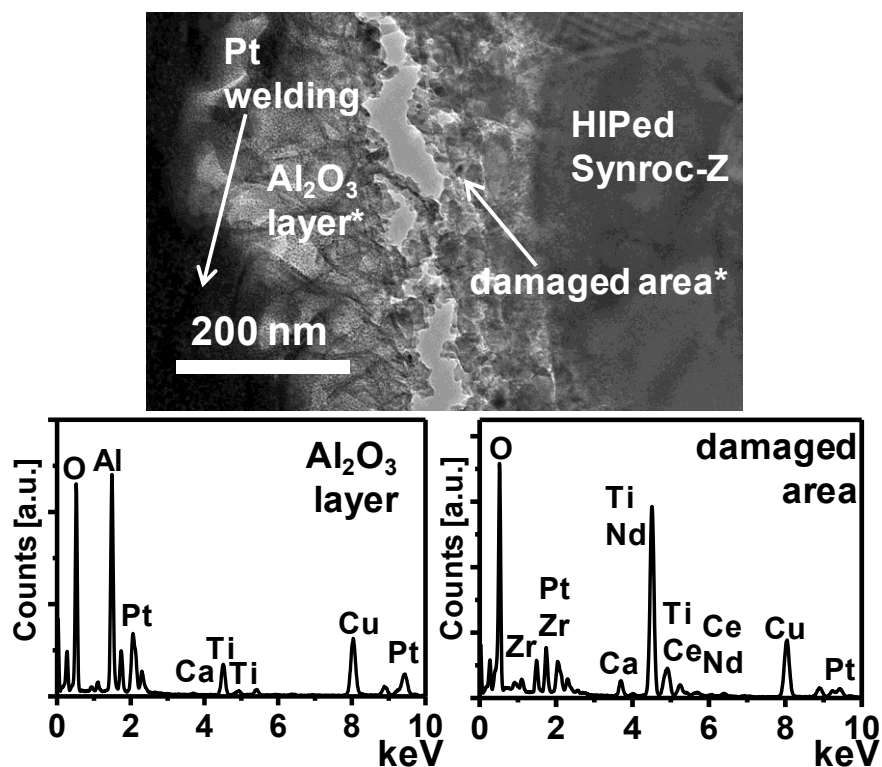


Figure 5.15 TEM images of the alumina layer on the leached Synroc-Z (HIP: T=1200°C, P= 20 MPa, t= 3 h for 28 days' MCC-1 test) surface with EDX spectra of alumina layer and leached/damage area. The EDX analysed regions were labelled with *. Cu and Pt present in EDX come from the Cu grid and Pt welding used for TEM preparation as described in section 2.2.5.

5.3 R7T7 glass

R7T7 glass prepared at 1200°C was selected for MCC-1 testing, as it dissolved most waste elements except Ru, Pd, and Te, as described in Chapter 4. The surfaces of R7T7 samples were either ground to 15 μm (coarse) or polished to 1 μm (fine) finishes. Two of the R7T7-1200 samples with the two different surface finishes (15 μm and 1 μm) were successfully obtained and leach tested.

5.3.1 Coarsely ground surfaces

The surfaces of R7T7 samples were ground to 15 μm to meet the standard requirement for the MCC-1 test and to compare with HUPed Synroc-Z. The pH values of leachant (fresh DI water) added were 5.5 - 6 while the pH values of leachates after 3, 7, 14, and 28 days testing were ~6.7, ~7.4, ~8.4 and ~8.9 respectively. Figure 5.16 reveals the normalized leach rates for the glass precursors and waste elements that had leach rates greater than 0.001 $\text{gm}^{-2}\text{d}^{-1}$. In general, the normalized leach rates sustained the same level during the leach testing period with most of the glass precursors and FPs exhibiting similar rates that fall in the range of 0.1-1 $\text{gm}^{-2}\text{d}^{-1}$. Losses of rare earths in the waste occurred at a rate below 0.0005 $\text{gm}^{-2}\text{d}^{-1}$.

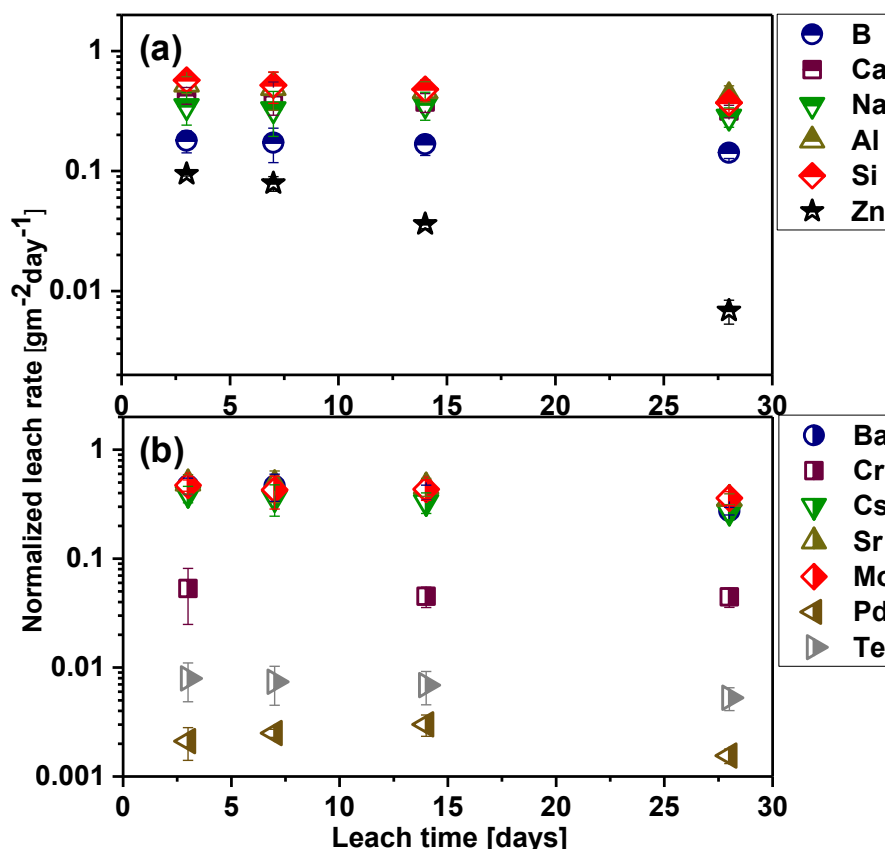


Figure 5.16 Logarithmic representation of normalized leach rates of (a) glass precursors and (b) waste elements in R7T7-1200 sample under MCC-1 test at 90°C. In general, the leach rates stayed at the same level during the whole testing period. Error bars represent the standard deviation from duplicates of leaching testing measurements.

Comparison of the GIXRD and XRD for the R7T7 samples before and after leaching showed some new crystal peaks for secondary phases formed during leach testing in Figure 5.17. Secondary phases which are silicates (Ca-silicate) and SiO_2 as detected via GIXRD and XRD (total thickness < 2 μm) were also observed by SEM (Figure 5.18). They covered ~52 area% of the glass surface after leaching. The secondary phase was mainly composed of Al, Si and Zn with a ratio of about 1: 2: 2, with Zr also detected. However, the layer with obvious cracks under the secondary phase is deduced to be a dried gel layer based on previous studies^{102, 105}. The composition of the dried gel layer region was different to the unleached glass sample as Na was found to be absent from the surface of the leached glass. Cracks observed in the gel layer probably formed on drying after sample removal from leachate.

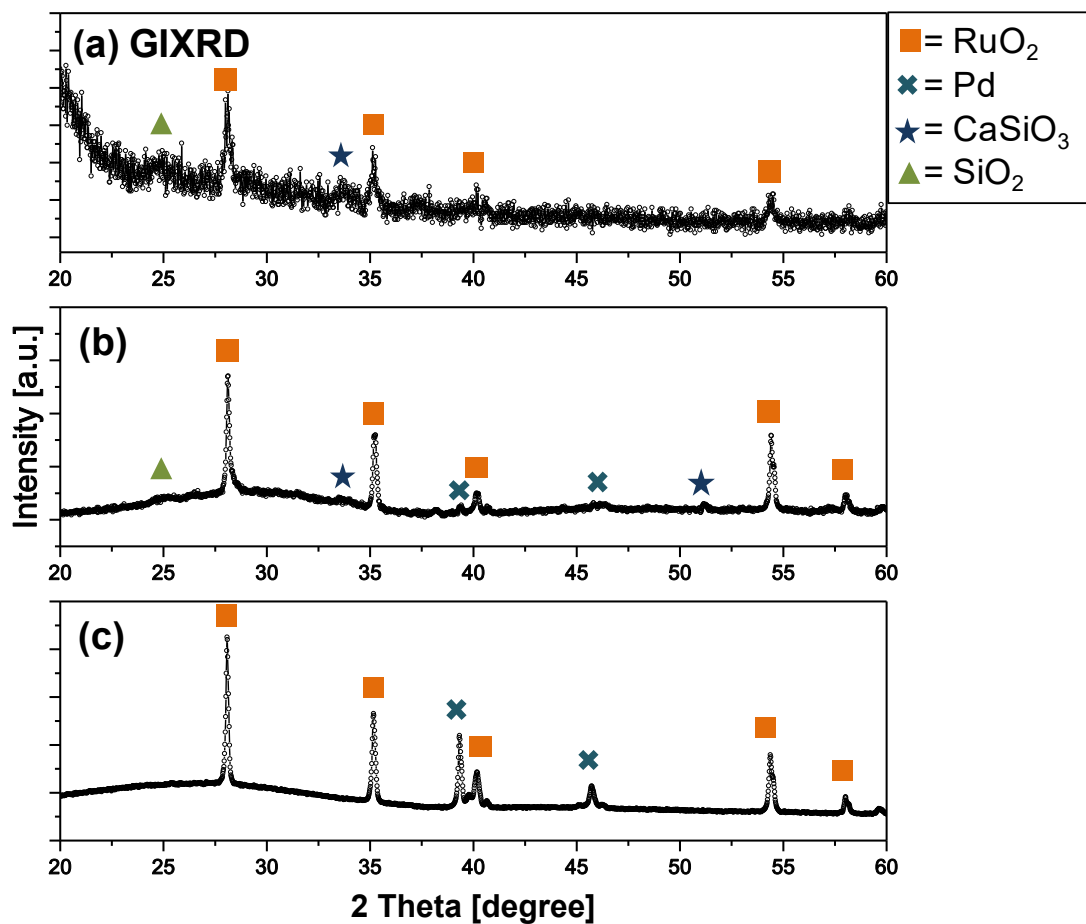


Figure 5.17 (a) GIXRD patterns of 28-day-leached R7T7-1200 at a fixed incident angle of 0.5° (penetration depth: $\sim 2 \mu\text{m}$) and normal XRD (penetration depth: $\sim 235 \mu\text{m}$) of (b) 28 days' leached and (c) unleached sample. The ICDD cards used for identification: RuO_2 (01-073-1469)¹⁵⁵, Pd alloys (Pd: 01-087-0641)¹⁵², CaSiO_3 (00-018-0306)¹⁶¹ and SiO_2 (01-083-0539)¹⁶⁴.

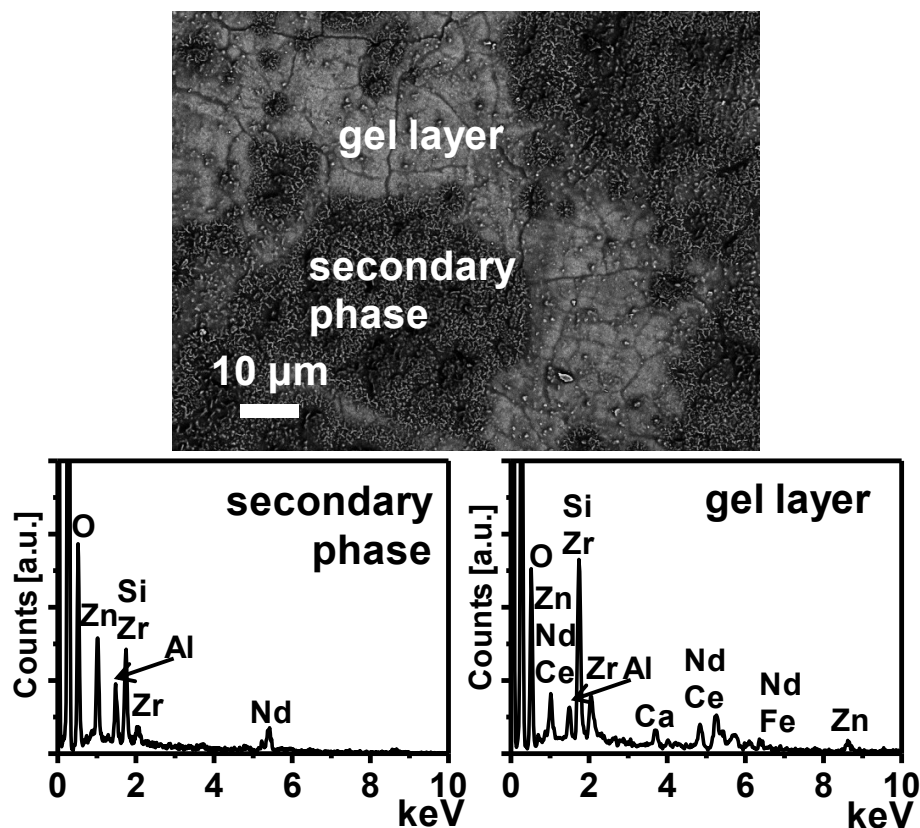


Figure 5.18 BSE image and EDX spectra of 28-day-leached R7T7 prepared at 1200°C with coarse surface. The light grey region was believed to be derived from a previous gel layer while the intermediate grey regions were the secondary phases (silicates).

5.3.2 Finely polished surfaces

Two R7T7 samples (fa and fb) were polished to 1 µm to examine the effect of surface roughness. Interestingly, there was considerable variation in the behaviour of both samples. One (R7T7-fa) showed similar pH values (Table 5.3) of leachates and leach rates (Figure 5.19a and c) to the coarsely ground sample while the other (R7T7-fb) displayed higher pH (Table 5.3) and faster leach rates (Figure 5.19b and d). In the first stage of leach testing, for most of the glass precursors (Table 2.8, except Zn), and Ba, Cs, Mo, Sr, Pd and Te displayed 10 - 100 times faster loss rates in R7T7-fb than R7T7-fa. However, the loss rates for Ba, Sr and Pd in the waste decreased as the test proceeded meaning their leach rates actually became lower in R7T7-fa after 28 days than in the R7T7-fb sample. The elemental loss of Ca and Al in R7T7-fb dropped to a similar level to R7T7-fa while B, Na, and Si in the precursors and Cs and Mo in the waste maintained the faster rates during the whole period.

The reason for the different behaviour of ostensibly identical samples may be due to failure to polish correctly. Figure 5.20 shows BSE images of a poorly polished R7T7 sample which contained many pores. The diamond particles used for polishing may have damaged the samples and thus produced pores. Those pores were difficult to observe in optical microscopy (easy in SEM) before leach testing.

Table 5.3 pH values of leachates for R7T7-fa and -fb samples during leach testing.

	3 days	7 days	14 days	28 days
R7T7-fa	6.4 ± 0.1	7.5 ± 0.1	8.2 ± 0.2	8.9 ± 0.1
R7T7-fb	9.2 ± 0.1	9.3 ± 0.2	9.5 ± 0.1	9.5 ± 0.1

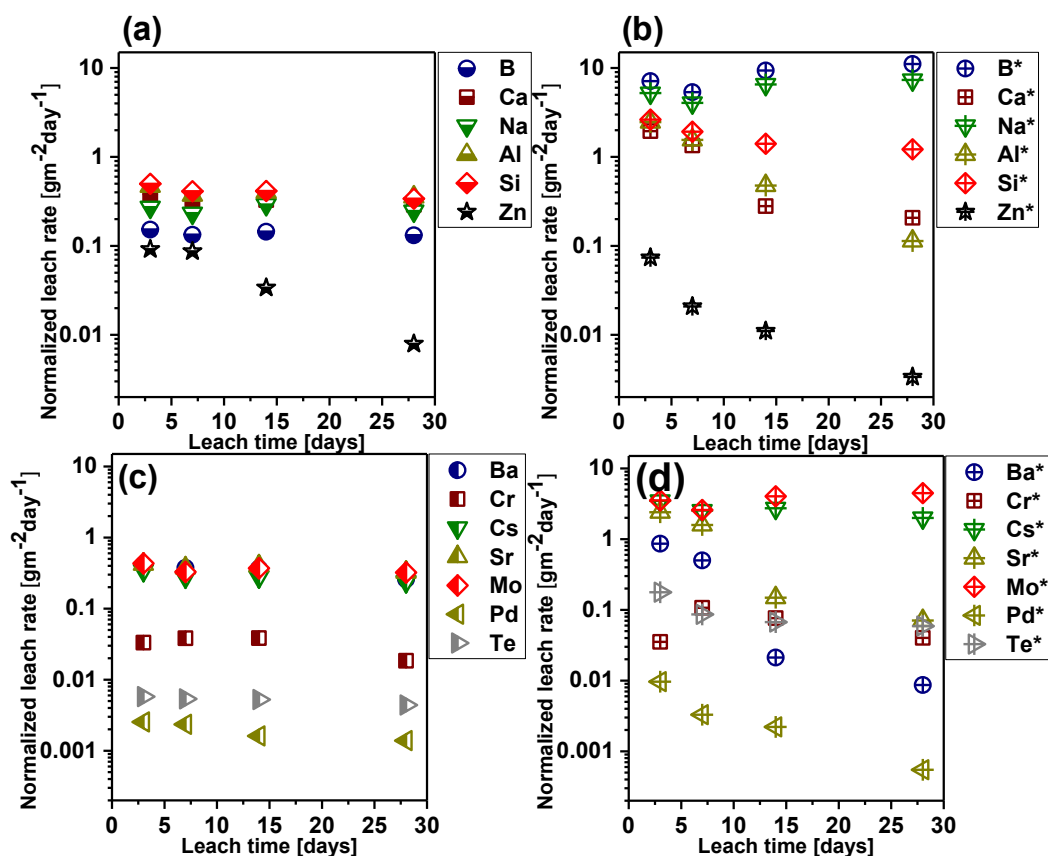


Figure 5.19 Logarithmic representation of normalized leach rates of glass formers in (a) R7T7-fa and (b) R7T7-fb and waste elements in (c) R7T7-fa and (d) R7T7-fb sample under MCC-1 test at 90°C.

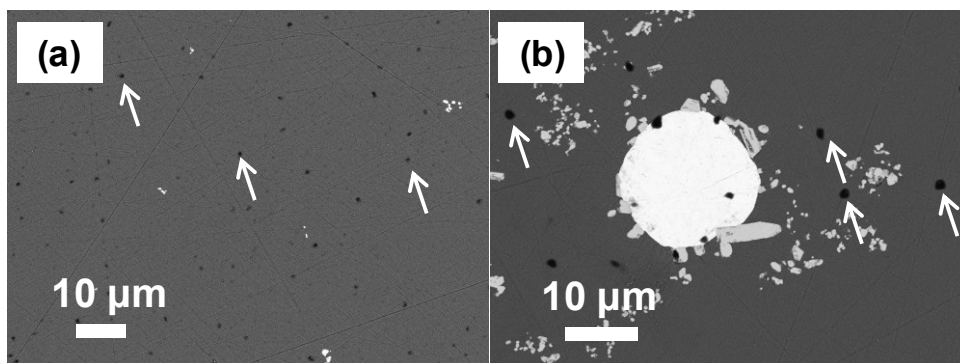


Figure 5.20 BSE images of a poorly polished R7T7 sample with pores (indicated as arrows) in (a) glass region and (b) RuO_2 and Pd-Te rich areas. The sample was damaged by 1 or 3 μm diamond powder during polishing.

The microstructure of leached R7T7-fa was similar to leached R7T7 samples with coarsely ground surfaces after the same time periods and testing conditions. Both of them displayed silicates (Figure 5.17b and 5.21b for XRD) and also a dried (previously gel) layer and secondary phases (silicates, total thickness $< 2 \mu\text{m}$) on the surface (Figure 5.18 and 5.22 for SEM images). Cracks were also observed in the gel layer regions while the main composition of the gel layer and secondary phases were also similar.

After the test, the surface of the R7T7-fb sample which displayed the faster leach rates was found to be covered by an amorphous layer as no obvious peaks appeared in GIXRD (Figure 5.21c). The amorphous layer which was composed of dried (previous gel) layer and phase precipitation was fragile with a thickness of $> 8 \mu\text{m}$ while a flatter surface (glass substrate) was exposed as the flakes were easily removed (Figure 5.23). This may be due to chemical processes (alkaline ion depletion, hydration of the layer) and/or physical changes (change in the structure and volume)²⁰⁰. Higher magnification BSE images also revealed open pore structures on the glass substrate surface indicating removal of some species or crystals from the bulk surface. The main composition of the glass substrate still contained Na at levels similar to unleached glass (Figure 4.11). Moreover, the ratio of Al, Si and Zn in the amorphous layer was about 1: 4: 2 and was different to all other leached glass samples as the amorphous layer contains more Si.

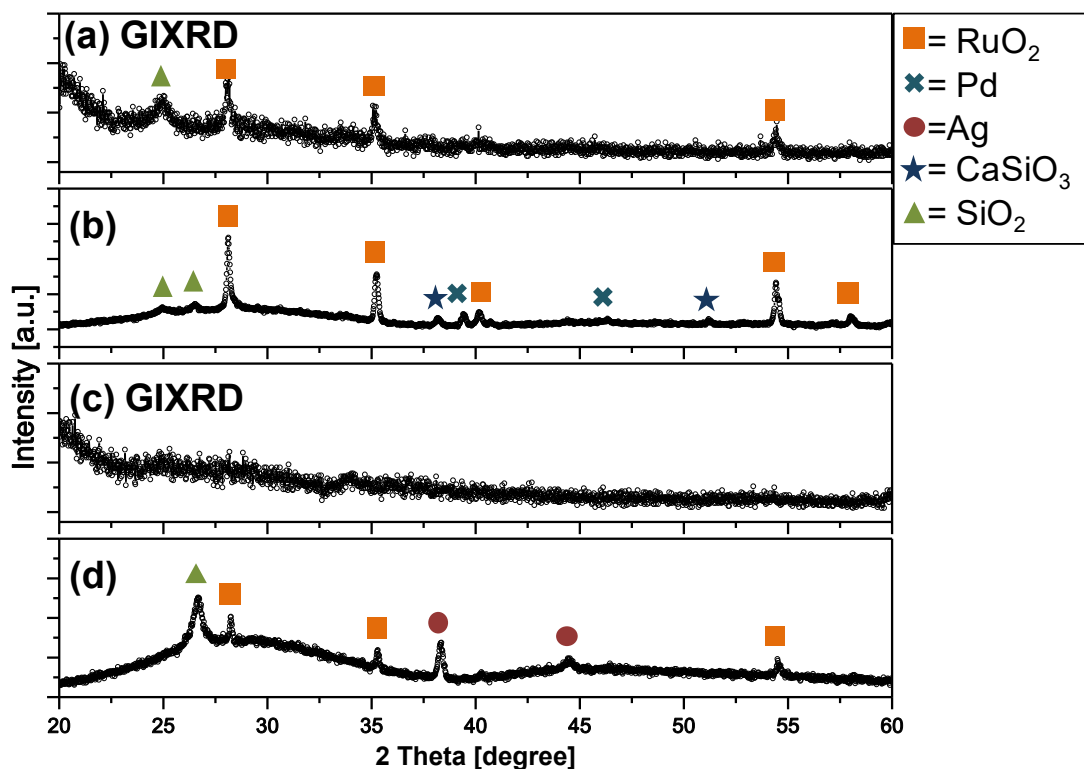


Figure 5.21 GIXRD patterns of 28 days' leached (a) R7T7-fa at a fixed 0.5° of incident angle (penetration depth: $\sim 2 \mu\text{m}$) and (c) R7T7-fb at a fixed 2° of incident angle (penetration depth: $\sim 8 \mu\text{m}$) and normal XRD (penetration depth: $\sim 235 \mu\text{m}$) of 28 days' leached (b) R7T7-fa and (d) R7T7-fb. The ICDD cards used for identification: RuO_2 (01-088-0322, 01-073-1469)^{155, 156}, Pd alloys (Pd: 01-087-0641)¹⁵², SiO_2 (00-050-1708, 01-085-0335)^{163, 165}, CaSiO_3 (00-018-0306)¹⁶¹ and Ag (01-087-0597)¹⁴⁶.

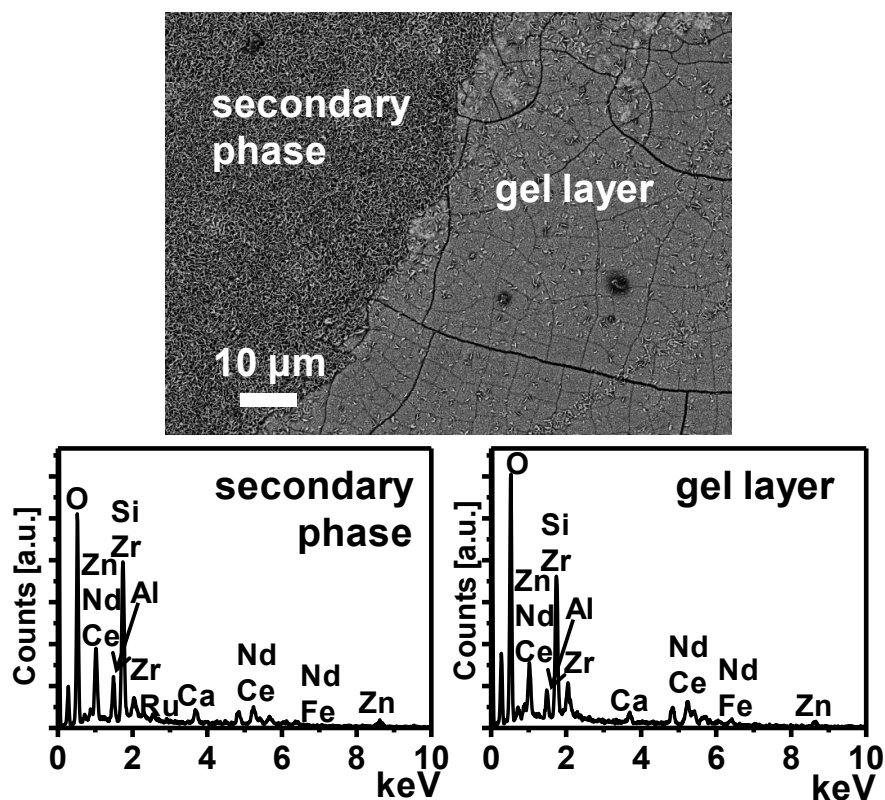


Figure 5.22 BSE image and EDX spectra of 28 days' leached R7T7-fa. The light grey contrast was gel layer while the intermediate grey regions were the secondary phase.

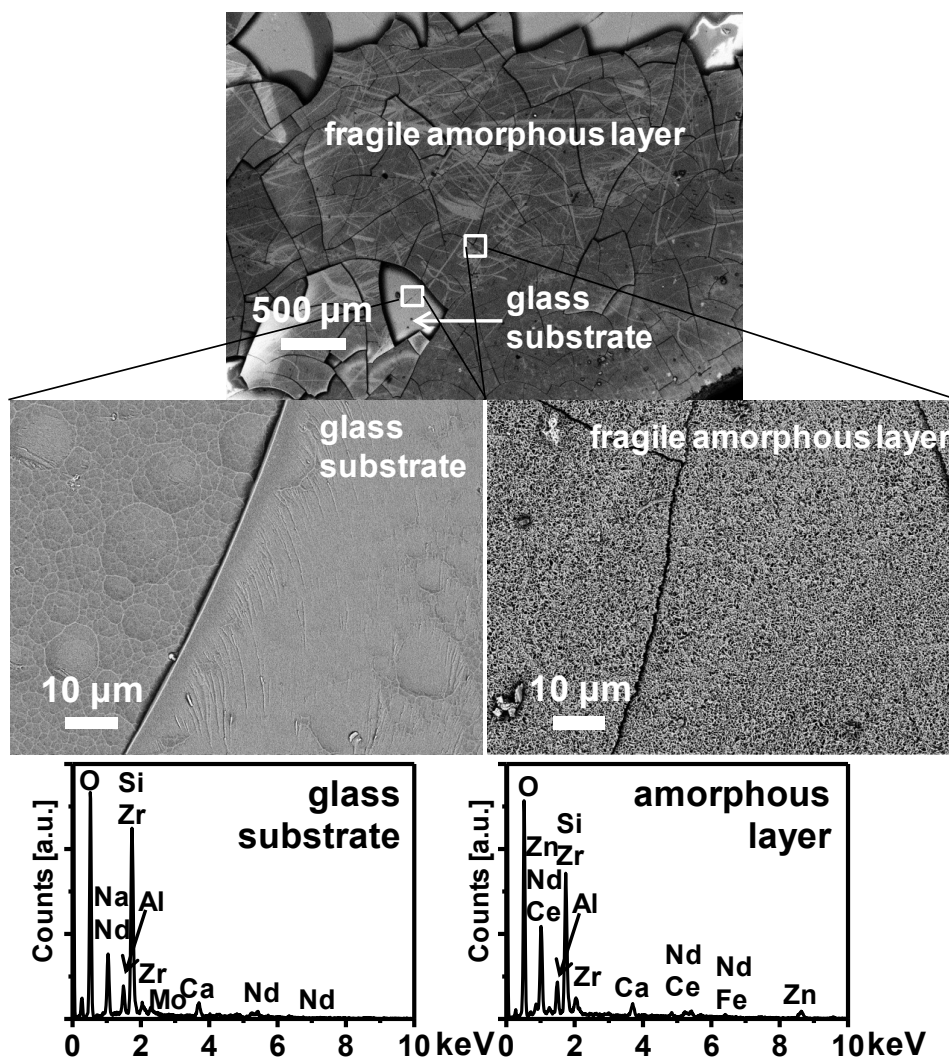


Figure 5.23 Low and high magnification of BSE images and EDX spectra of 28 days' leached R7T7-fb. The light grey region was glass substrate while the intermediate grey regions were the amorphous layer.

5.4 Summary

Table 5.4 summarises the durability results of both Synroc-Z and R7T7 samples used to immobilise the waste from the EURO-GANEX process via MCC-1 testing over 28 days. For HUPed Synroc-Z, HUPing temperature was the most significant processing variable for leach rates while the pressure and dwell time only showed minor effects. Synroc-Z was fully densified at 1150 and 1200°C while 2.5 vol.% of porosity was measured at Synroc-Z HUPed at 1050°C. The relatively higher porosity (2.5 vs. 0.5 vol%) caused faster leach rates than other HUPed Synroc-Z samples. HIPed Synroc-Z formed leachable Cs-Mo compounds and thus caused higher leach rates of Cs and Mo than HUPed Synroc-Z.

Anatase crystals were found after leaching in polished HUPed Synroc-Z mainly on perovskite grains. Well-aligned Ti oxide particles deposited on the surface after a thin film formed. It is likely that such Ti oxide film and particles offer some protection for the Synroc-Z perovskite phase from further aqueous attack as the perovskite limits contact with water. More details of the nature of the Ti oxides present will be discussed in the section 7.3.5. Conversely, the gel layer and secondary phases formed on the R7T7 glass provide little or no protection from aqueous attack as the elemental losses from R7T7 were only slowly decreasing (on average a 1.4 times decrease between 3 and 28 days compared to the 14 times decrease for HUPed Synroc-Z).

Table 5.4 Summary of leached samples in this chapter

	Porosity	Leach trend	Leach rates range (28 days)	Secondary phases formed after test
HUPed Synroc-Z	> 0.5 vol% (~2.5 vol%)	-	0.1-1 gm ⁻² d ⁻¹	Flake-shaped Ti-Fe oxide
HUPed Synroc-Z	< 0.5 vol%	decreased	0.01-0.1 gm ⁻² d ⁻¹	Anatase crystals + Ti-O thin film
HIPed Synroc-Z	~0.6 vol%	decreased (Cs,Mo)/ maintained (Ba, Sr, Ca)	0.1-10 gm ⁻² d ⁻¹	Anatase crystals, Al ₂ O ₃ layer
R7T7 glass	~0.1 vol%	maintained/ decreased (Zn)	0.1-1 gm ⁻² d ⁻¹	Gel layer, Si-Al-Zn rich phases

Chapter 6: Simulation of generated heat from real EURO-GANEX waste in wasteforms

6.1 Heat in HLW disposal systems

HLW from reprocessing must be isolated from humans and the environment for tens of thousands of years to allow the natural decay of the radionuclides^{201, 202}. According to the IAEA, the most likely method for the long-term management of HLW is to store it in deep (300 - 1000 m underground) repositories situated in stable geological formations^{201, 202}. The repository forms one of the outer layers of the so-called multi-barrier concept where several barriers are used to secure the radionuclides for a sufficient period of time until they are safe by limiting their release through migration to the biosphere. Inside the repository, several further barriers exist: the innermost being the wasteform which is itself surrounded by a metal canister that is then encompassed by buffer and backfill media^{201, 202, 203}. As a result, the safety of the disposal system is not solely dependent on a single barrier or phenomenon for its efficacy^{202, 203, 204}.

The wasteform materials discussed in this thesis represent the barrier closest to the waste elements in this concept. As they contain the repository's radionuclide inventory, the physical and chemical characteristics of the wasteform have an important effect on the overall performance of the disposal system. Radioactive decay of the nuclides incorporated into their structure may cause self-heating and other self-irradiation effects which may deleteriously affect their structure and durability²⁰⁵. Furthermore, exchange of energy, in the form of heat and radiation, between the wasteform, canister and backfill needs to be properly understood when defending a repository's safety case^{206, 207}. During the early stages of disposal, the wasteform is assumed to be protected by its metal canister. However, as time proceeds, a conservative safety case must assume that the canister will eventually be breached through corrosion leading to the wasteform becoming exposed to ground water^{208, 209}. Consequently, the leaching behaviour of the wasteform must be understood. To this end, matter exchange between wasteform and aqueous environments was studied in Chapter 5 using the MCC-1 leach test. This chapter is dedicated to

the other aspect, the exchange of energy.

During the first few decades following its production, the waste generates significant heat mainly due to the radioactive decay of relatively short-lived radionuclides, such as Sr-90 ($t_{1/2} = 28.8$ years) and Cs-137 ($t_{1/2} = 30.07$ years)⁵. This results in an initially high temperature within the wasteform. Thus, heat dissipation is an important factor that has to be taken into account when determining waste loading and emplacement in the repository and how this relates to the waste's performance. Most underground repository sites to store wasteforms are in saturated environments, as they are located underneath the water table. Only one proposed repository site, Yucca Mountain in the U.S, is located in the unsaturated zone (above the water table)^{208, 210}. During the design of geological disposal facilities, the maximum temperature for the outer surface of the waste canister is typically defined as $\sim 100^{\circ}\text{C}$ in a saturated repository whereas it is 200°C for the unsaturated Yucca Mountain repository²⁰⁸. The surface temperature can be controlled by the type of waste, the waste content, and the nature of the buffer and backfill materials used²⁰⁸. The amount of waste immobilised in a wasteform is usually determined in such a way that the central temperature of the wasteform does not exceed a specified value during disposal in the repository²¹¹. For example, the glass transition temperature for R7T7 glass is 510°C , therefore higher temperatures during storage may induce crystallisation which could negatively affect durability and the integrity of the glass²¹¹. A lower temperature of 450°C is therefore taken as the maximum temperature as it provides a good safety margin²¹¹. Moreover, different wasteforms can have very different leaching behaviour at high temperatures. For example, in accelerated leaching tests on borosilicate glass and Synroc in a closed system performed by Ringwood *et al.*²¹², the borosilicate glass completely disintegrated at 350°C under high pressure (~ 100 MPa) after 24 h, whereas the Synroc matrix showed breakdown only at 900°C and 500 MPa after 24 h. Moreover, the performance of R7T7 glass and Synroc at hydrothermal temperatures up to 350°C has also been examined in previous studies^{213, 214, 215, 216, 217, 218, 219}. R7T7 glass formed up to 30 μm in thickness of altered surface under water leaching at 200°C over 1000 days²¹⁵. However, Caurel *et al.*²¹³ observed formation of large cracks in the bulk R7T7 glass at leaching

temperature of 250°C and hence the cracks impaired the leaching performance of R7T7 glass. Comparing to Synroc, Myhra *et al.*²¹⁹ reported that Synroc only formed a modified layer extending to ~200 nm depth after hydrothermal attack at 350°C for 25 days. Based on the previous studies, Synroc generally can stand a higher temperature leaching without breakage than glass.

The KBS-3V repository for spent nuclear fuel at Olkiluoto, Finland, is used as an example repository to introduce an evolution repository operation plan²²⁰ and a reference for simulations in this chapter. Figure 6.1 shows an illustration of the KBS-3V repository design²²¹. The KBS-3V repository is located at a depth of 420 m in rock and is designed to store 5500 tU (tonnes of uranium) in spent nuclear fuel encapsulated in 3000 copper canisters. There is an operational stage for up to 100 years which begins with the emplacement of the first canister in the repository and ends with the closure of the KBS-3V repository^{220, 222}. One of the main processes occurring during the operational stage is the thermal effect due to decay heat. During the operational stage, only a small portion of the whole tunnel system in the KBS-3V repository will be open at a time. Just a few deposition tunnels will be excavated in advance and will be closed as soon as they are full. They will be backfilled and plugged soon after the canisters and buffer are placed in the deposition holes. At the end of operations, the repository will be sealed and permanently closed²²⁰. The wasteform is assumed to be emplaced in this operation mode of repository soon after production for the simulations in this chapter.

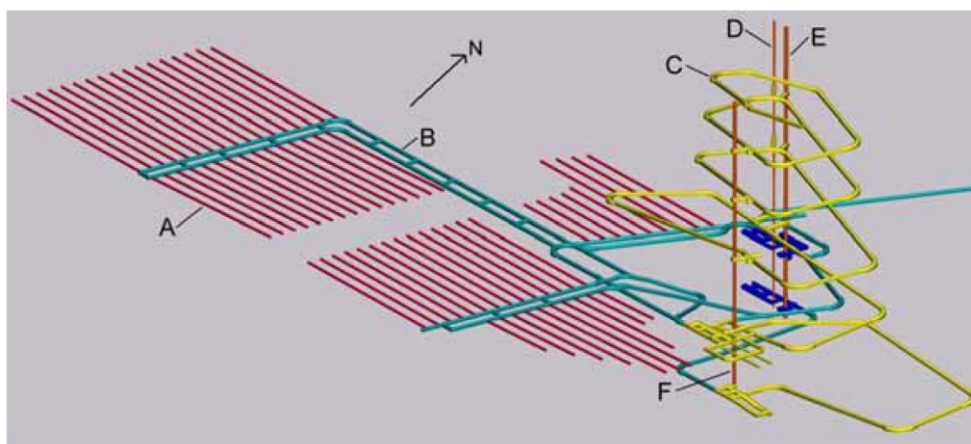


Figure 6.1 Illustration of KBS-3V repository cavities²²¹. A= deposition tunnels, B= transport tunnels, C= access tunnel, D= personnel shaft, E= canister shaft, F= ventilation shaft. Adapted from ref.²²¹

Due to safety and security regulations, EURO-GANEX waste is difficult to obtain for experimental studies. Moreover, studies are made more difficult by the fact that EURO-GANEX is still under experimental development (see section 1.2.2). In addition, the long timescales relevant to self-heating of waste tend to be inaccessible to laboratory experimentation. Instead, simulations were performed to predict heat generation and the changes in radionuclide inventory that occur during the decay of EURO-GANEX waste in Synroc-Z and R7T7. The results of these simulations are discussed in the following sections.

6.2 Simulation methods

The FISPACT-II software package^{223, 224, 225} was used to perform simulations of heat generation and activity from EURO-GANEX waste dissolved in the relevant wasteform matrices. FISPACT-II is a platform with a wide range of simulation methods maintained by the United Kingdom Atomic Energy Authority (UKAEA). The code works by iteratively solving the nuclear decay equation for systems containing multiple species. The result is a simulation of the time evolution of waste inventories, along with relevant properties such as generated heat and radioactivity. The FISPACT-II code can correctly account for the various branches in the decay chains that the radionuclides may take and track the compositional changes occurring in a sample over time. It also keeps a record of the energy released during decay events based on the library data during a calculation. The code is distributed with complete libraries of nuclear data^{226, 227, 228, 229} offering the cross-sections and decay constants for the rate equations which describe the decay of the initial inventory^{223, 225, 230}. In addition to these databases, the composition (precursors + waste) and the density of the wasteform at the initial time are the required input information.

The EURO-GANEX waste bearing Synroc-Z and R7T7 glass wasteform compositions used as inputs to the calculations are listed in Tables 6.1 - 6.4. These were derived by combining the basic composition of wasteform matrix with that of a known CANIGEN radionuclide inventory²³¹. The CANIGEN programme has been in use within the Fuel Reprocessing and Waste Management group at Whiteshell Nuclear Research Establishment (WNRE) in Canada for the generation of data on the radioactive decay properties of spent CANDU fuel. At the time of writing, no other publicly available source has been found providing the isotopic composition of spent nuclear fuel and hence its use here. The isotopic composition of wasteforms with 20 and 35 wt.% waste loading was a combination of the composition of reprocessed fuel and wasteform precursors. The waste composition represented fuel from which 99.9 wt.% of actinides (Pu+Am+Cm+Np+U) had been removed and had already been stored for 10 years as described for the CANIGEN programme²³¹. The proportions of wasteform precursors were expanded to given an isotopic composition by using the natural isotopic abundances of the species they

contained^{232, 233, 234}. As an input to each simulation, 1 kg of material was defined. The resulting composition of the 20 and 35 wt.% loaded R7T7 glass and Synroc-Z wasteforms are given in Tables 6.1 - 6.4 respectively, for these notional 1 kg samples. The initial densities of 20 and 35 wt.% waste loaded Synroc-Z and 20 wt.% waste loaded R7T7 glass were determined from their measured bulk density (4.47, 4.56 and 2.81 g/cm³, respectively) using values from the experiments in Chapters 3 and 4. In the absence of an experimental value, the density of the R7T7 glass with a higher waste load (35 wt.%) was estimated to be 2.95 g/cm³, which was calculated with ratio of waste-free glass²³⁵ (2.63 g/cm³) and 20 wt.% waste loaded glass. The time period considered by the simulations was from 1 day to 1000 years with data sampled increments of 1 day up to 1 year, and then in increments of 1 year up to 500 years and before using 10 year steps for the period between 500 and 1000 years.

Table 6.1 Composition of the 20 wt.% waste loaded R7T7 type glass wasteform isotopic composition in 1 kg used in the FISPACT-II programme.

Nuclide	Amount (g)	Nuclide	Amount (g)	Nuclide	Amount (g)
Li-6	6.8×10^{-1}	Zn-67	7.9×10^{-1}	Te-127	7.6×10^{-15}
Li-7	8.3	Zn-68	3.6	Te-127m	2.1×10^{-12}
B-10	8.3	Zn-70	1.2×10^{-1}	Te-128	6.4×10^{-1}
B-11	33	Sr-88	2.1	Te-130	2.3
O-16	4.3×10^2	Sr-90	2.7	Cs-133	8.3
O-17	1.6×10^{-1}	Y-89	2.5	Cs-134	1.3×10^{-2}
O-18	8.9×10^{-1}	Y-90	6.1×10^{-4}	Cs-135	1.0
Na-23	70	Zr-90	4.5	Cs-137	6.7
Al-27	25	Zr-91	4.8	Ba-135	2.2×10^{-6}
Si-28	1.9×10^2	Zr-92	5.5	Ba-137	1.3
Si-29	9.5	Zr-93	4.8	Ba-137m	7.0×10^{-7}
Si-30	6.3	Zr-94	6.4	Ba-138	5.9
P-31	1.5	Zr-95	2.0×10^{-17}	Ce-140	11
Ca-40	27	Mo-95	3.8	Ce-142	9.8
Ca-42	1.8×10^{-1}	Mo-96	3.9	Ce-144	7.3×10^{-4}
Ca-43	3.7×10^{-2}	Mo-97	4.0	Nd-143	5.7
Ca-44	5.7×10^{-1}	Mo-98	4.0	Nd-144	8.7
Ca-46	1.1×10^{-3}	Mo-100	4.6	Nd-145	5.2
Ca-48	5.1×10^{-2}	Ru-99	1.9×10^{-4}	Nd-146	4.1
Cr-50	4.7×10^{-2}	Ru-101	5.3	Nd-148	2.5
Cr-52	9.1×10^{-1}	Ru-102	4.9	Nd-150	1.2
Cr-53	1.0×10^{-1}	Ru-104	3.8	Sm-147	1.6
Cr-54	2.6×10^{-2}	Ru-106	1.8×10^{-3}	Sm-148	3.0×10^{-1}
Fe-54	3.2×10^{-1}	Pd-105	4.4	Sm-149	1.0×10^{-2}
Fe-56	5.0	Pd-106	3.4	Sm-150	1.3
Fe-57	1.2×10^{-1}	Pd-107	2.5	Sm-151	4.0×10^{-2}
Fe-58	1.5×10^{-2}	Pd-108	1.8	Sm-152	8.2×10^{-1}
Ni-58	3.2×10^{-1}	Pd-110	4.7×10^{-1}	Sm-154	1.9×10^{-1}
Ni-60	1.2×10^{-1}	Ag-107	2.2×10^{-6}	Gd-152	3.2×10^{-4}
Ni-61	5.4×10^{-3}	Ag-109	7.4×10^{-1}	Gd-155	1.7×10^{-1}
Ni-62	1.7×10^{-2}	Ag-110m	1.1×10^{-7}	Gd-156	1.0
Ni-64	4.3×10^{-3}	Te-125	6.4×10^{-2}	Gd-157	2.1×10^{-1}
Zn-64	9.4	Te-125m	5.9×10^{-5}	Gd-158	1.1×10^{-1}
Zn-66	5.4	Te-126	5.2×10^{-4}	Gd-160	2.7×10^{-2}

Table 6.2 Composition of the 20 wt.% waste loaded Synroc-Z wasteform isotopic composition in 1 kg used in the FISPACT-II programme.

Nuclide	Amount (g)	Nuclide	Amount (g)	Nuclide	Amount (g)
O-16	3.4×10^2	Zr-90	8.4×10^{-1}	Cs-135	1.0
O-17	1.3×10^{-1}	Zr-91	4.0	Cs-137	6.7
O-18	6.9×10^{-1}	Zr-92	4.3	Ba-130	5.2×10^{-2}
Al-27	28	Zr-93	4.8	Ba-132	4.9×10^{-2}
P-31	1.5	Zr-94	5.2	Ba-134	1.2
Ca-40	55	Zr-95	2.0×10^{-17}	Ba-135	3.2
Ca-42	3.7×10^{-1}	Mo-95	3.8	Ba-136	3.8
Ca-43	7.6×10^{-2}	Mo-96	3.9	Ba-137	6.8
Ca-44	1.2	Mo-97	4.0	Ba-137m	7.0×10^{-7}
Ca-46	2.3×10^{-3}	Mo-98	4.0	Ba-138	41
Ca-48	1.1×10^{-1}	Mo-100	4.6	Ce-140	11
Ti-46	30	Ru-99	1.9×10^{-4}	Ce-142	9.8
Ti-47	27	Ru-101	5.3	Ce-144	7.3×10^{-4}
Ti-48	2.7×10^2	Ru-102	4.9	Nd-143	5.7
Ti-49	20	Ru-104	3.8	Nd-144	8.7
Ti-50	19	Ru-106	1.8×10^{-3}	Nd-145	5.2
Cr-50	4.7×10^{-2}	Pd-105	4.4	Nd-146	4.1
Cr-52	9.1×10^{-1}	Pd-106	3.4	Nd-148	2.5
Cr-53	1.0×10^{-1}	Pd-107	2.5	Nd-150	1.2
Cr-54	2.6×10^{-2}	Pd-108	1.8	Sm-147	1.6
Fe-54	3.2×10^{-1}	Pd-110	4.7×10^{-1}	Sm-148	3.0×10^{-1}
Fe-56	5.0	Ag-107	2.2×10^{-6}	Sm-149	1.0×10^{-2}
Fe-57	1.2×10^{-1}	Ag-109	7.4×10^{-1}	Sm-150	1.3
Fe-58	1.5×10^{-2}	Ag-110m	1.1×10^{-7}	Sm-151	4.0×10^{-2}
Ni-58	3.2×10^{-1}	Te-125	6.4×10^{-2}	Sm-152	8.2×10^{-1}
Ni-60	1.2×10^{-1}	Te-125m	5.9×10^{-5}	Sm-154	1.9×10^{-1}
Ni-61	5.4×10^{-3}	Te-126	5.2×10^{-4}	Gd-152	3.2×10^{-4}
Ni-62	1.7×10^{-2}	Te-127	7.6×10^{-15}	Gd-155	1.7×10^{-1}
Ni-64	4.3×10^{-3}	Te-127m	2.1×10^{-12}	Gd-156	1.0
Sr-88	2.1	Te-128	6.4×10^{-1}	Gd-157	2.1×10^{-1}
Sr-90	2.7	Te-130	2.3	Gd-158	1.1×10^{-1}
Y-89	2.5	Cs-133	8.3	Gd-160	2.7×10^{-2}
Y-90	6.1×10^{-4}	Cs-134	1.3×10^{-2}		

Table 6.3 Composition of the 35 wt.% waste loaded R7T7 type glass wasteform isotopic composition in 1 kg used in the FISPACT-II programme.

Nuclide	Amount (g)	Nuclide	Amount (g)	Nuclide	Amount (g)
Li-6	5.5×10^{-1}	Zn-67	6.4×10^{-1}	Te-127	1.3×10^{-14}
Li-7	6.7	Zn-68	2.9	Te-127m	3.7×10^{-12}
B-10	6.7	Zn-70	9.7×10^{-2}	Te-128	1.1
B-11	27	Sr-88	3.6	Te-130	4.1
O-16	3.9×10^2	Sr-90	4.6	Cs-133	15
O-17	1.5×10^{-1}	Y-89	4.4	Cs-134	2.2×10^{-2}
O-18	8.0×10^{-1}	Y-90	1.1×10^{-3}	Cs-135	1.7
Na-23	57	Zr-90	4.4	Cs-137	12
Al-27	20	Zr-91	7.6	Ba-135	3.8×10^{-6}
Si-28	1.5×10^2	Zr-92	8.4	Ba-137	2.2
Si-29	7.7	Zr-93	8.5	Ba-137m	1.2×10^{-6}
Si-30	5.1	Zr-94	10	Ba-138	10
P-31	2.6	Zr-95	3.5×10^{-17}	Ce-140	19
Ca-40	22	Mo-95	6.7	Ce-142	17
Ca-42	1.4×10^{-1}	Mo-96	6.7	Ce-144	1.3×10^{-3}
Ca-43	3.0×10^{-2}	Mo-97	6.9	Nd-143	10
Ca-44	4.6×10^{-1}	Mo-98	7.0	Nd-144	15
Ca-46	8.9×10^{-4}	Mo-100	8.1	Nd-145	9.1
Ca-48	4.2×10^{-2}	Ru-99	3.4×10^{-4}	Nd-146	7.2
Cr-50	8.3×10^{-2}	Ru-101	9.2	Nd-148	4.4
Cr-52	1.6	Ru-102	8.6	Nd-150	2.2
Cr-53	1.8×10^{-1}	Ru-104	6.5	Sm-147	2.7
Cr-54	4.5×10^{-2}	Ru-106	3.2×10^{-3}	Sm-148	4.7×10^{-1}
Fe-54	5.6×10^{-1}	Pd-105	7.8	Sm-149	1.7×10^{-2}
Fe-56	8.7	Pd-106	6.0	Sm-150	2.2
Fe-57	2.0×10^{-1}	Pd-107	4.4	Sm-151	7.0×10^{-2}
Fe-58	2.7×10^{-2}	Pd-108	2.9	Sm-152	1.4
Ni-58	5.6×10^{-1}	Pd-110	8.1×10^{-1}	Sm-154	3.2×10^{-1}
Ni-60	2.1×10^{-1}	Ag-107	3.9×10^{-6}	Gd-152	5.6×10^{-4}
Ni-61	9.4×10^{-3}	Ag-109	1.3	Gd-155	3.0×10^{-1}
Ni-62	3.0×10^{-2}	Ag-110m	1.9×10^{-7}	Gd-156	1.8
Ni-64	7.6×10^{-3}	Te-125	1.1×10^{-1}	Gd-157	3.7×10^{-1}
Zn-64	7.6	Te-125m	1.0×10^{-4}	Gd-158	2.0×10^{-1}
Zn-66	4.4	Te-126	9.0×10^{-4}	Gd-160	4.7×10^{-2}

Table 6.4 Composition of the 35 wt.% waste loaded Synroc-Z wasteform isotopic composition in 1 kg used in the FISPACT-II programme.

Nuclide	Amount (g)	Nuclide	Amount (g)	Nuclide	Amount (g)
O-16	3.1×10^2	Zr-90	1.5	Cs-135	1.7
O-17	1.2×10^{-1}	Zr-91	7.0	Cs-137	12
O-18	6.3×10^{-1}	Zr-92	7.4	Ba-130	4.2×10^{-2}
Al-27	22	Zr-93	8.5	Ba-132	4.0×10^{-2}
P-31	2.6	Zr-94	9.1	Ba-134	9.6×10^{-1}
Ca-40	45	Zr-95	3.5×10^{-17}	Ba-135	2.6
Ca-42	3.0×10^{-1}	Mo-95	6.7	Ba-136	3.1
Ca-43	6.2×10^{-2}	Mo-96	6.7	Ba-137	6.7
Ca-44	9.6×10^{-1}	Mo-97	6.9	Ba-137m	1.2×10^{-6}
Ca-46	1.8×10^{-3}	Mo-98	7.0	Ba-138	39
Ca-48	8.6×10^{-2}	Mo-100	8.1	Ce-140	19
Ti-46	25	Ru-99	3.4×10^{-4}	Ce-142	17
Ti-47	22	Ru-101	9.2	Ce-144	1.3×10^{-3}
Ti-48	2.2×10^2	Ru-102	8.6	Nd-143	10
Ti-49	16	Ru-104	6.5	Nd-144	15
Ti-50	15	Ru-106	3.2×10^{-3}	Nd-145	9.1
Cr-50	8.3×10^{-2}	Pd-105	7.8	Nd-146	7.2
Cr-52	1.6	Pd-106	6.0	Nd-148	4.4
Cr-53	1.8×10^{-1}	Pd-107	4.4	Nd-150	2.2
Cr-54	4.5×10^{-2}	Pd-108	2.9	Sm-147	2.7
Fe-54	5.6×10^{-1}	Pd-110	8.1×10^{-1}	Sm-148	4.7×10^{-1}
Fe-56	8.7	Ag-107	3.9×10^{-6}	Sm-149	1.7×10^{-2}
Fe-57	2.0×10^{-1}	Ag-109	1.3	Sm-150	2.2
Fe-58	2.7×10^{-2}	Ag-110m	1.9×10^{-7}	Sm-151	7.0×10^{-2}
Ni-58	5.6×10^{-1}	Te-125	1.1×10^{-1}	Sm-152	1.4
Ni-60	2.1×10^{-1}	Te-125m	1.0×10^{-4}	Sm-154	3.2×10^{-1}
Ni-61	9.4×10^{-3}	Te-126	9.0×10^{-4}	Gd-152	5.6×10^{-4}
Ni-62	3.0×10^{-2}	Te-127	1.3×10^{-14}	Gd-155	3.0×10^{-1}
Ni-64	7.6×10^{-3}	Te-127m	3.7×10^{-12}	Gd-156	1.8
Sr-88	3.6	Te-128	1.1	Gd-157	3.7×10^{-1}
Sr-90	4.6	Te-130	4.1	Gd-158	2.0×10^{-1}
Y-89	4.4	Cs-133	15	Gd-160	4.7×10^{-2}
Y-90	1.1×10^{-3}	Cs-134	2.2×10^{-2}		

6.3 Simulations of wasteforms containing 20 wt.% EURO-GANEX waste

Figure 6.2 displays the results of simulated heat output by mass and by volume for Synroc-Z and R7T7 glass containing 20 wt.% EURO-GANEX waste. The main sources of heat generation are beta and gamma decay processes with the contribution from alpha radiation being negligible (owing to the absence of actinides in the wasteform). The heat output starts to decrease significantly after 1 year of decay and drops below the level used by the IAEA to define HLW (2 kW/m^3 or 0.0007 kW/kg) after a decay time of 105 years^{7, 17}. Despite this, it must be noted that the waste would still have to be classified as HLW due to its high specific activity. Figure 6.3 exhibits the specific activity release of the different wasteforms by mass. The activity decrease is similar to the generated heat as both of them start to reduce significantly after 1 year of decay. However, the activity does not decrease below the threshold for HLW ($2.5 \times 10^9 \text{ kBq/kg}$) until 140 years¹⁷.

By mass, both Synroc-Z and R7T7 wasteforms released the same amount of heat (Figure 6.2a and b). This is to be expected as they contain the same waste elements in the same proportions which undergo equivalent decay processes at the same rates. However, because of their different densities, Synroc-Z released ~1.6 times more heat than R7T7 for the same volume (Figure 6.2c and d). In other words, 1 kg of Synroc-Z and R7T7 with the same waste loading discharge the same amounts of heat while 1 m^3 of Synroc-Z gives off 1.6 times more heat than 1 m^3 of R7T7 glass.

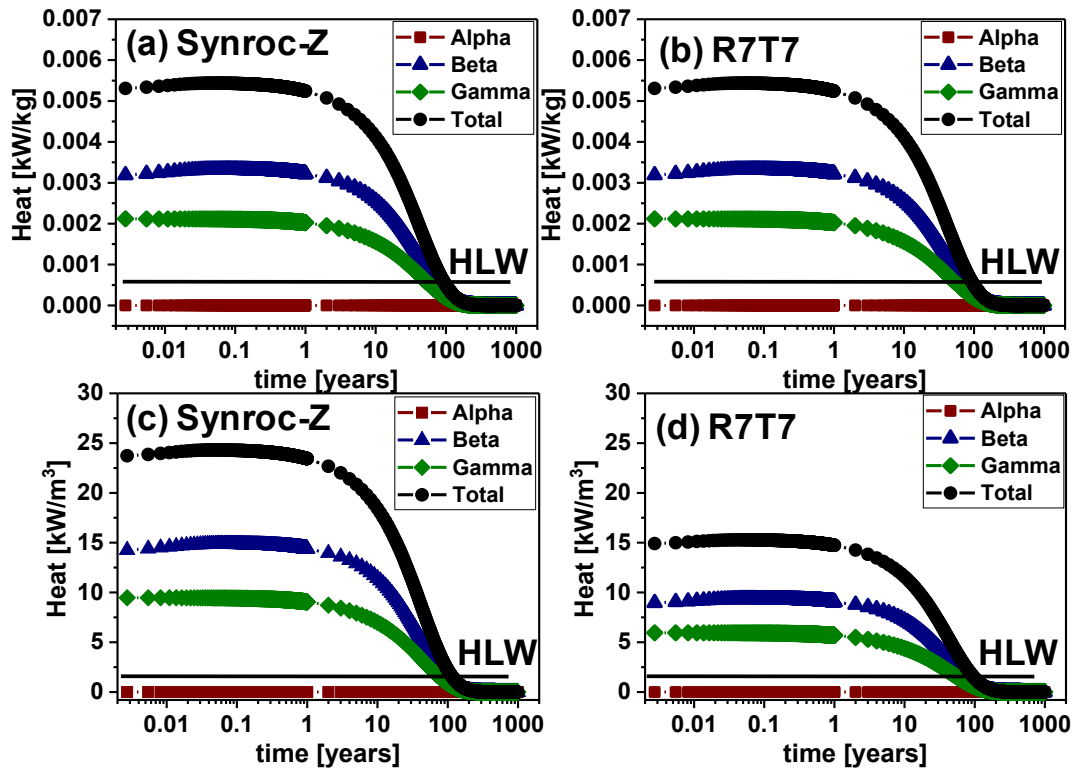


Figure 6.2 Generated heat decay in 20 wt.% waste loaded Synroc-Z and R7T7 by (a,b) mass and (c,d) volume. The IAEA threshold for HLW classification (2 kW/m^3 or 0.0007 kW/kg) is also given¹⁷.

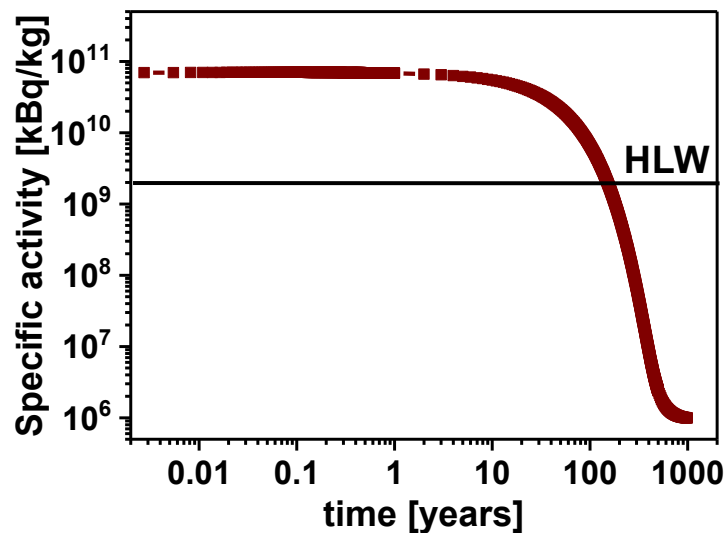


Figure 6.3 Specific activity release of wasteforms with 20 wt.% waste loading as a function of time. The threshold for HLW classification ($2.5 \times 10^9 \text{ kBq/kg}$) was determined based on IAEA safety guide¹⁷.

6.4 Main sources of heat generation and activity

In the first several hundred years, the heat generation is primarily due to Cs-137 and Sr-90 decay¹⁰. Figure 6.4 shows the beta decays of Cs to Ba and Sr to Y and Zr which are the principal sources of energy release due to their relatively high concentration among FPs in 10-year old HLW^{236, 237, 238}.

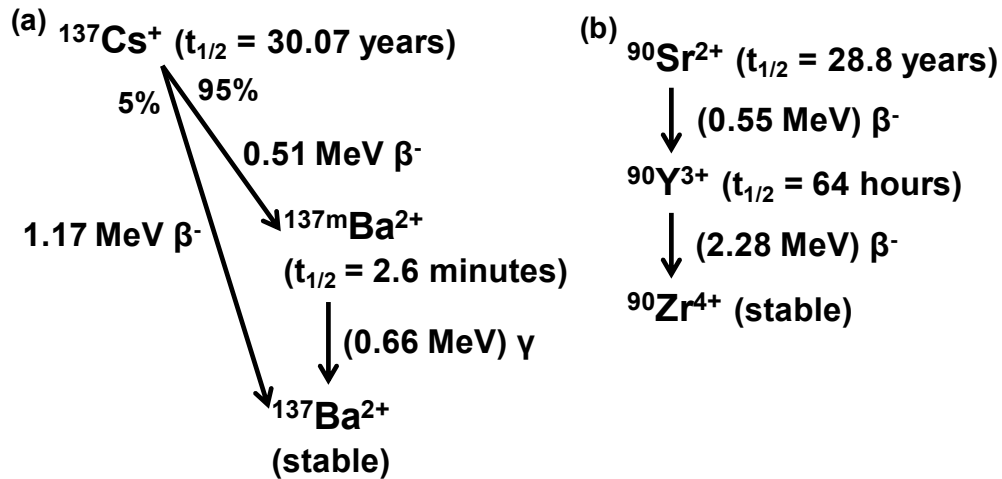


Figure 6.4 Decay level scheme of (a) Cs-137 and (b) Sr-90

This kind of decay is accompanied by changes of both ionic size and charge. Cs decays into Ba with charge change from 1+ to 2+ while the charge of Sr decaying into Zr via Y changes from 2+ via 3+ to 4+. In Synroc phases, Zr produced by decay of Sr-90 in perovskite is readily incorporated in this phase as CaZrO_3 which also has a perovskite structure. Similarly, since Cs is already substituting for Ba in hollandite, additional Ba from the decay of Cs is unlikely to cause a problem²¹². Figure 6.5 displays weight fraction changes of Cs-137 and Sr-90 in the wasteforms due to decay. The rate of change initially increases rapidly and then after 30 years of decay gradually slows down until it eventually stabilises at a significantly slower rate after 120 years of decay. Figure 6.6 shows the percentage of generated heat and activity produced from Cs-137 and Sr-90 in the wasteforms. In the first 10 years, Cs-137 and Sr-90 cause > 98 % of heat release and activity. This reaches its highest point (> 99.9 %) after 30 and 15 years of decay for the heat and activity respectively. Note that the isotopic composition at the start of the simulations represented material that had already been stored for 10 years; this means the predicted peak in heat occurs 40 years

after, and activity 25 years after, the fuel has been removed from the reactor. The proportion of the total heat output due to Cs-137 and Sr-90 displays a dramatic decrease after 350 years of decay while the corresponding activity exhibits a drop after 180 years. Cs-137 and Sr-90 are still the main source (>50%) of heat generation during the first 600 years and the main source of activity during the first 450 years after disposal. The heat and activity decreased at different time because of other competing reactions (i.e. Zr-93 and Sm-151 decay). The proportions of released heat and activity from other reactions vary with time and thus the proportion of the total releases heat and activity from the decay of Cs-137 and Sr-90 decreased at different rates. The contributions of Cs-137 and Sr-90 drop to a negligible level (< 1 %) of generated heat and activity after 800 and 670 years of decay respectively. Moreover, Zr-93 ($t_{1/2} = 1.53$ million years) and Sm-151 ($t_{1/2} = 88.8$ years) become the first and second largest contributors of heat and activity after 670 years of disposal.

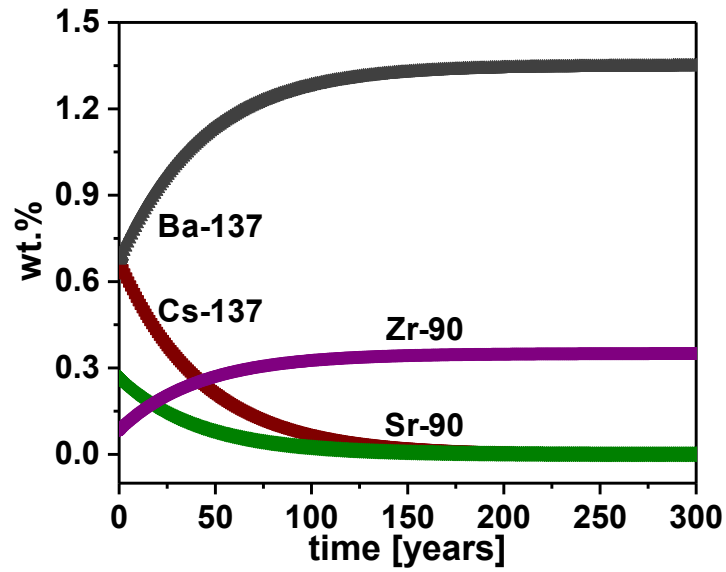


Figure 6.5 Weight fraction changes of Cs-137 (red line) and Ba-137 (grey line) and Sr-90 (green line) and Zr-90 (purple line) against time.

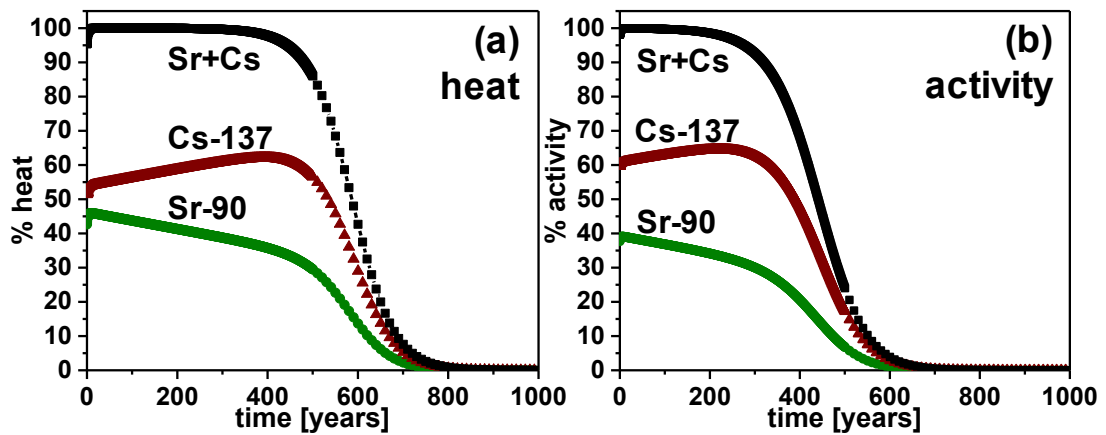


Figure 6.6 Percentage of (a) heat output and (b) activity in wasteforms from Sr-90 (green) and Cs-137 (red) decay against time.

6.5 Centreline temperatures in a typical waste package

The heat generated by EURO-GANEX waste tends to increase the internal temperature of the wasteform in which it is immobilised. This is determined by the heat transfer from the wasteform through its container and to the surrounding backfill materials. Predictions of the centreline wasteform temperatures are useful for geological repository designers and engineers responsible for optimising the waste loading and package design of the wasteforms to be placed in the repository. Earlier in section 6.1, the temperature limit of the outer surface of the wasteform canister was defined as being 100°C for a saturated repository to ensure the chemical and thermal stability of buffer/backfill materials (i.e. bentonite) and 200°C for the unsaturated repository^{208, 220}. In the following section, it is assumed that the repository under consideration has been with adequate cooling such that sufficient heat can be transported away from the canister surface, allowing a stable temperature to be maintained. As a results, the 100 and 200°C temperatures will be used as a boundary condition in the centreline temperature predictions that follow. A further simplifying assumption was made that the increase in wasteform centreline temperature due to the presence of the canister was negligible. This seems reasonable as the canister is only a thin layer of metal (i.e. copper or stainless steel) that has good thermal conductivity. The surface of the canister should be practically at a uniform temperature and the entire thermal gradient should be transferred to the backfill materials around the canister. The operational stage was assumed to be 100 years and the canisters are temporarily stored in an engineered air-cooled storage area based on the Finnish plan²²⁰. In the similar method, canisters of vitrified HLW in Sellafield in the UK are currently stored in natural air-cooled storage areas until they can be transferred to a geological disposal facility²³⁹. The surface temperature of canisters was assumed to be room temperature (20°C) during the operational stage in this section. The shape of the canister was assumed to be a cylinder based on the Finnish plan for operational simplicity in the orientation alignment²²⁰. The temperature increase from heat generated homogeneously throughout the centre of a solid cylinder can be calculated using the equation²⁴⁰.

$$T_c = T_s + \frac{qR^2}{4k}$$

with the following parameters:

T_c = the centreline temperature (K)

T_s = the surface temperature (K)

q = the heat released from waste (W/m³)

R = the diameter of the wasteform (m)

k = the thermal conductivity (W/mK)

Figure 6.7 shows the temperature rise for wasteforms with 20 and 35 wt.% waste loading as a function of time assuming a wasteform diameter of 36 cm based on a repository study for ceramic wasteform²⁴¹. Thermal conductivities are 1.1 and 2.1 W/mK for R7T7 glass and Synroc respectively^{92, 211}. The maximum temperature increase occurred at 17 days of decay. The maximum temperature increase for Synroc-Z with 20 and 35 wt.% HLW were 94 and 167°C respectively. However, due to its lower thermal conductivity, R7T7 glass showed higher maximum temperature increase which were 113 and 207°C for 20 and 35 wt.% waste loading respectively. After the increased temperature from heat generation has hit the highest point, the temperature increases for the 20 and 35 wt.% waste loaded wasteforms become negligible (<1°C) after 200 and 226 years of decay respectively.

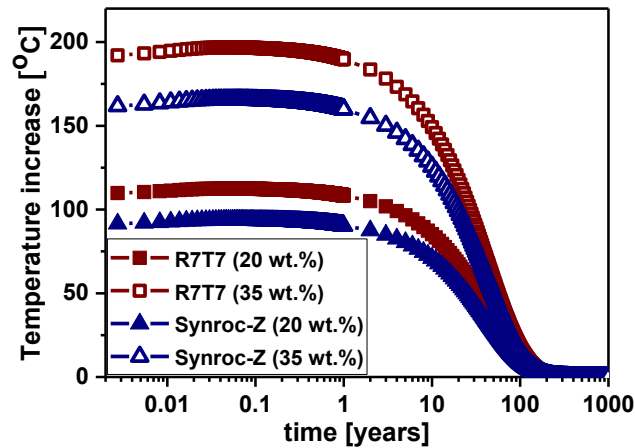


Figure 6.7 The centerline temperature increase (relative to outside environment temperature) of Synroc-Z (navy) and R7T7 glass (red) with 20 wt.% (filled symbols) and 35 wt.% waste loadings (open symbols). The diameter of canister was assumed to be 36 cm.

Figure 6.8 and Figure 6.9 predict the centreline temperatures of the canister in two scenarios. In Figure 6.8, the canister undergoes the initial operational stage while in Figure 6.9 it is placed in the repository without preliminary operational stage. The canister surface temperatures are set to 100 and 200°C in saturated and unsaturated repositories respectively.

Figure 6.8 displays the centreline temperatures of wasteforms in the saturated and unsaturated repositories as a function of time (100 - 1000 years) with operational stage (1 day to 100 years). During the operational stage (Figure 6.8a), the maximum centreline temperatures for Synroc-Z were 114 and 187°C for 20 and 35 wt.% waste loading respectively after 17 days of decay. The R7T7 glass displayed higher maximum centreline temperatures of 133 and 227°C for 20 and 35 wt.% waste loadings respectively. The temperature increase from surface to centreline in saturated and unsaturated repository (Figure 6.8 b and c) after closure (as described in section 6.1) was the same. The temperature changes from heat generation after the operational stage become minor effect. The maximum temperature increases for Synroc-Z with 20 and 35 wt.% waste loading were 9 and 16°C respectively while R7T7 glass exhibited a slightly higher temperature increase of 11 and 18°C for 20 and 35 wt.% waste loadings respectively.

Figure 6.9 predicts that the centreline temperatures of wasteforms in

saturated and unsaturated repositories would be if they were sealed without first requiring operational stage. The maximum centreline temperature in both repository types occurred at 17 days of decay. The highest centreline temperatures in the saturated repository (Figure 6.9a) of Synroc-Z for 20 and 35 wt.% waste loading were 194 and 267°C which were higher than when an operational period is included. For the unsaturated case (Figure 6.9b), the maximum centreline temperatures of Synroc-Z and R7T7 glass with 35 wt.% waste loading were up to 366 and 407°C respectively.

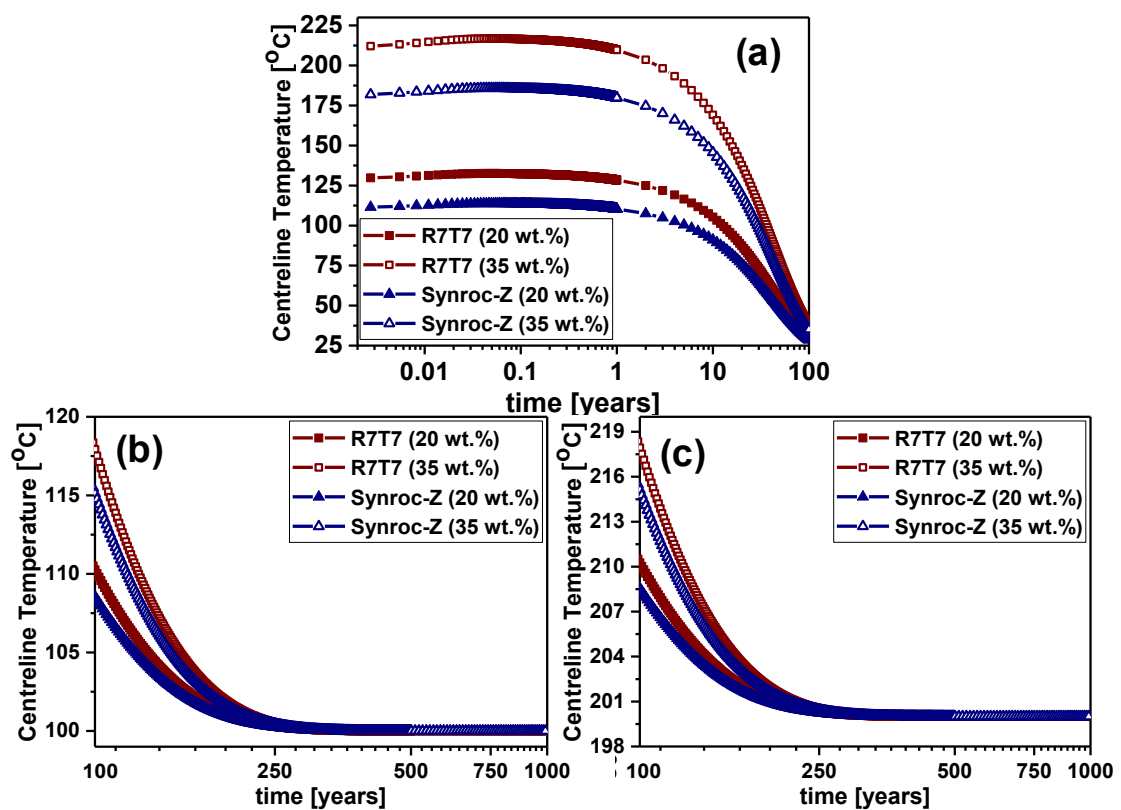


Figure 6.8 Centreline temperatures of Synroc-Z (navy) and R7T7 glass (red) with 20 wt.% (filled symbols) and 35 wt.% waste loadings (open symbols) during (a) operational stage for 100 years and after closing in the (b) saturated and (c) unsaturated repository, as a function of storage time. The wastefrom diameter was assumed to be 36 cm.

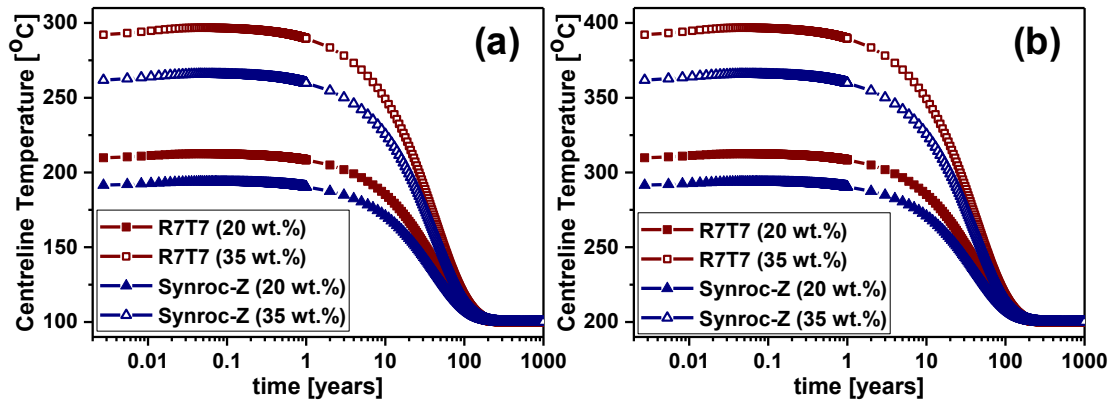


Figure 6.9 Centreline temperatures of Synroc-Z (navy) and R7T7 glass (red) with 20 wt.% (filled symbols) and 35 wt.% waste loadings (open symbols) in the (a) saturated and (b) unsaturated repository without operational stage, as a function of storage time. The wasteform diameter was assumed to be 36 cm.

An important consideration for repository designers is waste package dimensions. In the present case, the radius of the waste canisters could alter the basic dimensions of the galleries and tunnels in the repository and ultimately this would define the how many cylinders and how much waste could be disposed of. Given the extreme cost of such facilities making best use of space is important. In order to explore such issues, Figure 6.10 provides predictions for the maximum centreline temperatures of wasteforms for various cylinder diameters (from 30 to 100 cm) for the saturated and unsaturated repository conditions. Although the T_m of Synroc and R7T7 glass are high (~ 1600 and $\sim 1200^\circ\text{C}$)^{188, 242}, it is known that the Synroc matrix begins to breakdown at $T = 900^\circ\text{C}$ and $P = 500$ MPa after 24 h and that borosilicate glass will completely disintegrate at 350°C and ~ 100 MPa after 24 h in accelerated leaching tests²¹². To reflect this, maximum temperature limits of 800 and 330°C were chosen for the Synroc-Z and R7T7 glass respectively. Both are below the temperatures at which the materials start to degrade, which provides a good margin of safety. In the saturated repository (Figure 6.10a), the maximum diameters of Synroc-Z in these conditions are 95 and 70 cm for 20 and 35 wt.% waste loading respectively. However, the R7T7 glass shows less flexibility for the package size and waste loading due to the lower limit. The maximum diameters of R7T7 glass are 50 and 35 cm for 20 and 35 wt.% waste loadings respectively. Due to the design of unsaturated repository (200°C for the surface temperature, Figure 6.10b), the maximum diameter of Synroc-Z with 35 wt.% waste loading is 65 cm

while the maximum diameters of 20 wt.% waste loaded Synroc-Z and R7T7 glass are 90 and 35 cm respectively. The diameter of the wasteform for 35 wt.% waste loaded R7T7 glass in the unsaturated repository could be no larger than 30 cm. Overall, the safe diameter range of Synroc-Z for both 20 and 35 wt.% waste loadings and both repositories (saturated and unsaturated) is 30 - 65 cm. For R7T7 glass wasteform, it is 30 - 35 cm except in the case of the 35 wt.% loading in the unsaturated repository where it is no larger than 30 cm.

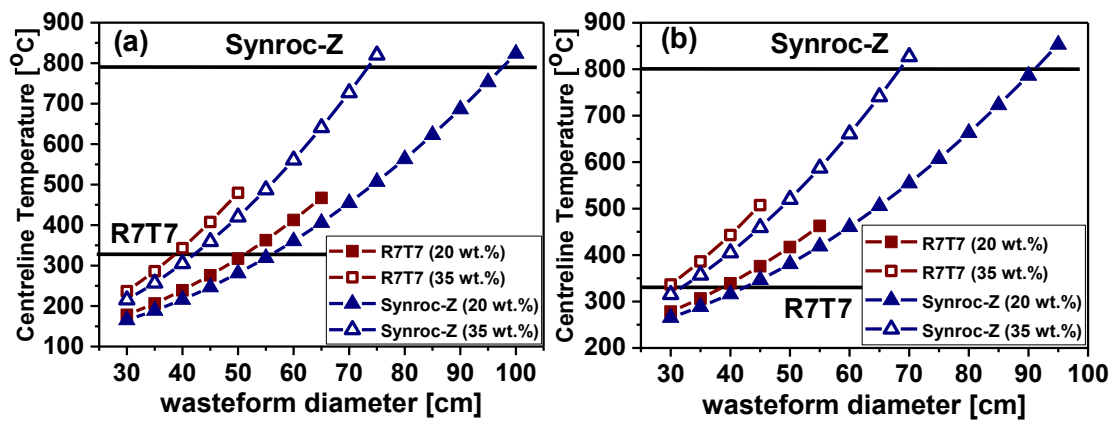


Figure 6.10 Maximum centreline temperatures of Synroc-Z (navy) and R7T7 glass (red) with 20 wt.% (filled symbols) and 35 wt.% (open symbols) waste loadings with different diameters in the (a) saturated and (b) unsaturated repository. The horizontal lines indicate the temperature limits for Synroc-Z and R7T7 glass.

6.6 Summary

Heat generation and temperature increase from EURO-GANEX waste in R7T7 glass and Synroc-Z wasteforms have been estimated via FISPACT-II simulations. Table 6.5 summarises the results of this chapter and reveals that Synroc-Z displayed several advantages when compared to R7T7 glass:

1. Higher density: Synroc-Z has a density ~ 1.6 times higher than R7T7 and thus needs less space than R7T7 while containing the same amount of waste.
2. Higher thermal conductivity: The higher thermal conductivity allows Synroc to experience a smaller temperature rise than R7T7 even through Synroc has a higher heat output for the same volume.
3. More flexibility in package size and waste loading: The better performance of Synroc-Z under extreme environments leads to a larger safe diameter range than R7T7 glass.

The effect of decay from Sr-90 and Cs-137 radionuclides reduces significantly after 200 years, as both heat and activity are $< 1\%$ of initial values meaning that after this period the centreline temperature increase due to decay heating is less than 1°C .

Table 6.5 Summary of heat generation properties of Synroc-Z and R7T7 in this chapter.

	Synroc-Z		R7T7	
Density (g/cm^3)	4.47	4.52	2.81	2.81
Thermal conductivity (W/mK)	2.1	2.1	1.1	1.1
Waste loading (wt.%)	20	35	20	35
Max heat generation by mass (kW/kg)	0.0054	0.0095	0.0054	0.0095
Max heat generation by volume (kW/m^3)	24.3	43.0	15.3	26.7
Max temperature increase ($^\circ\text{C}$) in 36 cm diameter in the saturated repository	194	266	213	297
Temperature increase $< 1^\circ\text{C}$ after decay of (years)	192	216	200	223
Max diameter (cm) with safe margin in the saturated/unsaturated repository	95/90	70/65	50/35	35/ < 30

Chapter 7: Discussion

A promising advanced reprocessing method, EURO-GANEX^{42, 43}, has been designed to separate the actinides as a group and thus one of the waste streams is likely to consist of only FPs without traceable actinides. Synroc-Z and R7T7 glass were used to immobilise a simulated actinide-free waste stream from EURO-GANEX and the heat generation (in Chapter 6) and durability of these wasteforms have been examined. This chapter discusses the fabrication of Synroc-Z and R7T7 wasteforms and compares their durability with those of similar wasteforms.

7.1 Synroc-Z fabricated by HUPing and HIPing

The waste stream from the EURO-GANEX process (containing only FPs without actinides) can be immobilised successfully in Synroc-Z with up to 35 wt.% waste loading. Synroc-Z contained less zirconolite (6.4 wt.%) which is the main host for actinides than Synroc-C (27.1 wt.%) and therefore more perovskite and hollandite (62.5 wt.% vs. 51.7 wt.%) which are the primary phases for FPs immobilisation (i.e. Sr and rare earths for perovskite and Cs and Ba for hollandite). Based on the phase composition, Synroc-Z is more suitable for EURO-GANEX waste. The unit cell volumes of the three main phases in Synroc-Z were similar to Synroc-C (Table 3.2). This suggests that the waste elements entered the same phases.

HUPing involves simultaneous heating and uniaxial die pressing (see section 2.1.2.1), and the processing temperature was the most important factor to obtain dense samples. The HUPed samples (1050°C, 20 MPa, 3 h) in Figure 3.10(d) contained pores and incompletely densified regions. This indicated that the processing temperature required to produce a dense sample should be 1100°C or above. Moreover, the higher processing temperature caused a larger grain size range (Table 3.3). The dwell time had a significant effect on phase composition between 0.5 and 3 h but at a lesser extent between 3 and 5 h (Figure 3.12). This suggested that after 3 h of dwell time the phase composition is largely equilibrated. The HUPing pressure and dwell time (>3 h) had minor or negligible effects when the processing temperature was sufficiently high.

However, to reach the target phase content (greater host phase content), higher processing temperatures and longer dwell times (> 1 h) are needed but limited at 1200°C to avoid waste volatilisation (Figure 3.1). The recommended HUPing conditions were thus $1150 - 1200^{\circ}\text{C}$ and > 10 MPa for 3 h. This HUPing condition range is similar to what had been suggested by Ringwood *et al.*²⁴³ for HUPed Synroc-C ($1150 - 1200^{\circ}\text{C}$, 14 - 21 MPa for 2 h) as both Synroc-Z and Synroc-C contain the same phases but in different proportions. Moreover, Synroc-Z can host up to 35 wt.% simulated waste without forming any new phases and still retain some of the rutile buffer phase (~ 8.2 wt.%) allowing for changes in the proportion of the host phases for the waste elements (Figure 3.15). The metallic phases' proportion increases with higher waste loading and hence the measured bulk densities of higher waste loaded Synroc-Z were higher. This may be an issue for leach testing which will be discussed in section 7.3.4.

Another hot-pressing technique, HIPing (see section 2.1.4), has been used to produce Synroc and its derivative (ceramic wasteforms) at ANSTO and other research centres^{90, 119, 244, 245, 246}. The advantages of HIPing when compared to HUPing are the negligible release of off-gas and more isotropic and higher applied pressure. Synroc-Z was prepared successfully via HIPing without undesired phases at ANSTO and exhibited no significant differences in texture and the distribution of waste elements when compared to HUPed Synroc-Z. However, there are more factors to consider such as the canister material employed and baking temperatures before HIPing to remove moisture, all of which need to be controlled when using HIPing technology. The interactions between the 316 stainless steel canister and Synroc under HIPing conditions has been examined by Li *et al.*²⁴⁶. The interface of canister and Synroc is < 10 μm but the contaminated (mainly with Fe) Synroc is found up to 300 μm from the interface.

Some undesired phases such as Cs-Mo compounds and Ca-Mo phases were observed in HIPed Synroc-Z samples in Figure 3.20 (for conditions of 1200°C , 20 MPa, 3 h and 1050°C , 100 MPa, 3 h). The Cs-Mo compounds observed in HIPed Synroc-Z were also discovered in Synroc-C prepared via melting under air¹¹⁸. The hollandite phase did not incorporate Cs, which formed

the Cs-Mo compounds instead. This is an issue for the wasteform durability as by comparison the Cs-Mo compounds are easily leached (Figure 5.12). In order to incorporate the Cs in the hollandite, the Synroc-C had to be processed under reducing atmosphere¹¹⁸. In addition, the Mo was supposed to be reduced to metallic Mo and form alloy phases¹¹⁷. However, the extra Ti metal added for redox control⁵ was not sufficient or reacted with other materials such as the canister during the baking stage. The insufficient amount of Ti metal powder prevented Mo from being reduced and thus allowed the formation of Cs-Mo and Ca-Mo compounds during HIPing. Moreover, the Cs-Mo compounds formed a layer deposited on the HIPed Synroc-Z and they easily came off from the Synroc-Z during the transfer of samples from FIB to TEM as they were weakly bound (Figure 3.25). This suggested that Cs and Mo may have volatilised and formed pores in the process of HIPing. In cooling, the gaseous Cs and Mo were then deposited on inside of the pore surfaces. This problem is currently being looked at in ANSTO using Synroc with 20 wt.% waste loading with varying additions of Ti metal powder (2 – 10 wt.%) prior to HIPing.

7.2 R7T7 glass fabricated by melting vitrification and HIPing

The waste stream from EURO-GANEX, containing only FPs, can be incorporated into a R7T7 glass matrix. The R7T7 glass composition, when mixed with waste prepared via the oxide route, did not exhibit full decomposition of the carbonates during calcination. The calcination temperature was not increased further because the threshold was deliberately chosen to be lower than the R7T7 glass transition temperature to avoid reactions between the powder and the alumina crucible. Instead, the powder prepared via oxide route decomposed during melting. The minimum processing temperature at which most of the waste dissolves in the glass, without leaving significant porosity, was found to be 1100°C (Figures 4.6 and 4.7).

The R7T7 samples produced via the melting route contained only RuO₂ crystals and Pd-Te alloy inclusions when the processing temperature exceeded 1100°C. This is not surprising since RuO₂ and Pd-Te alloys have often been reported insoluble or sparingly soluble in borosilicate glasses^{247, 248, 249, 250}. PUREX waste has previously been immobilised in R7T7 glass wasteform and it

has been reported that it is difficult to dissolve elements from the noble metal group in this glass^{85, 192}. This indicates that the platinoids are a recurring issue in borosilicate glass wasteforms even if the waste composition has changed.

Although vitrification technology has been used for nuclear waste for many years, it requires precise control of process conditions such as melt viscosity, and crystallisation(s) which notably depend on waste composition. Another method to produce glass, HIPing, currently used at laboratory scale for ceramic^{245, 251} and glass composite materials (GCMs)^{119, 252, 253}, was tested. The R7T7 glass sample was HIPed to determine the effect of pressure on R7T7 glass. There have been previous studies looking at sintered glass via HIPing using different pressure settings (0.2 – 2 MPa) to lower the required temperature (<1000°C) with the intention of lowering radionuclide volatilisation (e.g. Cs, Mo)^{5, 254, 255}. However, the application of pressure did not increase the solubility of elements with low solubility such as Mo, Ru, Pd, Te^{247, 248, 249, 250, 256, 257, 258, 259, 260}. Moreover, Cr-Fe metal crystals were visible at the edges of glass R7T7 HIP-1100-10-3 (Figure 4.14a) and could be detected via XRD in all HIPed samples (Figures 4.15 – 4.17). This indicated that the glass precursors and waste reacted with the canister (316 grade stainless steel) during HIPing. In addition, some pores appeared in all HIPed glasses leading to porosities of ~1 vol%, larger than that obtained from the melting route (< 0.3 vol%). Since the canisters were sealed, these pores may actually be bubbles which come from volatile elements (~1.2 wt% of mass loss, Figure 4.1) and oxygen from foaming during HIPing as they could not escape. Some volatile elements such as Mo were not found in the glass prepared via the melting vitrification route when examined with SEM/EDX but were found in HIPed glass samples. This may suggest that during the melting route these volatile elements may volatilise due to the high processing temperatures required for melting.

When considering these results and the process complexity, the HIPing process did not show significant advantages compared to melting vitrification. The advantages are that the sealed canisters avoided volatile elements escaping which would minimise secondary or operational wastes from off-gas systems during HIPing and glass does not need to be poured into another canister as it's already contained in one.

7.3 Durability of wasteforms

Understanding of the resistance to leaching of a wasteform is fundamental to being able to control radionuclide release into the biosphere, as corrosion of other barriers such as the waste canister may eventually lead to the wasteform being exposed to groundwater. The durability performance of Synroc-Z prepared via HUPing and HIPing and R7T7 glass fabricated via the melting route were examined in Chapter 5 via MCC-1 testing at 90°C over 28 days.

7.3.1 Leaching behaviour of Synroc and glass wasteforms

The HUPed Synroc-Z with a dense microstructure (< 0.5 vol% porosity) displayed a good durability with the leach rates of all elements decreasing with time (Figure 5.1). Conversely, the unexpected Cs-Mo compounds formed in the HIPed Synroc-Z (Figure 3.20) caused deleterious effects on the leach rates of Cs and Mo. This is due to insufficiently prevailing reducing conditions during HIPing and could be rectified by adding more Ti metal after calcinations. The R7T7 glass was another good wasteform for EURO-GANEX waste as it incorporated most wastes (except Ru, Pd, and Te) into the glass matrix and, as shown in section 5.3, displayed adequate leaching performance.

Figure 7.1 compares the leach rates of HUPed Synroc-Z and R7T7 glass samples in this thesis and PNL 76-68 glass⁸³ and Synroc-C²⁴³ from literatures using MCC-1 testing. In general, both Synroc displayed better durability than both glass wasteforms. Both glass wasteforms (R7T7 and PNL 76-68) maintained their leach rates at a similar level while PNL 76-68 glass generally showed the highest leach rates than other wasteforms. Both Synroc exhibited similar durability and a decrease trend for their dissolution rates when extending testing period.

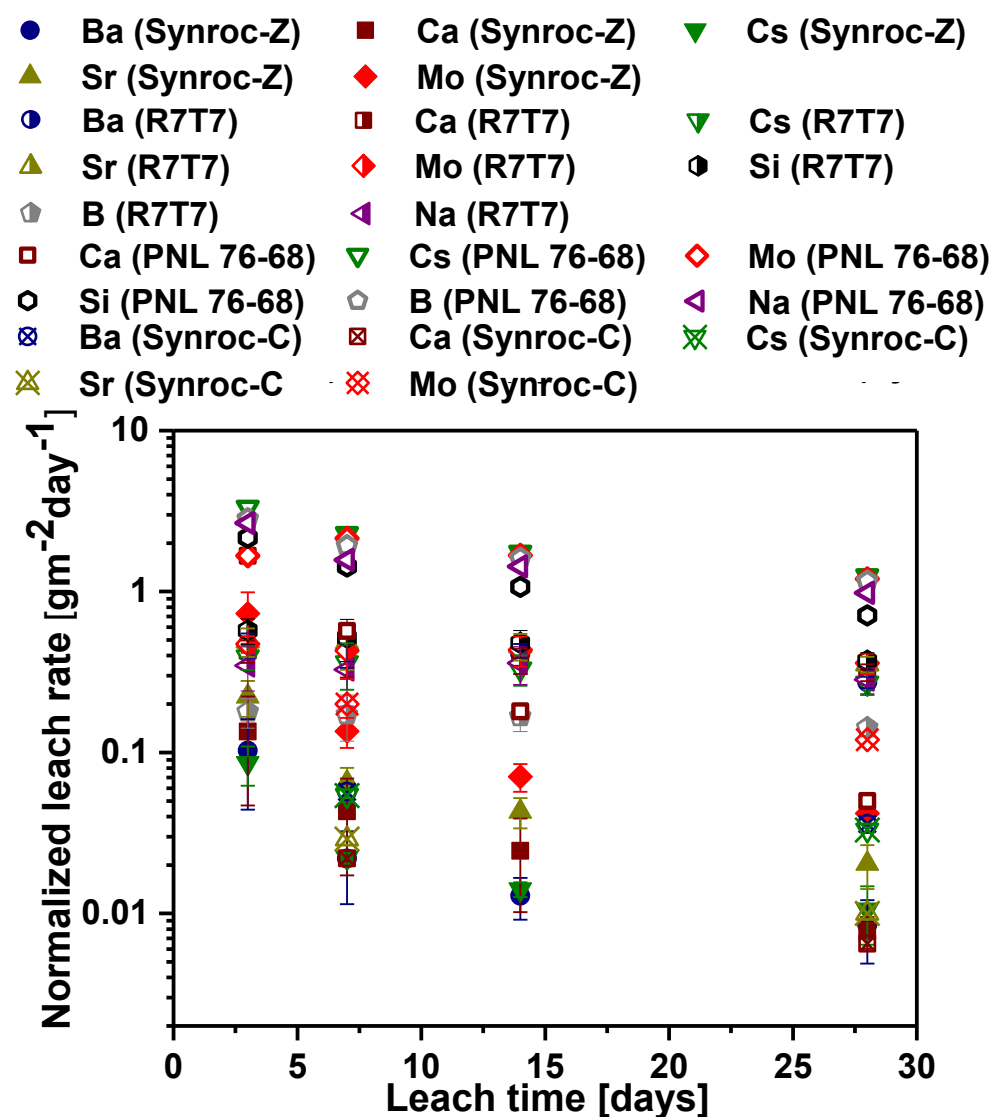


Figure 7.1 Log normal plot of leach rates of HUPed Synroc-Z (filled symbols), and R7T7 type glass (half filled symbols) in this thesis, and PNL 76-68 glass (open symbols)⁸³ and Synroc-C (open symbols with cross)²⁴³ from literatures under MCC-1 test at 90°C.

For the first three days, the Mo loss in HUPed Synroc-Z was ~1.5 times faster than in the R7T7 samples while the losses for other elements (Ba, Ca, Cs and Sr) were 2 - 5 times slower. A Ti-O film and anatase crystals formed on the surface of HUPed Synroc-Z (Figure 5.8) after leaching appear to have acted as a barrier mitigating the short-term elemental loss to some extent. However, the gel layer + secondary phase formed on the surface of R7T7 glass (Figure 5.18) did not improve its dissolution resistance much since the leach rates of most elements were at the same level during the whole test. The gel layer which is expected to form under the conditions of the test^{111, 214}, along with precipitation of secondary phases, should form a porous layer on the surface of borosilicate glass and thus is not able to mitigate the elemental loss as effectively as the Ti-O film and anatase crystals. This meant that Synroc-Z generally had 10 - 100 times slower elemental loss (Ba, Ca, Sr, Cs, Mo) than R7T7 glass after 28 days. HUPed Synroc samples have been compared with vitrified borosilicate glasses in many studies^{49, 89, 216}. The results in this project were similar to Synroc-C compared to a typical borosilicate glass, PNL 76-68 glass⁸¹, as Synroc-C obtained 10 - 1000 times slower leach rates of Ca and Cs during the testing period⁸⁹. Moreover, Oversby *et al.*²¹⁶ examined Synroc and PNL 76-68 glass for 7 days' leach testing in water at 200 and 85°C. Synroc showed no detectable weight change and leaching (detection limit < 0.005 gm⁻²d⁻¹) at both testing temperatures while the PNL 76-68 glass displayed a higher mean leach rate of 8.9 and 1.3 gm⁻²d⁻¹ at 200 and 85°C respectively²¹⁶. The durability of Synroc and borosilicate glasses were examined via accelerated leach testing by Ringwood *et al.*⁴⁹ at temperatures up to 1000°C with high pressure in pure water or 10 wt.% NaCl solution in a close system for 24 h. Synroc-B (containing 1 wt.% each of Cs, Sr and U) is unaffected by leaching in pure water or NaCl solution for 24 h at temperature up to 900°C and 5000 bar. In contrast, the borosilicate glasses were completely devitrified in the pure water or NaCl solution at temperatures of 350 - 400°C and 1000 bar for 24 h^{49, 212}. Based on the results from this project and previous studies, Synroc generally can maintain its performance without significant damage under more extreme environmental conditions than borosilicate glass.

7.3.2 Effect of HUPing and HIPing conditions in Synroc-Z

The process temperature was the key factor to produce the high quality of Synroc-Z samples, as indicated by changes in porosity as described in section 3.3. Generally, higher processing temperatures yielded lower porosities which in turn increased leach resistance. Synroc-Z samples HUPed at 1050°C had a relatively high porosity (~2.5 vol.%) compared to other samples (< 0.5 vol.%) which decreased the leach resistance by an order of magnitude compared to other HUPed Synroc-Z samples (Figure 5.2a). As a consequence, samples fabricated at 1050°C exhibited 2 to 60 times faster leach rates than other leach-tested HUPed samples. By contrast, varying the pressure and dwell times had a minor effect on the porosity as the leach rates changed only by a factor of 2 or so between the extremes of pressure and dwell time (Figure 5.2b). Woolfrey *et al.*²⁶¹ studied the durability of Synroc-C at various hot-pressing temperatures and pressures and reported that the effect of pressure was negligible when the hot-pressing temperature was 1150 - 1200°C which was similar to the conditions in this thesis.

The minor phases formed in HIPed Synroc are another factor affecting its durability. The HIPed Synroc-Z contained leachable Cs-Mo compounds (Figure 3.20a) and thus had high Cs and Mo leach rates (Figure 5.12). Murakami²⁶² studied three Synroc-C samples synthesized using HUPing, HIPing and sintering. The HUPing and HIPing conditions were 1200°C, 60 - 80 MPa for 1 - 3 h while the sintering conditions were 1300°C for 26 h. The sintered Synroc-C samples contained larger grain size range (1 - 20 µm vs. 0.5 - 2 µm) and a minor but preferentially leachable glass phase in about 1 µm regions. The glass phase caused initial leach rates 100 - 200 times faster for the sintered Synroc-C than HUPed and HIPed Synroc-C. Moreover, Synroc-C was prepared via inductive melting (1500°C) by Sobolev *et al.*²⁶³ to compare the microstructure and leach behaviour with HUPed Synroc-C. The major phase composition between Synroc-C prepared via melting and HUPing is similar. However, the melted Synroc-C had higher porosity (10 - 15 vol.%) and formed Ba-Ca, Ca-Sr and Cs molybdates under oxidizing melting conditions. The higher porosity and leachable molybdate phases in the melted Synroc-C increased its leach rates so they were 10 - 100 times greater than HUPed Synroc-C²⁶³. Based on the above

studies and the results from this project, the dense microstructure (low porosity, < 0.5 vol%) and minor phase composition (leachable molybdate phases and glass phase) are the main factors affecting the durability performance of Synroc. In other words, the Synroc-Z HUPed at 1050°C with relatively high porosity (2.5 vol% compared to < 0.5 vol%) and HIPed Synroc-Z containing Cs-Mo compound (leachable minor phase) affect their durability performance leading to more rapid leach rates than other HUPed Synroc-Z samples with dense microstructure and without leachable minor phase.

7.3.3 Effect of surface roughness

The polished surface in Synroc-Z did not appreciably affect the resistance to Ca and Cs chemical dissolution but did decrease the loss rates of Sr, Ba and Mo as shown in Figure 5.7. Faster leaching rates for these species agree with a study by Carter *et al.*²⁶⁴ on the effect of sub-surface damage by polishing on Cs-bearing hollandite. Hollandite with two levels of surface roughness was prepared either by $0.05\text{ }\mu\text{m}$ diamond polishing which contains more significant surface damage or by colloidal silica polishing which caused little damage. The damaged layer increased the leach rate by 10 - 50% for Cs and Ba during the 28 days of testing²⁶⁴. The $1\text{ }\mu\text{m}$ polish in HUPed Synroc-Z reduced the level of mechanical damage compared to $15\text{ }\mu\text{m}$ ground HUPed Synroc-Z, thus decreasing the effective surface area and the presence of crystalline defects, such as dislocations and point defects which can be introduced during mechanical deformation (Figure 5.4a).

However, there is no clear description to explain why the Ca and Cs dissolution rates were not affected by mechanical damage, but others (Sr, Ba and Mo) were. Ca leaching has been previously reported to be unaffected by mechanical damage by Zhang *et al.*²⁶⁵. They studied the effect of surface damage on the leaching of Ca in perovskite which was polished to $0.25\text{ }\mu\text{m}$ and annealed at 1320°C in air to remove the damage layer. The initial rate of Ca loss in mechanically damaged samples (with a rougher surface) was slightly higher but later caught up to the rate in the long-term²⁶⁵, which is therefore in agreement with the behaviour of Ca in this thesis. The leach rates tend to get closer with time which might reveal that leach rates are no longer controlled by

surface damage but by the secondary phases present instead. The nature of the Ti-O thin film and/or anatase crystals provides a partially protective layer from the aqueous attack formed on the perovskite surface^{217, 265}. However, it is not clear why Sr, the other component in perovskite, would not be similarly inhibited. It can be concluded that surface damage initially enhances the aqueous attack but only has a minor effect over longer periods.

Unlike Synroc-Z, the smooth surface (1 μm) of R7T7 glass showed little or no effect on leaching resistance (Figure 7.6 for R7T7-fa sample) compared to coarsely ground (15 μm) R7T7 sample. The leach rates and microstructures were similar in this thesis for both R7T7 glass with different surface roughness. Figure 7.6 compared the leach rates of B and Si for R7T7 samples with the study reported by Buckwalter *et al.*²⁶⁶ who compared commercial borosilicate glass with different surface finishes. The coarsely ground (15 μm) samples and finely polished (1 μm) samples showed scratch depths of 3 μm and 0.008 μm respectively with 17 % of average reactive surface area increase. However, both glass samples with different surface roughness displayed similar corrosion rates (less than a factor of 1.2). Dussossoy *et al.*²⁶⁷ performed Soxhlet test (dynamic test with constant flow²⁶⁸) at 100°C to R7T7 glass with different surface roughness for up to 28 days. The leach rates of B in 15 μm ground and 1 μm polished R7T7 glass samples were alike in Soxhlet tests. This indicated that the effect of surface finishes between 15 and 1 μm for glass is minor. However, one of the polished R7T7 glass samples obtained faster leach rates (Figure 7.6) and a different microstructure (fragile amorphous layer which was made up of gel layer and phase precipitation). This may have been due to damage caused during the polishing stage (Figure 5.20). Pores were observed in some polished glass samples when the applied load was too large (> 25 N) and not applied uniformly during polishing (Figure 5.20).

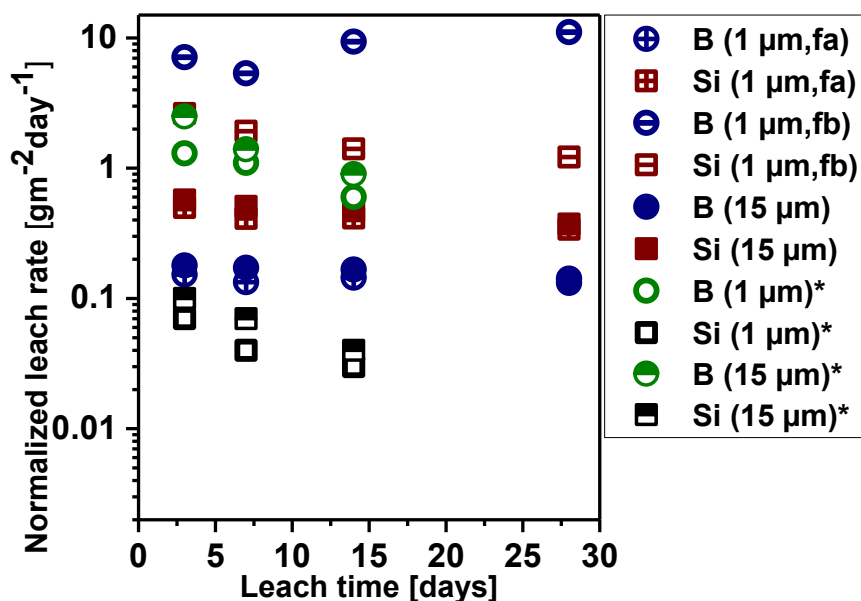


Figure 7.2 Comparison of leach rates of R7T7 glass in this thesis (navy and wine colour) and commercial borosilicate glass (green and black colour, labeled with ^{*)266} with 15 μm and 1 μm surface finishes via MCC-1 leach testing.

7.3.4 Durability of Synroc-Z vs. Synroc-C with different waste loading

A fabrication process of Synroc-Z via HUPing has been developed and it has been demonstrated that Synroc-Z can host up to 35 wt.% of simulated EURO-GANEX wastes without fundamentally altering the material by forming greater levels of the main waste-hosting crystal phases (section 3.4).

Synroc-Z was expected to display worse durability than Synroc-C because of the higher quantities of perovskite in Synroc-Z (Figure 3.7), which is the most leachable phase in Synroc^{54, 199}. However, Synroc-Z gave similar leaching resistance at low waste loading (< 20 wt.%) and actually maintained its durability performance at high waste loading (> 20 wt.%). Figure 7.2 plots the results of leach rates in Synroc-Z from Figure 5.5 (red filled symbols) to compare with the leach rates from typical Synroc-C samples (navy blue open symbols)^{5, 269}. The leach rate data of Synroc-C were reported using MCC-1 test at 90°C for 7 days which was adopted in this thesis^{5, 269}. The result is plotted as a function of various waste loadings.

In the Synroc-C data, the leach rates roughly overlapped⁵ between 5 and 23 wt.% waste loading and hence no trend in chemical durability for low waste loading (< 20 wt.%) was discernible. However, a clear trend reveals that the

increased waste loaded (> 20 wt.%) Synroc-C has increased leach rates. Synroc-C was not designed to host a waste loading greater than 20 wt.% and hence its leach resistance performance degrades significantly above 20 wt.% waste loading. Such degradation in Synroc-C containing greater waste loading (> 20 wt.%) has been attributed to the lower presence of the perovskite and hollandite phases due to the fact that there were insufficient phases formed to host all of the waste elements added^{270, 271}. This apparent transition in behaviour can be distinguished by a dividing line (shown in Figure 7.2) between leach resistant and leachable Synroc-C which occurs at a loading between 20 and 30 wt.%. At low waste loadings' (< 20 wt.%) leaching kinetics are thus controlled by the density and porosity while the high waste loadings' (> 20 wt.%) leaching rates are mainly dominated by the formation of host phases.

The results of Synroc-Z for leach rates between 20 and 35 wt.% loading in this thesis reveal a smaller increasing trend in Figure 7.2. The faster leach kinetics at low-waste loadings are expected based on the different amounts of the main phases in Synroc-C and Synroc-Z. Synroc-Z contained higher perovskite content (~30 wt.% vs. 20 wt.%) which is a more leachable phase compared to other host phases⁵⁴. Although 20 wt.% loaded Synroc-C generally displays slower leach rates than Synroc-Z, it is worth noting that the normalized leach rates are all within the same order of magnitude and one of the two main FP radionuclide, Cs, is retained better by Synroc-Z than by Synroc-C. Durability was mainly controlled by density and porosity at low-waste loading regions while the density should be at least 98% and preferably 99% of the theoretical value to obtain high quality Synroc²⁶¹. However, Synroc-Z maintained its performance with high waste loading (e.g. at 35 wt.%) as additional TiO₂ buffer leads to sufficient formation of the designated Synroc phases. The perovskite and hollandite still formed in sufficient amounts to host the waste in Synroc-Z (Figure 3.15) but Synroc-C which contained higher waste loading (nominal 35 wt.%) actually immobilised a lower amount (~ 23 wt.%) than expected²⁷¹.

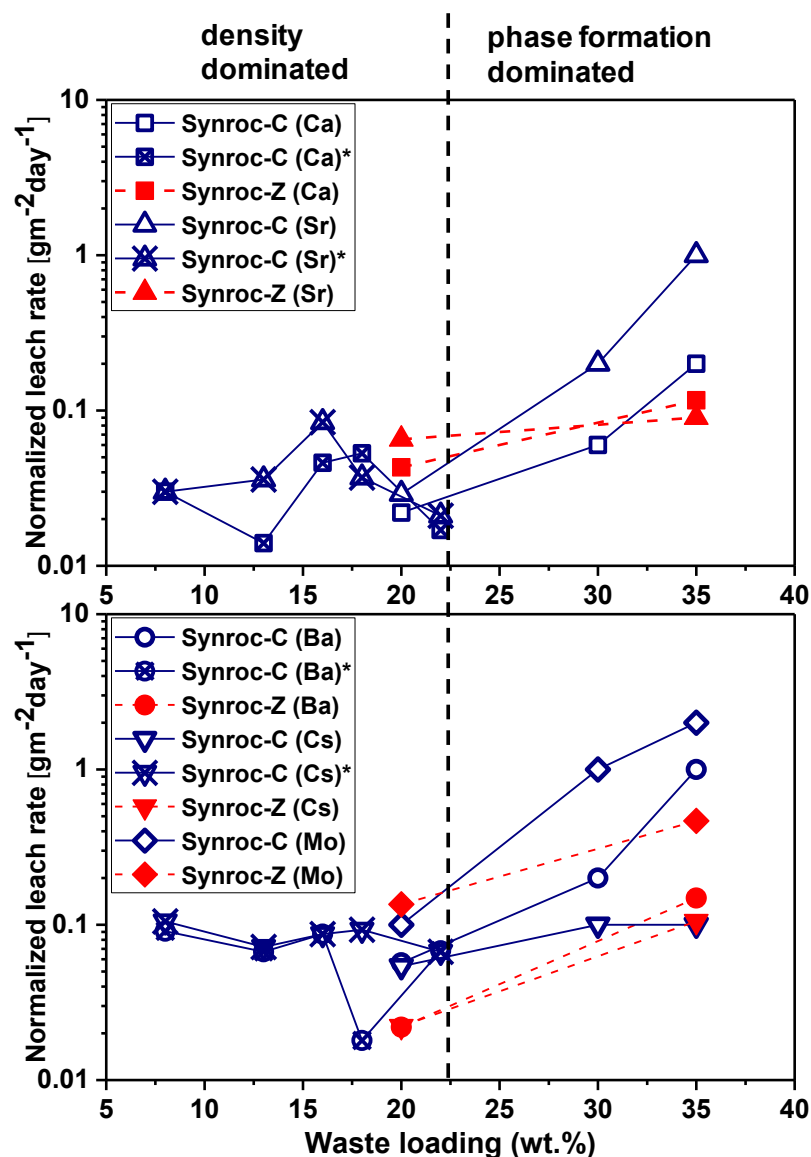
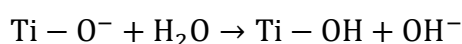
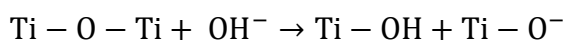


Figure 7.3 Comparison of leach rates of Synroc-C (open symbols)^{5, 269} and Synroc-Z (filled symbols) with different waste loadings for (a) perovskite (from Ca and Sr releases), and (b) hollandite and Mo-alloy phases (from Ba, Cs and Mo releases) via MCC-1 test at 90°C for 7 days. The low waste loading data⁵ is labelled as Synroc-C* while high waste loading²⁶⁹ is labelled as Synroc-C. The low waste loaded Synroc was dominated by its density and porosity while the high waste loaded Synroc was mainly dominated by the formation of host phases.

7.3.5 Secondary phases formed after leach testing of Synroc-Z

The formation of secondary phases during leach testing in HUPed Synroc-Z was compared with previous studies on other types of Synroc^{199, 217, 218, 272, 273}. Most of the previous literature focused on secondary phase formation during leaching at temperature of 70°C^{199, 217, 272, 273} and temperature of 150°C (hydrothermal temperatures, T = 100 - 240°C)^{199, 218, 272, 273}, while few studies reported the morphology of secondary phases formed during leach at 90°C. Based on the observations in this thesis, the anatase crystals (Figure 5.9a and 5.10) and thin Ti-O film (up to 10 nm, based on Pham *et al.*'s study²¹⁷ in Figure 5.11) formed mainly on the perovskite-rich region. However, the previous observations of secondary phases formed on the leached Synroc-C at different temperatures^{199, 218, 272, 273} displayed a different morphology. For example, elongated bipyramidal crystals were observed during leaching at 150°C and the crystals extended deeply into the perovskite substrate while only a thin amorphous film (up to 10 nm) was discovered at 70°C^{199, 217, 272, 273}. The growth mechanisms at these two temperatures occur at different rates as growth at 150°C develops a relatively faster perovskite dissolution rate and Ti solubility constraints while growth at 70°C displays the same type of dissolution behaviour but at a slower rate. Figure 7.3 displays a schematic diagram of such secondary phase morphologies after leaching at different temperatures. The observations in this thesis reveal that both morphologies at high temperatures (crystals) and low temperatures (thin films) coexist during leach testing at 90°C. This result suggests that the growth occurring from the perovskite dissolution with an initial release of Ca²⁺ into solution is a result of ion-exchange reactions. The rate of dissolution is dependent on the total area of solution and Synroc interface, surface damage on the Synroc, testing temperature and pH value^{217, 274}. Collapse of the Ti lattice occurs as a result of base-catalysed hydrolysis as shown in Equation 7.1.



Equation 7.1 Collapse of Ti lattice in the water

This reaction is accompanied by the formation of an amorphous Ti-oxide film due to Ti solubility constraints²⁷⁴. This film is stable at 70°C and below^{217, 275} but metastable at 90°C. Once the film grows thick enough (~10 nm), it becomes unstable, then precipitation and growth occurs preferentially along favourably-oriented crystallographic planes. This leads to the formation of pyramidal anatase particles observed in Figure 5.9(a). Kastrissios *et al.*²⁷⁶ performed leach testing at 110°C on Synroc-C and found similar morphologies suggesting the leaching between 90 and 110°C should lead to the formation of this combination of thin film and crystals. However, the crystallites of Ti oxides produced during leaching are different at different testing temperatures. In this thesis, only anatase crystals formed at 90°C for 28 days' leaching. When the testing temperature increases to 110°C and above, Kastrissios *et al.*²⁷⁶ and Pham *et al.*²¹⁷ found that brookite and anatase crystallites were formed on the perovskite regions after 4 days' leaching. Lumpkin *et al.*²⁷² observed that Synroc formed mainly anatase with minor brookite during leaching at 150°C for up to 28 days. However, the formation of brookite became more rapid with increasing exposure time. This indicates that for short-term leaching, the Ti oxides crystals formed at 90°C are expected to be anatase while at 110°C and above, major anatase with minor brookite is expected to form. For longer leaching times (> 28 days), the brookite growth appears to be faster than anatase. Moreover, another possibility of formation of TiO₂ crystals is precipitation from solution onto the surface^{199, 217, 274}. Whole surface layers may be corroded by dissolution and release some or all species into solution, in combination with formation of precipitate phases, depending on solubility constraints.

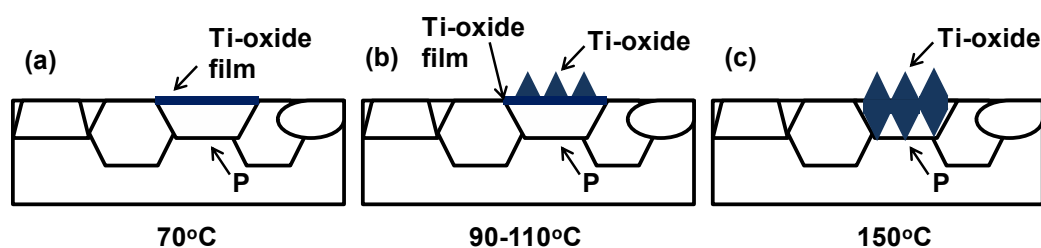
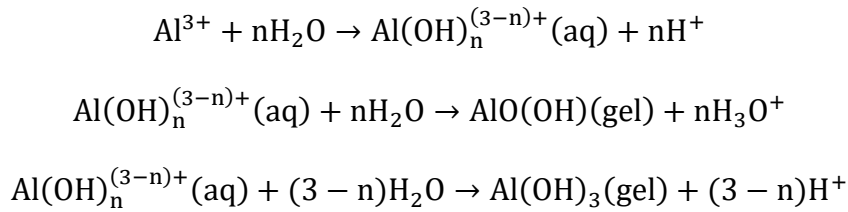


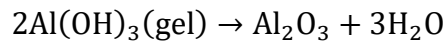
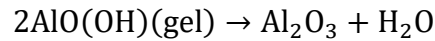
Figure 7.4 Schematic diagrams of leached Synroc after leach testing at (a) 70°C^{199, 217}, (b) 90-110°C^{217, 276}, and (c) 150°C^{199, 217}. P = perovskite.

The other secondary phase found on the leached HIPed Synroc-Z, alumina layer (Figure 5.14b and 5.15), may not represent phases present during the durability testing. This alumina layer may form on the hollandite-rich region as hollandite is the main phase containing Al (Figure 3.23). Lumpkin *et al.*¹⁹⁹ also found that Al oxides flakes as secondary phases on leached Synroc samples after exposing to water at 150°C for 28 days. Pham *et al.*²⁷⁵ studied the surface reactivity of hollandite in aqueous solution and observed the formation of an Al-rich gel layer. The ion-exchange of Ba and Cs from hollandite dissolution is similar to the release of Ca from perovskite while the release of Al from hollandite to solution occurs at the same time. The Al ions drive the water to low pH as a result of hydroxyl consumption reactions (Equation 7.2):



Equation 7.2 Al ions hydroxyl consumption reactions with water

The $\text{Al}(\text{OH})_n^{(3-n)+}$ are aqueous species and n may be 1 - 3. These species in solution constrain Al solubility so that precipitation occurs to form an Al-rich gel layer. The reactions could occur on either zirconolite or perovskite phases as they both contained minor Al in their structure before leach testing (Figure 3.23). The Al-rich gel layer only exists in aqueous conditions as the water in gel layer is removed during drying (Equation 7.3). The leached HIPed Synroc-Z was analyzed on dried samples and thus the dried layer observed may not be the phases present during the leach testing.



Equation 7.3 Formation of Al_2O_3 from Al-rich gel layer via drying.

7.3.6 Leaching mechanisms in R7T7 glass

R7T7 borosilicate glass is another candidate wasteform for EURO-GANEX HLW waste. Its optimal processing temperature range (1150 - 1200°C) has been determined in Chapter 4. The corrosion mechanism of R7T7 glass examined in this thesis is similar to other glass wasteforms as described in section 1.3.4. It is summarised and illustrated in Figure 7.4 and 7.5 which display the process of a phenomenological description including four rate regimes^{111, 277, 278} and the layer evolution during leach testing in this thesis respectively. The alkali ions, Na⁺ and Li⁺, were leached out from the R7T7 glass during the whole leach testing (Figure 5.16). This indicates that the ion exchange diffusion (alteration stage I, top figure in Figure 7.5) occurred as expected when the MCC-1 test started. The dissolution of the major glass networks (Si, B, Al etc.) occurs at the same time. Boron is a glass network former which is also fully soluble under the current standard leaching conditions (details in Table 1.2). The dissolved boron fraction can act as a tracer of the degree of glass corrosion^{104, 279, 280}. The normalized mass losses of the mobile elements (B and Na) indicate the quantity of glass leached per unit area¹⁰⁴. Hydrolysis (stage II) also occurred simultaneously with the ion exchange process. Stage III (middle figure in Figure 7.5) is observed when the dissolved silicon in solution reaches a sufficient concentration to form an amorphous, porous gel. A dried gel layer was observed after durability test (Figure 5.18) in leached R7T7 glass. Moreover, secondary phase formation (stage IV, the bottom figure in Figure 7.5) was also discovered in some regions on the surface of leached glass (Figure 5.18) while leached sample R7T7-fb (Figure 5.23) had secondary phases covering the entire gel layer. The alteration layer was observed as amorphous and contained not only sparingly water-soluble elements such as Ru, Ce, Nd, and Zr but also soluble species (Al, Ca and Zn). The pH values of leachates for sample R7T7-fb were higher than other glass samples (9.5 vs. 6 - 9), suggesting that the alkali ions were released faster due to polishing damage and hence the gel layer and secondary phase formed faster and was thicker.

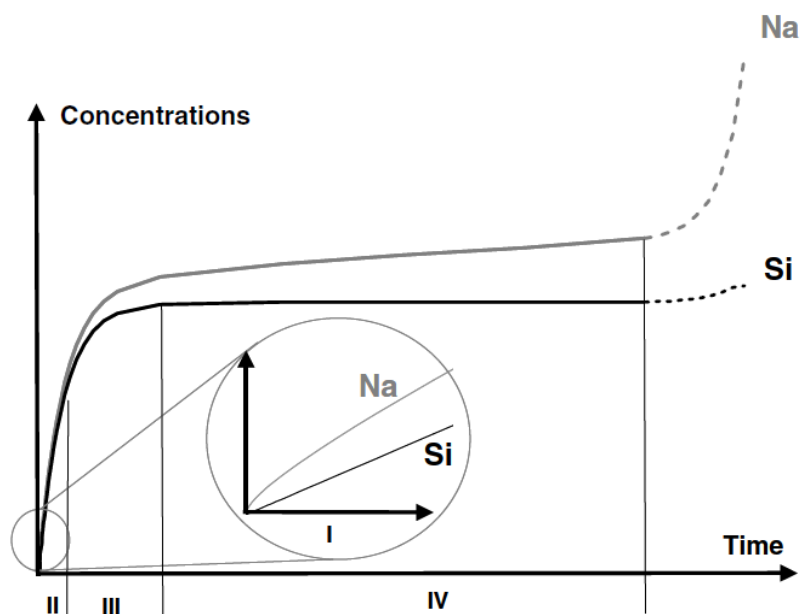


Figure 7.5 Different rate regims and Na and Si concentrations in solution against time. Regime I- initial diffusion (ion exchange), II – initial rate (hydrolysis), III – rate drop, IV – residual rate. Adapted from Frugier *et al.*¹¹¹

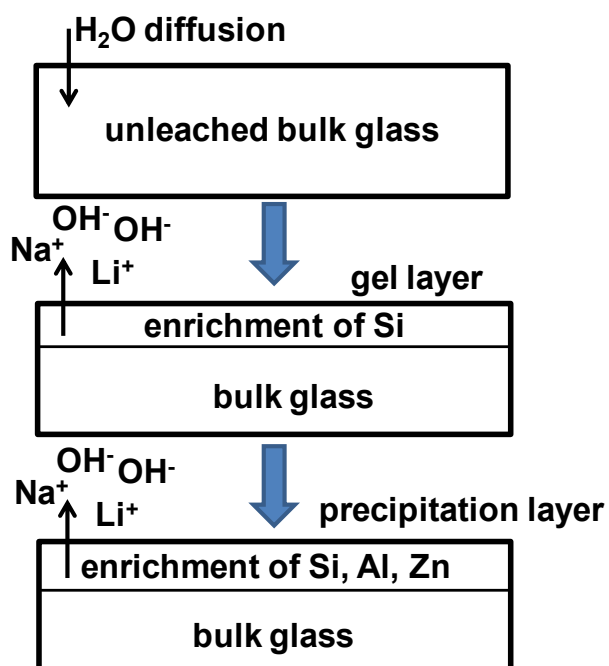


Figure 7.6 Schematic diagram of layer evolution of R7T7 glass during MCC-1 testing.

The secondary phases formed on the dried leached R7T7 glass in this thesis are Ca-silicate and quartz detected via XRD and Zn-Al silicate observed via SEM. Those silicates and quartz observed on the dried samples might be hydrosilicates and hydrosilica during leach testing¹⁰⁵. However, the water in the

hydrates was removed during drying and the secondary phases turned to dried compounds and formed cracks (Figures 5.18, 5.22 – 5.23).

The dissolution rate of Zn in R7T7 glass decreased against time (Figure 5.16a and 5.19a) as Zn in the glass acted as a strong network former. The formation of Zn-O-Si linkages increased and hence displayed improved durability on early dissolution kinetics^{281, 282}. Moreover, continuous ion exchange and hydrolysis caused elemental concentration in leachate to increase with time. Hydrolysis attacks bridging bonds of the network-forming elements (Si-O-X, where X = Si, Al, B, Zr) in the interphase created by the release of mobile elements²⁸³. The hydrolysis rate reduces when the activities of the gel forming elements (Si, Al, Ca, etc.) tend towards steady-state conditions in solution²³⁵. Al in the glass provides polymerized network and is related to the decrease of network hydrolysis with the decrease of non-bridging oxygens (NBOs). After aqueous corrosion, Al may be found in the gel layer and attached to the silicate network²⁸⁴. The normalized elemental loss data in R7T7-fb (Figure 5.19 b and d) that is obtained in this work showed such connection as the leach rate of Al decreased with time. Formation of this network is believed to strengthen the glass structure and improve the durability of the glass.

Different crystalline phases have been discovered on the alteration layer for different glass wasteforms in the longer-term durability test. Gin *et al.*²⁸⁴ performed short-term and long-term (up to 14.4 years) leach testing for 10 different borosilicate glasses containing 3 to 30 oxides. They found formation of Na-silicate hydrate, Ca-silicate hydrate as secondary crystalline phases after leach testing. Corkhill *et al.*²⁸⁵ carried out durability tests between 1 and 168 days for 25 wt.% simulated UK HLW glass. Mg-silicate hydrates and Ca-silicate hydrates were formed on the surface as secondary crystalline phases. However, in this thesis, the leached R7T7 samples were dried before analysis. No hydrates and hydroxides were observed as secondary phases although these phases would be expected to be found during leach testing.

Cassingham *et al.*²⁸⁶ and Zhang *et al.*²⁸⁷ examined the durability of UK HLW glass with addition of ZnO and CaO. The addition of these oxides to UK glass composition reduced the thickness of gel layer and alteration rate as they can improve glass network polymerisation^{286, 287}. Comparing with other glass

compositions, the addition of any modifier or intermediate elements can affect the glass network bonds during ion exchange or hydrolysis process^{286, 287} and hence the optimal glass composition needs to be compromised to achieve high glass durability.

7.4 Simulation of generated heat in wasteforms

Radiogenic heat production is an important factor which may affect wasteform durability. Simulations of radioactive decay are useful to understand and estimate the possible impact of self-heating on wasteforms over a long-term period. The FP only waste stream from EURO-GANEX exhibits beta and gamma decay with only negligible alpha decay for wasteforms in the first several hundred years (Figure 6.2). Beta particles and gamma rays emitted during the decay of FP can break covalent and ionic bonds, change valence, excite electrons and alter the mobility of ions²⁸⁸. The high ionization rates during the initial thermal period may cause decomposition, phase separation, and bubble formation in glass wasteforms²⁸⁸. This is similar to the current waste from PUREX process where short-lived fission products cause significant self-heating during the first 600 years of storage^{205, 288}. Moreover, both heat and activity levels of wasteforms for EURO-GANEX waste are found to decrease below the threshold for HLW classified by the IAEA after 140 years (Figure 6.2 and 6.3). This suggests that the HLW from EURO-GANEX could be classified as an ILW based on the IAEA classification after 140 years and the 140 years old wasteform could be disposed of more cheaply as ILW, saving expensive repository space.

However, it is worth noting that the radiation damage in PUREX waste primarily comes from the decay of actinide elements which emit high-energy alpha particles and recoil nuclei. This causes elastic collisions with wasteform constituent atoms, which results in atomic displacements^{289, 290}. The alpha decay effects would be much more significant in PUREX waste due to the presence of actinides and their long half-lives^{205, 212, 288, 291}. With only traces of actinides and alpha-emitters, HLW wasteforms for EURO-GANEX would be expected to avoid many of the issues arising from alpha-decay. The main radiation effect is volume changes in wasteforms. The volume change of glass wasteforms can decrease, increase (up to 1.2 % of initial volume) or maintain unchanged depending on the glass composition^{81, 290, 292, 293, 294}. A volume change of ± 1 % can be tolerated by the current canister design²⁸⁹. However, the radiation effects are more significant to Synroc. The volume expansion of Synroc-B was up to ~6.5 % of initial volume^{295, 296}. Moreover, the amorphization

of crystals and volume changes caused by radiation damage may result in the microcracking in the glass wasteforms^{290, 293} and modifications in composition of phases in Synroc²⁸⁹.

The estimated centreline temperature of wasteforms was described in section 6.5. The highest centreline temperatures for 35 wt.% EURO-GANEX waste loaded Synroc-Z and R7T7 glass with a diameter of 36 cm in saturated repository conditions were 266 and 307°C respectively. Comparing the results in Figure 6.8a with previous studies, Sizgek²⁴¹ modelled a three-dimensional (3-D) nuclear waste repository in granitic rock for both 20 and 10 wt.% HLW-bearing Synroc in the 36 cm diameter. The maximum centreline temperatures he reported were 160 and 247°C for 10 and 20 wt.% HLW loaded Synroc with a 10-year surface cooling period. Moreover, Weber²⁰⁵ studied the centreline temperatures of heat generation from glass wasteform with 25 wt.% HLW from PUREX in the 32 cm diameter canisters. The maximum centreline temperature for the glass wasteform was 290°C for 25 wt.% waste loading. Both Synroc-Z and R7T7 glass in this thesis only exhibits slightly higher centreline temperature but larger waste loading. This indicates that wasteforms can host up to 35 wt.% EURO-GANEX waste and their centreline temperatures are still comparable with the previous studies with even higher waste loading. Furthermore, Synroc-Z generally displays more flexibility with respect to package size and waste loadings than R7T7 glass (Figure 6.9). Lastly, the higher thermal conductivity of Synroc-Z actually leads to a lower centreline temperature. This suggests that heat generation from Synroc-Z loaded to 35 wt.% may be expected to insignificantly alter wasteform performance if the package diameter is kept within the safe range identified as 30 - 65 cm.

Chapter 8: Conclusions and future work

8.1 Conclusions

Potential wasteforms for EURO-GANEX waste, Synroc-Z and R7T7 glass, have successfully immobilized the EURO-GANEX waste in their matrix and have been studied their fabrication methods, leaching behaviour and effect of heat generation. Major findings were listed below:

1. Dense Synroc-Z samples can be produced via hot-pressing technique (HUPing and HIPing) within temperature of 1150-1200°C and pressure > 10 MPa for a dwell time of 3 h.
2. Sufficient metal powders added prior to hot-pressing for Synroc-Z can produce reducing conditions and hence avoid formation of undesired phases.
3. R7T7 glass still cannot dissolve all noble metal alloys and oxides even applying high pressure (up to 100 MPa).
4. Synroc-Z can maintain its leaching performance when the waste loading increases up to 35 wt.% due to sufficient buffer phase content.
5. Secondary phases formed on the surface of Synroc depend on the surrounding temperature. For example, if the surrounding temperature is 70°C, a Ti-O thin film is expected to form. The secondary phases formed are protective, decreasing the rates of element loss.
6. Compared to Synroc, the secondary phases formed on the R7T7 glass provide little or no protection from aqueous attacks since the leach rates only slowly decreased with time
7. Because of larger density, higher thermal conductivity and better durability than glass, Synroc exhibited more flexibility in package size and waste loading.

8.2 Future work

Synroc-Z and R7T7 glass have been studied as potential hosts for EURO-GANEX waste. However, further work is required if the durability of the wasteforms is to be fully understood. For example, the phase composition change during hot-pressing process is unknown. Characterization on interrupted HUP and HIP runs such as high temperature-XRD may be helpful to investigate how processing temperature influences phase composition. Moreover, various conditions for hot-pressing techniques can be considered e.g. larger sizes of die/canisters, different amount of different metal powder added to produce reducing conditions. In addition, the leach testing performed in this project is MCC-1 short-term (28 days) testing in DI water. Many different leaching conditions are available to examine the leach resistance of wasteforms such as long-term (up to several months or years) testing, product consistency test, the effect of solution composition for a range of pH values, a flow condition and hydrothermal temperatures with pressure. The secondary phases formed on the leached samples can be characterized by better techniques such as TEM/EELS to examine types of Ti oxides formed on leached Synroc and environmental SEMs for hydrated layers formed on leached Synroc and glass. Lastly, it would be ideal to study Synroc-Z and R7T7 glass containing real EURO-GANEX waste to examine the effects of heat generation and radioactivity. For the wasteforms with real waste, the phases formed in wet environments and under elevated temperatures caused by the decay of short lived FPs is another area worthy of investigation.

Although Synroc-Z and R7T7 have displayed good performance under aqueous attack, other potential wasteforms could be examined for their possibility to immobilise EURO-GANEX waste. This includes ceramics with different phase composition and different composition glasses. For multiphase ceramics, individual phases should be selected that are able to incorporate one or more waste elements, with the proportions of phases varying depending of the composition of the waste stream. Synroc-Z was the first design attempt for actinide-free waste, but its formulation could be further enhanced as the large volume fraction of perovskite will have detrimentally affected its durability. Possible future reformulations could therefore involve reducing the perovskite

volume fraction. Supercalcine ceramics and tailored ceramics are other well-known silicate-based and alumina-based ceramic phase assemblages respectively^{5, 52}. Moreover, glass composite materials (GCM) are another possible candidate^{51, 52} which combines both advantages of ceramics (generally superior chemical durability) and glass (easier fabrication process). There is also a need to study the effect of partial submersion in water on durability as highlighted by Chinnam *et al.*²⁹⁷ in their recent study. Such conditions affect the corrosion mechanisms and are highly likely in geological disposal facilities when they become saturated.

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