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Hot Isostatic Pressing - Reducing the proliferation risk of stored plutonium

Abstract

There is currently somewhere in the region of 550 tonnes of declared separated plutonium worldwide. This material carries a proliferation risk globally and will continue to do so until it is put beyond reach.

As reprocessing contracts have reached completion in the UK, it currently holds a stockpile of 150 tonnes of civil separated PuO_2, and the long-term management of the stockpile material is currently under significant review by the Nuclear Decommissioning Authority (NDA) and UK government. The NDA are considering multiple options for the long-term management of PuO_2 including reuse options as reactor fuel(s) and immobilisation options for long-term storage and eventual disposal in a geological repository.

One of the main technologies being developed as a process option for disposal is incorporation of the PuO_2 into a ceramic zirconolite matrix and consolidating via hot isostatic pressing (HIP). This involves subjecting the material to high temperature and pressure inside a hermetically sealed canister, which leads to a dense, durable wasteform; naturally occurring mineral analogues have been shown to have compositional stability for over 2 billion years.

The National Nuclear Laboratory (NNL) are currently developing the HIP100 active demonstrator facility to undertake the processing of the PuO_2 stockpile at the 100 g scale. This will provide valuable data on wasteform properties and performance which will feed into the wider geological disposal facility (GDF) programme and the NDA's roadmap for HIP technology which aims to be TRL 7 by 2031.

The facility will produce samples from the suite of PuO_2 produced over half a century of UK reprocessing operations, verifying that target wasteforms can be formed as well as feeding a process envelope over to full scale operations.

Introduction

The Magnox reprocessing plant operated from 1964 to 2022 at the Sellafield site in the northwest of England. The facility extracted plutonium and uranium from Spent Nuclear Fuel (SNF), primarily from Magnox reactors, using the PUREX process. Over its 58 year lifetime

the facility handled over 55,000 tonnes of SNF from the UK's Magnox reactor fleet. Magnox fuel from Italy and Japan was also reprocessed during this time as well as fast breeder fuel from Dounreay.[1]

In 2019 all Magnox reactors, except for the Yongbyon nuclear reactor in Democratic People's Republic of Korea, had all reached completion and been defueled. The last batch of SNF arrived at Sellafield in 2019 and was processed in 2022, after which operations ceased. 58 years of reprocessing SNF on the Sellafield site has left the UK with the world's largest stockpile of declared separated civil plutonium. The UK holds approximately 150 tonnes of plutonium dioxide, with 22.5 tonnes of this belonging to foreign countries.[2] The handling and disposal of this has been transferred to the UK though multiple long term contracts.[1] The Sellafield stockpile makes up a significant proportion of the declared global PuO_2 stockpile of 550 tonnes.[1]

In the UK the plutonium in the civil stockpile is stored as solid PuO_2 powder at a dedicated above ground storage facility within the Sellafield site. The PuO_2 powder is stored in individual cans to avoid criticality and contamination risks. Plutonium from UK Magnox SNF contains about 85% of the fissile isotopes Pu-239 and Pu-241.[1] The stockpile poses a large economic burden, costing around 73 million pounds annually to maintain,[3] as well as safety, health, environmental and security risks that will continue until the material is put beyond reach.

The civil plutonium stockpile is controlled under strict IAEA safeguards. The UK declarations on the stockpile are made to the IAEA, who independently verify this information and monitor storage and movements of the material to ensure it is not diverted for proliferation purposes.[4] Auditing of this material does not remove the security risk that the stockpile poses as the plutonium stored is of reactor grade. [5] Three potential security risks are; proliferation of nuclear weapons to other states through theft or illegal transfer of PuO_2, construction of nuclear or radiological explosive devices by terrorists following the theft of separated plutonium or a terrorist attack on the storage site to disperse the contained material. This risk will remain for as long as the plutonium remains in its current form and location.[6]

Plutonium management policy in the UK is defined by the UK government and is supported by the Nuclear Decommissioning Authority (NDA), a non-departmental public body who oversees the decontamination and clean-up of the UK's civil nuclear sites. A report conducted by the royal society in 2007 concluded 'continuing to stockpile a very dangerous material is

not an acceptable long term option' and urged the government to develop and implement strategy for the management of separated plutonium.[6]

Following this report, the NDA commissioned analysis of the credible options for long term plutonium management, following which 3 primary options for plutonium waste management were identified:[7]

- To continue with the current strategy of long term storage, followed by immobilisation and disposal
- Prompt immobilization and direct disposal
- Reuse as fuel through conversion to mixed oxide fuel (MOX)

In 2011 the UK government commissioned a consultation exercise to identify a preferred plutonium management option, choosing from the above identified credible options.[8] On behalf of the UK government, the department of energy and climate change concluded that the 'preferred policy for managing the vast majority of UK civil separated plutonium is to reuse and it therefore should be converted to MOX fuel for use in civil nuclear reactors. Any remaining plutonium whose condition is such that it cannot be converted into MOX will be immobilised and treated as waste for disposal'. The basis of this decision was the perceived maturity of this technology when compared to immobilisation of the stockpile for disposal. Combining this with the potential economic gain from energy production using MOX fuel made this the most cost effective option. However, it is clear in the policy statement that proceeding with a new MOX plant will not begin until the government is confident this option can be implemented safely, securely and offers value for money. If this cannot be established the way forward may need to be revisited.[9]

The NDA are considering multiple immobilisation options for long term storage and eventual disposal of plutonium dioxide. This technology will be implemented on the proportion of the stockpile that is not suitable for the manufacture of MOX fuel, currently estimated to be around 5% of the stockpile,[10] and will also be applicable should government policy change.[11]

It is UK government policy to dispose of the UK's higher activity legacy waste in a Geological Disposal Facility (GDF). This approach was recommended by Radioactive Waste Management (RWM, now Nuclear Waste Services) in 2006. It was then accepted by the UK government and in 2007 a framework for implementation of this facility was published.[12]

The focus of GDF disposal is ensuring that people and the environment are protected from the effects of exposure to ionizing radiation from material that will be stored for many thousands of years, which includes radiological hazards as well as safeguarding this material. Nuclear safeguards are of central concern with respect to the disposal of fissile material, such as separated PuO_2.

One of the leading technologies being developed as a process option for disposal is incorporation of the PuO_2 into a ceramic zirconolite matrix and consolidating via Hot Isostatic Pressing (HIP).

HIP consolidates a powder feed into a dense, durable wasteform inside a hermetically sealed canister. In a generic HIP process the pressure vessel is pressurised up to multiple hundreds of MPa using an inert gas, such as argon, within the vessel a furnace produced temperatures of up to 2000 ^{o}C.[13] As such, HIP is generic consolidation technology, applicable to many wasteforms subject to identification of the correct heat and pressure cycle.[14] The adaptability of the HIP process had resulted in selection of HIP to treat and immobilise: High Level Waste (HLW) from Australian Nuclear Science and Technology Organisation's (ANSTO) medical isotope production,[15] It is also being considered to dispose of Cs exchanged chabazite minerals to support decommissioning of Fukushima chabazite [16] and for disposal of a range of Plutonium containing waste and residues currently stored on the Sellafield site.[14] It is important to note that the PuO_2 stockpiles contain too high a concentration of plutonium to classified as 'plutonium containing'.

The applications of HIP technology expand beyond the immobilisation and encapsulation of radionuclides. HIP is used to manufacture nuclear reactor vessel heads and steam plenum chambers and their access ports.[17] HIP technology provides uniform density, elimination of porosity, fine grain structure, the possibility of composite parts and improved ductility and impact strength.[18] The HIP process also enables the forging or casting of solid shapes with complex internal and/or external geometries. HIP has been identified by manufacturers as a process that can offer potential improvements to material properties relative to more conventional forging/ casting techniques.[18]

To undertake the processing of the PuO_2 stockpile the UK National Nuclear Laboratory (NNL) are currently developing the HIP100 active demonstrator facility. The NDA have contracted NNL to support the technical and engineering development of this method of Pu disposition to bring it up to technology readiness level (TRL) 6. This programme of Pu active research and

development is to be conducted over a 5 year period with a range of PuO_2 feeds from throughout the Sellafield reprocessing plant lifetime, to further underpin the knowledge and understanding of wasteform behaviour with directly relevant feed material. To underpin this, active samples will also be used to support wasteform development, validate wasteform formulations and evaluate product performance.

HIP100

The HIP100 process is based on the incorporation of Pu into the crystal structure of the mineral zirconolite, $CaZrTi_2O_7$, through substitution via ambipolar diffusion.[19] Zirconolite is one of the mineral phases of the synroc (portmanteau of synthetic rock) materials developed in the 1970's for immobilisation of high level nuclear reactor wastes,[20] in which its purpose was the incorporation of actinide species. Since stockpile PuO_2 is quite a pure material, the other constituents of the original synroc are not necessary and thus zirconolite alone is used. Substitution of the Pu into the zirconolite crystal structure is controlled by the ionic radii of the ions, with Pu^{4+} substituting onto both the Ca and Zr sites with a preference for the Ca site, considered nominally as a 2:1 ratio.

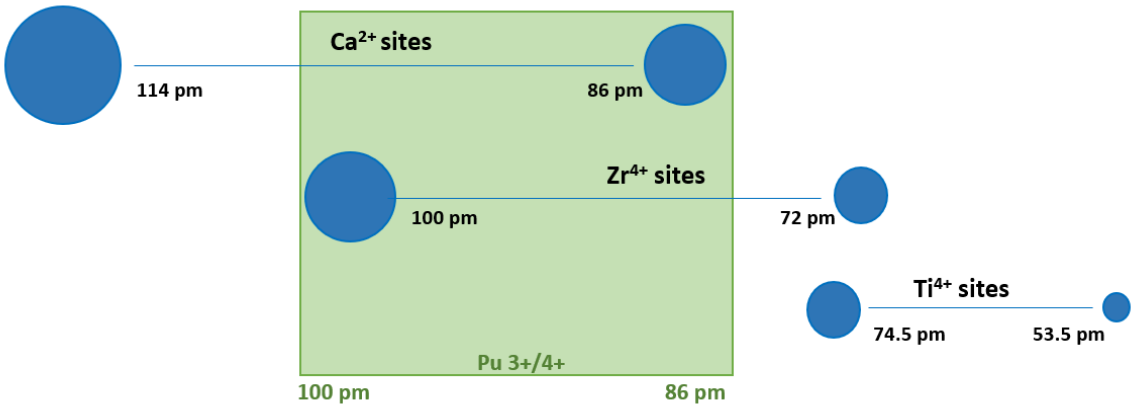

Figure 1. Schematic to illustrate substitution sites in zirconolite. The blue spheres show the nominal ionic radii range of the sites specified in this system. The green square shows the size range of Pu 3+ and 4+. Not to scale.[21]

Since a single substitution of Pu^{4+} for Ca^{2+} renders the structure charged, a charge compensator is required to balance the structure. This is achieved typically in the form of ions that preferentially substitute onto the Ti sites of zirconolite, such as Al^{3+} or Fe^{3+}. This leaves a nominal composition for a 20 wt% substituted zirconolite as:

$$(Ca_{0.8}Pu_{0.2})(Zr_{0.9}Pu_{0.1})Ti_{1.6}M_{0.4}O_7$$

Where M = 3+ cation, such as Al^{3+} or Fe^{3+}. In reality this composition is a solid solution with slight variations in Pu content across the two substitution sites. Pu incorporation can be varied up to 25 wt%, with incorporation above 20 wt% potentially leading to increases in secondary Pu bearing phases which is generally seen as deleterious due to potential mismatches in physical and chemical behaviours. Above 25 wt% incorporation the zirconolite becomes superseded by a pyrochlore structure.[22]

The HIP100 facility (Figure 2) consists of 5 gloveboxes containing the equipment required for the process, each piece designed and tested to be able to be maintained and used in a glovebox environment. Along with this, an existing HIP furnace and pressure vessel have been refurbished and adapted for automated loading and unloading within the active facility.

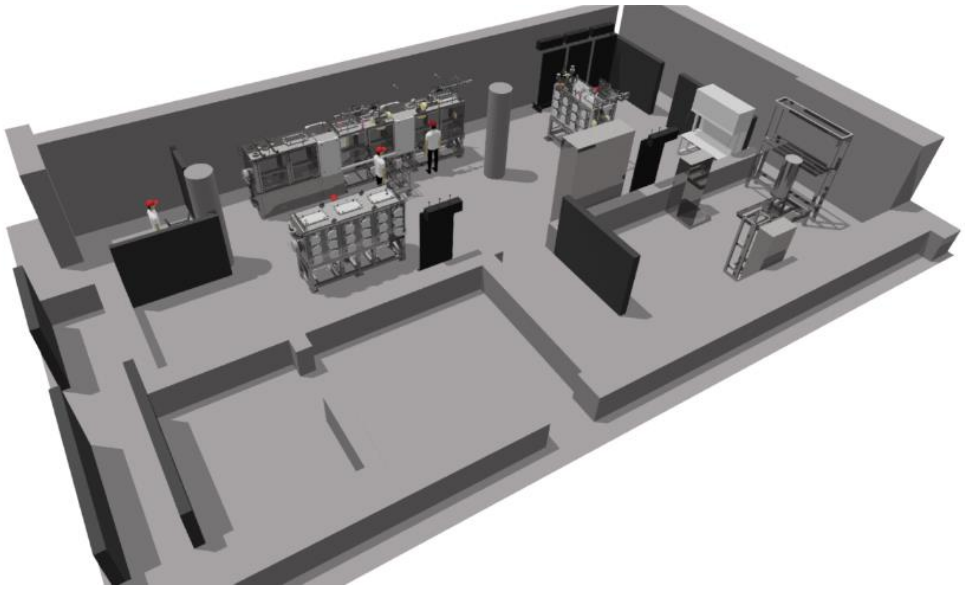

Figure 2.Schematic of the HIP100 facility

The HIP100 process begins with ceramic precursor materials which undergo solid state synthesis into zirconolite when sintering during the HIP itself. The ceramic precursors used are calcium titanate ($CaTiO_3$), zirconia (ZrO_2) and titania (TiO_2), with a charge compensator (typically Al_2O_3 or Fe_2O_3) and PuO_2 for incorporation, although surrogates are typically used in most studies, such as Ce, U or Th. [23,24,25] Neutron poisons will be added (Gd, Hf) to Pu containing products as part of criticality control for the UK's GDF, these can also be incorporated into the crystal structure of zirconolite.[26]

The powders are wet milled together in a planetary mill with isopropyl alcohol (IPA) and ZrO_2 milling media to produce a homogenous powder. Once dried the milled powders are pressed into the inner can of the HIP canister using a hydraulic press, for which the process following

is given in figure 3. The HIP100 process utilises a ‘can-in-can’ system where the HIP canister is actually two separate canisters; an inner and outer canister manufactured from 316 stainless steel, both with sintered steel filters within the lids for particle retention whilst allowing gas flow. This canister design allows for contamination control within the facility. After filling and lidding the inner canister, is it passed through a bulkhead, which segregates two halves of a glovebox directly, into a clean outer canister where the operator can handle the canister free from potential residual contamination from the filling process. The outer canister lid is then secured and then welded to the canister body using an automated orbital welder. The canister is then heated under vacuum to 600 ^{o}C to remove any volatiles and air from the canister, before being induction crimped along the evacuation line to form the hermetic seal and excess canister tail removed.

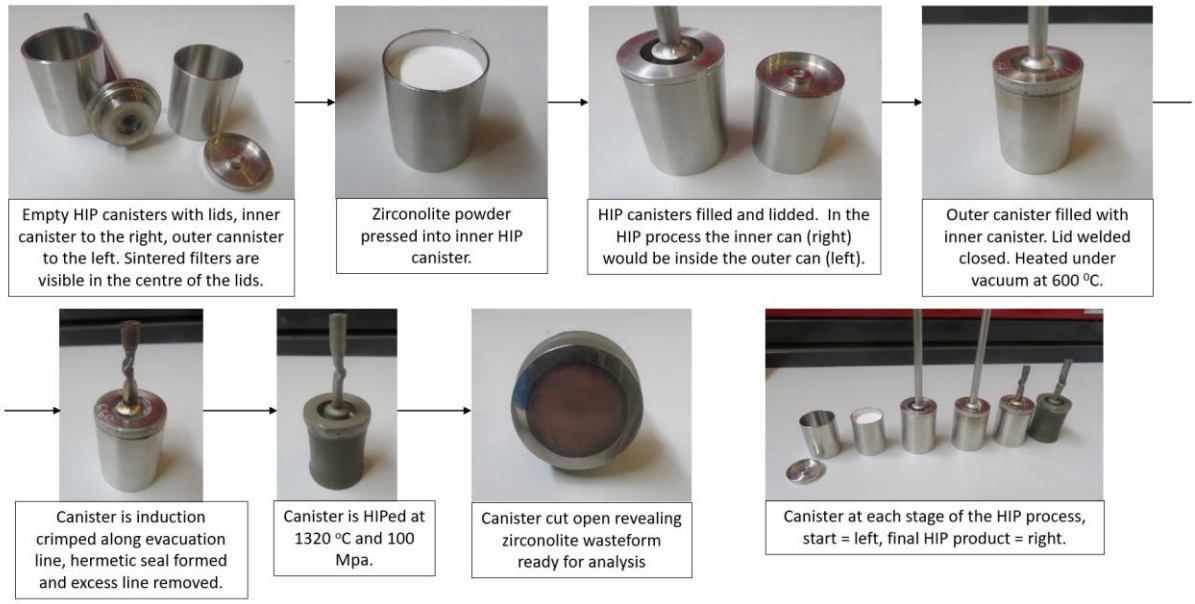

Figure 3: Flow diagram of the HIP100 process.

The completed canister is subsequently transferred into an active furnace isolation chamber (AFIC), which provides protection against powder release and allows the removal of the canister from glovebox to the HIP. The canister is then HIPed at 1320 ^{o}C and 100 MPa, where it undergoes solid state sintering and densification into the final zirconolite wasteform and is then ready to be prepared for analysis (Figure 4).

Figure 4: Small scale (44 g loaded) HIP canister before and after HIP.

The purpose of this facility is to demonstrate production of a ceramic wasteform suitable for the immobilisation of PuO_2 feeds using actual Sellafield PuO_2 materials and thus produced canisters are subsequently cut open and analysed to learn as much information as possible, using techniques such as X-Ray diffraction, Raman spectroscopy and scanning electron microscopy (SEM) (Figure 5). One of the aims of the facility is to produce a single Pu bearing phase of material, and these materials will be tested for durability under relevant disposal conditions. The data produced on the properties of the wasteform can then be fed forward to the UK's GDF programme.

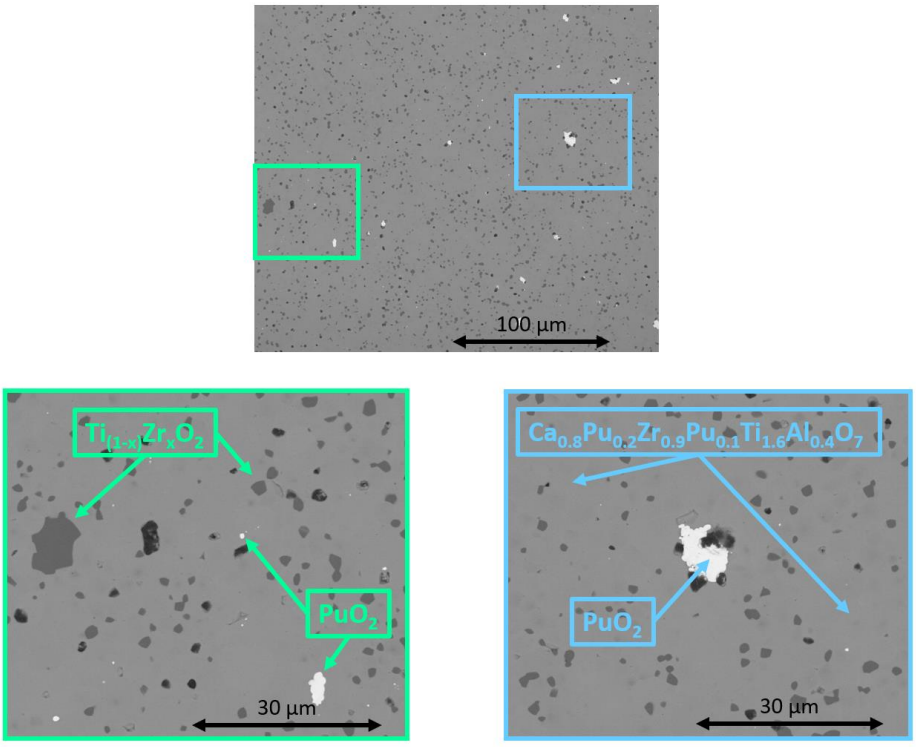

Figure 5: Backscattered electron SEM images of zirconolite with incorporated Pu. Produced at NNL in small scale active trials in support of HIP100.

Fissile isotopes make up the bulk of the PuO_2 stockpile, hence there are significant safeguards concerns regarding its long-term storage and disposal in a GDF. The IAEA estimates the time needed to convert PuO_2 to the quality of plutonium (Pu^{239} >95%) required to construct nuclear devices as 1-3 weeks,[27] highlighting the importance of the safe disposal of this stockpile. The attractiveness of the HIP100 process to dispose of the plutonium stockpile expands beyond its immobilisation and containment of the long-lived radioactive isotopes and their radiation. The incorporation of the fissile plutonium within the ceramic HIP100 wasteform is argued to be a proliferation resistant process. Should a potential proliferator access this wasteform the technology and capital required to separate and isolate the fissile isotopes from the zirconolite ceramic would be very significant.

Summary

The HIP100 research and development programme will provide valuable data on the properties and performance of the ceramic wasteform. This data will be invaluable in the planning and implementation within the wider UK GDF programme. HIP technology for Pu disposition aims to be at Technology Readiness Level (TRL) 7 by 2031, with a full scale inactive HIP in an operational environment.[28] It is the ambition of this facility that the success of HIP100 will lead to the development and construction of an industrial scale HIP100 plant on the Sellafield site to help process, immobilise and put the PuO_2 stockpile beyond reach.

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