Development of an Immobilisation Technology for Radioactive Waste Solution from Mo-99 Production

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ABSTRACT

Australian Nuclear Science and Technology Organisation (ANSTO) developed a method to immobilize the Intermediate Level Liquid Waste (ILLW) arising from its Mo-99 production process.

The immobilisation process involves impregnation of waste solution into ceramic precursor powders, drying, calcining and consolidation (Hot Isostatic Pressing, HIP) to produce final ceramic waste form. Ceramic precursor powder is produced by spray drying of a sol-gel based colloidal dispersion. These free-flowing, microspherical, 20-80 microns, precursors have porosity of 40-50%.

An in-house custom designed and manufactured microwave-heated and mechanically fluidised mixer-drier was used for impregnation of the precursor powder with the simulated waste (Depleted Uranyl Nitrate Hexahydrate, DUNH, and inactive Cs, Sr nitrates as fission products) and drying. During impregnation an evaporation rate of 1 l/h water per kW microwave energy in steady state was achieved by matching the feed rate of DUNH to produce equivalent of 35% UO_2 loading. It was demonstrated that the tuned microwave energy can be delivered to the mixer-drier during the entire impregnation process within very low reflection values.

The samples of the waste loaded free-flowing powder were subsequently calcined at 750°C under reducing atmosphere for thermal denitration and mineral phase nucleation. Calcined powders were filled into cans. After evacuation and sealing, the cans were isostatically pressed at 1260°C. The consolidated ceramic waste form produced from the DUNH run has been assessed by durability and material characterization tests.

Successful confirmation of each processing step at pilot and/or plant scale, has led to the design and construction of the overall process at full scale (equivalent of processing 8 kg U per batch) in a simulated hot-cell mock-up plant. The constructed plant mainly consists of a Microwave-heated Mechanical Fluidised Bed (MWMFB) mixer-drier a fluidised bed calciner, an off-gas unit, material transfer/holding and can filling units. Performance of the overall process by integrating each of the processing steps and material transfer operations are currently being tested with inactive simulants from the point of remote operated plant design perspective. Definitive design of a hot-cell production system has been initiated in parallel to the mock-up plant tests.

This paper describes the results of both full-scale DUNH impregnation run and inactive mock-up plant tests in developing unique Mo-99 waste immobilisation technology.

INTRODUCTION

Waste management experience of the major Mo-99 producers in the world is summarized in a report published by International Atomic Energy Agency (IAEA).[1] Although many producers have deferred treatment of the uranium-bearing waste fraction with the intention to reprocess for recovery of the U-235, ANSTO adopted long term immobilisation of its legacy Mo-99 waste.

At ANSTO, Mo-99 process waste arising from irradiation and processing of uranium dioxide enriched to 2.2% U-235 has resulted in a stockpile of 620 kg of uranium in solution. ANSTO’s processing route for the production of Mo-99 involves nitric acid dissolution of the irradiated targets that gives an acidic waste containing uranium and the remaining fission products. ANSTO commenced accumulating the acidic ILLW in a specifically designed storage facility in 1971.

Since 1999 ANSTO has been processing the stored liquid waste for volume reduction through a hot-cell process of concentration – deammoniation – solidification to produce a crystalline uranyl nitrate (hydrated) solid.[2] The solidified product is contained in single-use stainless steel vessels. This operation to date has processed over 5000 litres and reduced the volume of processed liquid by 97.4% to an Intermediate Level Solid Waste (ILSW) form. The solid product is being stored in the same facility and in the same manner as the other ILSW items. This process is an interim step only as the solid crystalline product is unsuitable for long-term disposal due to its solubility in water. Therefore, incorporation of the waste into a titanate based ceramic waste form (synroc) [3] was identified as an appropriate strategy for long-term immobilisation of the waste and future disposal to the intermediate level waste storage.

The Mo-99 Waste Immobilization (MoWI) process utilizes the technologies that have been developed and successfully tested on laboratory, pilot-plant and plant scales at ANSTO. The effort to develop a feasible production method for ceramic waste forms has focused on dry processing methods, rather than handling slurries, sludges or pastes. This approach originated from the earlier success in developing porous microspherical synroc precursor particles by spray-drying of inorganic multicomponent sol compositions. Development and deployment of this technology for production of precursor ceramic microspheres with custom designed compositions have been completed by 1995 and production of the precursor powders has been routinely carried out on 50 kg/batch scale.[4, 5]

MoWI technology involves a series of unit operations, Fig. 1. These mainly are:

1. Impregnation (infiltration) of porous precursor powders with liquid waste,
2. Calcination of the waste impregnated powders,
3. Consolidation of the calcined waste carrying powders.

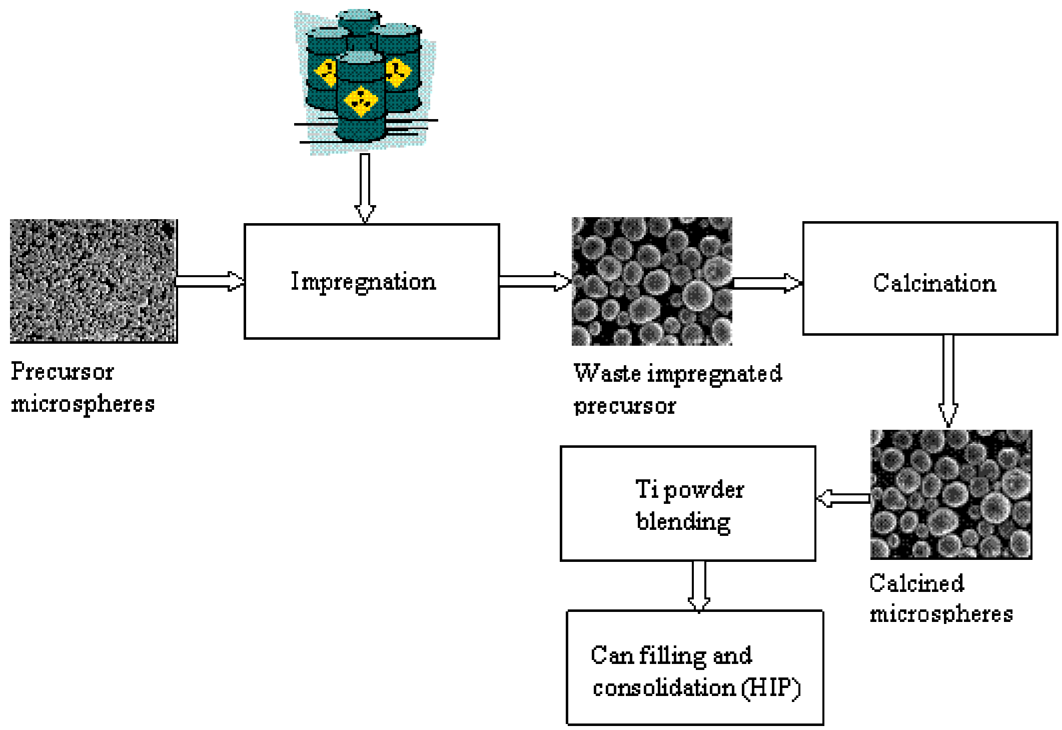

Fig. 1. Process flow diagram for ceramic waste process at ANSTO

Experimental investigation of various processing options to develop a suitable technology for impregnating precursor ceramic microspheres with liquid waste streams has been carried out following the precursor development activities.[6, 7] The experiments were carried out on 1, 5, 10 and 30 kg/batch scales by using liquid waste simulants and DUNH solution.

Subsequently the impregnated powders were calcined on 0.5, 2 and 10 kg/batch scale under reducing atmosphere for decomposing the nitrate salts to metal oxides. The calcined powders were consolidated on several scales in graphite dies and stainless steel bellows using both uniaxial and isostatic hot presses.

The development and demonstration activities led the overall liquid waste processing technology at ANSTO is directed towards construction of a synroc plant in a hot-cell for the long-term immobilisation of the accumulated legacy waste arising from Mo-99 production for indefinite storage or disposal in a geological repository.

An inactive mock-up facility has been constructed and is in testing stage to demonstrate the operability of the mixing/drying, calcination and can filling procedures within the hot-cell geometry.

PROCESS TECHNOLOGY AND RESULTS

The equipment for impregnating and calcining steps of the process are schematically illustrated in Figure 2.

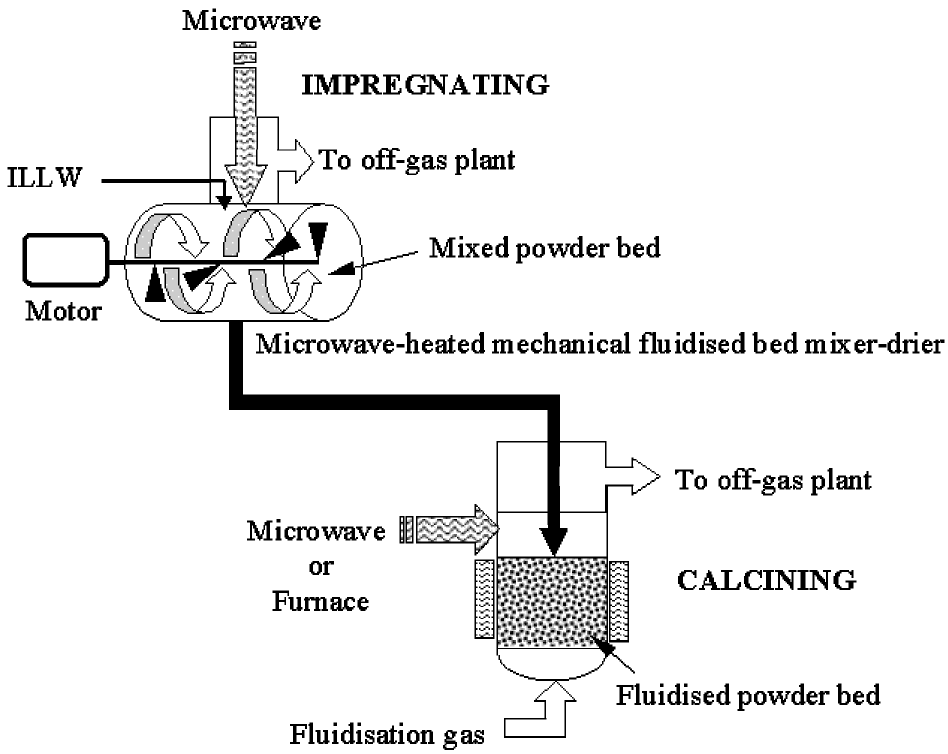

Fig. 2. Schematic illustration of impregnating and calcining systems

Waste Impregnation

Homogeneous distribution of U and fission products through the phases of the ceramic waste form was adopted as a prerequisite for the waste form. The results of the experimental technology development activities showed that morphology of the precursor particles, properties of the bulk precursor powders, both before and after the introduction of the waste species, influence the quality of the ceramic waste form to be obtained.

Experiments with various powder-liquid contacting and drying methods (fluidised bed, rotary drier, mixed bed and mechanically fluidised bed) showed that the porous precursor powders must be impregnated with the liquid stream without formation of any wet cake, sludge or slurry phases. Apart from the solid-liquid contact aspect, the experiments were carried out utilizing various heating methods (including: external electric heating, oil bath/jacket, hot gas, microwave and combination of these). The tests showed that the mechanism of the heat transfer to evaporate the water content of the impregnated ILLW in the microspheres is critical to eliminate formation of free water in the powder bed and segregation of the waste species on the surface of the precursor particles and in the bulk of the powder.

Therefore, incipient impregnation technique has been adopted to load the porous ceramic precursor microspheres with the dissolved salt compounds of ILLW stream. Microwave heating was chosen to achieve fast and selective heating of water content of the ILLW impregnated microspherical particles without involving any heat transfer coefficients of the jacket heated mixer-driers. Further conclusion made on the method of contacting ILLW with the precursor powder by using a ploughshare type mixer (mechanically fluidised bed) to achieve high efficiency mixing in three axis of the mixer vessel and contacting the atomised ILLW with the precursor powder.

Design and construction of a custom made prototype-1 MWMFB mixer-drier with a nominal capacity of 50L (plant scale) has been carried out at ANSTO. The sketch and a photograph of the MWMFB mixer-drier are shown in Fig. 2 and Fig. 3, respectively.

Fig. 3. MWMFB mixer-drier

MWMFB unit was installed into a custom made glove box to carry out tests with simulant salt solutions and DUNH. The tests with the simulant salt solution addressed optimization of mixing speed, liquid atomization rate and microwave energy aspects. The MWMFB unit was equipped with a 6kW microwave power supply and a magnetron (2450 MHz) system. The magnetron was protected from the possible reflected microwave power by a water-cooled microwave circulator. The microwave transmission system was installed with an impedance analyzer that commands to a motorised 3-stub tuner.

The operation campaigns with simulated acidic nitrate salt and DUNH solutions proved that microwave energy coupled perfectly to the drum of the mixer-drier and its contents without any significant microwave reflection back to the magnetron under both manual and automatic tuning conditions. Typical Voltage Standing Wave Ratio (VSWR) values for routine operation have been achieved at average value of 1.22 which corresponds to ~1% of the transmitted microwave power.

Both intermittent and continuous impregnation campaigns for several batches of the precursor powder proved that 6 l/h water can be evaporated at 6 kW microwave power level and at 10 kPa

vacuum under steady state operation of MWMFB mixer-drier,
Figure 4.

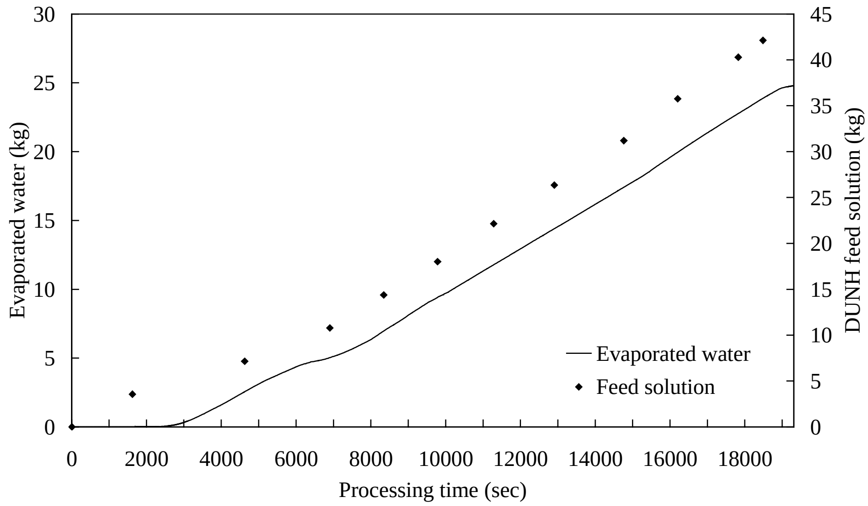

Fig. 4. Feed and water evaporation plots during impregnation of DUNH solution

The experimental campaign at plant scale produced a 30 kg batch of DUNH impregnated and free-flowing ceramic precursor with 35wt% oxide equivalent UO_2 loading in about 5.5 hours.

Calcining and Consolidation

Calcining of the waste impregnated powders was investigated on various scales using tray, rotary and fluidised bed calciners. Calcining is carried out at 750°C under reducing atmosphere till evolution of NO_x diminishes. Use of reducing atmosphere for calcination significantly reduces degree of volatility of Cs, Ru etc. and requires less space for off gas treatment. The experiments revealed that chemical reduction of the calcined product depends on the availability of sufficient hydrogen in the air tight calciner throughout the calcination process and the diffusion of hydrogen into the microspheres in an environment where competitive reactions between hydrogen and nitrous oxides occur.

On the basis of experimental findings and remote-operated hot cell design constraints, utilization of fluidised bed calcining technology on batch operation bases has been decided. External electric furnace and microwave heating of the fluidised bed calciner were chosen as the options to be investigated, Figure 2.

Utilization of a MicroWave-heated Fluidised Bed (MWFB) calciner has been considered for the following advantages:

- Rapid and bulk heating due to penetration of microwaves into the bed and direct delivery of energy to the bed material.
- Smaller foot print and elimination of heating utilities from the hot cell due to transmission of microwaves through simple waveguides.

Proof-of-concept calcination tests using the simulant salt solution impregnated precursors were carried out using a fluidised bed unit (~100 mm in diameter) equipped with an external electric furnace. Subsequently, a single mode (TE_{10}) cylindrical (~100 mm in diameter) MWFB calciner was designed and constructed. The microwave generator system of the MWMFB mixer-drier has been used to heat the MWFB calciner.

The complex dielectric constant of the bed is a function of the composition, the temperature and the density of the bed; and all these parameters continuously change during calcination process. Apart from that, the geometry of the bed also dynamically changes along the process, due to thermal decomposition, fluidisation dynamics of the bed and thermal expansion of the calciner superstructure.

The test campaigns with MWFB calciner revealed two of the utilised commercial microwave autotuners (based on an impedance analyser and a motorised 3-stub tuner) could not cope with the dynamics of the calciner to match the impedance of the magnetron to that of the calciner. However, a novel method for tuning microwaves to the fluidised bed was developed [8] and 1.3 kg of nitrate salt composition impregnated powder was successfully calcined at 750°C under reducing gas atmosphere (3.5% H_2 in N_2) for 1 hour to produce fully reduced calcine. The new tuning method achieved very low microwave reflections with less than 1% of the magnetron power output.

Samples from DUNH impregnated ceramic precursor produced from MWMFB mixer-drier was calcined in three 0.5 kg batches for characterisation purposes. A small-scale rotary calciner available in the active area was utilized for calcinations to avoid contamination of the fluidised bed units. Calcination was carried out under reducing gas atmosphere at 750°C for 1 hour and the calcined powders were filled into stainless steel cans and after evacuating and sealing. The cans were subsequently isostatically pressed at 1260°C and 100 MPa for 2 hours.

Samples were characterized by scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Diffused Reflectance (DR) analysis. This showed that the microstructure of the product was fine grained dense ceramic containing approximately 80% pyrochlore structured $CaUTi_2O_7$. The remaining phases consisted of brannerite, zirconolite, rutile and hollondite to immobilise fission products and process chemicals. The SEM investigations proved that the HIP'ed samples produced perfect synroc material and showed no residual UO_2 particles present in the ceramic matrix.

Ceramics produced from active tests were assessed for durability using MCC-1 static leach tests in deionised water at 90°C. The leaching tests on these ceramics yielded very good results better than those obtained on reference grade materials used for High Level Waste (HLW), Table I.

Table I. Normalised concentrations of the elements (g m^{-2} day^{-1}) in the leachate from MCC-1 test for 28-day period. Reference material is borosilicate glass.[9]

Element	**Synroc ceramic**	**Waste form criteria (reference material)**
U	$0.9x10^{-4}$	<0.1
Cs	0.08	1
Sr	0.0071	1

This demonstrates the suitability of ceramic waste form, which easily meets leaching standards for HLW. It should be noted that we are dealing with intermediate level waste. Synroc provides demonstrably secure long-term immobilisation barrier for geological disposal that is an important component of design systems that conform to the safeguards required for the public.

Mock-Up Test Facility

Design and construction of a mock-up facility have been carried out for integration of the previously proven individual processing steps of MoWI process using realistic equipment and procedures. The facility aims to investigate operability and maintainability of the process components at remote operating conditions to identify the areas of improvements and modifications.

The MoWI process has been designed to carry out one processing step at a time and it is based on a plant that immobilizes 190 kg uranium in a year. The design of the mock-up facility has been based on the geometry and configuration of the available hot-cells, which are proposed for MoWI process, at ANSTO. The mock-up facility is a demonstration facility to perform the tasks in a non-radiological environment replicating as much as possible remote operating conditions. The mock-up cell consists of a 3-D frame and a mock-up window simulating visual access and positions of two master-slave manipulators, Figure 5.

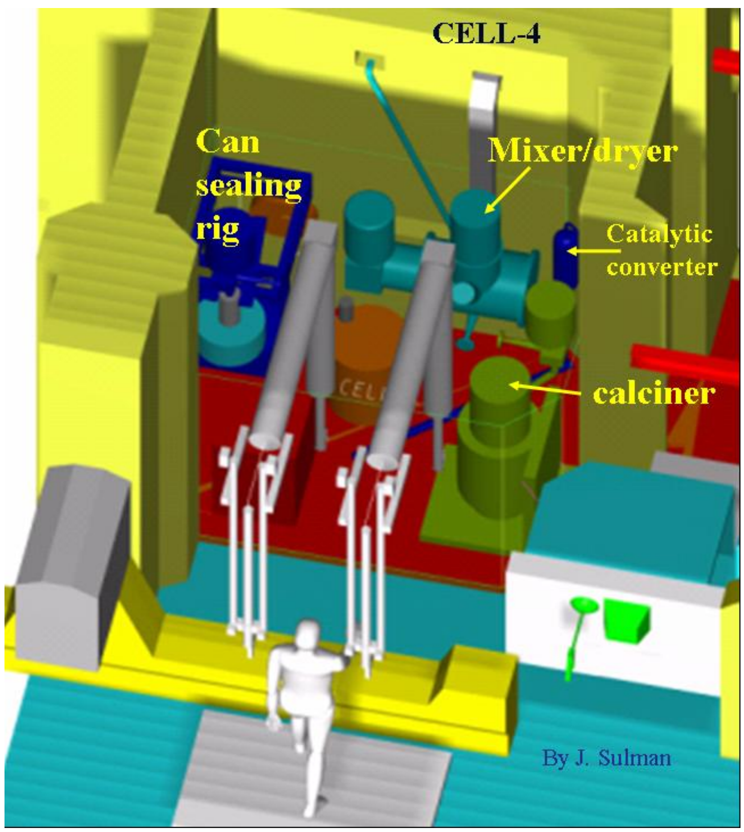

Fig. 5. Layout of MoWI process in hot cells

Mock-up facility consists of a custom designed prototype-2 MWMFB mixer-drier with a nominal capacity of 50L, a fluidised bed calciner (300 mm in diameter) with a split shell electric furnace and optional microwave heating provisions, off-gas treatment module, liquid waste transfer system and a preliminary apparatus to investigate can filling operations. A 6 kW microwave generator has been installed outside of the cell with appropriate waveguide configuration and microwave monitoring-autotuning instruments.

The facility is provided with pressurized air, nitrogen, reducing gas and vacuum supply utilities. Transport of the processed powders between the stages of the plant is carried out by pneumatic transfer aids. The facility has been installed with various safety features, instrumentation and interlock systems to simulate active plant operations. Process variables are downloaded using data logging software through real time graphical and numerical monitoring.

Following successful commissioning of the facility, the tests for assessing pneumatic powder transfer, integration of processing components and identification of the operation windows for variables are currently being carried out.

CONCLUSION

The experimental campaign on plant scale (30 kg) for impregnating (35wt% UO_2 loading) D-UNH solution into sol-gel microspheres proved that a synroc ceramic waste form with perfect microstructure and composition can be produced by utilising in-house developed MWMFB mixer-drier technology.

This work concludes that MWMFB mixer-drier is capable of producing free-flowing powders by continuous impregnation of a salt solution into porous precursor microspheres.

The concept of calcining waste containing dry powders by using a microwave-heated fluidised bed has been achieved by utilizing a novel impedance matching method.

As described in this paper there has been an orderly progression in the development of equipment and operations leading to a plant scale mock-up facility for immobilization of waste arising from Mo-99 production.

The mock-up facility with second generation prototype equipment has been designed and constructed on the bases of the in-house developed processing technologies. Test run campaigns to establish a design bases for the hot-cell plant to immobilize Mo-99 legacy waste are currently carried out.

ANSTO's decision of long term immobilisation of the waste arising from Mo-99 production process in synroc is a sound waste management solution and will be a valid demonstration of ANSTO technology.

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