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THE WATSS RECYCLING PROCESS – VALIDATION OF TRANSURANIC ELEMENTS EXTRACTION FROM SPENT FUEL OXIDE AT CNL

J.P. Zuniga[1], I. Scott[1], O. Gregoire[1], A. D. Warren[1], R. Brown[1], G. Cota-Sanchez[2], L. Bradford[2], D. Cluff[2], K. Kovack[2], D. Poff[2] and Rory O'Sullivan[1]
[1] Moltex Energy, Saint John, New Brunswick, Canada
[2] Canadian Nuclear Laboratories, Chalk River, Ontario, Canada
josezuniga@moltexenergy.com

Abstract

The extraction of transuranic elements from spent uranium oxide nuclear fuel can be obtained by the direct conversion in molten salt of transuranic oxides into chloride or oxychloride species, while uranium oxide remains as insoluble solid material. This is based on a pyrochemical processing technique relying exclusively on chemical redox potential for the extraction of components of spent fuel in molten salt. This is significantly less complex than pyroprocessing based on electrochemical separation.

Computational tools and experiments with simulant spent fuel have been combined to determine commercially viable extraction conditions, and a set of options have been tested with real spent fuel at the Canadian Nuclear Laboratories facilities in Chalk River. The results validate the viability of the selective extraction, which is the first stage of the broader Waste-to-Stable-Salt (WATSS) fuel recycling process.

1. Introduction

As the demand for electricity increases in daily life, from electric vehicles to data centers, the urgency to reduce our reliance on fossil fuels has never been greater. It also becomes evident that intermittent and seasonally driven sources need to be backed by a stable provision of baseload power, renewing interest in new nuclear capacity as a reliable and sustainable solution. Two fundamental considerations need to be addressed to ensure the long-term sustainability of this option: the continued availability of fissile fuel and the suitable management of wastes. Both factors may be addressed by realizing that the discharged fuel from the current fleet of reactors, considered as "spent fuel" still contains a significant amount of fissile material.

Whether it is for fuel availability or for waste management considerations, it becomes more and more important to view spent fuel recycling as a sustainable way forward, especially the grouped recycling of transuranics (TRU - unseparated Pu and minor actinides) for their consumption in fast-spectrum molten salt reactors. This is the purpose of the Waste to Stable Salt (WATSS) process developed by Moltex Energy.

Reprocessing and recycling of used fuel are traditionally considered as sensitive activities in terms of proliferation since the PUREX process, the process currently used at industrial scale to recover plutonium from spent fuel to produce MOX, may also be applied to (and initially was developed for) the production of weapons-grade material. Besides its proliferation concerns, this legacy method has

proved to be expensive and involves very large plants due to the large volumes of solvents required. However, if the recycled material is intended to be consumed in a fast spectrum reactor, such as the Stable Salt Reactor – Wasteburner (SSR-W) developed by Moltex, plutonium doesn't need to be separated from other actinides. This opens the door to different methods of recycling, with considerably increased potential for proliferation resistance [1]. Among these methods are a set of processes broadly referred to as pyro-processing where molten salts are used as the solvent for the chemical species instead of water and organic solvents.

In the WATSS process, the fuel is first mechanically stripped of its cladding. It then undergoes a pre-treatment stage in which the irradiated oxide material is subjected to a sequence of controlled oxidation and reduction steps. This process reduces the particle size of the oxide matrix and adjusts its oxidation state to the level required for subsequent processing. The single oxidation treatment is the well-established voloxidation process, while the sequence of alternating oxidation and reduction is known as OREOX (Oxidation-Reduction of Oxides) [2]. The next step (Stage 1) is the selective separation of TRU species from uranium, which constitutes the majority of the oxide matrix. This separation is achieved through direct extraction of TRUs into a molten salt medium, facilitated by a carefully controlled addition of a reducing metal in precise stoichiometric proportions. The reducing metal converts transuranic elements into salt-soluble species—either trichlorides or oxychlorides—while uranium reduces through a series of compounds to a final insoluble dioxide phase. In the subsequent stages of the WATSS process (Stages 2 and 3), the extracted TRUs are concentrated to produce molten salt fuel, while fission products are separated. The actinides are first selectively reduced into liquid bismuth, followed by re-extraction into clean molten salt through chlorination by bismuth chloride in the presence of magnesium chloride. This process yields a magnesium chloride-based salt infused with actinide trichlorides, which serves as a precursor for reactor fuel salt. For the production of fuel for molten salt reactors, precursor salts with precisely characterized elemental and isotopic compositions are stored and blended to achieve the desired actinide ratio. Conventional salts are then added to reach the eutectic point, such as sodium chloride for the SSR-W. The final stage can be adapted to produce either chloride- or fluoride-based fuel salts, depending on the specific requirements of the reactor developer.

2. TRU extraction in molten salt

The primary consideration of the whole process, and the purpose of stage 1, is to effectively separate TRU species from uranium, present in overwhelming proportion in the oxide matrix. This stage is based on the direct extraction from powdered spent fuel into a molten salt in the presence of a reducing metal that would turn transuranic elements into trivalent salt soluble species (trichloride or oxychloride), while leaving uranium as an insoluble dioxide. This is essentially based on the process identified by Wenz in the late 1960's [3]. He showed that oxidation of UO_2 spent fuel to U_3O_8 by a process known as voloxidation, followed by extraction in molten $MgCl_2$ based salts with a reducing metal added to reconvert the U_3O_8 to UO_2, resulted in as much as 95% of the plutonium dissolving in the salt while most of the uranium remained as solid oxide. Wenz used MOX as Pu-bearing feed material with a relatively high proportion of Pu. It has later been highlighted that all TRUs behave similarly and are separated as a group from the uranium compounds [4].

The reducing metal identified in the early work, tantalum, was not an economically viable option. Moltex has now revisited this approach with alternative, cheaper, reducing reagents identified using modern chemical computational tools [5].

An economic feasibility study by Moltex Energy is based on the assumptions of a nominal efficiency of 90% and a low overall efficiency of 75% extraction for the commercial operation of WATSS.

Moltex has identified 3 approaches for reaching the redox conditions, by addition of a reducing reagent, corresponding to uranium being largely tetravalent while other actinides are trivalent:

- Careful selection of a reducing reagent with a redox couple having the suitable potential (the approach described by Wenz with tantalum),
- Controlled addition of the stronger reducing reagent, with feed-back monitoring to prevent build-up of uranium trivalent species (titration),
- Over-reduction with a strong reducing reagent, followed by back-oxidation with an oxidizing reagent with a redox couple having suitable potential (in accordance with the first bullet point, the obvious example is tantalum oxide)

The last option would require quantities of tantalum species far smaller than the stoichiometric quantity required to reduce all actinides initially present in the oxide.

The present paper addresses the second and third options mentioned above, and the potential for magnesium to be used as a strong reducing reagent, either for a controlled addition or the over-reduction of TRUs with some acceptable uranium carry-over in the salt. Besides its low cost, a significant advantage of using magnesium as a reducing metal is avoiding the accumulation of by-products of oxidized metal in the process. Magnesium chloride is already a major component of the salt phase. This is an important aspect in terms of re-usability of the salt, and reduction of the volume of high-level waste.

The chemical behaviour of the spent fuel oxide matrix in molten salt, with the addition of a reducing reagent, has been studied in different configurations with the commercially available HSC Thermodynamic Modeling Software. HSC version 10.4.2.2 and built-in database was used in this study. The results from the system in which magnesium is added as the reducing agent are reported in figures 1 and 2 for uranium and plutonium species respectively.

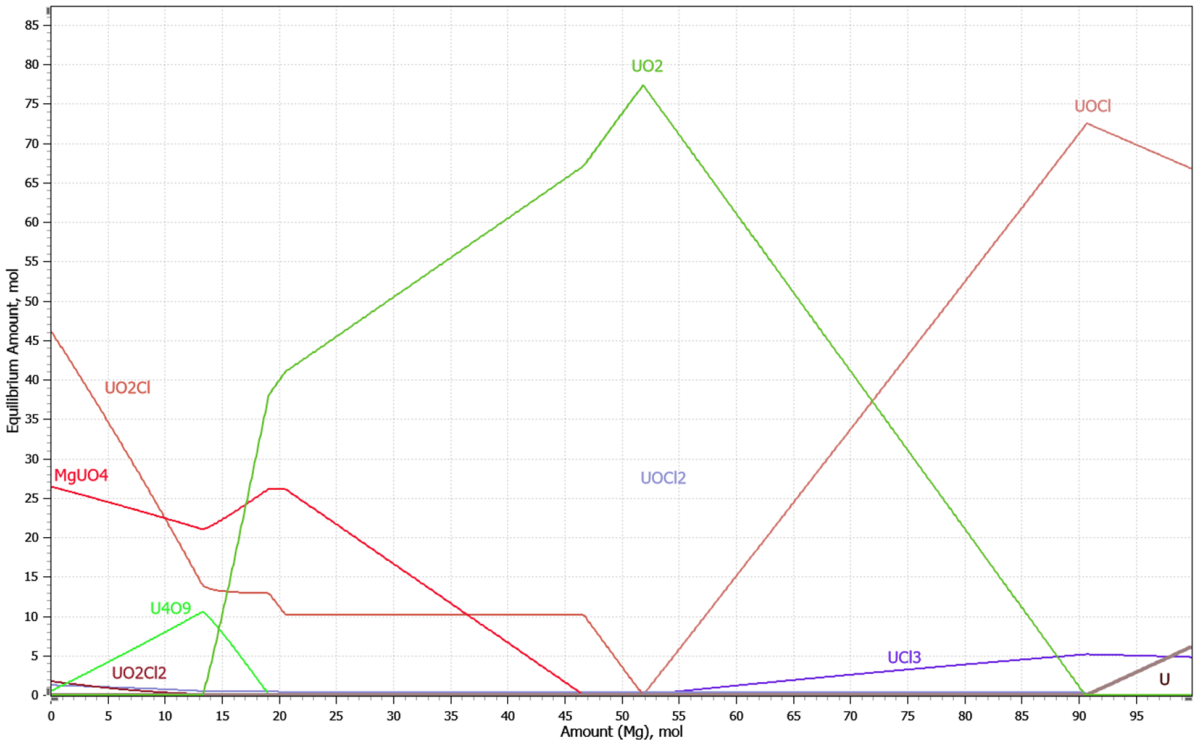

Figure 1 Thermodynamic stability of uranium species in a spent fuel – molten salt system with increasing amount of magnesium metal, as calculated with HSC software.

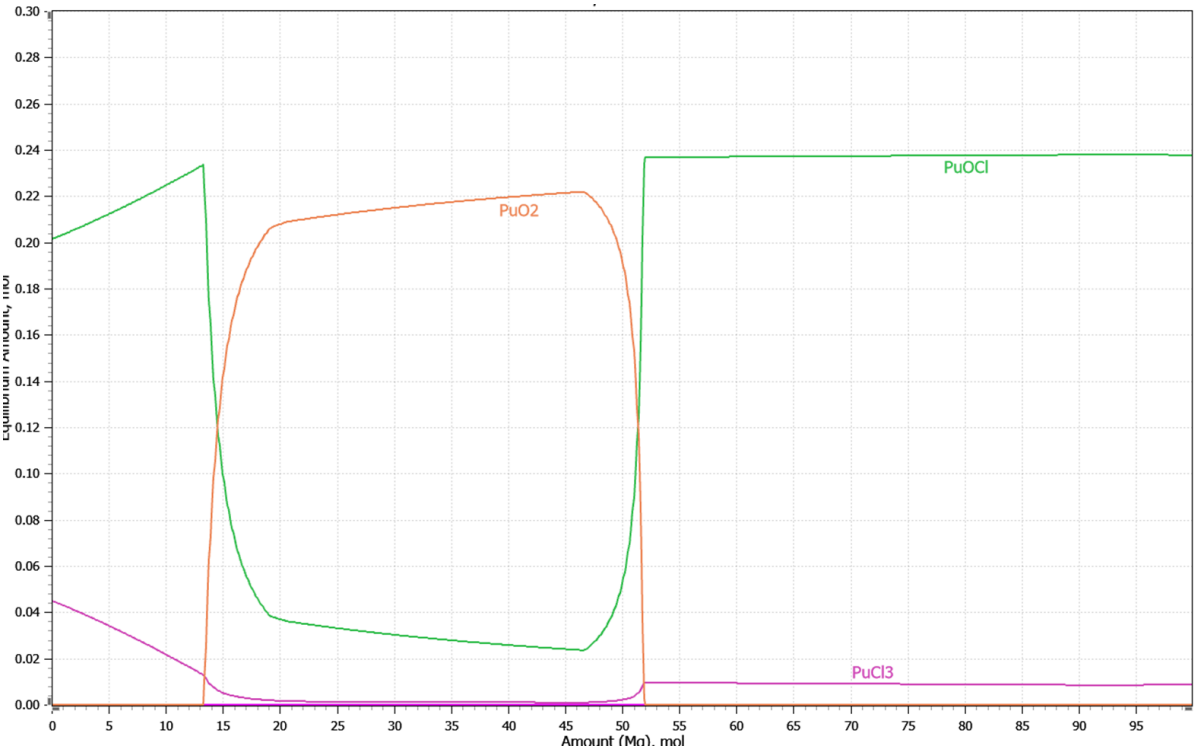

Figure 2 Thermodynamic stability of plutonium species in a spent fuel – molten salt system with increasing amount of magnesium metal, as calculated with HSC software.

From the thermodynamically stable equilibrium of species composition reported in figures 1 and 2, we can infer the different chemical processes at play when voloxidized spent fuel is contacted with $MgCl_2$ – based molten salt, and when magnesium metal is added. The proposed reactions (1-6) are reported below.

$$U_3O_8 + MgCl_2 \rightarrow MgUO_4 + 2\ UO_2Cl \quad (1)$$

$$PuO_2 + ½\ U_3O_8 + MgCl_2 \rightarrow MgUO_4 + PuOCl + ½\ UO_2Cl_2 \quad (2)$$

$$MgUO_4 + Mg \rightarrow UO_2 + 2\ MgO \quad (3)$$

$$UO_2Cl + ½\ Mg \rightarrow UO_2 + ½\ MgCl_2 \quad (4)$$

$$UO_2 + ½\ Mg + ½\ MgCl_2 \rightarrow UOCl + MgO \quad (5)$$

$$PuO_2 + ½\ Mg + ½\ MgCl_2 \rightarrow PuOCl + MgO \quad (6)$$

In contact with the divalent halide, U_3O_8 reacts to form a hexavalent oxide stabilized with MgO, as well as a salt-soluble oxychloride, in proportions consistent with equation (1). Plutonium (and other transuranics) also react, forming a trivalent oxychloride and a complement of hexavalent uranium species according to (2). With the addition of magnesium metal, hexavalent and pentavalent uranium react according to (3) and (4) respectively, leading to the formation of salt-insoluble UO_2. Such reaction consumes the uranium species allowing reaction (2), therefore largely leaving plutonium in its dioxide form, until all uranium has been reduced to its +4 oxidation stage. With a stoichiometric excess of Mg, actinides are further reduced according to (5) and (6), TRUs being reduced first, and then uranium with the remaining available reducing reagent. Trivalent species produced are in equilibrium between oxychloride and trichloride, both being soluble in the salt phase.

This process highlights the rationale for starting with a uranium matrix in a higher oxidation stage, producing a salt-soluble intermediary species that allows the reaction to propagate deep inside the grains.

From the experiments carried out by Wenz [3], it is known that the Ta / Ta_2O_5 redox couple stabilizes uranium in its +4 state while TRUs are in +3 forms. The addition of a small amount of tantalum oxide following the production of some uranium oxychloride due to an excess of magnesium is therefore expected to oxidize the salt-soluble uranium species back into insoluble UO_2, while leaving oxychlorides and trichlorides of TRUs in the salt.

3. Experimental extraction of surrogate material

Until the end of 2024, Moltex Energy used its own experimental facilities in Warrington, UK, equipped and licensed for the management of uranium species, but not plutonium-bearing compounds. Preliminary tests of different extraction chemistries, identified on the basis of computational modeling tools, were carried out with simulated spent fuel (simfuel), consisting in sintered UO_2 pellets containing cerium dioxide as a surrogate for PuO_2. A variety of extraction conditions have been investigated.

The cerium extraction profile reported in figure 3 highlights an experiment in which zirconium was first added as a reducing metal to reduce most, but not all, of the uranium species to UO_2, followed by the addition of magnesium metal in excess. In this case, a total of 50% excess relative to the calculated stoichiometric amount needed to turn all U_3O_8 into UO_2 form was added. The significant excess was required due to its being both consumed in the reaction and its high vapour pressure at 700°C, a reaction temperature required for the salt to be liquid.

Nearly 99% extraction of Ce was achieved with two different liquid phases. One phase was transparent like water and the other was dark red, which has been reported in previous work as an indication of U in the +3 state [6].

Ta_2O_5 was added to the extraction after 20 hours of operation. The UOCl reacted very aggressively and quickly with tantalum oxide, converting the two liquid salt phases to one clear salt phase, an indicator that there is low U content in the salt. The addition is shown in the Figure 11 labelled as "Back oxidation" in which a small decrease of Ce extraction from ~99% to ~95% was measured, however within the variability of other data points and likely not statistically significant.

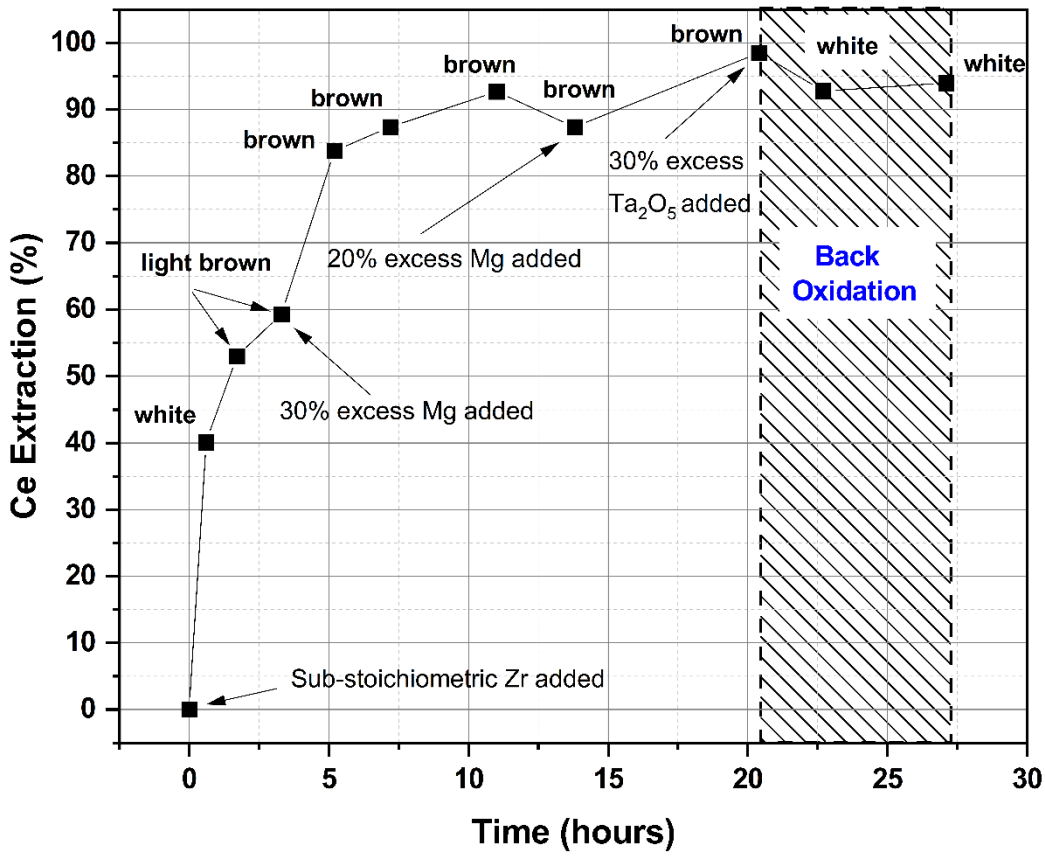

Figure 3 Extraction of cerium from SimFuel using excess magnesium metal and back oxidizing with Ta_2O_5. The reported colour for each data point corresponds to the colour of the salt, which is an indication of the content of uranium in +3 oxidation state.

4. Experimental extraction with actual spent fuel

The validation of the preliminary results obtained with simfuel requires extraction tests with real spent nuclear fuel. This needs to be carried out in a hot-cell environment. This test campaign has been done at the Chalk River facilities of the Canadian Nuclear Laboratories (CNL).

Unlike the experimental environment in the glovebox of the Warrington labs, where extraction and sampling could take place in an oxygen-free atmosphere, a glovebox cannot be fitted in the hot-cells available for experiments and are not equipped to have a controlled atmosphere. The test rigs to use in the hot cell should therefore be specifically designed to incorporate controlled atmosphere features, and alternative means to sample and/or analyse the extracted salt needed to be considered.

4.1 Modified experimental setup for hot-cell layout

4.1.1 Test rig design

The rig design, reproduced in figure 4, is intended to allow four independent tests to be performed on spent fuel powder simultaneously over multiple days without the need to break the controlled atmosphere. Each rig comprises four reaction vessels made of Ni201 (23 mm internal diameter; 129 mm high), in which different extraction conditions are tested. These four vessels are surrounded by a cylindrical containment vessel designed to be inserted in a furnace (see bottom part of Figure 5). A mechanical stirrer also made of Ni201 sits within each extraction vessel, connected to a respective motor mounted above the containment vessel's lid. A calibration-certified thermocouple penetrates the containment vessel lid to provide a measurement of the temperature of gas space in the rig. The motor assembly and stirrers can be lowered and raised thanks to a threaded rod.

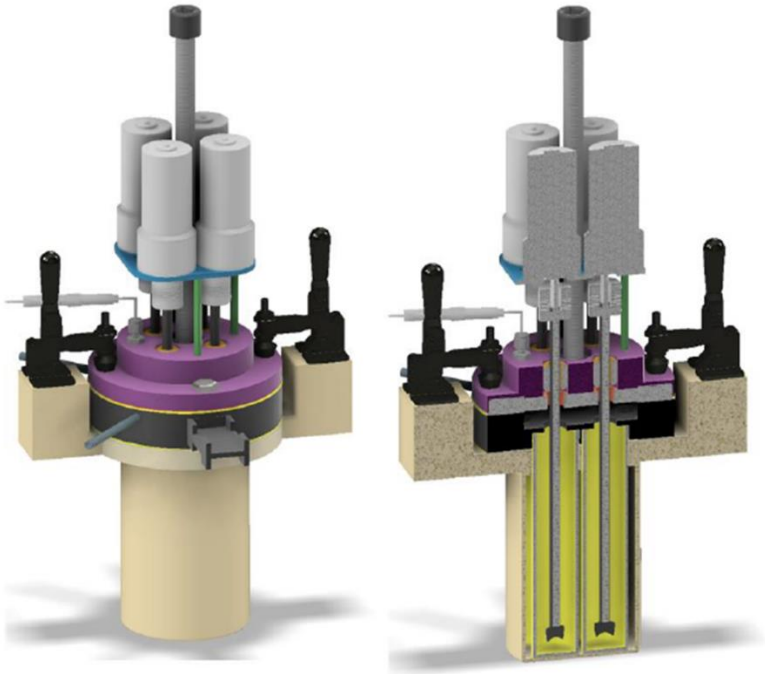

Figure 4 Computer-generated image of a test rig. Left: External view. Right: cross-section view.

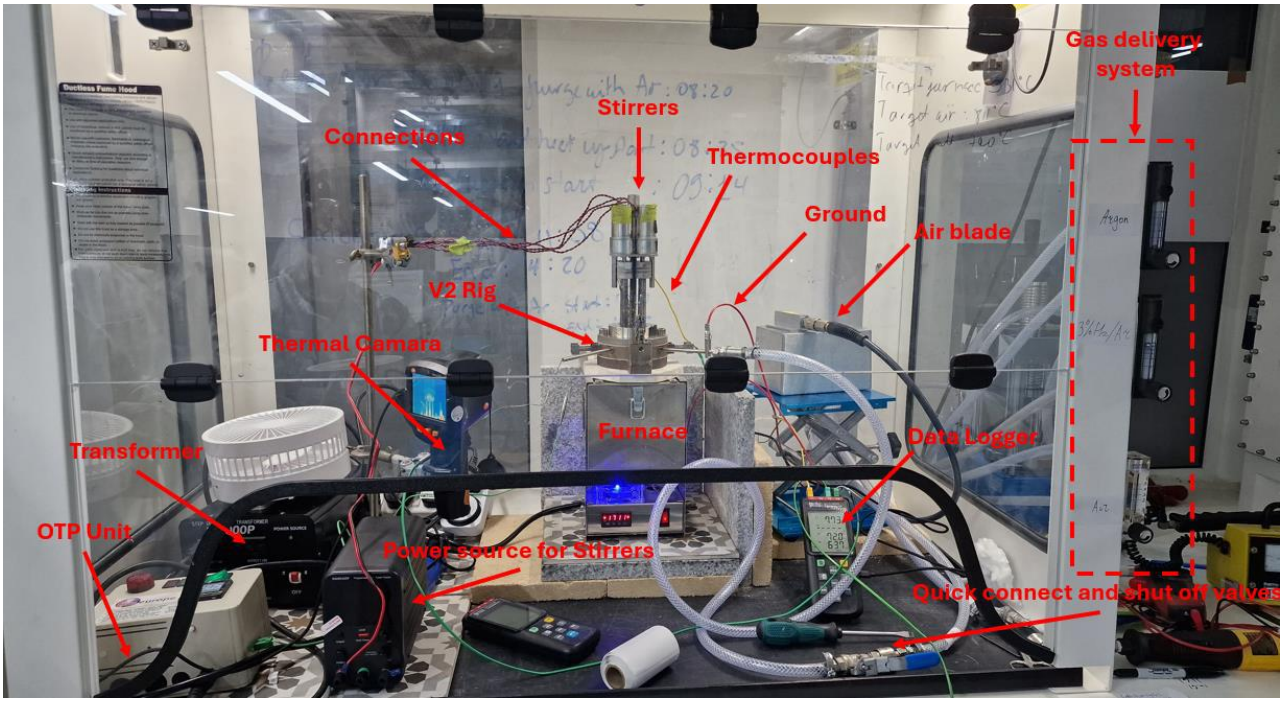

Figure 5 Extraction rig setup at UK lab. The motor assembly is in the raised position.

After the extraction time is passed, the stirrers are paused and withdrawn from the molten salt, and the furnace is switched off. A settling period allows for the salt to freeze before the rig is open by releasing two clamps on the sides of the rig, easily actionable with tele-manipulators. The experimental measurement of conversion of oxides to chlorides or oxychlorides is then carried out by dissolution of the solid cylinder of salt and powder as discussed in the following section.

4.1.2 Analytical method

The design of the rigs does not allow sampling of the molten salt during extraction. The analytical method identified to determine the conversion of oxide to chloride forms (trichloride or oxychloride) is the selective dissolution of chlorinated species with diluted acid, without dissolving oxides, followed by the composition analysis of the filtered liquid phase and of the retained solid oxide.

Preliminary tests of dissolution of salt samples containing UOCl, an isomorphous analogue of PuOCl, concluded that 0.1M HCl was insufficient to dissolve UOCl. With the increase of the acid concentration to 1M, the red slurry dissolved almost instantly and turned into a green solution, suggesting a change from +3 to +4 oxidation state. Spectroscopic analysis of the solution showed that almost all of the uranium turned into a soluble species.

A literature review highlighted that the dissolution of PuO_2 in 3M HCl at 100°C would not exceed 8% after several hours (see Figure 7 and Ref [6]). From a conservative extrapolation of published data, it is assessed that at 1M the dissolution would not exceed 3% at 100°C and it can be deduced to be negligible at room temperature.

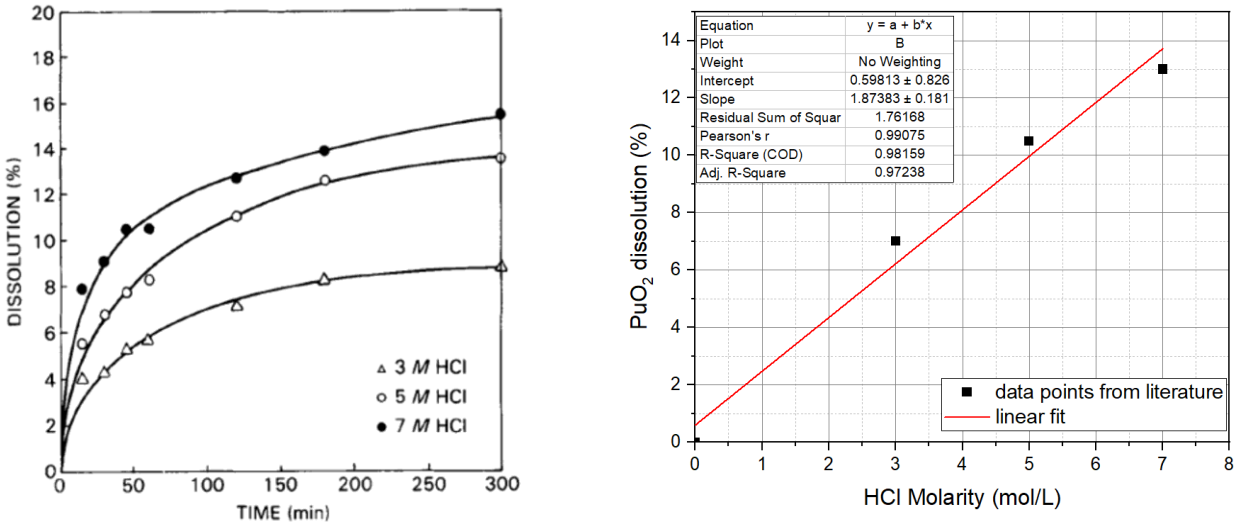

Figure 6 Left: Dissolution of PuO_2 in HCl medium at 100°C (reproduced from Ref [7]). Right: Linear regression of data points from Ref [7] corresponding to 120 min dissolution.

A dissolution test of UO_2 in 1M HCl displayed no measurable UV-visible spectrophotometric signal in the filtrate confirming that these conditions would have a negligible leaching of uranium oxide in the liquid phase.

The overall analytical method consists in (a) cutting the extraction vessel above the level of frozen salt with a precision cutting tool set at slow cutting speed to minimize heat generation and prevent contamination of the content, (b) placing the salt-laden section of the vessel horizontally in a container filled with 1M HCl and equipped with overhead stirring system, (c) operating the dissolution system until all salt and slurry is completely dissolved or dispersed, (d) extracting a sample of dissolved solution with a syringe fitted with a 0.22 micron pore size filter, and (e) measuring the concentration of extracted species (Ce or Pu and U). This last step is done by spectrophotometry at the UK labs (Ce and U, only) and TIMS at CNL.

Pictures reproduced in figure 7 show step (a) as reported above, while pictures of the setup for steps (b) to (d) are reproduced in figure 8.

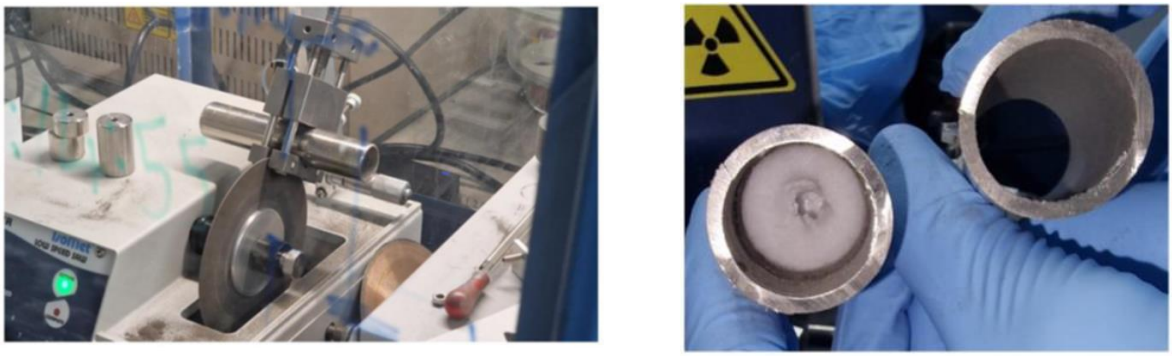

Figure 7 Left: Extraction vessels cutting set-up. Right: Horizontal cross-section of cut vessel.

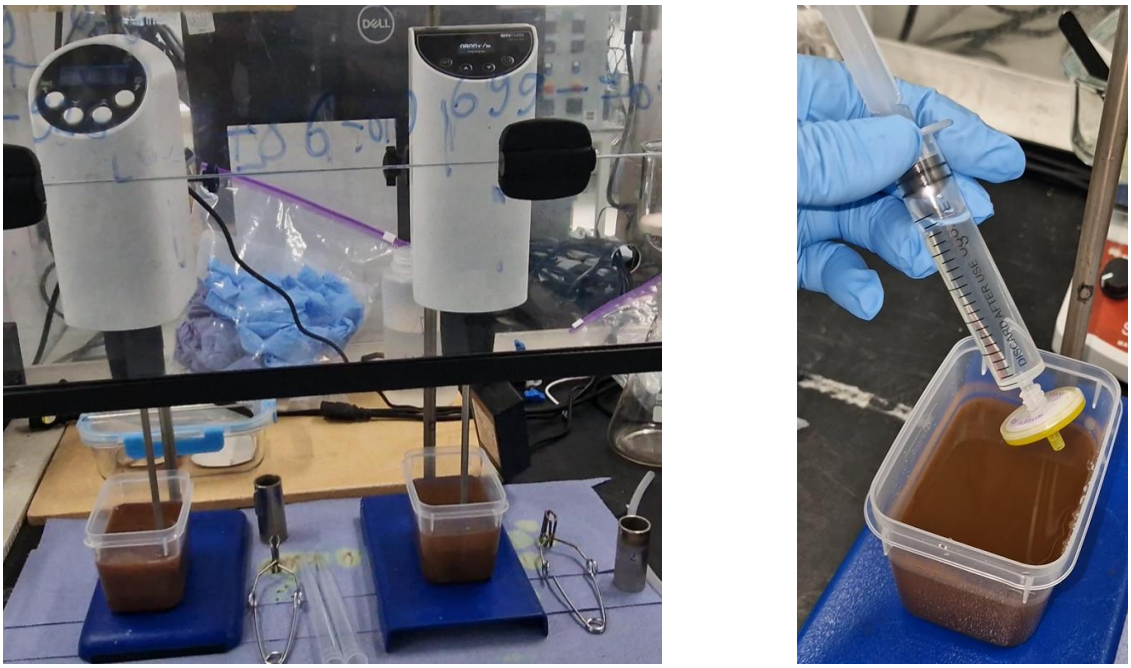

Figure 8 Left: Salt dissolution set-up, with overhead stirring systems. Right: Collection of filtered samples.

4.2 Experimental test results

Three test rigs have been used in the Universal Cell (UC) hot cell facilities at CNL, in a campaign labelled MIFE (Moltex Irradiated Fuel Experiments) by CNL. This corresponds to 12 different experimental conditions (different reducing reagents and reaction time), including some reference tests (with simfuel, or with real spent fuel and no reducing metal). Preparation for dissolution and sampling of the different reaction vessels were conducted in the Fuel and Materials Cells (FMC).

Taking into account the post-experiment treatment time and analysis of the samples, analytical data are only made available progressively, several months after the experiments. The first relevant test involved the addition of magnesium to a mixture of salt and OREOX-treated spent CANDU fuel, according to the composition reported in Table 1. This experiment corresponds to a 24-hour extraction. All tests are carried out at 700°C (internal temperature).

Table 1 Components included in the reaction vessel for the Mg test

Component	**Mass (g)**
Spent CANDU fuel oxide following OREOX treatment (U_3O_8 matrix)	7.4003
Salt ($MgCl_2$-NaCl-KCl eutectic)	31.0319
Magnesium metal	0.5640

From the amount of oxide added, the mass of uranium has been calculated as 6.2509 grams. The Pu/U ratio in the feed material had been measured earlier by CNL and was determined to be 0.4065 wt %. From these values, a mass of plutonium in the reaction vessel of 0.0255 grams is calculated.

Table 2 shows the results of Pu and U concentrations in the diluted samples as well as the back calculations performed to estimate the Pu extraction and U transfer efficiencies from the oxide matrix to the salt phase. As highlighted in section 2 and supported by experimental data [4], the behaviour of Pu is representative of all TRU elements. Pu and U analysis results of an undiluted HCl blank sample indicated that a negligible cross-contamination occurred from the hot cell to the fuel dissolutions during sample preparation.

Table 2 Pu and U in the salt phase after 24-hour extraction

	Concentration in diluted solution (µg/g)	**Concentration in dissolved solution (µg/g)**	**Concentration in salt (µg/g)**	**Mass extracted in salt (g)**	**Extraction efficiency (%)**
Pu	6.923 +/- 0.013	69.974	646.661	0.0199	77.92
U	20.680 +/- 0. 27	209.021	1931.67	0.0594	0.95

The Pu/U ratio in the extraction salt increased to 0.3348, from an initial value of about 0.004 in the spent fuel. The extraction efficiency of plutonium exceeds the success criteria for the test (75 %, the low-end of the range supporting the economic feasibility), with a surprisingly low transfer of uranium, giving a range of previously unanticipated design opportunities for this chemistry and potentially mitigating an additional process step of back-oxidation. It also has the potential to lead to an even cleaner waste product than previously envisioned.

With respect to the results themselves, it should be stressed that these constitute first-of-a-kind experiments, and that no optimization of parameters (*e.g.* temperature, dwell time, reactive surface area, stirring speed, etc.) has taken place. As such it is highly likely that with additional optimization further improvements to the extraction percentages and/or the extent of uranium carry over can be achieved.

5. Conclusion

The preliminary results reported here are exceptional. They highlight a significant extraction of transuranic species from real spent fuel. The success criteria supporting economic feasibility - at least one selective extraction exceeding 75% with low uranium content - has been met. The result opens up a clear route for a commercial process where magnesium is used as the sole reducing metal to achieve just the right level of reduction. A significant advantage of using magnesium as a reagent in a salt solution largely made of magnesium chloride is avoiding the accumulation of by-products in the extraction salt, easing its re-usability and reducing the volume of secondary waste generated.

The 78% Pu extraction would be the minimum that would be achieved with a high probability that the extraction could be improved substantially without increasing the extraction of uranium excessively, since previous experimental work indicated significantly improved extraction when additional Mg is added as the reaction progresses.

6. Acknowledgements and contributions

Moltex Energy developed the overall process and carried out theoretical simulations and experimental work with simfuel. CNL carried out extraction experiments and analytical work in hot cells with CANDU spent fuel.

The authors acknowledge the technical contribution of James Moffat, Ricardo Ortega, Phil Quayle, Eldar Rahimov, Connor Smith and Joe Vickers to the experimental activities in the UK.

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