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The Advanced Fuel Cycle Initiative is developing advanced technologies to allow for the safe and economical disposal of waste from nuclear reactors. An important element of this initiative is the separation of key radionuclides. One of the systems being developed to separate key radionuclides is the UREX+1 process. The Tc and Cs/Sr solutions from UREX+1 process will require treatment and solidification for managed storage.

This paper illustrates the benefits of HIPed tailored ceramic waste forms, to provide for the immobilization of separated Cs, Sr and Tc. Experimental data are presented for a Cs and Sr-bearing hollandite-rich tailored ceramic prepared with 12 wt% waste (on an oxide basis). Normalized MCC-1 type leach testing at 90^oC for 28 days revealed extremely low Cs and Sr release rates of 0.003 and 0.004 $g/m^2/day$ respectively. Experimental data on the immobilization of Tc in titanate ceramics containing up to 40wt% TcO_2 are also be presented.

I. INTRODUCTION

The Advanced Fuel Cycle Initiative (AFCI), funded by the Department of Energy's Office of Nuclear Energy, is developing advanced technologies to allow for the safe and economical disposal of waste from nuclear reactors. An important element of this initiative is the separation of key radionuclides. One of the systems being developed to separate key radionuclides is the UREX+1 process[1]. The UREX+1 process is a series of four solvent-extraction and one ion exchange process that perform the following operations: (1) recovery of U and Tc (2) recovery of Cs and Sr (3) group recovery of Pu, Np, minor actinides (Am and Cm) and lanthanides and (4) separation of actinides from lanthanides.

The Cs/Sr strip solution from these candidate separation processes will require treatment and solidification for managed storage. Safe interim storage will require a waste form that is stable, does not produce radiolysis products (e.g., buildup of potentially explosive gases like hydrogen), has high product density (to minimize storage volume), and has properties that enhance heat management (e.g., high thermal conductivity). Radioactive cesium produced by uranium fission includes three isotopes: 134, 135 and 137. $^{137}_{55}Cs$ has a 30.17 year half-life, and decays by a beta/gamma process to form barium. The highest radiation energy fraction emitted during the decay process is due to $^{137m}_{56}Ba$, which decays to its ground state with the emission of a gamma ray (2.6 minute half-life , 0.6616 MeV), to stable $^{137}_{56}Ba$. The isotope $^{134}_{55}Cs$ present in smaller quantities is a β and γ emitter with a 2.06 year half-life. The third active cesium isotope (roughly the same amount as $^{137}_{55}Cs$) is $^{135}_{55}Cs$, with a half-life of $2.3x10^6$ years, and which forms $^{135}_{56}Ba$ by β emission. Radioactive strontium-90 decays by a beta-only process to $^{90}_{39}Y$ with a halflife of 29 years. This in turn decays to $^{90}_{40}Zr$ by a beta emission and isomeric transition with a half life of 2.67 days for the beta process and 49.7 min for the isomeric transition.

In addition to withstanding the elevated temperatures generated mainly by the decay of the $^{137}_{55}Cs$, $^{134}_{55}Cs$ and $^{90}_{40}Sr$ isotopes, a waste form matrix for immobilizing Cs and Sr must ensure long-term durability and resistance to β radiation. It must also take into account that Cs is volatile at elevated temperatures and is highly mobile in the environment. The use of a titanate ceramic as a waste form to immobilize the Cs/Sr was therefore investigated.

Generically, synroc is an advanced crystalline ceramic comprised of geochemically stable natural titanate minerals, some of which have immobilized uranium and thorium in the natural environment for many millions of years[2]. However synroc can take various forms depending on its specific use and can be tailored to immobilize particular components in the high level waste (HLW) by incorporating them into the crystal structure of the mineral analog phases. The principal advantage of the synroc-C ceramic, targeted to PUREX HLW, is that the waste ions are incorporated % in durable titanate mineral phases(HLW loading can be varied between 0 and 35 wt), which are considerably more insoluble in water (at least two orders of magnitude) than the silicates and phosphates in supercalcine ceramics[3], as well as borosilicate glass[2]. The main titanate minerals in synroc-C are hollandite ($BaAl_2Ti_6O_{16}$), zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$). Zirconolite and perovskite are

the major immobilization hosts for long-lived actinides such as plutonium (Pu) and the rare earths, whereas perovskite mainly immobilizes Sr. Hollandite principally immobilizes Cs, along with rubidium (Rb) and barium (Ba). The hollandite group of minerals has the general formula $A_xB_yC_{8-y}O_{16}$. In the crystal structure of synroc-type hollandite the B and C cations are surrounded by octahedral configurations of oxygen. Each of these $(B,C)O_6$ octahedra share two edges to form paired chains running parallel to the c- axis. These chains are corner linked to neighboring paired chains to form a three-dimensional framework with tunnels running parallel to the c-axis. The large A cations are located in these tunnels. In synroc-type hollandite, the A position is occupied by Cs, Rb and Ba, the B position by Al and Ti^{3+}, and the C position by Ti^{4+} (ref. 2).

Cs host forms must be stable under (β,γ)-irradiation, chemically durable and must accommodate the changes in chemistry resulting from the Cs decay process to Ba^3 and Sr decay to Zr The use of Ti is important because, as Cs^+ and Sr undergo beta decay, a charge imbalance results. In order to compensate for this, Ti^{4+} cations in the lattice can undergo autoreduction to Ti^{3+}, conserving the charge balance. An additional concern for Cs/Sr waste form is the thermal heat generated from decay. The temperature of hollandite ceramics containing 5 wt% of Cs_2O and a corresponding amount of SrO could reach 300°C at the beginning of the waste storage, depending on the geometry of the ceramic. The extent to which the radioactive decay of Cs and Sr will produce permanent damage, notably structural changes, is strongly dependent on dose rate and on the availability of thermal energy for self-healing recombination mechanisms. It is difficult to predict the radiation-induced behavior of Cs immobilization hollandite because of the kinetic factors and the simultaneous irradiation and annealing but the suitable choice of geometry, i.e. the use of relatively small, well spaced waste forms, can minimize the temperature buildup[4].

Important factors in determining the applicability of using synroc for immobilization of Cs and Sr include the potential waste loading (to reduce storage space requirements), the chemical durability (to reduce leach resistance as compared to borosilicate glass) and the waste form flexibility (to allow for feed/process variations). The waste form design must mitigate volatility risk posed by these wastes, hence integration with best process technology is essential. Much research along these lines has been completed in the past 20 years on the development of synroc for various types of Cs and Sr waste streams.

Hart et al.[5] designed a hollandite-rich waste form composition consolidated by hot pressing at 1200 °C at 200 MPa. The waste form consisted of 70 wt% hollandite $(Ba_{0.8}Cs_{0.4}(Ti_{1.5}Al_{0.5})Ti_6O_{16})$ + 20 wt% perovskite $(Ca_{0.x}Sr_{0.t})TiO_3)$ + 10 wt% rutile, with 5 wt% Cs

nominally substituted in the hollandite and 2.5 wt% of Sr substituted in the perovskite. The resulting product had Cs and Ba leach values about double those of synroc-C^2 and this discrepancy was due to the very small quantities (<<1%) of the water-soluble $CsAlTiO_4$ phase in the sample. Both MCC-1 and PCT tests were completed at 90°C for 184 and 84 days respectively. Hart et al.[5] also demonstrated that up to 10 wt% Cs could be added to synroc-B, the standard synroc-C precursor[2], and that this could be hot-pressed to form a durable product.

Work on waste forms containing single phase or near single phase hollandite has been carried out by several workers[6-8] Carter at al.[6] reported on the fabrication, characterization and leach testing of Ba hollandite samples containing 0.5 formula units of extra TiO_2 as rutile and produced by the alkoxide route. The samples were hot uniaxially pressed in 40 mm diameter graphite dies for 10 hours at 21 MPa at temperatures between 1200°C and 1250°C. The normalized Ba and Cs release rates of these samples at 90°C in deionized water were <0.001 g/m^2/day after 56 days.

More recently Bart et al.[7, 8] developed a single phase Fe- substituted hollandite containing 5wt % Cs_2O. The composition was reported to be $BaCs_{0.28}(Fe_{0.82}Al_{1.46})Ti_{5.72}O_{16}$. The chemical durability was on a par with that of synroc-C^{11} for Cs.

Carter et al.[9] studied the aqueous durability of Rb-doped Synroc and hollandite. Rb hollandite and Synroc containing a modified Purex-type high level nuclear waste were produced by alkoxide/nitrate route. The samples were hot-pressed at 21 MPa, with and without 2 wt% Ti metal added, for 2-10 hours at temperatures between 1200-1250°C in a graphite die. The samples were leached at 90°C and showed the Ba, Cs and Rb leach rates to be broadly similar to those of reference grade synroc-C^2.

Carter el al[10, 11] reported that hollandite-rich (60-80 wt%) ceramic waste forms incorporating ~ 7.5 wt% Cs, with Cr-, Ni-, Zn-, Mn-, Fe- or Co- substituted for the Al in synroc-type hollandite, could be melted in air and result in a product with excellent aqueous durability. The normalized PCT-B Cs leachate concentrations for the melted samples are two orders of magnitude better than the Na concentration for reference EA glass.

The ^{99}Tc from the process will also require immobilization. ^{99}Tc has a half-life of 2.1 x 10^5 years, is very mobile in natural ecosystems, and has a high biological uptake. For these reasons ^{99}Tc figures heavily in long-term repository performance assessments, despite the fact that it is a weak beta-emitter with a relatively low specific activity, compared to many other isotopes.

Under oxidizing conditions Tc is heptavalent and is extremely mobile, forming the pertechnetate TcO_4^- ion. The higher Tc oxides (Tc_2O_7 and TcO_3) are also relatively volatile, so this generally limits the processing conditions to neutral or reducing atmospheres. Under reducing conditions Tc is metallic. In this state it can be

encapsulated as sub-micron metal alloy particles inside an inert matrix. For example, high level waste streams which contain Tc can readily be incorporated in synroc-C (see above), and consolidated via hot-pressing at ~ 1200°C with a Ti metal buffer. In this waste the Tc is diluted into metallic alloy particles with Pd, Ru, Rh, Ni and Fe[12], and these in turn are encapsulated by the ceramic phases to give a material with low leach rates. For example, in MCC-1 type tests on the above material in oxic conditions (open laboratory) at 90°C the Tc leach rates decreased from ~ 10^{-3} g.m^{-2}.d^{-1} after ~ 25 days leaching to ~ 10^{-5} g.m^{-2}.d^{-1} after ~ 100 days[12]. Under anoxic conditions in a glove box (P_{O2} < 20 ppm) the leach rates were 1000 and 100 times lower, respectively.

For wastes rich in Tc, alternative solutions need to be examined to achieve high waste loadings, the two approaches being encapsulation of the metallic Tc in a durable ceramic matrix or substitution of Tc^{4+} for a lattice ion in a ceramic wasteform. The Tc^{4+} ion has an ionic radius of 0.0645 nm[13] and can partially substitute for Ti^{4+} (ionic radius = 0.0605[13] nm) in titanate ceramics. In previous work attempts have been made to substitute Tc^{4+} for Ti^{4+} in synroc phases via hot-pressing in graphite dies and hot-isostatic pressing in stainless steel bellows/cans with Ti, Fe and Ni buffers[12 14-16]. A perovskite sample of $CaTc_{0.5}Ti_{0.5}O_3$ stoichiometry was made via hot-pressing at 900°C in graphite followed by sintering at 1500°C in Ar. In this sample the volatile losses were ~ 20 % of the Tc[12, 16]. The phases formed on hot-pressing were perovskite $CaTc_{0.1}Ti_{0.9}O_3$, CaO, plus Tc-metal. Upon sintering at 1500°C the material formed single-phase perovskite with the composition being measured as $CaTc_{0.42}Ti_{0.58}O_3$.

Perovskite ($CaTiO_3$) and spinel (Mg_2TiO_4) were suggested as matrices at Pennsylvania State University in the 1980s[17, 18], work which followed on from earlier crystallographic research on Tc-oxides[19]. Apatite has also been proposed as a waste form for Tc[20]. Some workers have looked at the incorporation of Tc in stainless steel[21, 22]. Keiser, et al. looked at immobilizing Tc in stainless steel alloys, similar to synroc-C work above[15, 16]. They were able to incorporate 2 wt% technetium into a stainless steel - 15 wt% zirconium alloy[21]. No Tc-rich phases were detected, with the Tc being distributed amongst the stainless steel phases.

The selection and integration of appropriate waste form processing technology is an essential component of developing waste form solutions for these separated waste streams. Hot-isostatic pressing (HIPing) offers significant advantages for these streams. Firstly there are zero off-gas emissions during high-temperature consolidation, which mitigates volatility concerns from Cs and Tc. Secondly the process places minimal constraints on the waste form chemistry which in turn permits significantly higher waste loadings. In addition, the HIP process readily produces a dense monolithic waste form, which both minimizes disposal volume and reduces surface area available for aqueous attack once emplaced in a repository.

This paper illustrates the benefits HIPed tailored ceramic waste forms, provide for the immobilisation of separated Cs, Sr and Tc.

II. EXPERIMENTAL

A hollandite-rich ceramic waste form was designed to immobilize Sr/Cs waste with a loading of 12 wt%. The sample consisted of 85 wt% of hollandite and 15 wt% rutile. Table I lists the composition on an oxide basis.

Table II lists the waste composition used in the hollandite-rich ceramic waste form. The organic materials were not added, as they would all be removed during the calcination step (see below). The sample was produced from nitrates (Ba, Sr, Cs and Rb) and alkoxides of Al and Ti. After drying, the powder was calcined in air at 750°C for 1 hour. The powder was ball milled prior to HIPing. Two wt% of Ti metal to reduce some of the Ti^{4+} to Ti^{3+}, was added to the powder before HIPing. Ti^{3+} assists the hollandite to accommodate the Cs and Rb at the required levels. HIPing was carried out at 1275°C/30MPa/1h.

To immobilise the Tc, a sample was designed to contain 80wt% rutile, 5wt% hollandite, 5wt% perovskite, 5wt% zirconolite and 5wt% NiO and contained up to 40wt% TcO_2 Table I lists the composition on an oxide basis. The sample was produced from nitrates (Ba, Ca, Ni and Al), NH_4TcO_4 and alkoxides of Zr and Ti. The precursor materials were mixed with water and then dried at ~90°C. After drying, the powder was calcined in argon at 700°C for 1 hour. The powder was ball milled prior to HIPing. HIPing was carried out at 1150°C/30MPa/1h.

A JEOL JSM6400 scanning electron microscope (SEM) equipped with a Noran Voyager energy-dispersive spectroscopy system (EDS) was operated at 15 keV for microstructural work. The X-ray diffraction (XRD)was carried out using a Philips PW 1050 instrument using Cu $K\alpha$ radiation. Leach testing was carried out using both the Product Consistency Test (PCT-B)[23] and a modified MCC-1[24] leach test. The PCT-B protocol involved crushing the samples and sieving them to obtain particles 75-150μm in diameter (100-200 mesh). The particles were washed in cyclohexane to remove the fines (non-polar cyclohexane was used, instead of water, to prevent pre-leaching of Cs that would otherwise influence the leach results) and 1g samples were leached in 10ml of water at 90°C for 1 and 7 days. Specimens for the MCC-1 test were polished (~0.25μm finish) disks (8x8x2mm) and were leached using a modified version of the ASTM C – 1998 standard[24], where the leachates were completely replaced with fresh water at the end of each time interval (1, 7, and 28 days) to avoid steady-state conditions being reached. An aliquot of each leachate was analysed for elemental releases.

TABLE I. Sample composition on an oxide basis.

Oxide	Hollandite-rich (Cs, Sr, Ba and Rb)	Rutile-rich (Tc)
	Wt %	Wt %
TiO_2	72.18	49.77
Al_2O_3	8.75	0.62
SrO	1.84	-
Rb_2O	0.85	-
Cs_2O	4.95	-
BaO	11.4	0.95
NiO	-	5.0
ZrO_2	-	1.47
CaO	-	2.34
TcO_2	-	39.85

TABLE II. Waste composition (Cs/Sr).

Component	
Guanidine carbonate (g/L)	100
DTPA (g/L)	20
Cesium (g/L)	0.30
Strontium (g/L	0.10
Barium (g/L)	0.28
Rubidium (g/L)	0.05

III. RESULTS AND DISCUSSION

III.A. Hollandite-rich Waste Form

Figure 1 shows the XRD pattern of the hollandite-rich ceramic containing 12 wt% waste after HIPing. Peaks in the XRD pattern correspond to hollandite and rutile, in agreement with expectations from the overall design of the starting composition.

The SEM analysis showed that Cs, Ba, Rb and Sr all entered the hollandite phase as predicted in the design. The backscattered SEM image (Figure 2) of a polished surface showed the sample to consist of hollandite, rutile and a small amount of Al_2O_3. The presence of alumina indicates that the redox environment in the HIP can was slightly more reducing than anticipated, insofar as some of the Al targeted to the B site of the hollandite was displaced by Ti^{3+}. This has no detrimental effect on the hollandite rich ceramic waste form.

The 1 and 7 –day PCT leach results showed (Table III) the normalized extractions of all waste elements to be below 0.7g/L, corresponding to 0.08 $g/m^2/d$ for 1 day, assuming a density of ~4.2 g/cm^3 for the hollandite-rich monolith. This result is in line with the Cs leach rate for hollandite-rich ceramics. Note that the normalized PCT-B leachate concentration for the reference EA glass for Na is ~20 times higher at 13 g/L. The extractions of all elements in the hollandite-rich ceramic are well below this limit.
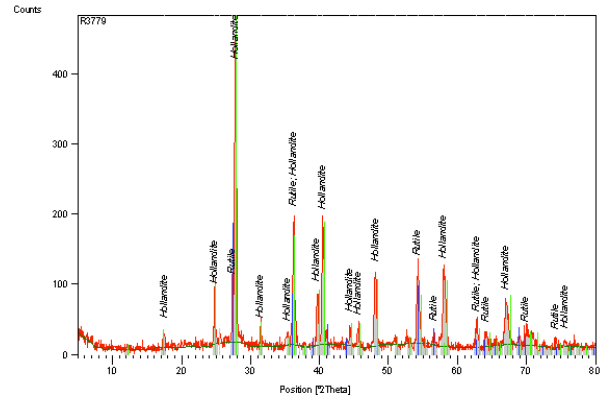

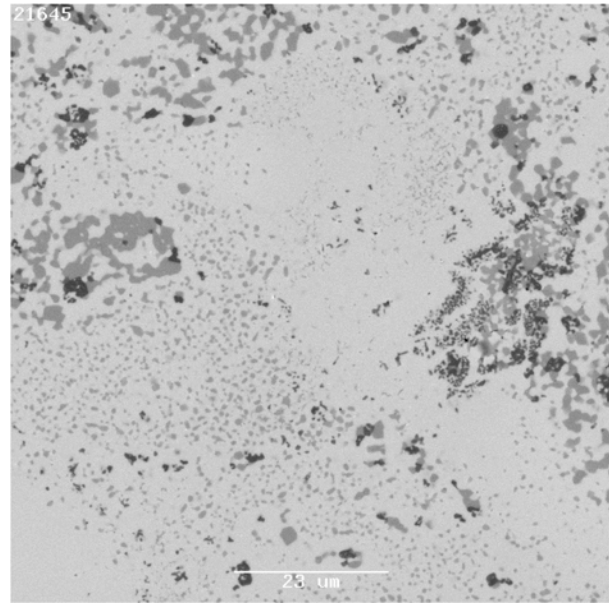Fig. 1. XRD trace of hollandite-rich ceramic HIPed at 1275°C/30MPa/1h. Cu Kα radiation.

Fig. 2. Backscattered electron image of hollandite-rich ceramic. Hollandite matrix (light gray), TiO_2 (mid gray) and Al_2O_3 (black).

The MCC-1 leach results are presented in Table VI. It is noted that the 7-day PCT result agrees quite well with the MCC-1 datum even though the SA/V ratios in the two forms of leach test differ by a factor of ~100. For ultimate disposal of this waste form, it may be thought that storage for ~ 300 years might allow the form to qualify as low-level waste, but the ongoing activity from the decay of [135]Cs would need to be taken into account: Additional shielding of the waste form could be necessary to reduce the contact dose to a value consistent with the specifications for low-level waste. Such considerations are also influenced by the size of the waste form packages.

TABLE III. PCT-B results for hollandite-rich waste form.

Element	Normalized Concentration 1 day (g/L)	Normalized Concentration 7 day (g/L)
Al	0.004	0.05
Ba	0.05	0.07
Cs	0.6	0.68
Rb	0.02	0.28
Sr	0.11	0.2
Ti	0.000002	0.00002

Errors on all elements were < 7%

TABLE IV. MCC-1 results for hollandite-rich waste form.

Element	Normalized Release Rate* 0-1 days	Normalized Release Rate 1-7 days	Normalized Release Rate 7-28 days
Al	0.021(1)	0.004(1)	0.001(1)
Ba	0.058(3)	0.0075(1)	0.0016(3)
Cs	0.28(4)	0.016(1)	0.0032(6)
Rb	0.11(1)	0.011(1)	0.0023(4)
Sr	0.093(6)	0.010(1)	0.004(3)
Ti	0.00023(1)	0.000040(1)	0.00001(1)

* $g/m^2/day$

III.B. Rutile-rich Tc Waste Form

The XRD pattern of the rutile-rich ceramic containing 40 wt% TcO_2 after HIPing showed the peaks to correspond to rutile, in agreement with expectations from the overall design of the starting composition and the other phases present were not present at a level to show in the XRD pattern.

The SEM investigation of the rutile-rich ceramic containing 40 wt% TcO_2 showed the sample to be very porous (see Fig. 3). The secondary electron image Fig. 4 showed the sample to contain ~ 80% $(Ti,Tc)O_2$. EDS analysis of the $(Tc,Ti)O_2$ revealed a composition of $Tc_{0.38}Ti_{0.62}TiO_2$ (50.6 wt% TcO_2) which would correspond to the ~40 wt% TcO_2 waste loading. The other phases identified were a Ba-Tc oxide and Ni-Al spinel. Due to the very porous (~40%) nature of the sample there were difficulties in identifying any other phases.

Although the sample was extremely porous the sample was prepared for PCT-B testing and leached. The 7-day PCT-B leach results showed the normalized technetium release rate was ~0.15g/L (Table V). These extraction results are very low, comparable to those for the hollandite waste form, and would be even lower if better densification was employed via either the use of, slightly higher temperatures, or pressures, and/or the use of sintering aids.
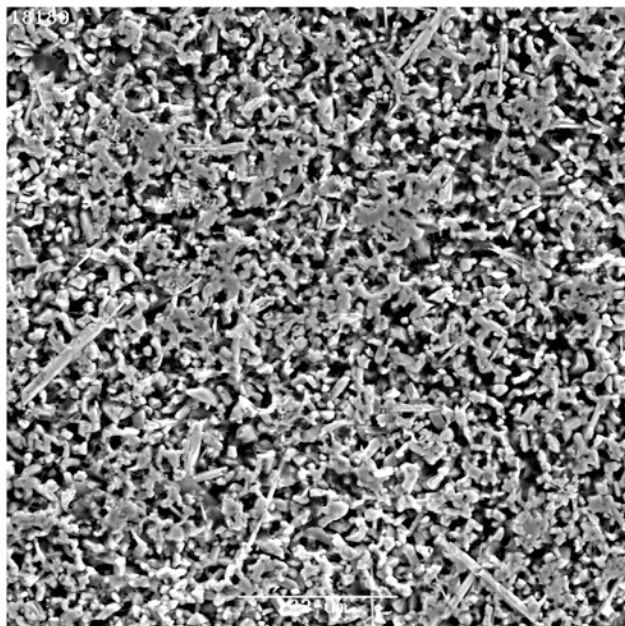

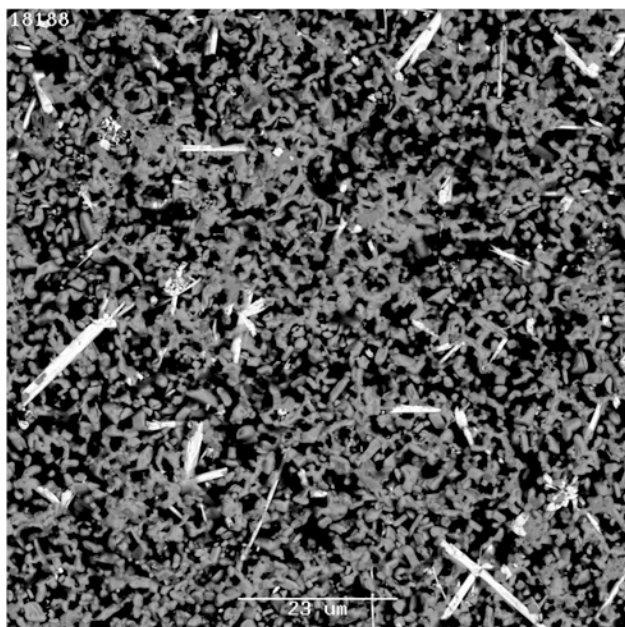Fig. 3. Secondary electron image of rutile-rich waste form showing very porous structure

Fig. 4. Backscattered electron image of rutile-rich waste form. $(Ti,Tc)O_2$ matrix (mid gray), Ba-Tc oxide (white), pores (black)

TABLE V. PCT-B results for rutile -rich waste form.

Element	Normalized Concentration 7 day (g/L)
Ti	0.00015
Ni	0.0019
Ca	0.50
Zr	<0.0001
Ba	0.054
Al	0.17
Tc	0.15

Errors on all elements were < 10%

IV. CONCLUSIONS

These further experiments confirm that immobilization of the separated cesium and strontium and Tc waste streams from advanced fuel reprocessing in a flexible hollandite-rich ceramic for the Cs/Sr and rutile-rich for the Tc is technically a very feasible process. A dense monolith results in the case of the hollandite–rich waste form with excellent aqueous durability. The use of hot isostatic press technology also avoided any potential cesium loss during the hot consolidation step. Although the rutile-rich waste form was porous, it resulted in a waste form with excellent aqueous durability and there is a high potential for improving the consolidation of this waste form over that achieved in the current experiments. In addition, the ability to tailor the waste form design chemistry in combination with the flexible hot isostatic press process enables a common synroc processing line to immobilize a range of different waste streams from the proposed advanced recycling initiatives.

ACKNOWLEDGMENTS

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