Evaluation of the Use of Synroc to Solidify the Cesium and Strontium Separations Product from Advanced Aqueous Reprocessing of Spent Nuclear Fuel

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ACRONYMS

AFCI   Advanced Fuel Cycle Initiative

ANSTO   Australian Nuclear Science and Technology Organisation

CCD   chlorinated cobalt dicarbollide

CCIM   Cold Crucible Induction Melter

CEA   Commissariat à l'Energie Atomique

DTPA   diethylenetriaminepentaacetic acid

DOE   Department of Energy

FPEX   Fission Product Extraction

FY   Fiscal Year

HIC   High Integrity Container

HIP   Hot Isostatic Press

HLW   High Level Waste

INL   Idaho National Laboratory

LANL   Los Alamos National Laboratory

LLW   low level waste

MAC   methylamine carbonate

MCC   Materials Characterization Center

NZP   sodium zirconium phosphate

PCT   Performance Consistency Test

PEG   polyethylene glycol

PNNL   Pacific Northwest National Laboratory

UREX+   Uranium Extraction +

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EXECUTIVE SUMMARY

To reduce the short-term decay heat load in the potential high–level radioactive liquid waste (HLW) to be generated by the proposed future nuclear fuel aqueous-based reprocessing schemes, research under the Department of Energy's (DOE's) Advanced Fuel Cycle Initiative (AFCI) is being conducted on the development of solvent extraction processes that specifically separate the predominant fission products of cesium (Cs) and strontium (Sr). To ensure reliable, safe, cost effective, and stakeholder acceptable waste forms for the nuclear fuel cycle of the future, this Cs/Sr strip solution will require immobilization for managed storage or disposal. To that end, the Idaho National Laboratory (INL) was tasked to complete a literature evaluation of the Synroc process, including determining the potential for its application in immobilizing this Cs/Sr strip product.

Synroc is an advanced crystalline ceramic comprised of geochemically stable natural titanate minerals, which have immobilized uranium and thorium in the natural environment. These natural analogs can incorporate into their crystal structures nearly all of the elements present in HLW, thus immobilizing them. Synroc can take various forms depending on its specific use and can be tailored to immobilize particular components in the HLW. 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 is principally for Sr. Hollandite principally immobilizes Cs, along with potassium (K), rubidium (Rb) and barium (Ba).

A significant amount of research in several countries, with Australia being the most predominant, has been completed and documented on the use of Synroc for the immobilization of Cs and Sr. This literature evaluation determined that Synroc is expected to provide a reliable and durable waste form for the Cs/Sr strip product. In general, the Cs sequestering hollandite mineral phase is chemically durable with a leach resistance two orders of magnitude higher than for the currently established HLW form of borosilicate glass. The use of tailored, high-performance, alternative waste forms that include ceramics and glass-ceramics, coupled with alternative near-mature process technologies, such as hot-isostatic pressing, sintering and cold-crucible induction melting, offer significant performance improvements and efficiency savings for wastes difficult to incorporate into glass. Consequently, the use of Synroc as an alternative for the immobilization of the Cs/Sr strip product must be further evaluated for future applications.

1. INTRODUCTION

The Advanced Fuel Cycle Initiative (AFCI) is conducting research on aqueous separations processes for the nuclear fuel cycle. This research includes development of solvent extraction processes for the separation of cesium (Cs) and strontium (Sr) from spent nuclear fuel to reduce the short-term decay heat load of the high-level waste (HLW). The Cs/Sr strip solution from candidate separation processes will require treatment and immobilization for managed storage and/or final disposal.

The thermal load on the repository is greatly reduced if the emplacement of Cs/Sr waste is delayed until these relatively short-lived (half-lives of ~30 yrs) materials decay. Separation of Cs and Sr along with plutonium and americium would allow a substantial increase in the repository loading, up to a factor of 40-50. The storage of Cs and Sr for the life cycle of the waste processing plant can be accomplished using existing casks and requiring a relatively small area (one to two football fields in size for the life of the plant). Safe interim storage will require a waste form that is stable, does not produce dangerous radiolysis products (e.g., buildup of potentially explosive gases like hydrogen), has a relatively high product density (to minimize storage volume), and has properties that enhance heat management (e.g., high thermal conductivity).

In fiscal year 2004, an Engineered Product Activity Team was formed from a subset of the members of the AFCI Separations Working Group.[1] This team identified the preferred storage forms and vehicles for the Cs/Sr waste stream arising from the treatment of spent fuel. For the Cs/Sr waste stream, this team reported that encapsulation in borosilicate glass, similar to that used for high level waste, may be considered a baseline against which other storage forms are judged. The four most promising alternative Cs/Sr storage forms identified by this team included:

- Ion-exchange of the Cs and Sr in zeolites, which are then immobilized in a cement matrix (Portland, apatite, phosphate-bonded, or refractory)

- Immobilization using Sodium Zirconium Phosphate (NZP) that is possibly diluted with a cement matrix

- Use of a steam reformer to produce a stabilized Cs/Sr mineralized granular product waste form (i.e., the Washington Group International storage form)

- Immobilization of Cs and Sr in an optimized Synroc crystalline assemblage

Research initiated by the Idaho National Laboratory (INL) in FY-05 is focusing on the development and testing of the steam reforming solidification process and ion exchange testing with the emphasis being on steam reforming. The FY-05 steam reforming testing successfully converted Cs/Sr strip products to a solid form without volatilizing the Cs.[2] Results also indicate that with optimization of the steam reforming operating parameters 100% mineralization is possible. The limited ion exchange batch contact testing results indicated that the crystalline silicotitanate inorganic ion exchange sorbent has high selectivity for Cs removal from dilute nitric acid and slightly alkaline strip solutions and

minimal selectivity for Sr removal from dilute nitric acid but good selectivity for Sr removal from a slightly alkaline strip solution.

In FY-06, INL work on the ion exchange was suspended but optimization of the steam reforming operating parameters is continuing.[3] The INL was also tasked to complete a literature evaluation of the Synroc process including determining the potential for its application to immobilization of the Cs/Sr strip product. This report summarizes the Synroc evaluation.

2. FEED PARAMETERS

The baseline process for separation of Cs and Sr from dissolved spent light water reactor fuel, as part of the Uranium Extraction Plus (UREX+) process, is a solvent extraction process utilizing chlorinated cobalt dicarbollide and polyethylene glycol (CCD/PEG) in a phenyltrifluormethyl sulfone (FS-13) diluent. Cs and Sr are stripped from the CCD/PEG organic stream with an aqueous solution of guanidine carbonate and diethylenetriamine-pentaacetic acid (DTPA) yielding a metal carbonate product solution. Alternative extraction processing methods are also under investigation. The first alternative is a variation of the baseline CCD/PEG process but uses a methylamine carbonate (MAC)/DTPA solution to strip the organic extractant. This yields a product containing the metals and DTPA (with small amounts of MAC) and allows the MAC to be recovered and recycled. A second alternative is the Fission Product Extraction (FPEX) process which extracts the Cs/Sr with a calixarene-crown ether extractant consisting of 4,4′,(5′)-Di-(t-butyldicyclo-hexano)-18-crown-6 (DtBuCH18C6), Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6), and 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB modifier) in a branched aliphatic kerosene (Isopar® L). With this process, the organic extractant is stripped with dilute nitric acid.

The estimated compositions of the Cs/Sr strip solutions/immobilization process feeds are summarized in Table 1.

Table 1. Estimated composition of Cs/Sr strip product feed streams.

Component	CCD/PEG Feed 1	CCD/PEG Feed 2	FPEX Feed 3
Guanidine carbonate (g/L)	100	---	---
DTPA (g/L)	20	60	---
Methylamine carbonate (M)	---	0.5	---
Nitric acid (M)	---	---	0.04
Cesium (g/L)	0.30	1.2	0.60
Strontium (g/L)	0.10	0.4	0.20
Barium (g/L)	0.28	1.12	0.56
Rubidium (g/L)	0.05	0.20	0.10

3. SYNROC DESCRIPTION

Synroc is a type of "synthetic rock", invented in 1978 by the late Professor Ted Ringwood of the Australian National University. It is an advanced ceramic comprised of geochemically stable natural titanate minerals, which have immobilized uranium and thorium in the natural environment. These natural analogs can incorporate nearly all of the elements present in HLW into their crystal structures thereby immobilizing them. Synroc can take various forms depending on its specific use and can be tailored to immobilize particular components in the HLW. Synroc-C was intended mainly for the immobilization of liquid HLW arising from the reprocessing of light water reactor fuel.

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 hosts for long-lived actinides such as plutonium (Pu) and the rare earths, though perovskite is principally for Sr. Hollandite principally immobilizes Cs, along with potassium (K), rubidium (Rb) and barium (Ba).[4] 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 $(B,C)O_6$ octahedral 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+}.[5]

To achieve maximum cost savings and optimum performance the Synroc waste forms are tailored to suit the particular characteristics of nuclear waste to be immobilized rather than adopting a single one-size fits all approach. The Australian Nuclear Science and Technology Organisation (ANSTO) has demonstrated that significant reductions in waste volume for the partitioning/conditioning strategy can be achieved through immobilization of the heat-generating radionuclides, i.e., Cs-137, Sr-90, and Cm-244 together with long-lived Tc-99 in Synroc, while remaining waste is immobilized in glass. The combination of partitioned Cs and Sr with Cu-244 ensures that the effects of alpha-decay processes on the waste form durability are minimized through self-annealing of alpha-decay damage due to the radiogenic decay heat.[4]

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.[6] The use of Ti is important because, as Cs^+ undergoes β-decay forming Ba^{2+} a charge imbalance results. In order to compensate for this, a Ti^{4+} cation in the lattice undergoes reduction to Ti^{3+} conserving the charge balance. Cs^+ can be immobilized in hollandites that contain Al^{3+} and Mg^{2+}. In these systems, the Al^{3+} and Mg^{2+} are present to ensure charge balance is maintained during formation, preventing the premature formation of Ti^{3+}. Such components are also used to modify the tunnel size allowing larger atoms to be accommodated.[7]

The temperature of hollandite ceramics containing 5wt% of Cs_2O could reach 300°C at the beginning of the waste storage. The extent to which the radioactive cesium radiation 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 behavior of hollandite because of the kinetic factor and the simultaneous irradiation and annealing.[8]

The principal advantage of the Synroc C ceramic is that the waste ions were incorporated (HLW loading could be varied between 0 and 35 wt%) in durable titanate mineral phases, which are considerably more insoluble in water (two orders of magnitude) than the silicates and phosphates in the supercalcine ceramics. "Supercalcine" ceramics based on crystalline silicates, phosphates and molybdates were formed by sintering in air at ~ 1100ºC and had very high fission product loadings. Typical phases for supercalcine were pollucite $CsAlSi_2O_6$; powellite $CaMoO_4$, and rare earth apatites and phosphates.[9]

In 1981, there was a selection process in the US for candidate waste forms for the HLW produced form nuclear weapons based reprocessing and stored at the Savannah River Site. Synroc came second behind borosilicate glass in this assessment because, although the leach resistance of Synroc C hollandite is two orders of magnitude higher than for the current borosilicate glass, the engineering development was lacking. Therefore, the Australian Government financed the construction of a Synroc Demonstration Plant at ANSTO in the mid-1980s. This plant can produce inactive Synroc monoliths at the 50 kg scale with a throughput of 10 kg/h.[9]

4. SYNROC PROCESSES

The literature has indicated several routes for making Synroc or hollandite. Multiphase ceramics are suitable for wastes that do not contain a significant proportion of glass forming components. They can be formed with a wide range of process technologies including sintering, hot-isostatic pressing (HIP) in argon and cold-crucible induction melting (CCIM).

Sintering

Sintering consists of pressing a pellet generally somewhat larger than the desired size and sintering it in a furnace to an appropriate temperature, via a carefully controlled heating/cooling cycle, under the desired atmosphere. Sintering is widely used in the nuclear industry for the production of MOX fuel pellets. To sinter a binder and lubricant must be added to press uniform "green" pellets, and the feed powder must be ground fine (~ 10 microns) and mixed to increase reactivity. This increased reactivity will allow the pellets to be sintered without cracking or unpredictable dimensional changes and will avoid sticking between sintered pellets and furnace equipment provided appropriate setter plates are used.[10]

HIP

A HIP consists of a pressure vessel surrounding a resistance-heated furnace. In hot isostatic pressing a stainless steel can is filled with calcined radioactive waste feed and is then evacuated at temperatures up to ~500ºC and sealed. The can is placed into a furnace and the HIP vessel is closed and pressurized using argon gas. The pressure is applied isostatically via the dense high pressure argon, which is also an extremely efficient conductor of heat. This combined effect consolidates and immobilizes the waste into a dense isotropic monolithic block sealed within the can. HIPs are used in the nuclear industry and are installed in hot-cell facilities.[10]

There are several methods of making the HIP precursor. In one approach, the waste is added to a mechanical mixture of the binary metal oxides necessary for formation of Synroc and calcined in a reducing gas. This mixture is sealed in canisters and HIPed at ~10^8 Pa and 1200-1400ºC.[11] A variation on this is known as the standard sol-gel route in which an alkoxide based liquid precursor is hydrolyzed by mixing with an aqueous waste stream, dried, calcined under reducing conditions and hot-pressed in metal bellows at 1200ºC / 14-20 MPa after adding 2 wt% Ti metal as an oxygen getter.[12] The Synroc precursor can also be made via a chemical processing route involving Ti and Zr alkoxide hydrolysis in the presence of NaOH to form a sodium titanate/zirconate powder which acts as a cation exchanger for Al, Ba, and Ca waste nitrate solutions. This form is dried and then calcined under reducing conditions and hot pressed and sintered at 1100-1170°C, with the addition of 2 wt% Ti to lower the mobility of the volatiles and keep Mo metallic to avoid the formation of water soluble molybdates.[13]

Cesium is volatile and is highly mobile in the environment, and together cesium and strontium account for the majority of radiogenic heat generated in fission product wastes. The integration of waste form and process design enables the elimination of volatility concerns during consolidation by the use of hot-isostatic pressing technology. This is achievable, even at high temperatures, since the waste form is sealed inside a stainless steel can prior to HIPing. By overcoming volatility concerns during consolidation, the tailored waste forms also relieve pressure on the off-gas requirements resulting in further cost savings. The combination of high temperature and high pressure used with the HIP can cause safety concerns in radioactive waste environments, especially those dealing with plutonium. In contrast, encapsulation of the waste in glass uses high temperatures but atmospheric pressures.

Melting/CCIM

Synroc can be formed by melting oxides into a glass composite material. Glass ceramics (crystalline) are made by melting to form a viscous glass, which is then crystallized on cooling or in a separate crystallizing heat treatment operation. Controlled crystallization can be used to form desired phases rather than uncontrolled devitrification of a vitreous waste form. Uncontrolled crystallization can lead to potential stress and cracking or reduced durability. With controlled crystallization, there is a potential for higher waste loadings, and improved mechanical and chemical properties compared to the parent glass.

The latter can be achieved by controlled partitioning to incorporate highly active species into crystals while leaving a continuous glassy phase of similar composition and durability to that of the current waste immobilization glasses. To reduce the number of processing steps it is desirable to use controlled cooling from the melt to give the desired microstructure and phase evolution rather than a separate heat treatment. The crystallization sequence in such systems is a strong function of waste loading and cooling history, often with undesirable surface and bulk nucleation. Synroc glass ceramic is an example of a glass ceramic with Synroc crystalline phases in a vitreous matrix, which was developed for sodium rich wastes such as those from the Hanford site.[13]

One technology capable of achieving this melting scheme is the cold crucible melter, which consists of water-cooled metal fingers that surround the material to be melted. The crucible, surrounded by an induction coil, is essentially transparent to the electromagnetic field and direct heating of the material in the crucible is possible without an electrode inside the melter. Once melting is established, a frozen skull of the material being melted solidifies on the cold walls and forms a protective self-healing and corrosion-resistant barrier that protects the rest of the melter from melt corrosion. Cold crucible melters are better suited to large scale continuous rather than batch operation, as startup can be difficult. However they operate at higher temperatures than joule melters and produce less secondary waste. To initiate each melt batch, species susceptible to conductive material need to be added. These are typically refractory metals (such as Ti or Zr), which allows the surrounding material to be heated to a temperature where it can couple directly with the induction field. This coupling requirement can place a relatively narrow specification on the waste form chemistry as the overall composition of the melt needs to meet certain electrical properties and thermal conductivity requirements, as well as viscosity and melting rate characteristics, to allow the process to be sustainable without breaching its confining chilled skull and yet be poured safely.[10]

5. IMMOBILIZATION OF Cs AND Sr WITH SYNROC

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). Much research has been completed in the past 20 years on the development of Synroc for various types of Cs and Sr waste streams and a small portion of that work is related here.

Leach test definitions

Before discussing the results of some of the testing, an understanding of the various leach tests conducted may be helpful. In general, leach testing was conducted on the various Synroc-type products to compare the chemical durability with that of borosilicate glass. The main vitreous waste form leach tests include:

- MCC-1 uses deionized water in static conditions on a monolithic specimen with the sample surface to water volume usually $10m^{-1}$ and is usually conducted at

90°C. (MCC is the Materials Characterization Center of Pacific Northwest National Laboratory (PNNL).)

- MCC-2 uses deionized water in static conditions on a monolithic specimen at an elevated temperature in a closed system.
- MCC-3 (or Performance Consistency Test (PCT) - ASTM C1285-94) uses deionized water at 90ºC on a powder sample in a closed system with a surface area to water volume of ~1000m^{-1}.
- MCC-4 uses a single pass flow-through test with deionized water in a system that is open to the atmosphere
- MCC-5 uses a high flow Soxhlet in a system that is open to the atmosphere.

Results of literature search

Following are brief descriptions of the results of a literature survey that focused on the immobilization of Cs and Sr.

<u>Australia, 1996</u> [12]

In 1996, ANSTO reported on immobilization of Tc, Cs and Sr in Synroc. Cs-doped samples were made by the sol-gel route in which an alkoxide based liquid precursor plus nitrates and TcO_4^{-2} is hydrolyzed, dried, calcined under reducing conditions at 600-750ºC and hot pressed at 1200ºC/20 MPa in stainless steel. Leaching studies on the resulting samples were then completed.

For Cs/Sr incorporation in a Synroc-related mixture, ANSTO used a 70 wt% hollandite, 20 wt% perovskite and 10 wt% rutile material containing 5 wt% Cs nominally substituted in the hollandite and 2.5 wt% of Sr substituted in the perovskite. The formulation was based on a hollandite composition of $Ba_{0.8}Cs_{0.4}(Ti_{1.5}Al_{0.5})Ti_6O_{16}$, with the perovskite composition being given by $Ca_{0.79}Sr_{0.21}TiO_3$. The material had a composition of 2.3 wt% Al_2O_3, 10.8 wt% BaO, 6.1 wt% CaO; 5.1 wt% Cs_2O; 3 wt% SrO; 72.7 wt% TiO_2. The grain size was <1μm and the overall density was 4.2 g/cm^3. Both MCC-1 and PCT tests were completed at 90ºC for 184 and 84 days respectively. Cs leach rates were 0.15 g/m^2/day for the first 7 days and then fell to 0.01-0.03 g/m^2/day. Sr leach rates were <0.01-0.02 g/m^2/day.

Cs and Sr, in a molar ratio of 2:1, were also added to a Synroc-B form with an approximate composition of 5.4 wt% Al_2O_3, 5.6 wt% BaO, 11wt% CaO, 71.4 wt% TiO_2 and 6.6 wt% SrO_2. It was not experimentally clear whether Cs preferentially entered the hollandite or reacted to form Cs aluminates such as $CsAlO_2$ or $Cs_2Al_{22}O_{34}$ although there was no indication that the Cs was in phases other than hollandite.

At high Cs loadings, the presence of enough TiO_2 is important in allowing incorporation of Cs in hollandite. If enough is present, it is assumed that all Cs and Ba form hollandite according to $Ba_xCs_y(Al, Ti^{3+})_{2x+y}(Ti^{4+}_{8-2x-y})O_{16}$. The limiting case can be calculated as x=0.40 and y=0.81 corresponding to a Cs loading of 9 wt.%. The effect of small additions of Sr, in a 1:2 molar ratio relative to Cs, was found to affect the maximum Cs loading by <0.5 wt.%.

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Cs loading may be more limited by the temperature requirements at the storage facility or repository. For a Synroc bellows 0.35 m in diameter, and containing 100 kg of Synroc, the heat loading from the Cs at 10 wt.% Cs_2O would correspond to a centerline temperature of 300-400°C, disqualifying it from any repository where the temperature was required to be < 100°C.

The conclusion from this study was that Cs and Sr can be suitably immobilized in hollandite-rich Synroc variants, when precautions are taken to suppress formation of $CsAlTiO_4$.

Australia / RUSSIA, 1997 [14,15]
In 1997, ANSTO worked with the SIA "Radon" and the Institute of Geology of Ore Deposits in Moscow, Russia on a comparative study of Synroc ceramics. Since 1990 development and testing of the cold crucible technology for Synroc production have been carried out at SIA "Radon". Three Synroc-C samples containing simulated high level waste were studied. One was produced by the conventional hot-pressing method at ANSTO (sol-gel precursors, calcination, hot-pressing at 1150-1200°C and 14-21 MPa) and the others were obtained using cold crucible technology at Radon, Russia using an air atmosphere. One of the melted samples was prepared using the ANSTO sol-gel precursor and the second one was obtained from an oxide-nitrate mixture.

The specimens had closely similar mineral compositions with major hollandite, perovskite, zirconolite, and rutile phases. Molybdenum in the melted Synrocs exists in the form of Ba-Ca and Ca-Sr molybdates rather than metal alloy as in hot-pressed Synrocs. Cs in the melted samples enters molybdates, while in the hot-pressed Synroc this element enters hollandite. Thus fixation of the Cs in the melted Synrocs was substantially lower compared to the hot-pressed Synroc due to the formation of molybdates under oxidizing melting process conditions. In order to avoid molybdates formation, the melting process must be performed under reducing conditions. Leaching of other components (Ti, Zr) was comparable with that in hot-pressed Synroc.

Samples prepared from the various routes described above were used for additional leaching tests. The leaching experiments were conducted on powdered samples at room temperature, 100°C, and 200°C by repeated static tests with regular replacement of deionized water leachant.

Leaching behavior of the CCIM generated samples was mainly governed by the presence of alkali molybdates. The results indicated that 40-50% of the Cs is present in the molybdates. The Cs concentration in the leachate for the CCIM prepared samples was 40-160 ppm and in the hot-pressed sample was 0.5 ppm when leached at room temperature. At elevated temperatures Cs exhibited the highest leach rate for the CCIM samples (~0.1-5 $g/m^2/day$). These rates were approximately the same as those obtained from borosilicate glass (~1-10$g/m^2/day$) and about two orders of magnitude higher than the leach rates for hot-pressed Synroc samples (~0.005-0.1$g/m^2/day$).

In summary, Cs and Mo leachability of samples prepared by inductive melting in the cold crucible indicate that the cesium leachability is close to that of borosilicate glass. The yield is determined by the presence of highly soluble alkali molybdates, which contain about half of total Cs. In order to avoid the formation of alkali molybdates the Synroc melting should be carried out at strongly reducing conditions where the alkali molybdates are thermodynamically unstable or alkali elements must be separated from HLW according to HLW partitioning concept.

Australia, 2001 [16]
In 2001, ANSTO 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. This method involved the mixing of the correct molar quantities of Al sec-butoixde, tetrabutyl zirconate and isopropyl titanate in ethanol with nitrates dissolved in water, while continuously stirring. Mixtures were then heated and stirred to drive off the alcohol and water. The dry product was calcined in air for two hours at 750°C and then ball-milled. 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 Synroc samples were leached at 90°C and showed the Ba (~0.01 g/m^2/day initially, falling to ~0.08 g/m^2/day at 128 days) and Cs (~0.8 g/m^2/day initially, falling to ~0.007 g/m^2/day after 128 days) leach rates broadly similar to reference grade Synroc-C. Rb leaching from all samples was relatively low and broadly similar to that of Cs and Ba in hollandite. However, the Rb normalized leach rates did not continue a downward trend with increasing time as do the Ba leach results. Earlier work on a hollandite rich Synroc showed that when very low quantities (<1%) of the water-soluble $CsAlTiO_4$ phase were present in the Synroc sample, the Cs normalized leach rates did not follow a downward trend. As there is not an Rb analog of the $CaAlTiO_4$ phase and only a very small amount of Rb was found in some of the perovskite, the exact reason for the Rb leach rates not following those of the Ba-hollandite, or behaving like Cs in hollandite, is not known.

Australia, 2002 [5]
In 2002, ANSTO reported on hollandite studies that included fabrication, characterization and leach testing. Ba hollandite samples containing 0.5 formula units of extra TiO_2 in the rutile form were produced by the alkoxide route. This method involved mixing the correct molar quantities of aluminum sec-butoxide and titanium (IV) isopropoxide in ethanol with Ba nitrate (and Cs nitrate where necessary) dissolved in water, under continuous stirring. The mixture was then heated to approximately 110°C to drive off the alcohol and water and stirred. The dry product was then calcined in air for two hours at 750°C and then wet milled. 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, and decreased with increasing leaching times. Varying the pH of between 2.5 and 12.9 affected only the Ba dissolution rates of hollandite by half an order of magnitude. The dissolution rates of all species decreased with increasing

leach time due to the formation of partly impervious surface coatings of Al and Ti rich species.

Australia, 2004 [17]
In 2004, ANSTO reported on studies conducted with hollandite-rich ceramic melts for immobilization of Cs. The titanate Synroc phase hollandite ($Ba_xCs_yM^{3+}{}_{2x-y}Ti_{8-2x-y}O_{16}$ where trivalent M = Al in oxidizing conditions and Al and Ti in reducing conditions) is well known for its ability to incorporate Cs when produced by hot pressing with excellent leach resistance. But attempts to melt (hollandite-bearing) Synroc C under air atmospheres resulted in all Synroc titanate phases, including hollandite, being formed, but leachable Cs molybdate phases due to the presence of Mo^{6+} were also observed. They found that the Cs did not enter the hollandite phase in melted Synroc-C and in order to incorporate the Cs in the hollandite the Synroc-C metals had to be processed under reducing atmospheres.

ANSTO's criteria for a suitable waste form included (a) could be melted in air; (b) no readily leachable phases were apparently present; (c) leach rates were low (<1 g/l, PCT-B) and (d) low Cs volatility. Samples for melting were produced by mixing the correct molar quantities of aluminum sec-butoxide (where necessary), titanium (IV) isopropoxide and zirconium tertbutoxide in ethanol with nitrates of other components dissolved in water, while continuously stirring. The mixture was then heated to ~110ºC to drive off the alcohol and water, while continuously stirring. The dry product was then calcined in air for two hours at 750ºC. The samples were placed in Pt crucibles and melted in air at 1450-1550ºC. Samples for sintering were prepared up to the calcination stage then wet ball milled in cyclohexane and sintered in air at 1300ºC for 20 hours. All sintered samples were made with an additional 0.5 moles of TiO_2.

PCT leach testing was carried out on a selection of samples, which were free of Cs_2O and Cs titanate phases. The normalized Cs leachate concentrations for the M=Cr, Ni and Co samples were 0.15 g/l, 0.15 g/l and 0.08 g/l respectively. These results are similar to those of other titanate hollandite-rich melts. The PCT leachate concentrations for Na, Li and K in EA glass are around 14 g/l and as Cs, Na, Li, and K are all alkalis they should have comparable normalized leach rates in such tests. The alkali normalized leachate concentrations in glass have values, which are two orders of magnitude above these studies lowest Cs concentrations. The normalized Cs leachate concentrations are comparable to those from reference Synroc-C.

In summary, leach resistant titanate hollandite-rich ceramics incorporating ~ 7.5 wt% Cs can be prepared with the hollandite in the sample containing Cr^{3+}, Ni^{2+}, Zn^{2+} or Co^{2+} (compensated by Ti^{4+} where necessary) by melting in air, as well as by ceramic technology. The normalized PCT-B Cs leachate concentrations for the melted samples are two orders of magnitude better than the Na, B and Li concentrations for reference glass. A hollandite-rich melted ceramic containing Mg did not result in the Cs being incorporated in hollandite and was thus not a feasible waste form. The hollandite-rich Mn sample melted in air designed to investigate the minimum number of phases showed feasible waste forms could be made with only the addition of perovskite and rutile to the

major hollandite. Cs could be fully substituted for Ba in single-phase hollandite $Ba_xCs_y(Cr^{3+})_{2x+y}Ti_{8-2x-y}O_{16}$ and $Ba_xCs_y(M^{2+})_{x+y/2}Ti_{8-x-y/2}O_{16}$ where M=Ni or Co in air-sintered samples.

Australia, 2004 [18]

In 2004, ANSTO reported on testing on hollandite-rich titanate ceramics prepared by melting in air by replacing the Al in the hollandite with cations of larger ionic radii (Ga, Fe, and Mn) to expand the tunnels in the structure and thus facilitating the entry of Cs. This was done by replacing the Al_2O_3 in the precursor mix with the same wt% of Ga, Fe and Mn oxides (assuming they were in the +3 state). The samples were produced by the alkoxide route.

The Synroc-B with 7.5 wt.% Cs_2O in hollandite-rich Al was melted in air at 1550ºC. It contained about 50% hollandite plus zirconolite, perovskite, rutile and $Cs_2Al_2Ti_2O_8$. The small amount of highly leachable $Cs_2Al_2Ti_2O_8$ (containing <1% of the Cs inventory) rendered the sample unsuitable for a waste form. Analysis of these sample results indicated that the addition of additional titanate phases would not only reduce melting temperature but also aid in the incorporation of the Cs in the hollandite structure.

The hollandite-rich Ga sample was melted in air at 1550°C and contained mostly hollandite, which contained the majority of the Cs, and rutile with minor components being zirconolite, perovskite, $Cs_2Ga_2Ti_2O_8,$ and Cs titanate. Since $Cs_2Ga_2Ti_2O_8$ is very reactive in water, samples containing this phase were regarded as unsuitable waste forms.

The hollandite-rich Fe samples were melted in air at 1500°C and hollandite-rich Fe/K sample in air at 1450°C and contained Cs-bearing hollandite, zirconolite, perovskite, rutile and Cs titanate. The addition of more Fe_2O_3 and BaO to the precursor resulted in a sample that did not contain the leachable Cs titanate phase. Therefore, this mixture was deemed to have a composition suitable for a waste form. The K was added to the mix in an attempt to lower the melting temperature and the hollandite-rich Fe/K composition was also deemed to be suitable as a waste form as it contained no leachable phases.

The hollandite-rich Mn sample was melted in air at 1550ºC and contained mostly Cs-bearing hollandite, zirconolite and perovskite and rutile. It lacked any easily leachable Cs-rich phases, which suggests this also would be an appropriate waste form composition.

PCT-B leach testing was carried out on the air melted hollandite-rich Fe and Mn samples. The leach results for the samples containing Fe (normalized Cs leachate concentration of 2.39 g/l) were appreciably higher than those for the other samples reflecting the presence of Cs titanate in this sample. In the modified sample containing Fe, which did not contain Cs titanate, the normalized Cs leachate concentration was reduced to 0.12 g/l. The leachate concentration for the Fe/K sample was 0.62 g/l and for the Mn sample was 0.27 g/l. For comparison, the leachate concentration for reference EA glass is 13-16 g/l.

In summary, leach resistant titanate hollandite-rich ceramic melts incorporating ~7.5 wt% Cs_2O were prepared when the hollandite in the sample contained Fe (when BaO added with extra Fe_2O_3) or Mn.

France, 2004 [6]
The synthesis, characterization and study of the radiation effects on hollandite ceramics developed for Cs immobilization were studied. Several hollandite samples having the $Ba^{2+}_xCs^{+}_y(Al,Fe)^{3+}_{2x+y}Ti^{4+}_{8-2x-y}O_{16}$ composition type (1.16≤x≤1.28; 0≤y≤0.28; with or without Fe) were prepared in air. One sample was chosen near the lower limit of the compositional range of Ba-Al hollandite (without Fe) in order to insert Cs more easily. In another sample, part of the Ba was substituted by 0.1 Cs/formula unit, keeping constant the Al/Ti ratio. Another sample used Fe^{3+} to partly replace Al^{3+} ions to facilitate incorporation of Cs into the tunnels. All samples were prepared by mixing Al_2O_3, Fe_2O_3, TiO_2, $BaCO_3$ or $CsNO_3$ powders, pelletizing and calcining the mixture for 4 hours at 810°C. The calcined powders were ground and sintered at 1320°C for 96 hours or at 1200°C for 30 hours.

This study showed that single phase hollandite ceramics in the $Ba_x(Al,Fe)^{3+}_{2x}Ti^{4+}_{8-2x}O_{16}$ compositional range can be obtained by natural sintering under air of oxide powders (oxide route). To insert Cs in the structure, the substitution of Al^{3+} by Fe^{3+} ions in hollandite composition, which increases the lattice parameters, seems to be necessary. Thus, iron-substituted barium hollandite, prepared by either an alkoxide or an oxide route produces waste forms suitable for Cs immobilization.

France, 2004 [19]
Additional work by the CEA (Commissariat à l'Energie Atomique) in 2004 included other studies on iron-substituted barium hollandite for Cs immobilization. A five wt% Cs_2O-doped Fe substituted hollandite was synthesized on a laboratory scale (100g), using an alcoxide route. The hollandite crystallization was achieved after a 5-hour calcination at 1000°C, in air atmosphere. After milling and cold pressing steps, ceramic pellets were sintered in air at 1250°C for 15 hours. The resulting materials were dense single phase pellets. The leaching resistance of this material was measured in pure water at 100°C using Soxhlet tests. The initial alteration rates in pure water at 100°C are in the range of 10^{-3} g/m²/day for tests conducted for 56 days in a continuously renewed pure water flow (0.02 g/m²/day on first day, 0.0006 g/m²/day between 25 and 56 days).

France, 2005 [20]
Continued testing on the chemical durability of iron-substituted hollandite ceramics for Cs immobilization was reported in 2005 by the CEA. Samples from the 2004 tests were leached under static conditions for 1 year at 90ºC. Under static conditions the mean alteration rate measured between 0 and 7 days was about $2x10^{-3}$ g/m²/d. Between 7 and 30 days the rate dropped to about $8x10^{-5}$ g/m²/d. The residual rate over longer durations was less than 10^{-5} g/m²/day. These results confirm the Cs-specific immobilization potential of iron-substituted hollandite ceramics.

CEA is continuing characterization of the material performance with emphasis on the effects of temperature, pH and surface area/volume ratio on the alteration rate, and on the self-irradiation behavior of the material. Other work is also in progress to determine the parameters related to the technological feasibility of these matrices, and in particular to establish a composition range around the reference composition for suitable management of chemical impurities liable to be present in the waste stream.

U.K., 2004 [7]

The U.K. has also been involved in studies of hollandite-based radioactive waste forms. In 2004, they reported on structural studies on hollandites with compositions $Ba_{1.2-x}Cs_xMg_{1.2-x/2}Ti_{6.8+x/2}O_{16}$ and $Ba_{1.2-x}Cs_xAl_{2.4-x}Ti_{5.6+x}O_{16}$ (x=0, 0.1, 0.25) that were made using a modified alkoxide/acetate precursor route and then either using HIP or sintering for the final product. X-ray powder diffraction showed that both methods yielded samples with tetragonal hollandites. When prepared by HIP the samples showed a greater degree of crystallinity. The data showed that the Cs is located within the channels in the structure, with no evidence of secondary phases.

Russia, 2003 [21]

In 2003, the Russian Academy of Sciences reported on the synthesis and study of isomorphous miscibility limits of crystalline phases with hollandite-type tunnel structure in the CsO(*Me*O)-Al_2O_3-TiO_2 (*Me*=Ba,Sr) systems. Samples were prepared by the solid phase synthesis of TiO_2, Al_2O_3, $BaCO_3$, Cs_2CO_3, and $SrCO_3$. The Cs containing samples went through a three-stage heat treatment with intermediate grinding of cakes after sintering at 650°C, 950°C and 1300°C for 18-36 hours. After heat treatment the sample was quenched in air. The Sr containing samples were sintered at temperatures of 950°C and 1300°C.

The variations in the temperature and duration of heat treatment in the course of synthesis resulted in the formation of the final products containing, as a rule, a mixture of two phases, namely hollandite and rutile. Through optimization of compositions, it was determined that the composition of the initial mixtures used in the synthesis must be calculated from the following hollandite empirical formula $BaAl_2Ti_5O_{14}$.

The studies suggested an insignificant volatility of Cs under the experimental conditions indicating the Cs^+ cations are embedded in the hollandite tunnel positions. They concluded that the region of existence of $Cs_xBa_{1-x/2}Al_2Ti_5O_{14}$ solid solutions lie in the concentration range 0≤x≤0.7. It should be noted that the value x=0.7 corresponds to a rather high cesium content (13.3 wt.%) in the crystal lattice of hollandite. For this reason, it would be appear to be appropriate to use these compounds as ceramic matrixes to immobilize cesium-containing radioactive wastes.

In the SrO-BaO-Al_2O_3-TiO_2 system hollandite based solid solutions were not observed over a wide range of concentrations. At x>0.2, the experimental conditions described above provide the formation of multiphase samples that contain TiO_2 and $SrTiO_3$ impurities in addition to the hollandite phase.

<u>**U. S., 1996**</u> [11]
In 1996, Los Alamos National Laboratory (LANL) performed tests on Synroc-B that had been synthesized at atmospheric pressure from freeze-dried nitrate precursors. By calcining atomically mixed precursors prepared by freeze drying (the cryochemical technique) of rapidly frozen nitrate solutions, the intimate mixing of ions inherent in a solution is conserved. Subsequent removal of the solvent by low temperature sublimation prevented phase separation and transferred this intimate mixture of ions into the solid state. As a result the conventional diffusion limited solid state reaction was circumvented and product formation was allowed to occur very rapidly at lower temperatures.

LANL demonstrated that the complete Synroc-B phase assemblage can be synthesized at ambient pressure (600 torr) through the calcination of atomized mixtures of nitrate salts prepared by freeze drying. Thermal processing of the freeze dried precursor for 10 min at $1100^{\circ}C$ or 15 hr at $1000^{\circ}C$ (in a 6% H_2/Ar atmosphere) yielded the desired product. The Synroc phases included $CaTiO_3$, $CaZrTi_2O_7$ and $BaAl_2Ti_{15}O_{14}$). The freeze dried powders would still need to be sintered but this should be simpler (lower temperatures) due to their uniform small particle sizes rather than the large and nonuniform particles resulting from calcination of a mechanical mixture.

<u>**U. S. and Russia, 2003**</u> [22]
Results from collaboration between Savannah River Site, INL, PNNL, the V. G. Khlopin Radium Institute and SIA Radon to evaluate CCIM to immobilize Department of Energy (DOE) HLW surrogates was reported in 2003. These lab scale tests with surrogate DOE HLW were promising. Slurry feeding, which had not been widely demonstrated, was proven viable. Batch pouring through a bottom and side drain configuration was also successfully demonstrated. The glass product demonstrated acceptable durability as measured by the PCT. Additional information is needed on the retention of the Cs and Sr at the high operating temperatures. Crystal species were detected in some of the products, however, they did not appear to impact processing or measured durability but specific leach rates for Cs were not reported.

<u>**U.S., 2004**</u> [23]
The INL and ANSTO conducted testing to evaluate the feasibility of using a fluidized-bed to convert uranium-bearing liquid waste solutions into a Synroc G precursor. The details of the testing are considered proprietary, but the tests verified the technical feasibility of this approach.

6. SYNROC / STEAM REFORMING COMPARISON

As previously stated, safe interim storage of the immobilized Cs/Sr product will require a waste form that is stable, does not produce dangerous radiolysis products (e.g., buildup of potentially explosive gases like hydrogen), has a relatively high product density (to minimize storage volume), and has properties that enhance heat management (e.g., high thermal conductivity). Basically, to meet these fundamental requirements the Cs/Sr

waste stream must be converted from a liquid to a solid while preventing the Cs from volatilizing.

Because simple drying of the Cs and Sr in a carbonate solution produces a waste form with unacceptable high aqueous solubility and at high temperatures will decompose and produce CO_2, this method will not suffice. In addition, calcination to an oxide form is possible, but the low melting temperature of Cs_2O (490ºC) limits the size of the disposal container. Regardless, cesium oxide is also hygroscopic and has a low thermal conductivity. In light of these simple processing shortcoming as outlined above, it will be important to identify a immobilization processing technology that also destroys the organics (to prevent a buildup of gases) and ensures no environmental NOx releases - preferably by destroyed them.

Since, the specific criterion for the Cs/Sr waste form leachability is currently undefined for the ~ 300-500 year decay storage time, it may be sufficient to consider the waste canister as the environmental barrier to leaching. Such an assumption may be appropriate, since the criteria for Class C low-level waste (LLW) does not require the material to be stabilized against leaching by allowing the high integrity containers (HICs) to serve as the leachability barrier. Short-lived Cs-137 ($t_{1/2}$=30.17 years) contributes to the short term heat load, but Cs-135 ($t_{1/2}$=3X10^6 years) contributes to the long term radiotoxicity. Current regulations do not limit the quantity of Cs-135 in LLW, but the quantities associated with spent fuel may cause concerns enough to require deep geological disposal. Therefore, to ensure that the Cs/Sr product will not require further treatment after the decay storage time, the most conservative approach is to ensure the leachability of the Cs/Sr waste form is at least equivalent to that obtained with HLW in borosilicate glasses.

Two extensively developed methods of obtaining a stable Cs/Sr waste form equivalent to borosilicate glass include ANSTO's developed Synroc waste form and a steam reforming process that creates a stable mineralized waste form. In steam reforming, the waste feed, superheated steam, and co-reactants are introduced into a fluidized bed steam reformer system where liquids are evaporated; organics are destroyed; and reactive chemicals, radionuclides, and non-volatile heavy metals are converted into a mineralized solid waste product. Ongoing laboratory evaluations of steam reforming for the Cs/Sr stream have indicated the Cs and Sr in the solutions can be converted into leach-resistant aluminosilicate minerals, such as pollucite.[24] In order to produce pollucite and other mineral analogs of the alkaline metals, the feed must be mixed with alumino-silicate compounds such as natural clays and subsequently thermally sintered or calcined to activate solid-state crystal formation.

A preliminary evaluation of the effectiveness of employing Synroc's crystalline based waste formulation compared to the use of steam reforming to obtain a stable mineralized waste form has been conducted and is summarized in Table 2. The table highlights various areas of each technology's effectiveness in its ability to sequester the Cs and Sr fission products that may be selectively removed from any HLW generated by future nuclear fuel reprocessing scenarios.

TABLE 2. Comparison of Synroc and Steam Reforming

ATTRIBUTES	STEAM REFORMING	SYNROC
Cs/Sr capture	Ongoing tests indicate that a mineralized granular product is formed with very little volatilization of the Cs.[28,29,30]	Studies indicate that Synroc processes capture Cs/Sr in the waste form with very little volatilization. [25,34]
Waste Form Durability	Some Cs/Sr waste stream mineralized product has been produced, however, further validation and leach testing is required. The process destroys the organics, which could form dangerous radiolysis products.[28,29,30]	Numerous studies indicate that the leach rates of Cs/Sr and fission products from tailored crystalline waste forms, such as Synroc, are at least an order of magnitude less than for the currently accepted borosilicate glass for HLW. The process also destroys the organics which could form dangerous radiolysis products [25,26,27,31,32,33,34]
Waste Form Packaging	Granular product may require development of high integrity packaging to meet existing or future disposal requirements. Additional processing may be required, such as putting the granular product into a monolithic form, to meet waste disposal requirements.[28,29,30]	Monolithic waste form in current standard HLW canister should meet existing or future disposal requirements.
Formulation and Processing Complexity	Simple to slightly complicated. Many steam reformers in production scale operation for both low level radioactive waste, hazardous and hydrogen production.[28,29,30]	Complicated although technology for processing has been tested at all scales.[32]
Offgas Generation /Secondary Waste	Offgas generation is less than incineration –but much greater than melting or HIPing, Offgas scrubbing solutions greater than melting or HIPing –but may be recycled back to the reformer. NOx is destroyed in the steam reforming process.[28,29,30]	Low offgas , low offgas scrub solutions.[32]
Processing Flexibility (Robustness)	Ability to effectively produce acceptable waste forms for other high –level waste separated components, such as Plutonium and Uranium, is unlikely.	Numerous test indicate Synroc can sufficiently immobilize any radionuclides existing in HLW.[25,34]

7. CONCLUSION AND PATH FORWARD

Although this was not an exhaustive literature survey, the articles cited do indicate that immobilization of Cs and Sr in a Synroc-type matrix is very feasible.[25,33,34] In general, the hollandite with Cs is chemically durable with a leach resistance two orders of magnitude higher than for the current glass waste forms.[31] The use of tailored, high-performance, alternative waste forms that include ceramics and glass-ceramics [26,27],

coupled with alternative nearly mature process technologies, such as hot-isostatic pressing, sintering and cold-crucible induction melting [32], offer significant performance improvements and efficiency savings for wastes difficult to incorporate into glass. Many wastes, including those containing Cs and Sr, are problematic to incorporate in glass, since the limitations of the Joule heated melters used for glass restrict operating temperatures to below 1200°C, which may be insufficient for fully dissolving the fission products in the glass matrix. In addition Joule heated melters suffer from equipment corrosion, produce a secondary waste, and are susceptible to hazardous/radioactive volatile component losses.

Synroc is expected to provide a cost effective, reliable, and durable waste form. These fundamental and significant benefits are the result of the Synroc formulation method – in that the Cs/Sr can be placed in a natural analog crystalline/mineral matrix empirically proven to be nearly insoluble over long time periods [26,34]. Such formulations will decouple the *waste form* from the *waste form disposal environment* since there is no alpha decay and no corresponding crystalline waste form decay damage over the relatively short half lives of the Cs and Sr.[26,33] This decoupling furthermore greatly simplifies, and therefore increases the accuracy, of any models required to predict the Cs and Sr release rates over long time periods in the proposed disposal location. Steam reforming has yet to demonstrate it can produce a Cs/Sr waste form of equivalent durability, so as to provide the same level of waste form/disposal site decoupling.[28,29,30]

The use of Synroc as an alternative for the immobilization of the Cs/Sr strip product must continually be evaluated. In particular, optimization of the correct Synroc assemblage matrix for the various Cs/Sr feeds would need to be conducted. Some preliminary tests are being conducted by ANSTO (at their expense) this fiscal year to indicate further feasibility of the Synroc waste form for the Cs/Sr streams. The results from this testing can then be compared to the tests currently being conducted with a steam reforming approach to Cs/Sr immobilization. At this point, a more detailed comparison of fabrication ease, flexibility, chemical durability (leach rate), and costs between the two technologies can be completed to decide between steam reforming and Synroc immobilization.

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