

IMMOBILIZATION OF HIGH-LEVEL DEFENSE WASTES IN SYNROC-D:
RECENT RESEARCH AND DEVELOPMENT RESULTS ON PROCESS SCALE-UP*

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ABSTRACT

SYNROC is a titanate based ceramic waste form being developed to immobilize high-level nuclear reactor wastes. SYNROC-D is a unique variation of SYNROC designed to contain high-level defense wastes, particularly those in storage at the Savannah River Plant (SRP). We review recent research and development on SYNROC-D processing options and report on work in progress on various unit operations. The overall immobilization process can be divided into three general parts:

1. Slurry preparation (formulation, reactant addition and blending)
2. Powder processing (spray drying, calcination/redox control)
3. Mineralization (densification)

Powder processing research is directed toward development of a slurry-fed, fluidized-bed calciner based on the ICPP design. Densification research is focused on use of hot isostatic pressing (HIP) or hot uniaxial pressing (HUP). The successful use of both have been demonstrated.

INTRODUCTION

SYNROC (synthetic rock) is a titanate-based ceramic waste form currently being developed as an alternate to borosilicate glass for immobilizing high-level nuclear reactor wastes¹.

The idea of putting radwastes into a synthetic mineral form is not new; it was originally suggested as far back as the early 50s.² There are many natural minerals that can accept radwaste-type elements (Cs, Sr, and U) into their crystalline structure. Furthermore, several of these minerals possess the important property of having a very low solubility in groundwater and, thus, are strongly resistant to leaching and alteration in the geologic environment.

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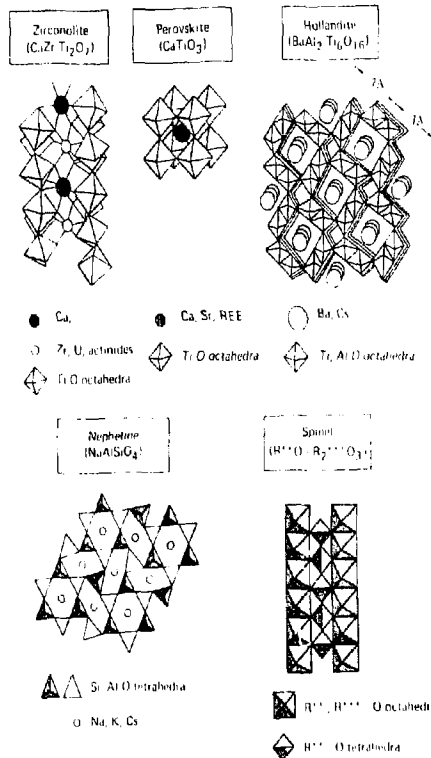


FIGURE 1. Crystal Structures Of The Minerals In SYNROC. SYNROC-C Is Comprised Of Zirconolite, Perovskite, And Hollandite. SYNROC-D Is Composed Of Zirconolite, Perovskite, Nepheline, And Spinel. Note That Because Of The Na And Si In The Defense Wastes, We Have Chosen To Incorporate Cs In Nepheline Rather Than Hollandite.

The SYNROC concept is unique because it suggests: a) using a titanate-based mineral system of extremely low solubility, and b) incorporating the radionuclides into these "host minerals" at low concentrations (i.e., as dilute solid solutions). The host minerals for the radwaste elements in SYNROC are zirconolite, perovskite, hollandite, and nepheline (Fig. 1). Analogs of these minerals can be found in nature. Many of the natural minerals contain radwaste elements (U and Th, for example) and have retained these elements in their crystal structures for up to 500 million years.³

SYNROC-C VS. SYNROC-D

The SYNROC composition originally proposed by Ringwood was designed for storage of commercial reactor wastes. This material is called SYNROC-C (C for commercial). At LLNL we are working on a modification of this original form for the storage of defense wastes, i.e. SYNROC-D (D meaning defense).

There are two major crystal-chemical differences between SYNROC-C and SYNROC-D. First, an additional inert (i.e., contains no radionuclides) spinel mineral phase (Fig. 1) is formed from the large quantities of aluminum and transition metals (mainly Fe, Ni, and Mn) in the defense waste. Secondly, due to the presence of Na and Si in much of the defense waste, a silicate phase (nepheline) is used as a Cs host.

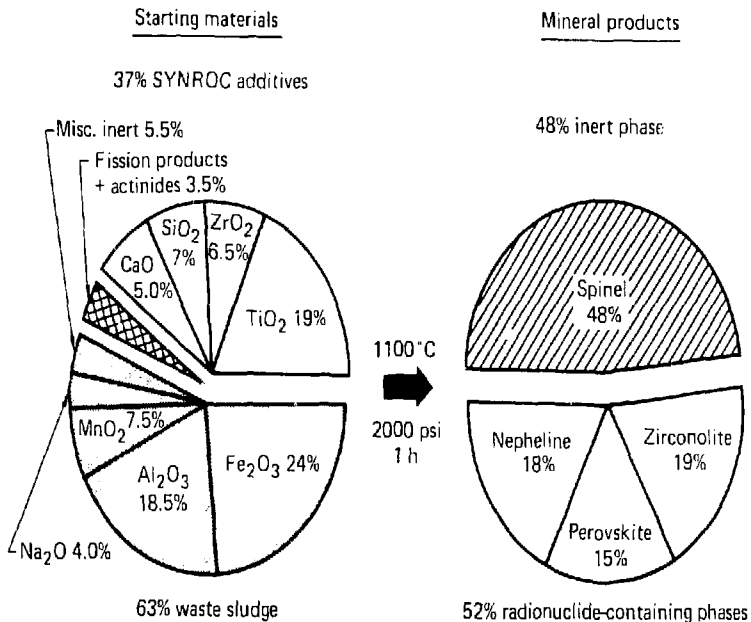


FIGURE 2. Pie Chart Showing The Composition Of The Starting Materials And Mineral Products During Preparation Of SYNROC-D Containing SRP Composite Sludge.

STATUS OF SYNROC-D DEVELOPMENT

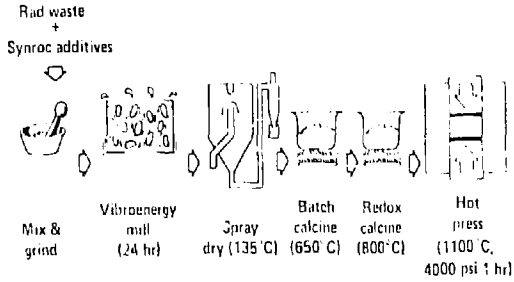
In October 1981 SYNROC-D was selected as the reference alternate waste form to borosilicate glass for immobilization of defense wastes. A total of eight candidate waste forms competed in this selection process. The decision of which alternate waste form to use was primarily based on performance properties. For example, SYNROC-D shows an improvement of 10^3 in actinide leach rates over borosilicate glass (SRL waste glass 131). Also the waste loading of SYNROC is three times that of the reference glass giving SYNROC a marked economic advantage for interim storage, transportation, and repository storage. These savings offset the additional costs associated with the processing facility.

In a recent series of papers, we have addressed the formulation⁴, preparation⁵, characterization^{6,7} and performance testing^{7,8} of SYNROC containing SRP defense wastes. We have also recently published a brief description of the SYNROC process flow sheets and a schematic layout of an associate processing facility⁹. In this brief paper we summarize current data on (i) pilot plant R&D on SYNROC preparation, and (ii) recent reductions in complexity of the SYNROC process.

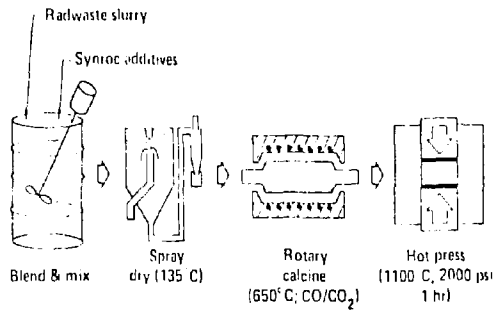
In regard to formulation, it is important to realize that only four additives (TiO_2 , ZrO_2 , CaO and SiO_2) are used in the preparation of SYNROC containing SRP defense waste (Fig. 2). Further, we have found that components in the waste sludge feed can vary by as much as $\pm 50\%$ in composition without affecting either the quantity of SYNROC additives needed or the quality of the final product. Our experience shows the SYNROC formulation to be very tolerant of wide variations in feed composition and thus very forgiving of feed stream upsets¹⁰.

The SYNROC-D process, at the present state (two years R&D) is less developed than the more mature (greater than 15 years) borosilicate glass process. This is expected. SYNROC is a new waste form and nearly all research has been directed toward lab synthesis and testing of the product. As a result of engineering R&D, significant simplification in SYNROC-D processing has occurred over the past 18 months. In our initial scheme, (Fig. 3a) we blended and sometimes milled the additives with the waste slurry. After spray drying, this mixture was calcined and then reduced in two separate batch operations. Often the powder was reground prior to hot pressing. The initial capacity was only about 50g/day. In our present preparation procedure, (Fig. 3b) we have eliminated all grinding operations and simply blend the waste and additives in a 55 gallon drum prior to pumping to a large (5 kg/hr) spray dryer. The spray dried powder is simultaneously calcined and reduced in a large rotary calciner and then hot pressed. By March 1982, (Fig. 3c) the spray dryer and rotary calciner will be replaced by a slurry-fed, fluidized bed calciner. This unit will eventually increase our powder production capacity to about 100 kg/day. We expect further significant reductions in the number, size and complexity of the SYNROC process steps as engineering R&D continues.

Past method (capacity ~0.05-1 kg/d)



Present method (capacity ~1-20 kg/d)



Future method (capacity ~10-100 kg/d)

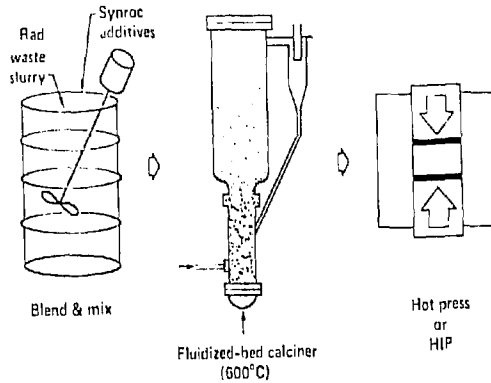


FIGURE 3. Comparison Of Past, Present And Future SYNROC Pilot-Plant Operations And Output Capacities.

ENGINEERING SCALE-UP

THE SYNROC-D PROCESS: AN OVERVIEW

During FY1981, a preliminary SYNROC reference process was developed based on laboratory preparation steps used to produce our first SYNROC samples. The reference process was used by SRL¹¹ to develop a preliminary engineering layout of the process cell. In this initial process layout, the washed sludge and Cs/Sr (separated from the supernate) are mixed with SYNROC additives and ball milled to particle sizes of less than 10 microns. The resultant slurry is spray calcined at a temperature between 650°C (minimum for 99% decomposition) and 800°C (maximum to prevent premature mineralization). The spray calcined powder is blended with a metal powder (Ni, Fe or Ti) for in-situ redox control and the mixture loaded and sealed in large containers for hot isostatic pressing (HIP). The HIP unit has a large diameter furnace in which the sealed metal containers of SYNROC are subjected to high temperature (1000-1100°C) and pressure (15,000 psi) to produce a monolith of greater than 92% theoretical density. Since the time this preliminary engineering layout was developed, significant advances have been made in the SYNROC process technology. In the next several sections, we will highlight these developments.

REDUCTION OF PROCESSING CELL AREA AS A RESULT OF RECENT R&D

Based upon the first laboratory preparation procedure, the initial processing flow sheet and plant layout (Fig. 4a) included a ball milling operation⁹. Also, for redundancy, two hot isostatic units (HIP), each with complete support facilities were also included. After critically reviewing the particle size requirements and HIP size/cycle time relationships (see following sections), we conclude that the ball milling operation and one HIP unit may be eliminated (Fig. 4b). The effect of this on processing cell area requirements is significant as shown at the left where the initial layout length of 390' is reduced to 270'. Other areas of possible size reduction involve consolidation of the two separate off gas scrubber tank systems for the calciner and canister preheat into one system and replacement of the metal powder redox control step by a gas phase redox method. This gas phase method is done as part of the calciner operation and would eliminate the powder blending operation. Replacement of the spray calciner with a more compact fluidized bed unit is also under development. This should result in additional simplifications in the flow sheet and allow cost savings in plant layout.

POWDER PROCESSING

Measurements of particle size distribution¹² on samples from waste storage tanks show a large fraction are less than 20 microns (Fig. 5). Particles greater than 20 microns are mostly inert sand or similar components. One operating scenario is to screen these out (including the grit blast material used for final decontamination) and handle as a separate low level waste stream or add them separately to the spray calciner through a larger orifice spray nozzle. Intimate mixing of these relatively inert particles with the main stream is not required since final product performance is unaffected by the presence of a few inert particles (TiO_2 , Al_2O_3 , SiO_2 , etc). Our laboratory preparations are presently done routinely without a grinding operation and produce a good product. Furthermore, the particle size distribution of the powders we are currently spray drying and hot pressing is greater than that reported for the SRP waste sludge (Fig. 5). Consequently, ball mill reduction of the sludge particle size is not required for the current SYNROC process.

The reference SYNROC flow sheet calls for in-situ redox control using metal powders. However, our present laboratory redox control is by gas phase reaction using a 1/10 CO/CO_2 gas mixture. Reaction kinetics are very fast at temperatures of 400°C or higher (Fig. 6) and the 1/10 mixture is below the combustion limit. Reaction with the calcined powders further reduces the CO content so the system is inherently explosion safe. Proper redox control may be effected with CO/CO_2 ratios as low as 1/100 or 1/1,000 (Fig. 7) although enough CO must be provided to react with the specific amounts of Fe_2O_3 , MnO_2 and U_3O_8 . The gas phase redox control may be carried out in the spray calciner or in the collection bin at the exit from the calciner. Maximum temperature is limited to 800°C to prevent premature mineralization.

Laboratory scale experiments are currently underway at LLNL to investigate the use of a fluidized-bed redox-calciner¹³. The unit is more compact than an equivalent spray calciner. The allowed operating temperature range is 400-800°C. This is a larger temperature range than the spray calciner (650°-800°C) since the longer residence time of material in the fluidized bed unit allows the decomposition/ reduction reactions to proceed to completion at lower temperatures.

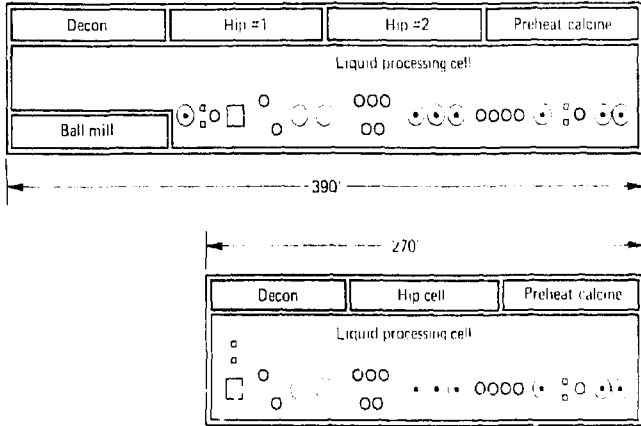


FIGURE 4. Schematic Plan View Of Processing Cell For Preparation Of SYNROC-D. Note That The Elimination Of Ball Mill And One HIP Unit Results In Significant Reduction In Length Of Process Cell. (a) Preliminary Design, (b) Current Design.

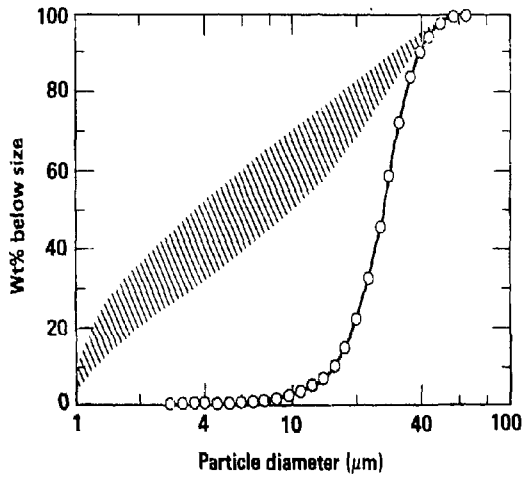


FIGURE 5. Comparison Of Particle Size Distribution For Current LLNL Calcined SYNROC-D Powder (Solid Line) With The Reported Distribution Range For SRL Waste Sludges (Shaded Area).

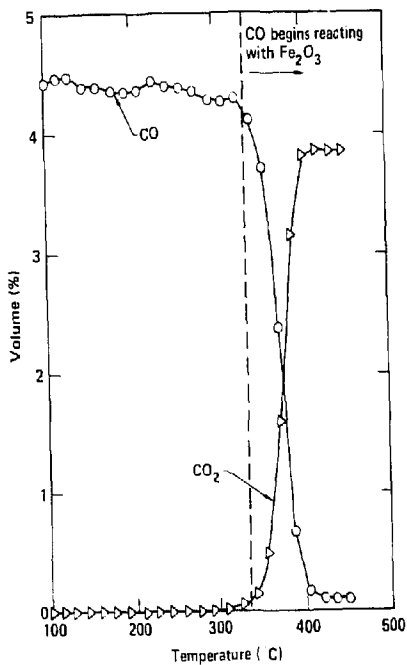


FIGURE 6: Extent Of Oxidation Of CO As It Flows Through A Heated Packed Bed Of Fe_2O_3 . Note That Above $400^\circ C$ The Reaction Becomes Very Fast Kinetically.

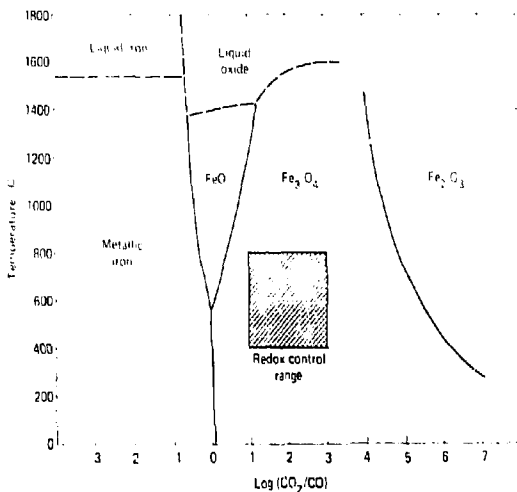


FIGURE 7: Gas Phase Redox Control Can Be Carried Out At Temperatures As Low As $400^\circ C$ With CO/CO_2 Ratios Below Combustion Limits.

DENSIFICATION (i.e. MINERALIZATION)

REQUIRED POWDER PROPERTIES

Calcined SYNROC powders ready for high temperature consolidation (i.e. mineralization) need to meet the following specifications: (1) pyenometric density = 3.7-4.0 g/cm³, (2) particle size less than 70 microns with mean size approximately 15 microns, and (3) a powder tap density greater than 1.0 g/cm³. The final, fully dense waste form has a density of about 4.0g/cm³.

An important powder characteristic is its packing density. HIP experience has shown that for powder with packing densities greater than 45% theoretical (i.e., less than 55% porosity), simple cylindrical canister designs can be used reliably. In this case the packed powder provides sufficient internal support to the metal canister to prevent buckling and distortion during densification. In the event that packing densities fall in the range of 25-35% theoretical, a special bellows-type canister is employed which allows most of the densification to take place in the axial dimension¹⁴.

DENSIFICATION METHODS

Laboratory experience has shown that two high-temperature fabrication processes currently employed in industry have potential for the large scale processing of SYNROC-D. Both of these processes, HIP (Hot Isostatic Pressing) and HUP (Hot Uniaxial Pressing) employ pressure as well as temperature in the consolidation process. In HIP (Fig. 8) a gas is used to uniformly apply pressure to all sides of the canister during densification. Large monoliths are possible with this process which makes it very attractive for HLW processing. In HUP, the waste cylinder is compressed axially between two pistons. Intermediate size cylinders (e.g. approximately 8" diameter) with height/diameter ratios less than 0.5 can be produced at high speed production rates. We have utilized HUP in the laboratory to establish the hot pressing parameters (time, temperature, and pressure) for SYNROC-D powders.

We have explored large scale HUP processing with the Greenleaf Corporation using simulated SYNROC-D powder. This company uses HUP to produce high quality ceramic cutting tool inserts of various shapes and sizes at very high throughput rates. Greenleaf Corporation has produced a few 7" diameter cylinders of SYNROC-D at simulated production rates of about a ton/day. As a result of this work, we are encouraged that relatively small high speed hot presses have the potential to process SYNROC-D HLW at high throughput rates.

A typical SYNROC-D powder can be hot pressed over a large range of temperatures and pressures. The region of acceptability is defined by those conditions which will produce a high density waste form with only a small amount of residual closed porosity. The time at temperature and pressure is more significant to the HIP process because high throughput rates for medium size monoliths require short time periods at maximum temperatures. Our data show that densification can be achieved in 5-10 minutes, at 4000 psi pressure.

In the case of HIP, there is considerable flexibility in the required temperature and pressure. We have calculated the required time to thermally equilibrate a large waste powder compact. In our calculations we have assumed a packing density of 35% and an initial bellows canister size of 26" diameter by 58" high. Our laboratory studies have shown that packing densities near 35% can be achieved by controlling the solids/liquid ratio of the slurry feed during spray calcination.

EFFECTS OF HIP CANISTER SIZE ON CYCLE TIME AND THROUGHPUT

HIP shrinkage studies for bellows canisters have shown that a 26" diam. by 58" canister compresses to approximately 22" diam. by 31". At a waste loading of 60%, each canister would contain approximately 0.45 metric ton of SRP waste.

It will take less than 24 hours to preheat the HIP canister to a center line temperature of 800°C before charging the canister to the HIP furnace. Large industrial HIP furnaces are always loaded hot in a continuous process. Once loaded into the HIP unit, it will take about 11 hours to process the canister and cool the HIP to 800 C for recharging. This includes a three hour hold period at maximum temperature. After cooling the HIP unit to 800°C, the canister would be transferred to a controlled cooling furnace. The total HIP cycle time is expected to be approximately 11 hours. The consolidation pressure needs to be greater than 3000 psi. Industrial experience has shown that large HIP systems can be operated on a 12 hour cycle under similar time-temperature-pressure profiles. Therefore, a single HIP unit can be projected to process two canisters/day.

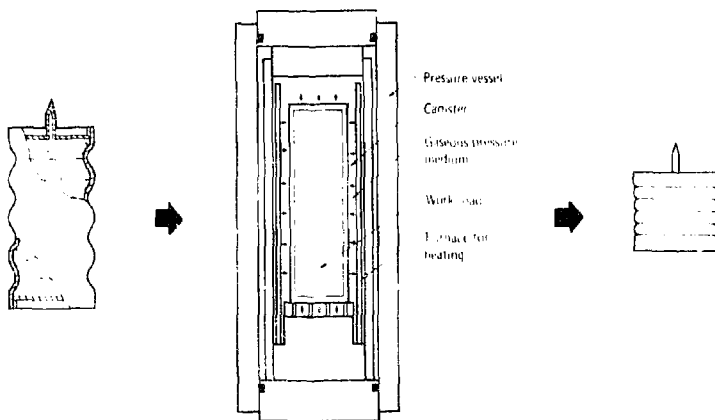


FIGURE 8. Schematic Of HIP Cycle Using A Bellows Canister.

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