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INCORPORATION OF HIGH-LEVEL WASTES IN SYNROC: RESULTS FROM RECENT PROCESS ENGINEERING STUDIES AT LAWRENCE LIVERMORE NATIONAL LABORATORY*

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INTRODUCTION

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 and the decision of which alternate waste form to choose was based primarily on performance properties.

The major advantage of SYNROC-D is that it gives a 10^3 improvement 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 facility¹, thus making the total system cost for SYNROC comparable to borosilicate glass.

In a recent series of papers, we have addressed the formulation², preparation³, characterization^{4,5} and performance testing^{5,6} of SYNROC containing Savannah River Plant defense wastes. We have also recently published a brief description of the SYNROC process flow sheets and a schematic layout of an associate processing facility⁷. In this brief paper we summarize highlights from recent engineering research and development, in particular, results from fluidized bed calcination studies of SYNROC slurry.

SYNROC-C VS. SYNROC-D

The SYNROC composition originally proposed by Ringwood⁸ 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 is formed from the large quantities of aluminum and transition

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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.

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. 1). 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 tolerant of variations in feed composition and thus quite capable of handling reasonable feed stream upsets⁹.

Fig. 1. Pie chart showing the composition of the starting materials and mineral products during preparation of SYNROC-D containing SRP composite waste sludge.

STATUS OF SYNROC-D PROCESS DEVELOPMENT AT LLNL

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 to date has

been directed toward lab synthesis and testing of the product. However, as a result of recent engineering R&D, significant simplification in SYNROC-D processing has occurred over the past 18 months.

In our initial lab process, (Fig. 2a) 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 to insure homogeneity. The initial capacity was only about 50g/day.

In our first improvement of the process (Fig. 2b), we eliminated all grinding operations and now simply blend the waste sludge and SYNROC additives in a 55-gallon drum (for small batches) or a 350 gallon tank (for large batches). This slurry is fed to a large spray dryer having an output of approximately 5-10kg solids per hour. The spray dried powder is then simultaneously calcined and reduced in a large rotary calciner. This product can be densified by hot uniaxial pressing (HUP) or hot isostatic pressing (HIP).

More recently, we have demonstrated further improvement through use of a slurry-fed, fluidized-bed calciner as a replacement for the spray dryer and rotary calciner (Fig. 3c). This initial work was done in cooperation with the Idaho Chemical Processing Plant using a 10cm (4 in.) diam. fluidized bed. (Further details of this work are given below.) The fluidized bed will eventually increase our calcined powder production capacity to about 100 kg/day. We would expect further significant reductions in the number, size and complexity of the SYNROC process steps if engineering R&D were to continue.

POWDER PROCESSING: FLUIDIZED BED CALCINATION

Calcined SYNROC-D powders ready for high-temperature consolidation need to meet the following specifications: (i) pycnometric density greater than 3.2 g/cm^3 , (ii) reactant grain size less than or equal to 70 microns (with a mean approximately equal to 15 microns), (iii) tap density greater than 1.0 g/cm^3 , and (iv) volatile content less than 1.0 wt%. Some control of the oxidation state of elements such as Fe, Mn, and U is also necessary. However, recent work at LLNL⁹ and Rockwell Science Center¹⁰ shows that the range of allowed oxidation state is quite large and thus control of this parameter is less critical.

Laboratory-scale experiments are currently underway at LLNL investigating the use of a slurry-fed, fluidized bed calciner. This calciner is similar in design to the units in operation at Idaho Chemical Processing Plant (ICPP) and offers several advantages for preparing SYNROC powders:

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

(b) (capacity ~1-20 kg/d)

(c) (capacity ~10-100 kg/d)

Fig. 2. Evolution of SYNROC processing from (a) a laboratory to various stages [(b) and (c)] of pilot-plant scale operation.

- (1) High throughput with moderate-to-long residence times.
- (2) High heat transfer rates and a broad range of operating temperatures.
- (3) No internal moving parts.
- (4) A fully-calcined product with high packing density (greater than 35% T.D.).
- (5) Twenty years of operating experience on real radwaste feed (at ICPP).

A schematic diagram of our 10cm (4 in.) laboratory-scale fluidized bed calciner is given in Fig. 3. Fluidizing gas (air) is introduced through a bottom plenum and the waste slurry is sprayed into the bed through a nozzle driven by high pressure air. Another nozzle is used to introduce a kerosene/O₂ mixture that provides the heat for drying and decomposition reactions. We have also added a series of band heaters to the vessel walls that provide an alternate heat source for operations up to 500°C.

Typical calciner operating conditions for processing a SYNROC slurry feed are given in Table 1. These data were derived from a series of experiments done under contract at ICPP. These tests involved over 70 hours of operation on a 10cm (4 in.) diam. calciner.

As mentioned above, one of the most desirable features of the fluidized bed calciner is the high packing density of the powder product. This high density is achieved by continuous deposition of a coating of product on a seed particle; the coating has a low porosity and consists of an intimate mix of microcrystalline grains of SYNROC additives and waste feed. Thus, although the product particle size is quite large (0.2-0.8mm), the reactant grains composing each particle are small enough (micron size) to give high reactivity during consolidation.

The fines produced during calcination (about 25% of the total product) are carried overhead and collected by a cyclone separator. These fines can be selectively introduced into the bed to provide the "seed" material for continued particle growth.

CONSOLIDATION VIA HOT ISOSTATIC PRESSING (HIP)

In HIP processing, the packing density of the powder is important because it impacts the design, size, and number of HIP cans needed to achieve a given throughput (Fig. 4). The expected plant throughput is about 1.45 metric tons SYNROC at 60% waste loading. At a powder-packing density of 35%, this quantity of SYNROC can be loaded into a single can having an initial height of 1.47m (58 in.) and a diameter of 0.91m (36 in.) or two canisters 0.65m

Fig. 3. Schematic of laboratory-scale fluidized bed calciner.

TABLE 1

SUMMARY OF TYPICAL OPERATING CONDITIONS FOR FLUIDIZED-BED CALCINATION OF SYNROC FEED (DATA FROM 10cm DIAM. UNIT AT IDAHO CHEMICAL PROCESSING PLANT.)

Bed cross-sectional area; (m ²)	7.85x10 ⁻³
Slurry feed rate; (l/h)	2.0
Solids loading: dissolved; (kg/l)	0.27
suspended; (kg/l)	0.093
Calcining rate; (kg oxide/m ² /h)	43
Fuel feed rate (kerosene); (cm ³ /h)	942
Oxidizer feed rate (oxygen); (m ³ /h)	1.6
Fluidizing air (at 600°C, 1 atm); (m/s)	0.32-0.35
Bed pressure; (psig)	3.5
Δ P across the bed; (in. H ₂ O)	21-25
Bed temperature; (°C)	595-610
Product packing density ^a ; (g/cm ³)	1.6-1.7
Particle (pycnometric) density (g/cm ³)	3.6-3.8

^a loose packed, without vibration or compression

Fig. 4. Effect of powder packing density and canister dimension on throughput.

(26 in.) diam. by 1.47m (58 in.) high. HIP experience has shown that for powders with packing densities greater than approximately 50% theoretical (i.e. less than 50% porosity), simple, cylindrical canister designs can be consolidated reliably. This is because the packed powder provides sufficient internal support to the metal canister to prevent buckling and distortion during densification. In the event of packing densities less than 35% T.D. a special bellows-type canister¹¹ is used which allows most of the compaction to take place axially. A bellows canister is currently proposed for use in SYNROC-D consolidation.

Recently Ringwood¹² has successfully densified SYNROC in bellows cans measuring 25cm (10 in.) diam. x 60cm (24 in.) high; the final can sizes after consolidation were about 20x20cm (8x8 in.). Work is currently underway at LLNL on preparing two 30x30cm bellows canisters (dimensions are after consolidation), each containing 100kgm of SYNROC-D.

Estimates of Cycle Times for HIP Operation

SYNROC-D powder densifies very rapidly at modest temperatures and pressures. For example, our experiments have shown that densification can be achieved in about 10 minutes at 4000 psi and 1100°C. Applying these results to large HIP canisters indicates that the time required for actual consolidation is small compared to the time required to preheat the canister to the necessary densification temperature.

We have calculated the cycle time for densifying a 0.65m (26 in.) diam. by 1.47m (58 in.) can containing SYNROC-D at 35% packing density. After consolidation this can is approximately 56cm (22 in.) diam.x79cm (31 in.) and contains 0.45 metric ton of SRP waste. The finished can is designed to fit the reference 61cm (24 in.) diam. waste canister. Our estimates show that it will take less than 24 hours to preheat the HIP canister to a center-line temperature of 800°C before charging to the HIP furnace. Large industrial HIP furnaces are usually loaded hot to maximize throughput (i.e., reduce cycle times). Once loaded into the HIP unit, it will take about 11 hours to process the canister and then cool to 800°C for recharging. This includes a three hour hold period at maximum temperature. Therefore a single HIP unit can be projected to process two canisters a day. Our estimates agree well with actual industrial experience that shows large HIP systems can be operated on a 12 hour cycle under similar time-temperature-pressure profiles.

A schematic diagram of the envisioned SYNROC process (at this stage of development) is given in Fig. 5. It shows the use of a fluidized bed calciner to prepare SYNROC powder that is then fed to a storage hopper. Bellows-type canisters are filled, evacuated, sealed and preheated. The preheated canisters are loaded into a HIP unit where they are densified, then removed and cooled and finally loaded into a waste storage container. After sealing, this container is decontaminated and transferred to the interim storage facility and then, ultimately, to an underground repository.

Fig. 5. Schematic of SYNROC-D process.

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