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SYNROC PRODUCTION USING A FLUID-BED CALCINER

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ABSTRACT

SYNROC is a titanate-based ceramic developed for immobilization of high-level nuclear reactor wastes in solid form. Fluid bed SYNROC production permits slurry drying, calcining and redox to be carried out in a single unit. We present results of studies from two fluid beds; the Idaho Exxon internally-heated unit and the externally-heated unit constructed at Lawrence Livermore National Laboratory (LLNL). Bed operation over a range of temperature, feed rate, fluidizing rate and redox conditions indicate that high density, uniform particle-size SYNROC powders are produced which facilitate the densification step and give HUP parts with dense, well-developed phases and good leaching characteristics.

INTRODUCTION

SYNROC is a titanate-based ceramic material which is being developed as a medium for immobilizing high-level nuclear reactor waste [1]. The minerals Zirconolite ($\text{CaZrTi}_2\text{O}_7$), Perovskite (CaTiO_3) and Hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$) are used as the major hosts to retain wastes in solid solution. SYNROC is made in three basic formulations [2]: (1) SYNROC-B, the basic three-phase material with no waste. (2) SYNROC-C, containing simulated high-level commercial waste. (3) SYNROC-D, containing simulated high-level defense waste. The SYNROC materials have exceptionally high stability and are able to accommodate waste loadings as high as 70% [2,3].

As shown in Figure 1, SYNROC process designs include steps for blending of SYNROC precursors with waste, drying, calcination, redox adjustment, and powder densification [4,5]. The use of a fluid bed results in a minimum space requirement as it permits drying, calcining and redox control to be carried out in a single process unit. Considerable experience at the Exxon Nuclear Idaho Company Plant has demonstrated the reliability of a remotely operated fluid bed unit for reducing high-level waste to powder form [6].

This paper presents research on fluid bed production of precursor powder and densification of the powder into a SYNROC product. In this work, we have concentrated on SYNROC-C production. Initial tests were carried out on a kerosene fired fluid bed by personnel at the Exxon Nuclear Idaho facility near Idaho Falls, ID [7]. Later tests were performed using an electrically heated unit of similar design built at LLNL.

Apparatus

Both apparatus used for production of the SYNROC calcines are represented schematically by Figure 2. They are constructed of stainless steel with nominal dimensions of 10-cm diameter by 50-cm high for the fluid bed section and 15-cm diameter by 50-cm high for the disengaging section. For the tests described here the LLNL calciner was electrically heated by external band elements of approximately 4.5 kW total power. Fluidizing gas (Air, Argon or an Argon-H₂ mixture) entered the bed through an electric preheater at bed

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Figure 1. Processing Steps for Large Scale SYNROC Production.

operating temperature. The gas distributor/bed support was a sintered porous stainless steel plate, with a central product withdrawal tube.

Feed slurry was supplied by a metering pump to an external-mix spray nozzle mounted 12 cm above the bed support.

Exhaust gas is cleaned first by a 10-cm diameter cyclone separator, which is effective to about 10 μm , and then by passage through a spray column/demister which collects particles to 1 μm .

The apparatus used at Exxon Nuclear Idaho is of similar design (and in fact served as a model for the LLNL unit). The major difference is that the Idaho unit is heated by an internal kerosene-oxygen burner, shown in Figure 2, with a capacity of 10.5 kW (31,000 BTU/hr). The offgas cleanup system consists of a venturi scrubber and condenser which provide excellent particulate removal.

Operation

Normal operation of both calciners is identical: the bed is charged with 3-4 kg of Alumina or SYNROC, a gas flow providing 1.3-1.5 times the minimum fluidization velocity is established*, and the bed is heated to operating temperature. Feed is then established, first using water or 4N HNO_3 in place of slurry. The feed mixture is a nitrate solution with titanium dioxide added as a fine powder (0.2 μm -anatase 56.5 wt%). The other SYNROC components (as oxides) are: CaO (14%), ZrO_2 (10%), Al_2O_3 (8.4%), and BaO (6.2%). To simulate the waste Cs, Sr, Gd, Nd and Mo are present in 1% quantities. Final density of the feed slurry is 1.22 g/cm³. Normal feed rates for the LLNL unit are in the range of 1.2 kg slurry per hour, which represents a production rate of 26.6 kg of oxides per hour for each m² of bed area (the Idaho production rate is 54 kg oxides/hr m²).

*The minimum gas fluidization velocity U_{mf} , is estimated using the correlation of Wen and Yu [8,9], and has been verified experimentally in this apparatus for Alumina and SYNROC particles [10].

Figure 2. General Fluid Bed Unit for SYNROC Production.

Fluidizing gas velocity, nozzle gas rate and feed rate influence the establishment of a stable particle size distribution in the calciner. Low superficial gas velocity and low nozzle gas ratios tend to produce larger size particles. Samples of the bed are withdrawn periodically and a sieve analysis performed to determine particle size.

The temperature difference between the calciner wall and the bed is quite small, (10-15°C) at heat fluxes of 1 watt/cm² due to the rather high wall heat transfer coefficient (650 Kcal/m²-hr-°C). Operating conditions for the Exxon Idaho unit and the LLNL unit are summarized in Table 1.

The purpose of these tests was to demonstrate stable powder production with greater than 95% calcination. During the Idaho tests we encountered problems with particle agglomeration and size control. Conditions were adjusted until agglomeration was largely overcome. Stable particle size was not achieved at 600°C however, both 500°C/air tests achieved size control. Run F03 used an H₂/argon mixture for redox control but this failed to achieve stable particle sizes.

Fluid Bed Products

The fluid bed powder is removed (1) as bulk product through a pipe into the distributor plate, (2) as fines in the cyclone, and (3) as fines in the scrubber. The fines passing through the scrubber escape in the offgas. In a commercial fluid bed unit fines removed by the cyclone would be recycled to provide seed particles for growth. The properties of these powders are summarized in Table 1.

As might be expected, the 600°C product (I-36) has a higher conversion than the 500°C product (I-70) and F02), however, under reducing conditions the conversion is high even at 500°C.

The attrition index correlates with the percentage recovered as cyclone product (Table I). Operating under reducing conditions gives the least fines or highest attrition index.

TABLE I
Summary of Fluid Bed Operating Conditions and Product Characteristics

	Exxon Idaho		LLNL	
	36 hr Air	70 hr Air	F02 Air	F03 Argon 6% H ₂
Temperature °C	600	500	500	500
Operating time hrs	36	34.1	15	38
Fluidizing Gas L/min STP	44	67	75	78
Combustion Gas L/min STP	27	27	NA	NA
Nozzle Gas rate L/min STP	31	39	13	19
Water Vapor Rate L/min STP	40	37	20	20
Total Gas Load L/min STP	142	170	108	117
Superficial Velocity cm/sec at operating conditions	91	97	61	66
Slurry feed rate gm/min	40.7	31.8	19.7	20.0
Feed as oxides, kg (%)	13.9(100)	12.4(100)	2.89(100)	6.82(100)
Product recovered, kg (%)	8.5(61.1)	8.8(71.1)	1.88(65.1)	5.10(74.7)
Fines recovered, kg (%)	2.5(18.0)	1.3(10.5)	.31(10.7)	.3 (4.3)
Scrubber/loss, kg (%)	2.9(20.9)	2.3(18.4)	.7 (24.2)	1.42(21.0)
Bulk Product				
Particle Size (mm)	.615	.624	.618	.850
Tap Density(g/cm ³)	1.66	1.71	1.67	1.53
Porosity (%)	31.	23.	26.	35.3
% Conversion (1)	99.6	97.8	97.4	99.5
Attrition Index (2)	34	94	80	98
Fines - Cyclone				
% Conversion (1)	91.2	90.4	81.	89.

(1) Conversion percentage is determined by heating product at 650°C for 16 hours. Then % Conversion = 100 x final wt./initial wt. (2) The Attrition index is a measure of the resistance of the particles to abrasion [7].

The conversion percentage of the fines is much less than for the bulk since the fines are rapidly swept into the cyclone. The character of the fines changed in F03 becoming smaller so that only a small fraction of the total fines was picked up in the cyclone (4%). Because of the small fines production in F03 we were not able to control particle size during the run.

We have observed some chemical fractionation in the products. About half the feed cesium is lost from the bulk product, and appears in the fines. The cesium fractionation is caused by high vapor pressure compounds produced during calcination. Thus there is greater cesium loss at 600°C than at 500°C and also greater loss under reducing conditions. There appears to be little fractionation of calcium, barium, strontium, or molybdenum. Titanium is also lower in the bulk product and enriched in the fines, possibly due to being fed to the bed as small (.2 µm) slurry particles which are rubbed from the growing SYNROC particles more readily than the oxides produced by nitrate decomposition.

Densifying and Mineralizing

The product of the fluid bed goes through a high-temperature densification step to form the SYNROC phases. Two industrial processes have the potential for large-scale fabrication of SYNROC parts [5,11]. Both of these processes, HUP (Hot Uniaxial Pressing) [12] and HIP (Hot Isostatic Pressing) [13] have been used to evaluate densification of the fluid bed product.

Small HUP parts have been produced by placing calcine powder between pistons in a graphite die. During densification, the temperature was raised to 1150°C, and the pressure to 4 KSI and held for one hour. The resulting densified SYNROC is a cylinder 19 mm in diameter by 12.7-mm thick. HIP densification takes place in a stainless steel can 38-mm O.D. by 44-mm

long. Densification occurs in a fluid pressurized chamber where the final conditions of 1250°C and 30 KSi are held for two hours. A summary of the densification tests are given in Table II.

TABLE II
Fluid Bed Powder Densification Results

Hard Bed Powder Densification Results				
Sample	Densification(1)		Final Density	% Porosity
	Prep.	Method	% Theoretical (2)	
Idaho Powder				
36 Hour HUP-1A		HUP	99.3% (4)	NA
70 Hour HUP-1A		HUP	99.3% (4)	NA
HIP-1A	AC	HIP	Low (6)	NA
HIP-2A	AC+TA	HIP	93.8% (5)	3.5
HIP-3A	AC+HC	HIP	94.5 (5)	1.0
F02 Powder				
HUP-1A		HUP	91.7% (4)	NA
HUP-2A	HC	HUP	94.1% (4)	NA
HIP-1A	AC	HIP	Low (6)	NA
HIP-2A	AC+TA	HIP	99.9% (5)	0.4%
HIP-3A	AC+HC	HIP	95.8% (5)	2.2%
F03 Powder				
HUP-1A	AC	HUP	95.7% (4)	NA
HUP-2A	AC	HUP	97.9% (4)	NA
HUP-3A		HUP	95.7% (4)	NA
HUP-4A	AC+TA	HUP	96.6% (4)	NA
HIP-1A		HIP	Low (6)	NA
HIP-2A	TA	HIP	89.1% (5)	8.7%
HIP-3A	HC	HIP	92.3% (5)	3.9%

(1) See text for preparation and HUP or HIP conditions, (2) Theoretical Density = 4.23 g/cm³ [11], (3) As produced powder with no further processing, (4) Density by calculated volume, (5) Density by mercury porosimetry, (6) Gas generation in HIP capsule prevented full densification.

Note that results are shown for unmodified as well as modified fluid bed powder. Pretreatment of the powder prior to densification was used to attempt to modify the product for better densification and leachability: (AC)-Additional air calcination (650°C for 16 hours) was used to reduce gas generation during densification. (HC)-Hydrogen calcination (700°C for five hours) completed calcination and reduced the powder (Mo to Mo⁺² state). (TA)-6 wt% Titanium metal powder getters the generated gas and sets the redox state of the powder.

HUP densification produced good dense parts under all conditions, probably because gas generated during densification escapes and does not interfere with densification. The graphite die used also sets the redox state of the powder. HIP densification was sensitive to gas generation and did not produce good parts with unmodified powder or air calcined powder (I-70-HIP-1A, F02-HIP-1A, F03-HIP-1A). Modifying the powder by H₂ calcination or Ti addition seemed to be equivalent. The F02 powder produced the best densities in HIP experiments while the F03 and I-70 powder produced the best densities in HUP experiments. The higher tap density of the fluid bed produced powder (40-50% TD) as compared to spray dried powder (20-25% TD) produce a smaller volume change on densification. This greatly simplifies the densification step increases the amount of waste per canister, and reduces the number of pressings required in the process[14].

Mineral Phase Characterization

Samples of fluid bed powders have been characterized by SEM techniques both prior to and after HUP densification. Backscattered electron images

before densification indicate only small variations in sample composition along the sphere radius (Figure 3A). X-ray images confirm some concentric compositional segregation [10]. The SEM images indicate some internal porosity.

In the densified HUP ceramics, the backscattered electron images indicate dramatic concentric chemical zonation (Figure 3B). Hence, hot pressing has amplified the chemical inhomogeneities present. Since XRD indicates that the predicted phases have been formed, the various rings will vary only in the relative proportions of phases present.

The brightest regions, located at the rims of every "particle" are enriched in barium and depleted in calcium relative to the rest of the material. This is in contrast to SYNROC-C microstructures from spray dried powders which show more homogeneous phases [15]. Further work is necessary to fully understand the nature of this zonation. In addition to the major SYNROC-C phases XRD studies show the alpha-alumina start-up material with some evidence of a Magneto Plumbite phase ($\text{CaAl}_{12}\text{O}_{19}$) probably formed due to the large excess of alumina. We expect a metallic molybdenum phase, but this remains to be verified. SEM studies of HIP ceramics are beginning.

Figure 3. Backscattered Electron Images of Idaho 70-hour fluid bed powder: (A) Before hot pressing each particle shows a concentric ring structure. (B) After hot pressing the densified SYNROC shows a deformed ring structure. Dark occlusions are unreacted alumina start up material. The powder was hot pressed in graphite at 1150°C , 4 KSI for one hour.

Leach Test Results

Table III summarizes the results from standardized MCC-3 leach tests that have been used to evaluate SYNROC [3]. The table compares the cesium and molybdenum leachability of fluid bed produced samples with: S27, the Reference SYNROC-D formulation for SRL composite sludge [3]; S08, the PW48 containing SYNROC-C [15] and; S0B, a SYNROC-C containing AGNS-type waste [15]. Cesium leach rates drop rapidly and after the first day are similar

for most samples while the molybdenum leach rates are somewhat higher for the fluid bed samples. The leach rates for the other simulated waste elements neodymium and gadolinium are below the detectability limits similar to S29, S08, and S38. Leach rates for barium and strontium are similar to other SYNROC-C materials.

The fluid bed ceramics, despite being less homogeneous than spray-dry produced SYNROC-C, show good leach results. This seems to indicate that the simulated radwaste elements are going into the proper phases. It also seems to indicate that fluid bed temperature has little effect on the final product. Leach results from HIP samples show high rates indicating poor phase development. The reasons for this are not clear at this time and are being investigated.

TABLE III

Results of MCC-3 Leach Tests Conducted on Crushed (150-300 μ m) Samples at 150°C

Material	Leach Rate Percent/day					
	Day 1		Day 2		Day 3	
	Cs	Mo	Cs	Mo	Cs	Mo
S29 SYNROC-D	7.6	(1)	0.4	(1)	0.3	(1)
S08 (Pw4b-waste)	0.8	1.6	0.1	0.2	0.06	0.1
S38 (AGNS waste)	0.7	2.4	0.2	0.5	0.1	0.3
I-36 HUP1A HUP	1.5	(1)	0.3	(1)	0.4	(1)
I-70 HUP1A	3.3	(1)	0.7	(1)	0.1	(1)
F02 HUP-1A	7.3	1.1	0.5	1.3	0.2	1.1
HUP-2A	9.2	2.0	0.6	1.6	(2)	(2)
F03 HUP-1A	7.0	(2)	0.5	1.0	(2)	(2)
2A	7.0	1.1	0.6	1.3	0.3	0.8
3A	9.1	2.2	0.7	0.7	0.4	0.4
4A	11.2	0.8	0.9	0.9	(2)	(2)

(1) not present in sample, (2) not measured

CONCLUSIONS

There are no fundamental problems in making SYNROC by fluid-bed calcination. In summary, our results have shown:

- o Bed operation at 500-600°C for long periods with no unforeseen problems.
- o Greater than 3/4 of the product above 200 microns, but sufficient attrition to produce the necessary seed particles.
- o Particle diameter and particle agglomeration can be controlled.
- o High tap density SYNROC powders can be made which are readily densified in HIP or HUP operation.
- o The HUP product shows dense microstructure with good SYNROC-C phase development and low leach rates typical of SYNROC.

Several questions remain to be answered:

- o The effect of reinjection of fines into the bed.
- o Bed scale-up parameters.
- o Optimum bed operating conditions to obtain good product with minimum cesium loss.
- o The HIP densification conditions needed to get good phase formation.

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