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SYNROC POWDER PREPARATION: Preliminary Fluid-
Bed Tests in a Cold-Flow Unit

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I. INTRODUCTION

SYNROC is a titanate-based material which is being developed as a medium for immobilizing high-level nuclear waste. 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. At its present stage of development, SYNROC is made in three basic formulations:

- (1) SYNROC B, a test material containing the three titanate phases only, with no waste loading.
- (2) SYNROC C, containing simulated high level commercial waste.
- (3) SYNROC D, containing simulated high level defense waste in high Iron, high Aluminum or a composite form.

The SYNROC materials have exceptionally high stability and are able to accommodate waste loadings as high as 70%, which gives them a substantial advantage over competing forms for long-term storage.

Designs for the SYNROC D production process must include the steps of additive blending with waste sludge, drying, calcination and adjustment of redox state prior to the powder hot-pressing operation in which the SYNROC minerals are formed. Figure 1 is a process flow diagram showing several options in powder processing.¹ Replacing the processing units shown in options A and B with a single fluid-bed unit as shown in option C would significantly reduce the process volume over that of a spray dryer plus calciner or a spray calciner and would also allow drying, calcining and redox control to be carried out in a single process step.

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FIGURE 1. Basic Synroc processing options. The process may be divided into three areas, i.e., slurry processing, powder processing, and mineralizing and densifying.

The use of a fluid bed unit for production of SYNROC powder has a precedent in the use of a fluid-bed calciner for high-level waste processing at the Idaho Chemical Processing Plant (Idaho Falls, ID). Considerable experience has shown the fluid-bed unit to be reliable and maintainable in a remote environment.²

In order to facilitate the design of a fluid bed and demonstrate its use for SYNROC production, we have constructed two small units, one for low temperature use and a second for actual SYNROC production at temperatures up to 800°C. The low-temperature unit is constructed with glass walls to allow observation of the fluidization process, including the onset of fluidization, bed and gas bubble behavior and mixing phenomena. We have also examined disturbances caused by side streams entering the bed. Side streams may represent fuel and oxidizer admission or slurry feed with subsequent flash vaporization of the carrier liquid.

The metal fluid bed is constructed of stainless steel and will be operated at 500-800°C to produce actual SYNROC powders. In this second apparatus we will be able to study the flash evaporation process, in bed-combustion processes and concurrent calcination and redox adjustment.

This report is a summary of the initial tests made with the low-temperature, glass-walled fluid bed. The tests described include:

- (1) The measurement of basic fluidization parameters.
- (2) Measurement of the effect of distribution-plate design on bed fluidization.
- (3) Observation of jet penetration, bubble formation and coalescence, and surface behavior.
- (4) Studies of mixing within the bed.

- (5) Determination of some of the effects of side streams on fluidization and mixing.
- (6) Correlation of the results using a simple model developed to describe fluidization processes in the test apparatus and aid in design of a full-scale process unit.

II. APPARATUS DESCRIPTION

The apparatus is shown schematically in Figure 2 and consists of a test section of 10.2-cm internal diameter by 45.7-cm height, constructed of glass pipe. A 16.2-cm internal-diameter glass disengaging section 39.4-cm high is connected to the upper end of the test section by a 6.4-cm conical adapter.

Air is admitted to the test section through an easily exchanged distributor plate mounted between the bottom of the test section and a lower plenum chamber. Distributor plates with various numbers and sizes of holes as well as porous metal plates have been used.

Feed air is metered through F1 and then warmed in a heat exchanger to 34 to 60°C in order to prevent adsorption of moisture by the bed materials. Exhaust air is filtered to remove entrained particles.

Provision has been made for admitting a metered (F2) air stream through the side of the test section to allow observation of the effects of feed-nozzle design and side-stream flow rates.

Instrumentation is quite basic and is shown in the schematic. Figure 3 is a photograph of the glass unit.

FIGURE 2. Low-Temperature Fluid-Bed Unit

FIGURE 3. Photograph of the glass fluid-bed unit.

III. FLUIDIZED BED EXPERIMENTS

Experiments have been performed in the 10-cm glass apparatus using beds of glass spheres or crushed alumina. The glass spheres had a particle density of 2.5 gm/cm^3 , and the alumina had a particle density of 3.8 gm/cm^3 . The fluidizing gas in all cases was filtered air obtained from the building compressor. All experiments were performed with reactor temperatures between 24°C and 60°C .

Incipient Fluidization Velocity

Two common definitions of incipient- or minimum-fluidization velocity exist. The first is known as the minimum bubbling velocity and is defined as the minimum-upward superficial velocity at which the pressure drop is equal to the weight of the bed.³ Under these conditions it is not uncommon for the bed particles to rearrange themselves into a looser packing arrangement and then require a slightly greater velocity to again become fully supported by the flowing fluid. This velocity can be calculated from correlations for pressure drop in fixed-bed reactors. The second incipient-fluidization velocity is known as the minimum-bubbling velocity and is defined as the minimum-upward superficial velocity at which the solids are agitated by bubbles. This second velocity is the more significant rate. Unfortunately, no adequate correlation for minimum-bubbling velocities are available. The minimum-bubbling velocity can be assumed to approximate the minimum-buoyancy velocity.

Experimental measurements of particle size, particle density, void fraction, and minimum-bubbling velocity were obtained for three sizes of glass spheres and two sizes of crushed alumina. These data are presented in Table I and are plotted against the Ergun equation^{4,5} for packed beds in Figure 4a.

TABLE I. Minimum fluidizing velocity data

All measurements were made at 60°C and 1 atm.

Particle Type	Harmonic Mean Diameter (cm)	Particle Density (g/cm ³)	+ Shape Factor	Void Fraction	Minimum Fluidizing Velocity (cm/sec)
Glass Sphere AG	.0045	~2.4	1.0	.47	.80
Glass Sphere AG	.0220	2.461	1.0	.42	2.97
Glass Sphere B	.0442	2.460	1.0	.47	16.15
Crushed Alumina 61-100	.010	3.392	.6	.54	.994
Crushed Alumina 28-48	.037	3.664	.6	.53	19.51

+ Shape factor is the area of the particle divided into the area of an equivalent sphere.

FIGURE 4a. Minimum Fluidization Velocity Correlation

It is interesting to note that the data for glass spheres appears to be scattered equidistantly on either side of the line representing the Ergun equation. The data for the alumina is shifted to the right, but a shape factor of approximately 0.6 can account for part of this discrepancy. Substituting the weight of the packing for the pressure drop in the Ergun equation and rearranging gives this expression the root of which is the minimum-fluidization velocity:

$$1.75 \rho_g \phi D_p V_{mf}^2 + 150(1 - \epsilon) \mu V_{mf} - \epsilon^3 g (\phi D_p) (\rho_s - \rho_g) = 0.$$

See reference 4 for other forms of this equation.

The equation is solved for V_{mf} (cm/sec) using the quadratic formula.

where:

D_p = mass mean particle size (cm)

ϕ = shape factor

ρ_s = particle density (g/cm³)

ρ_g = mean gas density (g/cm³)

μ = mean gas viscosity (poise)

ϵ = void fraction

g = gravitational acceleration (960 cm/sec²)

$G_o = V_{mf} \rho_g$ fluidizing gas mass flux (g/cm²·sec)

A much simpler correlation for predicting the minimum fluidization velocity has been proposed by C. Y. Wen and Y. H. Yu⁶:

$$(N_{Re})_{mf} = \left(\sqrt{(33.7)^2 + 0.0408 N_{Ga}} \right) - 33.7$$

where

N_{Re} the Reynolds number is given by

$$N_{Re} = D_p \rho_g V_{mf}/\mu$$

and

N_{Ga} the Galileo number by

$$N_{Ga} = D_p^3 \rho_g (\rho_s - \rho_g) \mu^2$$

They found an overall standard deviation of $\pm 34\%$ based on 284 points. The correlation appears to represent our data very well as shown in Figure 4b. The one point which is considerably off is for a particle diameter slightly outside the limits of the correlation.

Note that this correlation has eliminated the dependence of Φ and ϵ . For non spherical particles the particle diameter can be replaced by ΦD_p ; however for this a good approximation is to use a particle diameter determined by the geometric mean of two consecutive sieve openings.⁶ In our data, except for the smallest glass spheres, particle size has been determined by sieve analysis.

Distributor Plate/Bed Activity

Experiments using two types of distributor plates were performed on both glass and alumina beds. The first type of distributor plate was a non-porous plate drilled out with 19 discrete holes in a regular pattern that covered the cross-section of the bed. The second type of distributor plate used was a porous-metal frit. The effects of these two plates on the measured pressure drop of the bed were compared in terms of a bed-activity parameter: the dead height. The dead height is defined as:

FIGURE 4b. Minimum fluidization velocity correlation proposed by Wen and Yu.⁶

$$h_d = [1 - \Delta P_{\text{exp}} / \Delta P_{\text{calc}}] h_{\text{bed}}$$

where:

ΔP_{exp} = the experimental bed-pressure drop. (cm-H₂O)

ΔP_{calc} = the bed-pressure drop calculated from the bed weight. (cm-H₂O)

h_{bed} = the height of the bed. (cm)

Physically, the dead height represents the depth of bed near the distributor plate that is not fluidized. This region is not fluidized because it is bypassed by the jets of gas from the distributor plate that penetrates deeply into the bed. The height is minimized in good design. The data for the discrete hole-type plate is presented in Figures 5a, 5b, and 5c. The pressure drop across the distributor plate and the pressure drop in the bed both influence the gas distribution at the plate. Increasing the pressure drop across

the plate enhances the gas distribution. Figure 5a indicates the presence of maldistribution at the plate by showing that the dead height increases with increasing bed weight (and therefore, increasing bed-pressure drop). This conclusion was verified in the laboratory by the direct observation that two of the nineteen holes were plugged during that run. The opposite trend for bed height with increasing bed weight is observed in Figures 5b and 5c indicating that all the holes are flowing during those runs. In all of the runs for the discrete-hole distributor plate the dead height was observed to be increasing with increasing velocity. If allowances are made for maldistribution and the height of the pressure tap above the distributor plate, this increase in dead height with increasing velocity correlates reasonably with the gas jet penetration at the plate:

$$\frac{P}{D_0} = 33.34 \log_{10} (V_0 \sqrt{\rho_g}) - 61.25$$

Figure 5a

Contour Plot of Dead Height for a Fluidized Bed using a 19-hole Distributor Plate with 0.16-inch Holes. Bed contains Glass Beads 270 μ m in diameter.

Figure 5b

Contour Plot of Dead Height for a Fluidized Bed using a 19-hole Distributor Plate with .055 inch Holes. Bed Material was 525 μ m Diameter Glass Beads.

Figure 5c

Contour Plot of Dead Height for a Fluidized Bed Using a 19-Hole Distributor Plate with .055 inch Holes. Bed Material was 408 μ m Diameter Alumina Particles.

where:

P = jet penetration length (cm)

D_o = orifice diameter (cm)

V_o = superficial velocity through orifice (cm/sec)

ρ_g = gas density upstream of orifice (gm/cm^3)

This data is presented in Figure 6. The reason for this is that the bed material between the gas jets would be partially or wholly supported by the distributor plate rather than the fluidizing gas.

The data for the sintered metal distributor plates are presented in Figures 7a, 7b, and 7c. Some maldistribution is present in Figure 7a at the lowest velocity, but all other data for the sintered metal plate show decreasing dead heights with increasing bed weight. All of these data show decreasing dead heights with increasing gas velocities (distributor-plate pressure drops), but the magnitude of these dead heights is much less than those for the discrete-hole plates. The sintered metal-plate dead heights are practically equal to the height of the pressure top above the plate, and the entire bed may therefore be assumed to be active.

Side-Stream Vapor Load

The effect of introducing a gas side-stream into a fluidized bed was investigated using a bed of glass beads. Side-streams with narrow-coherent jets, and therefore high-jet velocities, were found to be unstable only for small diameter beds because these streams could penetrate the entire diameter of the bed and impinge on the far wall of the reactor. This instability was not investigated thoroughly because it was determined that side-streams with diffuse-jet patterns (flat cone) did not greatly disturb the bed, although enhanced solids mixing was observed above the point of side-stream

FIGURE 6. Comparison Between Jet Penetration, and Dead Height from Bed-Pressure Drop Data

Figure 7a

Contour Plot of Dead Height for a Fluidized Bed Using a Sintered Metal Distributor Plate. Bed Material was 270 μ m Diameter Glass Beads. (Pall Trinity Micro Corp. Grade H.)

Figure 7b

Contour Plot of Dead Height for a Fluidized Bed Using a Sintered Metal Distributor Plate (Pall Trinity Micro Corp. Grade G). Bed Material was 525 μ m Diameter Glass Beads.

Figure 7c

Contour Plot of Dead Height for a Fluidized Bed Using a Sintered Metal Distributor Plate (Pall Trinity Micro Corp. Grade G) Bed Material was 408 μ m Diameter Alumina.

introduction. Side-streams of up to 40 l/min of air in a 10-cm reactor were found to be feasible as long as the side-stream was introduced at least 10 cm below the bed surface. This rate is the same order of magnitude as the air rate used to fluidize the whole bed.

Mixing Characteristics

The mixing behavior of the solids in a fluidized bed was investigated by loading the reactor with two layers of differently-colored material which were subsequently fluidized. The mixing of these two colors was recorded photographically. Figure 8 shows a photo of the unmixed bed containing glass spheres. Figure 9a is a photo of the bed during Test 2 after approximately three seconds showing the mixing occurring in the bed; Figure 9b shows the same bed after nine seconds. The bed looks completely mixed. Table II gives a summary of the mixing experiments. In all cases the mixing of the glass spheres was observed to be very rapid. The total time required to completely mix the two zones was less than 10 seconds when using fluidizing velocities of only $(1.5)V_{mf}$. The mixing of the crushed alumina was observed to be slower. With gas velocities greater than $(2)V_{mf}$ the two zones were not quite completely mixed even after one minute of mixing. This could be a result of either the difference in particle shape and/or the difference in particle density between the glass and the alumina particles.

Similar experiments were conducted when a side-stream of 40 l/min of air was introduced into the fluid bed. The only observed difference being that the region of the bed above the side-stream mixed more rapidly than that below the side-stream. The side-stream had no discernible effect upon the region of the bed below it. All mixing experiments were performed on beds with heights of approximately 30 cm.

FIGURE 8. Photograph showing unmixed bed of glass beads.

FIGURE 9a. Photograph of fluidized bed at three seconds. Glass-bead particle diameter is .0525 cm and gas flow is $2.0 \times V_{mf}$.

FIGURE 9b. Photograph of fluidized bed at 9 seconds.

TABLE II. Mixing experiments (no side-stream)

Experiment	Material	D_p (cm)	ρ_p (gr/cm ³)	V_{mf} (gr/cm ² sec)	V_f/V_{mf}	Mixing time (sec)
1	glass	.0525	2.49	.0171	1.6	10
2	glass	.0525	2.49	.0171	2.0	5
3	glass	.0525	2.49	.0171	3.0	< 2
4	alumina	.0408	3.78	.0207	1.3	>60
5	alumina	.0408	3.78	.0207	1.7	>60
6	alumina	.0405	3.78	.0207	2.3	60

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APPENDIX

FLUID-BED PRESSURE DROP DATA

PRESSURE DROP DATA

Gas Velocity (cm/sec)	Bed Weight (gr)	ΔP (in H ₂ O)	Height (cm)
1) 270 micron diameter glass beads; 19 x .016-inch hole distributor plate.			
3.62	1700	6.85	14.5
3.62	1999	8.15	17.0
3.62	2301	9.50	19.6
3.62	2601	10.90	22.1
3.62	2901	11.85	24.9
3.62	3201	13.20	27.4
4.53	1800	6.70	15.5
4.53	2099	8.00	18.0
4.53	2400	9.35	20.6
4.53	2700	10.75	23.2
4.53	3001	12.10	25.9
5.40	1904	7.15	16.3
5.40	2204	8.50	19.0
5.40	2505	9.80	21.8
5.40	2806	10.95	24.5
5.40	3107	12.25	27.3

2) 270 micron diameter glass beads; Grade H sintered metal distributor plate.

3.62	1718	7.6	14.7
3.62	2502	11.35	21.2
3.62	3318	15.2	28.6
4.53	1718	7.65	14.7*
4.53	2502	11.6	21.2*
4.53	3318	15.75	28.6*
5.40	1718	7.9	14.7*
5.40	2502	11.75	21.2*
5.40	3318	15.8	28.6*

*estimated

PRESSURE DROP DATA (Cont.)

Gas Velocity (cm/sec)	Bed Weight (gr)	ΔP (in H ₂ O)	Height (cm)
3) 525 micron diameter glass beads; 19 x .055-inch hole distributor plate.			
21.74	1539	6.25	14.2
21.74	2284	9.75	21.0
21.74	2784	12.25	25.8
21.74	3475	16.0	--
24.85	1539	6.25	14.7
24.85	2284	9.75	21.5
24.85	2784	12.25	26.4
24.85	3475	16.0	--
27.93	1539	6.0	15.0
27.93	2284	9.75	22.2
27.93	2784	12.25	27.3
27.93	3475	16.0	--
31.04	1539	6.0	15.3
31.04	2284	9.50	22.8
31.04	2784	12.25	28.0
31.04	3475	15.75	--
4) 525 micron diameter glass beads; Grade G sintered metal distributor plate.			
21.74	1885	8.75	18.2
21.74	2529	12.0	24.1
21.74	3269	16.0	30.5
21.74	4031	20.0	--
24.85	1885	8.90	18.4
24.85	2529	12.25	24.9
24.85	3269	16.0	30.9
24.85	4031	20.25	--
27.93	1835	9.0	19.1
27.93	2529	12.5	25.6
27.93	3269	16.25	--
27.93	4031	20.50	--
31.04	1885	9.0	19.5
31.04	2529	12.5	26.0
31.04	3269	16.5	--
31.04	4031	20.5	--

PRESSURE DROP DATA (Cont.)

Gas Velocity (cm/sec)	Bed Weight (gr)	ΔP (in H ₂ O)	Height (cm)
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5) 408 micron diameter alumina particle; 19 x .055-inch hole distributor plate

21.74	2800	10.5	20.3
21.74	4482	20.75	--
21.74	5723	27.5	--
24.85	2800	10.25	20.9
24.85	4482	20.5	--
24.85	5723	27.25	--
27.93	2800	10.25	21.4
27.93	4482	20.5	--
27.93	5723	27.0	--
31.04	2800	10.25	21.4
31.04	4482	20.25	--
31.04	5723	26.75	--

6) 408 micron diameter alumina particle; Grue G sintered metal distributor plate.

21.74	2246	10.5	16.1
21.74	3346	16.0	23.8
21.74	4055	19.75	29.0
21.74	5399	26.25	--
24.85	2246	10.75	16.8
24.85	3346	16.25	24.6
24.85	4055	19.75	29.6
24.85	5399	26.50	--
27.93	2246	10.75	17.2
27.93	3346	16.50	25.8
27.93	4055	20.0	30.3
27.93	5399	26.5	--
31.04	2246	10.75	17.7
31.04	3346	16.50	26.2
31.04	4055	20.25	--
31.04	5399	26.75	--