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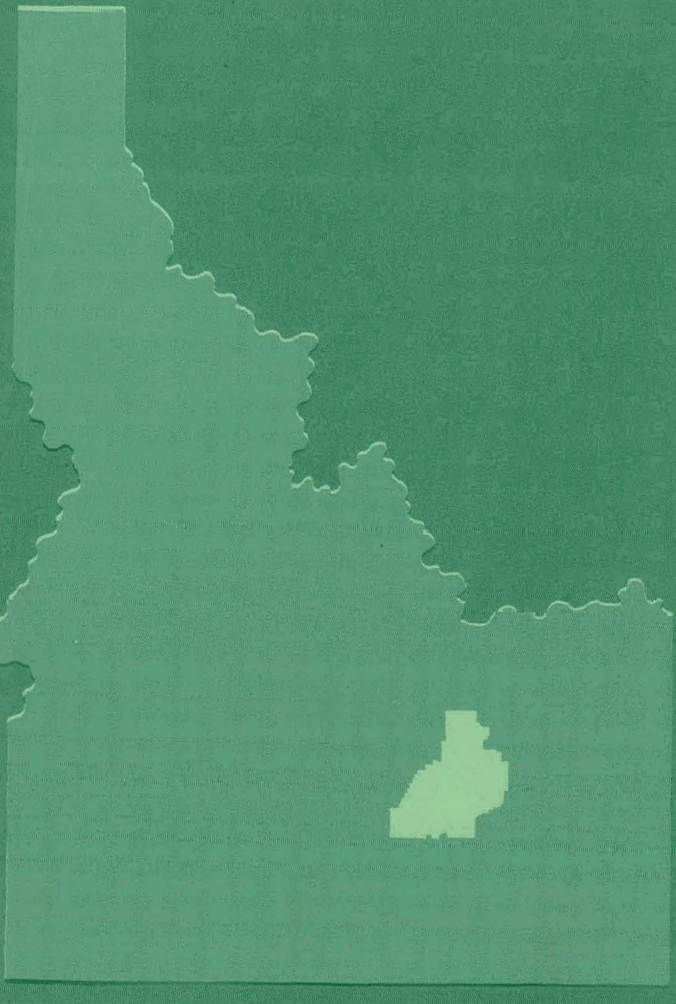
IDAHO CHEMICAL PROCESSING PLANT
TECHNICAL PROGRESS REPORT
RADIOACTIVE WASTE DISPOSAL PROJECTS

July - September 1959

July 22, 1960



PHILLIPS PETROLEUM COMPANY

ATOMIC ENERGY DIVISION

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IDAHO CHEMICAL PROCESSING PLANT

TECHNICAL PROGRESS REPORT
RADIOACTIVE WASTE DISPOSAL PROJECTS
JULY-SEPTEMBER 1959

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I. ABSTRACT

The progress of extensive laboratory and pilot plant investigations on the fluidized bed process for the conversion of radioactive liquid wastes to solids is reported. These studies are directed toward obtaining information on the dynamics of fluidized bed operation, the removal of volatile fission products and solids particles from gases, the development of equipment and operating techniques, and the various long term disposal aspects of all radioactive wastes.

Laboratory studies on the removal of volatile ruthenium from a simulated calciner off-gas showed the removal efficiency of silica gel to decrease with successive wetting and drying cycles. Electrostatic precipitators were found to have a higher removal efficiency for solid particles (alumina) when a wetted wall rather than a dry wall type was used.

Tests to determine the distribution of ruthenium in a pilot plant calciner were performed. Pilot plant data on particle growth in a fluidized bed were compared with theoretical equations. Operating experience with a NaK heat transfer system, and with liquid flow controllers is reported. The results of a series of qualitative tests to determine the likelihood of an explosive reaction should NaK leak into a fluidized bed calciner indicated that such a reaction is unlikely. A NaK leak that occurred at a welded junction was attributed to thermal overstressing of the metal and not due to corrosion. Calcium fluoride-impregnated Teflon was found to be a superior gasketing material, both chemically and mechanically, to pure Teflon.

A literature survey on the chemistry of zirconium in a calcination process suggested the possibility of calcination in contact with silica and a laboratory unit is being installed to study the process. The hydraulics of a pulsed plate solids-liquid contactor and its associated equipment were determined. A preliminary investigation was started of the possibility of using metallizing techniques to surface coat solid particles and thereby reduce the leaching of fission products when contacted with ground water.

Construction of a demonstrational fluidized bed calciner was approximately half completed; however, the national steel strike has slowed the construction schedule and the completion date cannot be estimated until the strike is settled. Process and equipment reviews of the facility and the results of thermal conductivity measurements on Idaho sands are reported.

II. SUMMARY

Laboratory and pilot plant work on the disposal of radioactive wastes was concentrated on the fluidized bed technique of reduction-to-solids and its associated problems. The work carried out during the reporting period defined further the operability limitations of equipment and materials of construction, the complex interrelationship of process variables, and the effects of operating techniques upon process components as well as determining the efficiencies and capacities for various process components. Review of engineering designs and plant construction of a Demonstrational Waste Calcining Facility was continued.

A. Research and Development in Laboratory and Pilot Plant

The use of D/P cell transmitters equipped with integral orifices in place of rotameter type controllers in the liquid feed stream to the six-inch diameter calciner resulted in smoother operation. A NaK leak in the heat exchanger for the two foot square calciner was determined to be the result of a transgranular crack in the welded zone which was presumed to have been caused by thermal overstressing of a poorly designed header. The heat exchanger is being redesigned. Qualitative tests which were conducted to determine the effect of NaK leaking into a fluidized bed calciner demonstrated that an explosive reaction was unlikely, since no rise in pressure could be detected by a 0-50 psi pressure transducer and high speed recorder. The use of a powder-metallizing gun in a fluidized bed to produce an impervious coating on the calcined particles is being considered as a means of immobilizing soluble fission products in the calcine.

Synthetic waste containing 6.6N nitric acid and 0.017 milligram per milliliter of ruthenium traced with ruthenium-106 was decomposed at 400°C to provide a simulated off-gas for laboratory test of the effectiveness of silica gel for ruthenium removal. Silica gel which had gone through ten wetting and drying cycles, thereby having its absorptive capacity for water vapor reduced from 40 to 30 percent on a dry weight basis, was tested for ruthenium removal efficiency. The average decontamination factor for the as-received silica gel was 164 while for the aforementioned silica gel was from 11 to 22; however, wide limits were found for the standard deviation in all tests. It was concluded that the effectiveness of silica gel as a ruthenium adsorbent will decrease with number of washing and drying cycles although it is not expected to have a significant effect in the operation of the Demonstrational Waste Calciner. The evaluation of a test to determine ruthenium distribution in pilot plant equipment using a ruthenium spike is awaiting analytical results.

A wetted wall electrostatic precipitator operated with a potential of approximately 20 kilovolts and a residence time of 3.98 seconds gave a removal efficiency of over 99 percent for particles larger than 0.3 micron and 93.8 percent for particles smaller than 0.3 microns. For dry wall operations at a potential of 24 kilovolts the efficiency was over 97 percent and 86.8 percent, respectively. It was concluded that the removal efficiency of an electrostatic precipitator for alumina particles was in the range predicted by theory and that wetted-wall operation is more efficient than dry wall operation even at a lower voltage. Theoretically, it is possible to predict the typical S-shaped curve for particle size versus weight for the calciner product from feed rate, weight of bed, seed rate and diameter, density and particle growth rate. However, the correlation between the theoretical equation and meager experimental data is not good.

Pulsed-plate solids-liquid contactors such as might be used for leaching fission products from calcined solids were incorporated into a process flow scheme. This scheme uses air lifts to remove the slurry at the bottom of the contactor and transport it to a separator for removal of the liquid. The performance curve for a ½ inch diameter air-lift showed it to have a capacity in excess of 2.25 liters per minute at air flow rates between 0.3 and 0.75 scfm and to be practically independent of the solids flow rates between 30 and 75 grams per minute. As the air flow rate was increased from 0.75 to approximately three scfm at the above solids rates the slurry capacity decreased linearly with the greatest decrease found for the highest rate of solids transport.

The resistance of a calcium fluoride-impregnated Teflon gasket material (Garlock 9428) to chemical service is greater than for the materials presently used at the ICPP. Estimated thermodynamic functions appear favorable for calcining fluoride containing zirconium wastes with silica. An apparatus is being constructed to evaluate experimentally the feasibility of the proposed reactions.

B. Waste Calcining Facility

Construction of a 60 gallon per hour demonstrational fluidized bed calcining facility for high level aluminum type wastes is approximately 45 percent complete. Completion of the facility originally estimated as February, 1960, will be deferred an unknown length of time because of the national steel strike.

Engineering review of construction drawings and specifications continues to demand considerable time. Inspection of high efficiency filters of the AEC-type disclosed deficiencies, e.g., tears, severe curvature of the media, etc., such as found by many other AEC contractors.

During the development of conceptual designs for a High Temperature Demonstrational Solids Storage Facility it became apparent that a greater knowledge of the thermal conductivity of locally available sands would be necessary. Therefore, thermal conductivity measurements were made on Idaho windblown and pit-run sand with the following results:

Idaho windblown sand - $k = 0.136 + (1.04 \times 10^{-3}T)$
Idaho pit-run sand - $k = 0.208 + (6.3 \times 10^{-4}T)$

where k and T are Btu/(hr)(ft^2)(°F/ft) and °F, respectively. These values were found to be essentially independent of pressure between 0 and 50 psig.

III. RESEARCH AND DEVELOPMENT IN LABORATORY AND PILOT PLANT

A. Equipment Operation and Development

During the reporting period the ruthenium adsorption equipment(18,22,25) was operated routinely in a series of experiments. Equipment is being assembled to construct a laboratory calciner for work on zirconium wastes containing fluorides.

The operation of the 6-inch diameter electrically heated fluidized bed calciner was improved significantly by replacing the rotameter-type controllers on the liquid feed stream with D/P cell transmitters equipped with integral orifices. The rotameter controller tended to stick momentarily, causing a surge in the feed stream and contributing to caking in the bed and to poor heat transfer, which in turn caused overheating and resulted in the destruction of many electrical heaters. Since the installation of the D/P cell controller, calciner operation has been improved in several ways: (1) the static pressure above the bed has been subject to less fluctuation, (2) the screen size of the product has been subjected to less cyclic variation, and (3) heat transfer has improved as evidenced by the fact that heater destruction has been eliminated for long periods of operation.

A leak occurred in the NaK heat exchanger of the two foot square calciner during the seventy-third start-up of the system. Prior to this leak the system had been operated for 2280 hours above 1000°F and 600 hours below. The crack occurred at the point where the first of twelve Carpenter-20 alloy tubes was welded to a manifold of stainless steel type 316. The NaK loop was dumped, the crack repaired by welding, and the calciner put back into operation. After three start-ups and 60 hours of service, a leak was detected at the point where the twelfth tube was welded to a tube sheet of similar composition; i.e., Carpenter-20 alloy. Following the second leak, the coil and a short section of the loop were removed for metallurgical examination. Both fractures in the coil were preceded by operation of the loop at the boiling temperature of the NaK. It has been observed that boiling reduced the overall pumping efficiency by approximately 20 percent and caused considerable vibration of the loop components. No one single factor can be isolated as the cause of the tube fractures but it is believed that the many thermal cycles imposed on a coil of poor thermal design was the primary cause of failure. A redesigned coil has been fabricated and the loop is being reassembled. Modifications in the fluidizing air system for this calciner will make it possible to use either high pressure air to operate a jet for recycle of solids to the bed and fluidize the bed or use low pressure air for the fluidization.

A 12-inch diameter calciner is being designed to replace the 6-inch unit. The larger unit should provide a more flexible experimental tool and eliminate many of the fluctuations in the 6-inch diameter unit which are attributable to its small size. The 12-inch diameter calciner is being designed as a prototype for a hot pilot plant. This unit and its auxiliaries should permit determination of (1) the effects of recycle of off gas as the fluidizing media, (2) the effect of subatmospheric pressure on the calcination process, (3) the relative value of steam versus air fluidization, (4) the effect of feed nozzle position, (5) the effect of various types of fluidizing air distributors, and should allow study of the pneumatic transport of calciner product from the calciner to a simulated storage area. Detailed design of the unit is under way and tests are being made on auxiliary equipment as well as on components of the calciner. For example, a perforated air distribution plate containing 3/16-inch diameter holes on a $1\frac{1}{4}$-inch triangular pitch has been fabricated and appears to give a much more uniform fluidization than was achieved by the bubble cap distributor plate.

A three-inch diameter glass column equipped as shown in Figure 1 was erected in a remote area to determine the effect of a NaK leak into a fluidized bed of calcined alumina under various conditions. Motion pictures were taken of a portion of the tests.

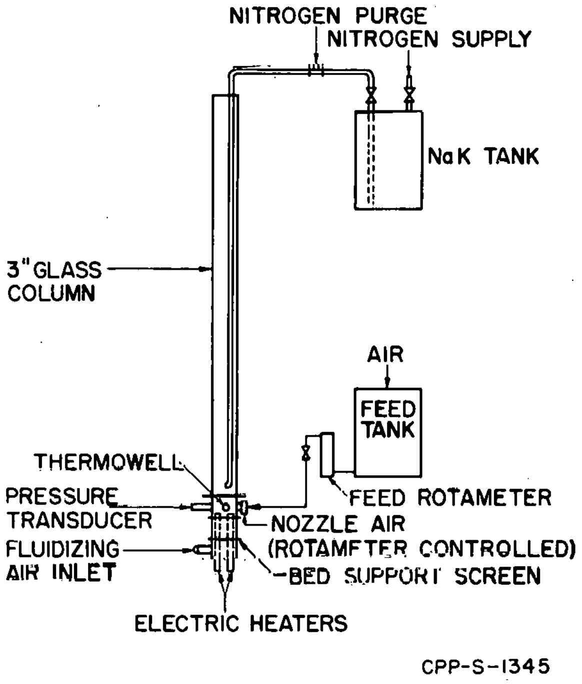

Fig. 1 - Equipment for Determining Effect of NaK Leakage Into A Fluidized Bed of Alumina

An electrostatic precipitator shell having a 4.00 inch inside diameter and a probe length of 14.5 inches was installed and a commerical power pack capable of 40,000 volts potential was obtained. Initial tests of this equipment indicate a potential of 25,000 volts should be attainable for appreciable periods of time when the unit is operated as a wetted-wall precipitator. In an attempt to obtain increased removal efficiency at lower voltages for submicron alumina particles from air another electrostatic precipitator was operated with dry Dowex-50 ion exchange resin being fluidized in the shell. Efficiency at the maximum voltage attainable without short circuiting (400 volts) was only 60 percent. The plates of the cascade impactor used for downstream sampling collected large amounts of the resin, thereby making accurate measurements impossible and the test was terminated.

Shake down runs on a four-inch diameter pulsed-plate liquid-solids contactor were made with calcined alumina and water. These runs were generally good except for occasional dumping of the calcine from one or more of the beds. This unstable action would start, most frequently, on a bed about half way up the column, although it has started at one time or another on every bed, and would progress down the column. The beds above were not affected, but the affected beds were left with only about one-fourth of the volume filled with calcine. This phenomenon was thought to be caused by insufficient seal depth of the downcomer in the bed of calcine contained on this plate. In an effort to correct this instability and to add additional measuring devices, the column was disassembled and the following changes made:

(a) The bed dimensions were changed to increase the downcomer seal depth from a $\frac{1}{2}$ inch to 1 inch. Figure 2 shows the new bed dimensions.

(b) The glass column was replaced with an acrylic column so that the column could be tapped, thereby permitting differential pressure drop measurement of a greater precision to be made.

(c) Air and liquid rotameters were added on the slurry air lift for determining performance.

The shakedown tests were continued after the column was reassembled and operation was satisfactory. The changes made in the bed dimension seem to have corrected the dumping of the alumina.

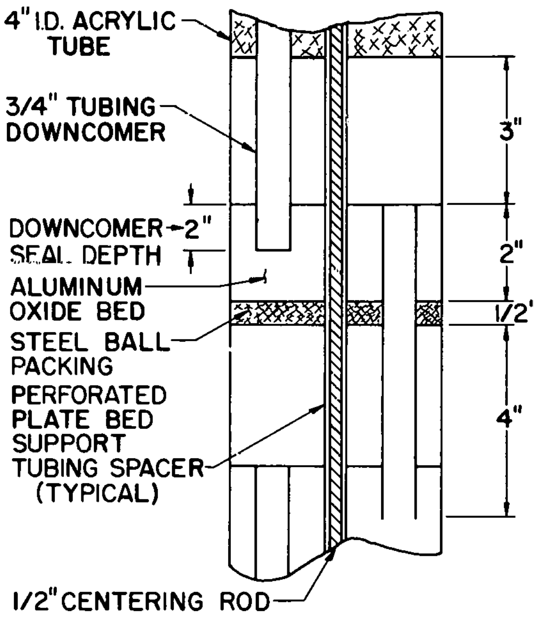

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Fig. 2 - Details of Four-Inch Diameter Liquid-Solids Contactor for Leaching of Calcined Solids

Air lifts were used successfully for continuous removal of the slurry discharged from the liquid-solids contactor. Since air lifts will perform continuously, are mechanically simple, and provide reliable remote operation they are desirable from both a process and operational viewpoint. Therefore, rotameters were installed to measure the air and liquid flows in order to determine the performance of these air lifts.

Several possible methods for treating calcined aluminum oxide waste to reduce leachability were investigated. One method is the application of metal or ceramic coatings from a powder-metallizing gun in a fluidized bed followed by a heat treatment of the particles to produce an impervious coating. A second method is an adaptation of the ORNL flame-calcination process to granular solids having the particle size characteristic of calcined aluminum type waste, in which the surface would fuse and reduce the number of surface pores, thereby reducing fission product leachability. Scoping tests are planned for the first method.

B. Process Studies

1. Off-Gas Problems

A high removal efficiency for both solid particles and volatile fission products from the Waste Calciner off-gases will be required before these gases can be released to the environment. Research on the removal of a volatile ruthenium species by a solid adsorbent (silica gel) and on the removal of solid particles by scrubbing, precipitation, etc., is in progress.

a. Ruthenium Adsorption by Silica Gel, D. W. Rhodes, Problem Leader; D. R. Anderson

Synthetic waste containing 6.6N nitric acid and 0.017 milligram per milliliter of ruthenium traced with ruthenium-106 was pumped continuously into a calciner tube, which was maintained at a temperature of approximately 400°C. Preheated air was introduced into this calciner and the off-gas was passed through a column containing 3 parts of 8-10 mesh Davison Grade 40 silica gel to 1 part of Davison indicating 6-16 silica gel. A sample of the same type of silica gel, which had been subjected to ten cycles of water vapor saturation and dehydration, thereby making the gel more resistant to decrepitation, was also used for the ruthenium adsorption studies. A caustic scrubber downstream from the silica gel column collected any ruthenium passed by the column, the concentration of ruthenium in this solution was determined by a gamma counting technique.

The results of these experiments indicate that ten successive wetting and drying cycles prior to the ruthenium adsorption cycle reduced the ruthenium decontamination factor of the silica gel to approximately one-tenth of its value in the as-received gel. The only known property of the silica gel that was altered by the wetting and drying cycles was its ability to absorb water. The absorption of water was reduced from 40 to 33 percent on a dry-weight basis as a result of the ten wetting and drying cycles; however, this apparent reduction of surface area is insufficient to account for the lower ruthenium adsorption. Rather, the lessened effectiveness for adsorbing ruthenium is suspected to be due more to a change in the type of surface available than a reduction of total surface area. The investigation of ruthenium adsorption by silica gel using the laboratory continuous calciner is being discontinued since the limit of its usefulness has been reached.

b. Ruthenium Distribution Determined in Pilot Plant Equipment, E. S. Grimmett, Problem Leader; B. R. Wheeler

A second run was made in the 6-inch diameter calciner with a ruthenium spike to determine the distribution of the ruthenium between the solids and the off-gas system since the first run, at a lower ruthenium concentration, was inconclusive because of poor material balances. Evaluation of the run is awaiting analytical results.

c. Removal of Solids From Off-Gases, E. S. Grimmett, Problem Leader; E. Hylsky

The studies on the use of an electrostatic precipitator to remove submicron alumina particles were extended to a previously described larger unit and runs were made with both dry and wetted-wall operation. The results are shown in Table 1.

Table 1

EFFICIENCY OF ELECTROSTATIC PRECIPITATOR

Type	Voltage (Kilovolts)	Length of Run (Hours)	Residence Time (Seconds)	Average Inlet Loading (gms/ft^3)	Removal Efficiency (Percent)
Dry Wall	24.5-25.5	6.7	3.98	(3 micron and less) 5.1×10^{-4}	97.7
				(1.2 micron and less) 5.0×10^{-4}	97.3
				(0.3 microns and less) 7.4×10^{-5}	86.8
Wetted Wall	19.5-20.5	55.1	3.98	(3 micron and less) 9.75×10^{-4}	99.3
				(1.2 micron and less) 6.62×10^{-4}	99.1
				(0.3 micron and less) 1.89×10^{-5}	93.8

2. Fluidized Bed Dynamics, E. S. Grimmett

Since particle size distribution of the calciner bed, and therefore of the product, is one of the more important dependent variables, a mathematical equation was derived for the relationship between particle size distribution and some of the operating variables. This equation, which is presented in an earlier report,(19) is:

$$A = \frac{S_o \pi \rho_p}{6Fa^3} \left[\left\{ 6 + 6\,al_o + 3(al_o)^2 + (al_o)^3 \right\} - \left\{ \frac{6 + 6\,al_t + 3\,(al_t)^2 + (al_t)^3}{e^{a\,(l_t - l_o)}} \right\} \right] \qquad (1)$$

Where

A = cumulative weight fraction of solids
F = equivalent solids feed rate, grams/hour
W = weight of bed, grams
S_o = number of seed particles entering the bed, number/hour
g = particle growth rate, cm/hour
ρ_p = density of particles, grams/cc
a = the function $\frac{F}{gW}$
l_o = diameter of seed particle, cm
l_t = the largest particle size in any specified cumulative weight fraction, cm

For a given feed rate assume that the system reaches steady state conditions. Assume further that the size of the seed particles is so small that equation (1) reduces to:

$$A = \frac{S_o \pi \rho_p}{6Fa^3}\left[6 - \frac{6 + 6al_t + 3(al_t)^2 + (al_t)^3}{e^{al_t}}\right] \qquad (2)$$

Now when $l_t \rightarrow \infty$, A is equal to unity and the equation becomes

$$A = \frac{S_o \pi \rho_p}{Fa^3 6}(6) = 1 \qquad (3)$$

therefore the group

$$\frac{S_o \pi \rho_p}{Fa^3 6} = 0.166 \qquad (4)$$

Now substitute equation (4) into equation (2) to get

$$A = .166\left[6 - \frac{6 + 6\,al_t + 3(al_t)^2 + (al_t)^3}{e^{al_t}}\right] \qquad (5)$$

From this it can be seen that the cumulative fraction, **A**, is a function of a and l_t. Since for any given run the value for a is constant, the cumulative size distribution obtained from that run can be predicted if a is known. This is illustrated in Figure 3, where cumulative fraction versus l_t is plotted for a number of different values of a. It will be noted that at large values of a the prediction is for small particle sizes as well as narrow size distribution ranges.

Equation (3) can be rearranged to show that:

$$\frac{S_o \pi \rho_p}{Fa^3} = 1 \qquad (6)$$

or

$$a = \sqrt[3]{\frac{S_o \pi \rho_p}{F}} \qquad (7)$$

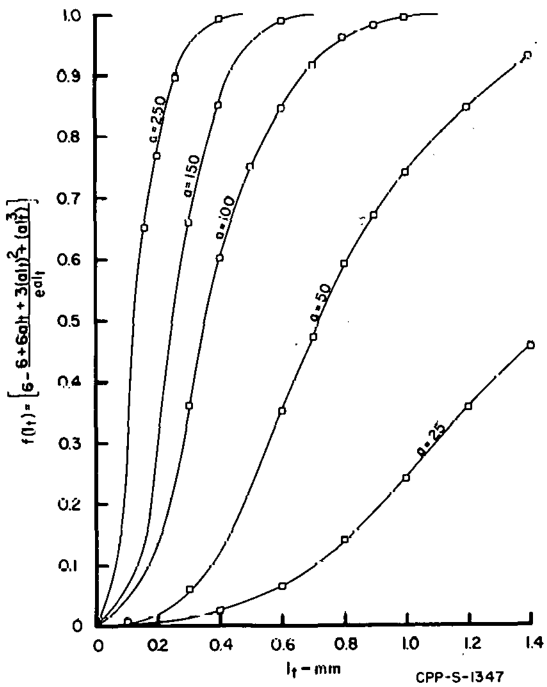

Fig. 3 - The Effect of the Function a on Particle Size Distribution in a **Fluidized Bed** Calciner

Examination of this equation shows that a, or the particle size distribution, is dependent only upon the feed rate and the number of seed introduced into the bed per unit of time. A plot of equation (7) is shown in Figure 4, with a plotted versus the feed rate, with S_o as a parameter, and ρ_p assumed to be 1.8.

Iron instead of the previously used manganese was utilized in a chemically **traced** run to determine particle growth rate. Curves comparing the actual particle size distribution found in the calciner with calculated values for three runs are shown in Figures 5, 6 and 7. In all cases l_o was assumed to be zero. Although the calculated curves do not coincide with the experimental ones, it will be noted that the experimental curves have the same general shape and shift into the correct area.

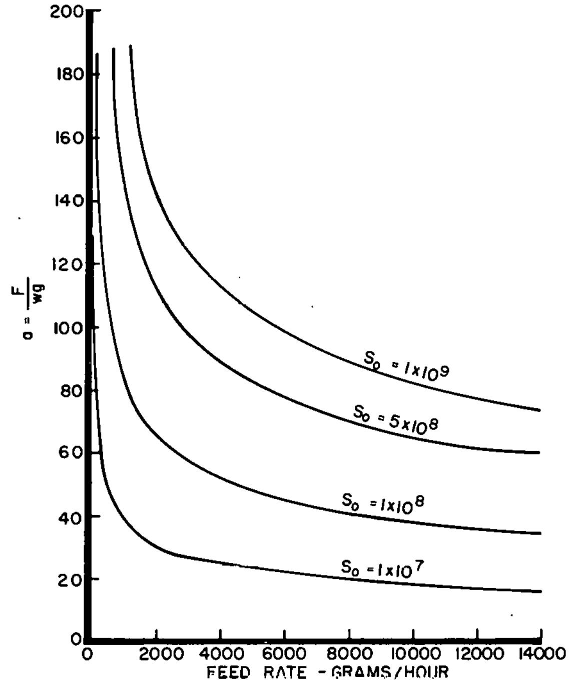

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Fig. 4 - The Effect of Seed Particle Rate, S_o, and Feed Rate, F, in a Fluidized Bed Calciner on the Function a

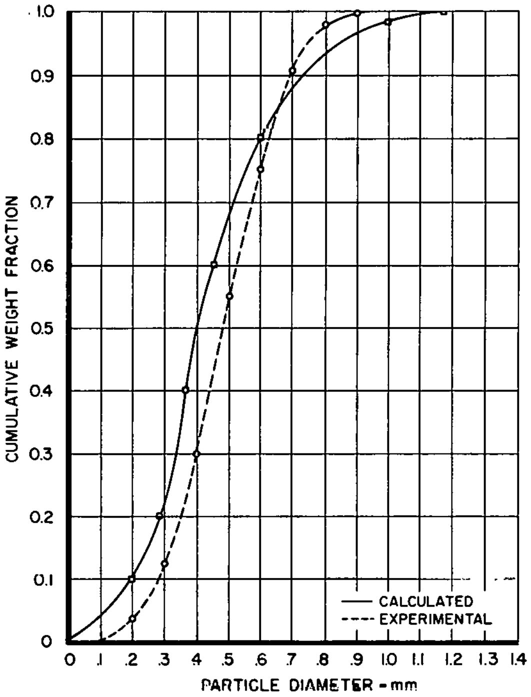

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Fig. 5 - Calculated vs Experimental Particle Size Distribution for Calciner Run SA-1, Feed Nozzle Air-to-Liquid Ratio = 505

Table 2 shows the calculated number of seed entering the bed per hour as well as the calculated number of seed entering the calciner

Table 2

SOME RESULTS OF THREE 100 LITERS PER HOUR CALCINER RUNS

	SA-1	SA-2	SA-2R
Seed Rate, S_o, - number/hour	4.4×10^8	3.05×10^8	1.44×10^7
S_o/hour	5.5×10^7	3.8×10^7	1.8×10^6
A	90.4	72	25.8
Feed Nozzle - $\frac{\text{Air Volume}}{\text{Liquid Volume}}$	505	410	270

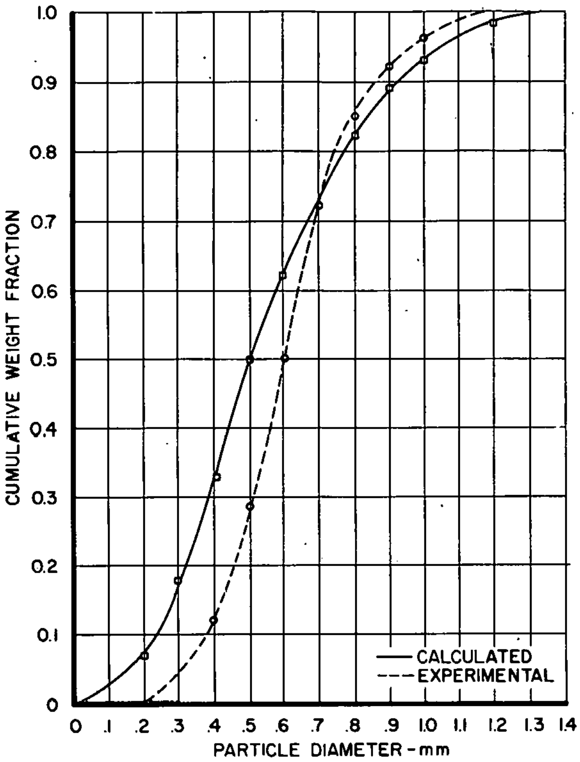

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Fig. 6 - Calculated vs Experimental Particle Size Distribution for Calciner Run SA-2, Feed Nozzle Air-to-Liquid Ratio = 410

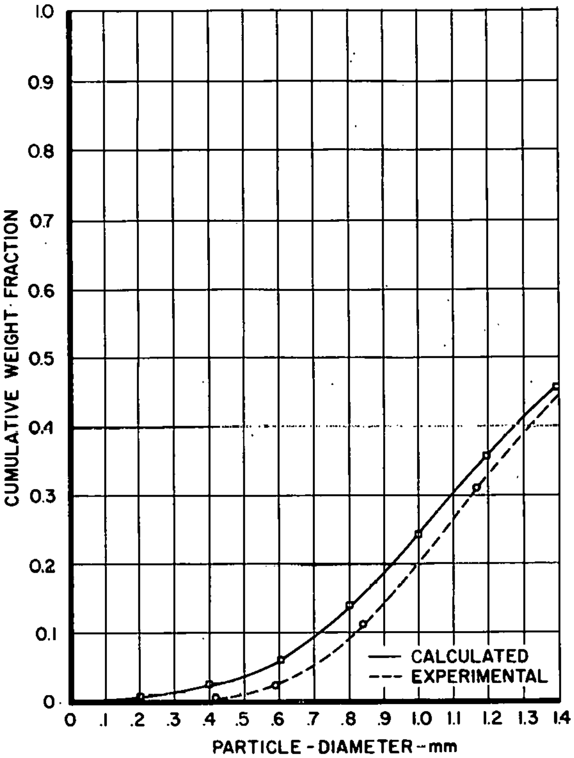

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Fig. 7 - Calculated vs Experimental Particle Size Distribution for Calciner Run SA-2R, Feed Nozzle Air-to-Liquid Ratio = 270

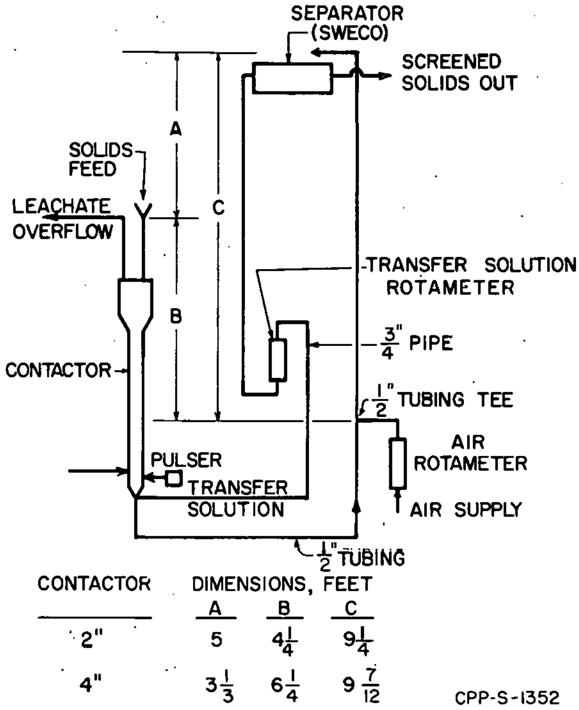
per cubic foot of bed, the values of a, and the ratio of feed nozzle air volume to feed volume. It will be noted that run SA-2R had a much smaller seed rate than the other two runs and that the average particle size is larger, as would be expected. Inspection of Table 2 will indicate a general trend to the relationship between the seed rate and feed nozzle air to feed volume ratio.

3. Handling and Disposal of Solid Product

a. Leaching, E. S. Grimmett, Problem Leader; B. P. Brown

The pulsed plate solids-liquid contactors were incorporated into a process flow scheme as shown in Figure 8. The leached solids progressing down the contactor are transferred as a slurry from the contactor bottom to a Sweco Separator. This continuously screens the slurry, discharging the screened solids and returning the slurrying solution through a rotameter to the bottom of the contactor. The air addition device for the air-lift was a standard $\frac{1}{2}$-inch tubing tee with air bled into the side inlet.

When determining performance of the air lift, suction and discharge heads, pulse frequency and amplitude were held constant. During testing a solids rate was set and the air rate varied to determine the curves shown in Figure 9. The reference curve is the



CONTACTOR	DIMENSIONS, FEET A	B	C
2"	5	$4\frac{1}{4}$	$9\frac{1}{4}$
4"	$3\frac{1}{3}$	$6\frac{1}{4}$	$9\frac{7}{12}$

Fig. 8 - Flow Schemes for Slurry Air Lift Tests

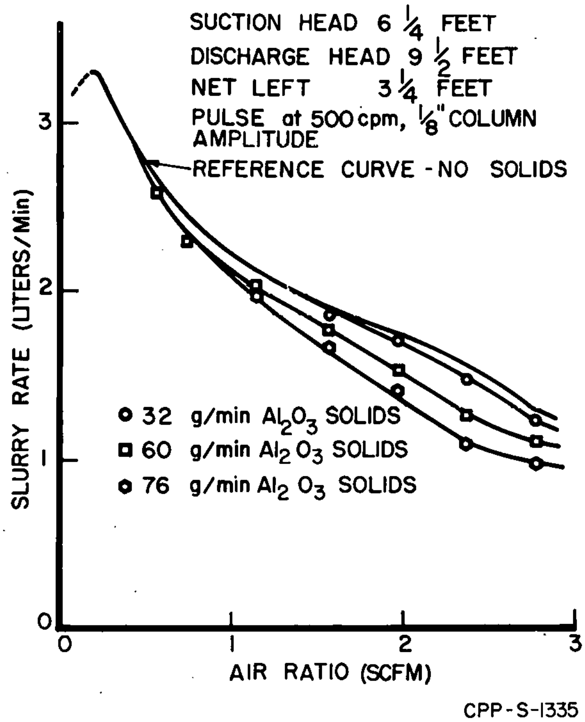


Fig. 9 - Performance Curves for a $\frac{1}{2}$-Inch Air Lift With Different Slurries

performance curve for the air lift with no solids flow. The other curves show the effect of increasing solids flow rate. The effect of solids at air rates less than 0.75 scfm and when the liquid rate is high, is negligible, since the amount of liquid compared to the amount of solids is large. At the higher air rates where the liquid-to-solids ratio is not so great, the effect of the solids is to decrease the amount of liquid by from 2 to 4 times the weight of the solids when compared with the reference curve. This is probably due to increased energy required to overcome the additional friction caused by the solids as well as the greater density of the slurry. Runs are planned on the air lifting of ion exchange resin slurries as well as studying higher flow rates of alumina solids.

The preparation of a new ion exchange equilibrium curve for the system copper-hydrogen on Dowex-50W, 8x, resin with nitrate as the common anion and a total cation strength of 0.5N is awaiting analytical results. A series of ion exchange runs is planned for the 2-inch contactor to compare efficiencies with other contactors.

4. <u>NaK Leak Test</u>, E. S. Grimmett, Problem Leader; G. E. Lohse

Numerous tests have been conducted to determine the effect of a NaK leak into either the pilot plant or demonstrational calciner. Results of these tests are given below:

(a) A fire occurred after two to three minutes of continued manual agitation when approximately 250 milliliters of NaK was added to one liter of cold calcined alumina. The burning mixture did not explode when dipped into a pool of water.

(b) When NaK was introduced into a fluidized bed of alumina at room temperature the immediate result was a complete mixing of the NaK throughout the bed. Continued fluidization caused voluminous amounts of oxide smoke to appear, followed by flames after approximately five minutes. This test and those described below were carried out in the equipment shown in Figure 1.

(c) When NaK was introduced at a constant rate into a heated bed of fluidized alumina, the initial reaction produced voluminous amounts of smoke. This reaction did not appear to be affected by the simultaneous introduction of the liquid feed. As time progressed a visible flame was produced. Reactions were not violent enough to expel calcined solids from the bed. No rise in pressure could be detected by a 0-50 psi pressure transducer and high speed recorder. Small masses of solids which contained unreacted liquid metal produced no explosions when dropped into a pool of water. Hydrogen evolution appeared to be uniformly continuous over a three to four minute period from a mass of solids three inches in diameter by four inches long. When water was allowed to drip on small masses of the alumina-NaK mixture a reaction similar to that of sodium dropped on water was observed.

(d) When hot gases produced by the combustion of propane were used to fluidize and heat the calcined solids in the test vessel the results were similar to those described previously. The residue remaining in the test apparatus contained potassium and sodium carbonate among other chemical compounds indicating that a reaction had taken place between the NaK and the carbon dioxide of the combustion gases.

As a result of these qualitative tests, it is believed that if a NaK leak were to develop inside the calciner that the reaction between NaK and oxygen from the air would predominate but that the reaction is unlikely to be of an explosive nature.

5. Materials of Construction

a. Corrosion in NaK Heat Exchanger, N. D. Stolica, Problem Leader; O. R. Klemens

Microscopic examination of the welded zone (stainless steel type 316 to Carpenter-20) that failed in the NaK heat exchanger of the two-foot square calciner revealed a transgranular crack, indicating that the failure was the result of overstressing, probably thermal, because of the large number of thermal cycles which had been imposed on the system. Metallographic examination revealed that the stainless steel type 316 has undergone a recrystallization in the high temperature (over 1000°F) NaK service, although recrystallization of stainless steel type 304 and Carpenter-20 in this service has not been observed.

A small amount of surface corrosion on the NaK side was observed, but this was judged to be an insignificant amount.

b. Evaluation of Gasketing Material, D. W. Rhodes, Problem Leader; J. S. Madachy

A test was made to determine the resistance to chemical attack of a calcium fluoride-impregnated Teflon gasket material (Garlock 9428), which had been proposed for use in the demonstrational calciner. The results clearly indicated that this material was superior to the material presently in use at the ICPP where resistance to attack by chemicals is the prime consideration. It must be assumed; however, that the Teflon gasket will be affected adversely by high radiation fields in much the same manner as pure Teflon.

C. Other Studies of the Reduction-to-Solids Method

1. Calcination of Zirconium Wastes, D. W. Rhodes, Problem Leader; R. L. Hickok

The conversion to solids by high temperature calcination of aqueous zirconium wastes containing fluoride would create several problems not encountered in the calcination of aluminum nitrate wastes. These problems arise from the physiological toxicity of hydrogen fluoride which would prohibit release to the environs and would necessitate recovery of the hydrogen fluoride in a decontaminated form prior to disposal in some acceptable manner; also, because of the highly corrosive effect during condensation and collection, a severe corrosion problem would be encountered in the materials of construction. A literature search on the chemistry of zirconium was initiated in an attempt to find approaches to the calcination of fluoride-containing zirconium wastes that would reduce both the corrosion and the toxicity problems.

One possible approach is calcination of the waste in contact with silica. Reaction of the fluoride with the silica under the proper conditions should produce volatile silicon tetrafluoride, which would be relatively noncorrosive. Information in the literature suggests that the volatile silicon tetrafluoride may be removed from the off-gas by a sodium fluoride solid adsorber at elevated temperature to produce sodium fluosilicate. Another approach to the removal of fluoride from the off-gas involves hydrolysis of the silicon tetrafluoride and collection of fluosilicic acid. No free hydrogen fluoride would be present by either method.

Estimates of the enthalpy changes and free energies of the calcination reactions appear favorable; however, the accuracy of the data available for these calculations is subject to question. Apparatus is being constructed to evaluate experimentally the feasibility of the proposed reactions.

IV. DEMONSTRATIONAL WASTE CALCINING FACILITY

Demonstrational Waste Calcining Facility, J. I. Stevens, Problem Leader; L. T. Lakey

Under construction at the ICPP is a 60 gallon/hour fluidized bed calciner for conversion of first extraction cycle aluminum waste to a granular solid. This facility will demonstrate the process operability and economics of the fluidized bed technique and obtain information on the long-term storage aspects of highly radioactive solids. Conceptual designs of a solids storage system capable of safely containing masses of solids with high temperatures at the centerline have been considered and a design concept has been chosen for which a detailed mechanical design will be made.

Construction of the Demonstrational Waste Calcining Facility was slowed considerably by the steel strike and the architect-engineer must re-estimate the completion date upon settlement of the strike. At the end of this reporting period, the overall estimated completion of the project is 45 percent which is broken down into the following categories:

	Percent
Building	70
Solids Storage	65
Process and Piping	20
Solids Transfer System	15
Sampling System	5

The off-gas filters, which consist of a primary roughing filter and a secondary high-efficiency filter of the AEC-type encased in a stainless steel box equipped with inlet and outlet valves, were rejected upon visual inspection. These filters were found to have tears in the filter media and severe curvature of the media and its dividers. These deficiencies are similar to those found by contractors at other sites. It is not known whether these deficiencies are attributable to poor manufacturing techniques, damage during encasement, or damage in shipment. However, the encasement will be redesigned and the filter will be inspected at this site by all interested parties before final assembly and installation.

The NaK dump tank, its catch basin and fire protection system was found to be considerably undersized when final design of the calciner heat exchanger, headers, etc., was completed. This will be corrected by installing a duplicate tank in parallel with the present tank and enlarging the catch basin and increasing the size of the fire protection system.

The rate of temperature rise of the waste storage tank currently receiving waste solution was measured. Apparently this tank has not been receiving waste for a sufficient time to create a thermal reservoir of appreciable magnitude in its environment. As a consequence the time-temperature curve exhibited no sharp change in slope and it was impossible to obtain a reasonably accurate estimate of heat generation rate and environmental losses. This test will be repeated after further thermal saturation of the environment by the tank contents.

The review of drawings and specifications was continued and the review of the detailed process calculations was begun. The evaluation of sampling techniques and preparations for technical evaluations of the calciner are underway.

During the course of developing various conceptual designs for a high temperature demonstrational solids storage unit it became apparent that the practicality of several attractive schemes would be dependent upon a greater knowledge than presently exists of the properties of ground materials at the erection site. One of these properties was the thermal conductivity of sands. Investigations by the architect-engineer showed that the thermal conductivity could be rapidly determined with sufficient accuracy for engineering design purposes by measuring the thermal diffusivity. The architect-engineer performed these tests in a 5-inch outside diameter by 20-inch long stainless steel type 304 cylinder which was instrumented by twenty gauge chromel-alumel thermocouples. The tests were conducted over the temperature range of 300° to 1400°F and at pressures of 0 and 50 psig. The following equations of the linear relationships of thermal conductivity and temperature were obtained:

Idaho windblow sand - $k = 0.136 + (1.024 \times 10^{-3}T)$
Idaho pit-run sand - $k = 0.208 + (6.3 \times 10^{-4}T)$
where k and T are $Btu/(hr)(ft^2)(^{\circ}F/ft)$ and $^{\circ}F$ respectively

Literature values for clean silica sand which had a thermal conductivity nearly equal to that of Idaho pit run sand at 800°F but with a temperature coefficient (slope) approximately that of Idaho windblow sand were used to check the test equipment. Corrosion of thermocouples imbedded in the sand was encountered. Furthermore, it is apparent that because of the high temperatures involved, it will be necessary to evaluate some of the materials of construction proposed for the vessel containing the solids.

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