ICP-1169

ICPP DEVELOPMENT PROGRAMS FOR FLUIDIZED-BED CALCINER HEAT INPUT

J.T. NICHOLS

September 1978

Allied Chemical
IDAHO CHEMICAL PROGRAMS

IDAHO NATIONAL ENGINEERING LABORATORY

DEPARTMENT OF ENERGY

IDAHO OPERATIONS OFFICE UNDER CONTRACT EY-76-C-07-1540

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $5.25; Microfiche $3.00

ICP-1169

DISTRIBUTED UNDER CATEGORY:
UC-70
Nuclear Waste Management

ICPP Development Programs for Fluidized-Bed Calciner Heat Input

by

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Date Published - September 1978

Abstract

The fluidized-bed calcination of ICPP radioactive wastes has been under development since 1955. The development program described in this report consisted of operation of pilot-plant fluidized-bed calciners which provided engineering data for a demonstration, plant-size facility for solidifying radioactive waste. The demonstration facility has been in operation since 1963 with first a recirculating sodium-potassium eutectic (NaK) method of heating and since 1970 an in-bed combustion method of heating. A New Waste Calcining Facility (NWCF) has been designed and is under construction. The facility also uses in-bed combustion for process heat. The development program for fluidized-bed calciner heat input is described.

Summary

In 1955 Argonne National Laboratory attempted to solidify simulated aqueous radioactive wastes in a fluidized-bed calciner at the request of personnel at the Idaho Chemical Processing Plant (ICPP). Because operation of the fluidized bed was successful, investigations were initiated at ICPP to further study the process using a six-inch-diameter fluidized-bed calciner. The six-inch-diameter calciner was built in 1955 and operated until 1960. The process looked feasible for solidifying ICPP aluminum nitrate wastes so another pilot-plant fluidized-bed calciner was designed and built. This two-foot-square calciner provided additional data for a plant-scale fluidized-bed calciner.

In 1956 the Atomic Energy Commission accepted a proposal to build a plant-scale fluidized-bed calciner for processing ICPP aluminum nitrate wastes and to provide engineering information for general use of the fluidized-bed calcination process. The construction of the Demonstration Waste Calcining Facility (DWCF) was completed in 1961. After two years of testing and modification, radioactive waste was fed to the calciner. During the ten-month campaign, 1.94 km^3 (512,000 gal) of radioactive aluminum nitrate waste was converted to 213 m^3 (7500 ft^3) of granular and powdered solids. The second and third campaigns resulted in conversion of 3.7 km^3 (980,000 gal) and 1.2 km^3 (320,000 gal) of waste, respectively, to solids of which 1.6 km^3 (420,000 gal) was zirconium fluoride waste. After the third campaign, an in-bed combustion system was installed in the facility. The system was installed because operational problems developed with the recirculating sodium-potassium eutectic (NaK) system and because the in-bed combustion system would allow increased feed rates. Processing of radioactive wastes continued in 1970 with the in-bed combustion system. A total of 4.3 km^3 (1,130,000 gal) of aluminum nitrate and zirconium fluoride wastes have been converted to solids in the four completed campaigns with the in-bed combustion system.

The data from the six-inch-diameter calciner constructed in 1955 provide the design basis for fluidized-bed calcination of radioactive wastes at ICPP. The six-inch calciner used electric cartridge heaters which allowed a feed rate of 6 L/h (260 $L/m^2 \cdot h$) maximum. Heater burnout was frequent; the lowest incidence of heater burnout was achieved with superficial fluidizing velocities of 0.61 to 0.76 m/s (2 to 2.5 ft/s), so the DWCF was designed with a fluidizing velocity in this range.

The two-foot-square calciner was built to provide additional engineering data for the DWCF. A recirculating liquid metal was selected for the heat transfer medium since it would provide the highest heat transfer rates in the fluidized bed with the least amount of surface area. The NaK heating system for the two-foot calciner produced 147 KW of power at the fluidized bed. Heat transfer coefficients ranged from 228 to 569 $W/m^2 \cdot K$ on the 2.6 m^2 heat transfer bundle.

Operation with this calciner showed that fluidizing velocities as low as 0.21 m/s (0.7 ft/s) would give good heat transfer coefficients. The major effect on heat transfer coefficients was particle size and bulk density.

The DWCF was initially tested at the design fluidizing velocity of 0.683 m/s (2.24 ft/s), but the fluidizing velocity was lowered to 0.31 m/s (1 ft/s) to reduce the elutriation rate. The DWCF operated well at that velocity; a feed rate of 349 L/h (299 $L/m^2 \cdot h$) (92 gph), 15% above design capacity, was obtained while calcining radioactive wastes. Forty-two bayonet tubes provided 440 KW of heat to the fluidized bed at a bed temperature of 400°C. Before radioactive waste processing began, the DWCF was renamed the Waste Calcining Facility (WCF). WCF operation during campaign 1 was good; only 57 hours of down time occurred, mostly due to NaK leaks. Campaign 2 operation was much worse, NaK leaks, NaK pump failures, and a leak in a bayonet tube caused most of the 100 days of down time during the two-year campaign. The bayonet tube leak was never repaired; operation was conducted with the helium leak detection system filled with NaK. The NaK loop performed exceptionally well during the third processing campaign with only 36 hours of down time for repair of the NaK system.

Because of the poor performance of the NaK loop in campaign 2, another form of heat input was investigated. The system selected was in-bed combustion. The process was examined in a 30-cm diameter calciner in 1968 and 1969. With 600 hours of operation in the 30-cm calciner, a system was designed for the WCF. Additional safety studies were conducted in the 30-cm-diameter calciner and the in-bed combustion system was installed in the WCF. The initial operation of the WCF in-bed combustion system was poor. Further pilot-plant nozzle testing indicated a different nozzle design and increased oxygen were necessary. These modifications provided satisfactory performance in the WCF. Since installation of the in-bed combustion system, performance has been good with the exception of high elutriation rates apparently caused by increased attrition from the high velocity nozzle flame and some off-gas plugging problems possibly caused by unburned hydrocarbons. The gross feed rate with in-bed combustion has been 455 L/h (389 $L/m^2 \cdot h$) (120 gph); the limiting factor on feed rate is the WCF off-gas system which must maintain a vacuum in the calciner vessel. Higher feed rates would overload the off-gas blowers. Additional work is needed to solve the associated elutriation problem.

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I. Introduction

The Idaho Chemical Processing Plant (ICPP), by the nature of the operations performed, generates significant quantities of high-level radioactive wastes. The wastes are intermediate level sodium-bearing solutions and acidic zirconium fluoride-aluminum nitrate solutions resulting from the solvent extraction reprocessing of spent nuclear fuels. They contain the fission products formed in the reactors in which the fuels were used and are highly radioactive. At the present time, ICPP waste solutions are being stored in underground stainless steel tanks until they can be converted to solids. In the 1950's, the wastes were primarily acidic aluminum nitrate solutions. At this time, it was determined that some form of solid storage of radioactive wastes was necessary. Among the methods considered were batch calcination, continuous calcination in a fluidized bed, continuous calcination in a rotary calciner, and adsorption of fission products on clays with subsequent sintering. For most wastes, conversion to the solid phase offered the advantages of a large volume reduction and, potentially at least, a substantial reduction in the storage costs. After analysis of the advantages and disadvantages of the different methods of waste disposal, fluidized-bed calcination was selected for extensive evaluation. This process offered the best balance of technical and economic feasibility with high ultimate radiological safety. Research programs at Argonne National Laboratory demonstrated fluidized-bed calcination on a pilot-plant scale,[1] initiating further research at ICPP.

The fluidized-bed calcination process involves spraying an aqueous solution of metal salts through a pneumatic atomizing spray nozzle into a heated, gas-fluidized bed where the salts are largely converted to oxides in the form of free-flowing granular solids. The solids are continuously removed from the bed; water vapor, some solids, and volatile decomposition products leave with the fluidizing gas. In 1955, a six-inch-diameter calciner was constructed at ICPP for preliminary testing. The six-inch-diameter calciner was extensively modified in 1956 and further testing conducted. To provide design information for a demonstration calcining facility, a two-foot-square calciner was constructed in 1956 and operated from 1957 to 1963. In 1956, the AEC accepted a proposal to build a waste treatment facility at ICPP, and the contract for design and construction was awarded to the Fluor Corporation.[2] "A net feed rate of 225 L/h (60 gph) was selected for the demonstrational unit because this rate would utilize equipment sufficiently large to obtain reliable design data, would provide adequate quantities of waste to develop and demonstrate adequate storage facilities, and would permit some reduction in the backlog of stored liquid waste. The WCF was not intended as a production unit; therefore, no attempt was made to arrive at a size compatible with ICPP production capacity. The size selected for the demonstrational facility held to a minimum both the initial investment and the cost of correcting any system deficiencies that were observed during operational testing."[3]

Construction of the DWCF was completed in early 1961 and testing completed in late 1962.[2] The facility name was changed to the Waste Calcining Facility (WCF) before radioactive waste was processed through it in 1963. The recirculating NaK heating system was used during the first three processing campaigns up to June 1969. The NaK system was replaced the following year with an in-bed combustion system which has been used since.

The purpose of this report is to describe the ICPP development of heating systems for calcination of ICPP radioactive wastes in a fluidized bed. These development programs led to the selection of an in-bed combustion system for NWCF calciner heat input. Selection of fluidizing velocities and distributor plate design will also be discussed.

II. DEVELOPMENT AND OPERATION OF THE WASTE CALCINING FACILITY NaK HEATING SYSTEM

1. Operation of Six-Inch-Diameter Calciner[4]

The six-inch-diameter calciner was constructed in 1955 to further investigate the process of fluidized-bed calcination demonstrated at Argonne National Laboratories with simulated aluminum nitrate waste. The research was conducted at ICPP using simulated aluminum nitrate waste, zirconium fluoride waste, and stainless steel waste. Aluminum nitrate waste was used in all long runs. The original six-inch-diameter calciner used strap-on electric heaters, but this technique did not provide sufficient calcination capacity. The capacity of the unit was increased by increasing the area available for heat transfer and by eliminating excessive heat losses using internal cartridge heaters substituted for the external strip heaters. Also, manual temperature control prohibited maintaining a reasonably constant bed temperature. Automatic adjustment of one of the four autotransformers was accomplished by installing an electronic-pneumatic controller sensing the signal from a thermocouple in the bed opposite the spray nozzle. The controller was connected by a flexible coupling to the shaft of the autotransformer through a pneumatic positioner. The redesigned calciner had eighteen 1000-W cartridge heaters in a triangular pitch on 3.8 cm centers. The cartridges were 23 cm long with 15 cm heated sections. In order to operate at reasonable capacities, the cartridge heaters had to be operated at high flux densities resulting in high surface temperatures. Under these conditions, if a significant reduction in the heat transfer rate (due to caking in the bed, poor fluidization, large particle size, etc.) occurred, even in a highly localized portion of the bed, the surface temperatures of the heaters in that portion of the bed would rise and the heaters would burn out. The replacement of heaters, in addition to being an expensive annoyance, required that many potentially useful runs be terminated prematurely. Even under the best conditions, the feed rate was never greater than 8.2 L/h, and the normal maximum feed rate was only about 6.0 L/h. A fluidizing velocity of 0.61 to 0.76 m/s was necessary to minimize the burnout of cartridge heaters.

2. Operation of 2-Foot-Square Calciner[5,6,7,8]

Even though the results of the six-inch-diameter calciner studies were very encouraging, it became apparent in early 1956 that studies would have to be extended to a larger calciner and to development of a better heating system. The electrical heating elements used in the six-inch-diameter calciner were a constant source of trouble; momentary dead spots near heater elements caused localized hot spots which usually burned out the heater elements. It was obvious that it would be extremely risky to operate a calciner in a remote cell using such an unreliable heating system.

Preliminary planning was underway at that time for a Demonstrational Waste Calcining Facility (DWCF) to calcine a feed stream whose rate (227 L/h) would be an increase of some 25-fold over the highest feed rate used in the six-inch-diameter calciner.

Scale-up problems of this magnitude were completely undefined, and design data that could be used for such a large unit were, for the most part, unavailable.

Several heating systems for a larger pilot-plant calciner were considered, including high-temperature fluidizing gas, recirculating liquid metal, recirculating fused salts, and recirculating Dowtherm. The final choice was a liquid metal heat transfer system using a 22 percent sodium-78 percent potassium alloy (NaK) as the heat transfer medium. This choice was based on the following considerations:

1. High-temperature operation reduces the amount of heat transfer surface required for a given heat load and bed operating temperature. (For the NaK system, temperatures as high as 760°C can be employed.)

2. For a given calciner feed rate, a smaller heat transfer surface requires less space, thus a smaller calciner vessel.

3. For a given calciner feed rate and fluidizing velocity, a vessel with a smaller diameter requires less fluidizing gas, and hence, less off-gas must be treated in the off-gas cleanup system.

4. A properly designed liquid metal heat transfer system was reliable and temperatures could be controlled easily.

These considerations led to the design and installation of a two-foot-square pilot-plant calciner having a feed capacity of 100 litres per hour of aluminum nitrate-nitric acid solution. The unit was heated with an oil-fired NaK heat transfer system. A fluidizing vessel with a square cross section was chosen because it simplified considerably the design of the calciner heat exchanger and permitted construction of the vessel in local shops with available material. Except for unimportant corner effects, it was assumed that fluidization would be as good in a square vessel as in a round vessel, an assumption substantiated by tests in a one-foot-square plastic model. Major purposes of this unit were: (1) to develop further the calcination process, (2) to provide engineering design data for the DWCF, (3) to test and operate the NaK heat transfer system, and (4) to help train operators for the DWCF.

The later studies in the 2-foot-square calciner were conducted after the DWCF was constructed. Excessive rates of elutriation of solids from the DWCF calciner and excessive carry-over from the DWCF cyclone had been experienced in start-up testing of that facility.[2] Consequently, a considerable amount of the work was directed at determining the effect of operating variables on the generation of elutriatable solids. The variables studied included: feed rate, nozzle air rate, superficial fluidizing velocity, the return of fines to the bed, and feed introduction positions and methods. Characteristics of the cyclone fines were also studied as part of this problem.

The off-gas system on the two-foot-square calciner consisted of a primary cyclone followed by a venturi scrubber, demister and condenser. The venturi scrubber was operated on fresh water; no scrub recycle system was in use because a pump could not be found to circulate an acid slurry solution. Fines from the primary cyclone were usually returned to the fluidized bed through an air-jet pump, as in the six-inch-diameter calciner, to provide new seed particles.

Delivery of the NaK heating system was delayed several months beyond completion of the calciner and other auxiliaries. During this interim period, an electrical heating system and a tube-side-fired heat exchanger were used to check out the calciner system.

Feed rates up to 30 litres per hour were possible when using a 24-unit, 0.47 m^2 electrical heating system in conjunction with the use of hot combustion gases as the fluidizing medium. Feed rates up to 30 litres per hour were possible with a special tube-side-fired heat exchanger. Tubes for this unit were made from 3/4-inch Type 316 stainless steel tubing having a 1.65 mm wall thickness; total heat transfer surface was 0.93 m^2. Hot gases (up to 650°C) were supplied to the unit from a 360 kPa oil-fired combustion chamber. Over-all heat transfer coefficients obtained with the tube-side-fired heat exchanger ranged from 45 to 285 $W/m^2 \cdot K$.

An oil-fired furnace was used to heat the recirculating NaK. The hot NaK passed through a 2.6 m^2 U-bend exchanger placed directly in the fluidized bed of the calciner, and was then recirculated back to the furnace by means of an electromagnetic pump. The heating system was designed to deliver 147 KW to the calciner at a NaK inlet temperature of 760°C and an outlet temperature of 705°C. The heat exchanger tubes were constructed of 3/4-inch, 14 BWG Carpenter-20 tubes welded to 316 stainless steel manifolds. The heat input to the two-foot-square calciner was slightly above design values. During the testing program, feed rates were varied from 40 to 150 L/h and temperatures from 400 to 500°C. Over-all heat transfer coefficients ranged from 228 to 569 $W/m^2 \cdot K$. High coefficients were associated with beds having small particle sizes and high fluidized bed densities, whereas low coefficients are associated with beds having large particle sizes and low fluidized bed densities.

The electromagnetic NaK pump wiring failed after 2100 hours of operation. The wiring was replaced with a larger sized wire resulting in good operation for the remainder of the program (13,000 hours). A NaK leak external to the calciner developed after 2800 hours of operation and 73 start-ups. The leak occurred at a point where the Carpenter-20 tube was welded to the 316 stainless steel manifold. The crack was repaired by welding and the system put back into service. After 60 more hours of operation, another leak developed at a Carpenter-20 and 316 stainless steel weld. The failure of the weld zone was due to transgranular attack, probably caused by repeated thermal cycle overstressing. Insignificant amounts of surface corrosion on the NaK side of the tubes were measured at this time.

The direct-fired, Type 316 stainless steel NaK heat exchanger bundle in the furnace and the Carpenter-20 heat exchanger bundle in the fluidized bed of the calciner were inspected for corrosion or erosion after a total of 13,144 hours of operation (9,087 hours with the temperature of the NaK to the calciner above 540°C). During this period, the system was started up a total of 225 times. The inspection of the direct fired bundle revealed that the tubes were covered with a porous, non-uniform scale that had been-observed during previous inspections; it was easily removed with a wire brush. Gamma ray photographs of the headers and tubes of the furnace bundle showed that the thickness of the walls were still adequate, and that all thickness values so obtained exceeded the specified minimum dimensions for wall thickness of new pipes and tubes. The 147 KW burner was supplied with ASTM D 396-48T grade No. 2 fuel oil during this period. No obvious defects in the fluidized-bed heat transfer bundle were observed by visual inspection. Spot measurements of the diameters of the tubes of this bundle showed the outside diameters to be essentially equal to the outside diameter of new tubes.

3. DWCF Design and Operation[2]

Construction of the DWCF was completed in 1961. The main processing building of the WCF is a concrete structure in which the processing cells are underground in two banks with service corridors between the banks. Non-radioactive service areas for the WCF are housed in a concrete block structure above the processing cells. Like the ICPP fuel reprocessing facility, the WCF processing building was designed for direct maintenance of equipment. Critical equipment items, such as those with moving parts, were either installed in duplicate or placed in lead shielded cubicles outside the process cells. Sprays and piping were provided so that both equipment and process cells can be decontaminated remotely. Ladders and platforms facilitate access to equipment for maintenance. With few exceptions, process equipment items were fabricated from austenitic stainless steels, because these alloys satisfactorily resist corrosion from the acidic process and decontaminating solutions. A more detailed description of the process equipment is available in Reference 9.

The DWCF testing program consisted of 10 runs which lasted 22 months. The facility was designed to calcine 227 L/h of radioactive aluminum nitrate wastes, with 79 L/h of scrub recycle solution, at a temperature of 400°C.

The heat required for evaporation and decomposition of the liquid calciner feed was supplied by means of an indirect heat transfer system utilizing a sodium-potassium eutectic mixture (NaK) as the heat transfer medium. NaK flowed through a three-inch stainless steel pipe, by means of an electromagnetic pump, into an oil-fired radiant heater where it was heated to a maximum temperature of 760°C. The heated NaK then flowed through the fluidized bed heater, where it was cooled approximately 110°C, and back to the pump. Tanks were provided for thermal expansion of the NaK and for draining the system. The fluidized-bed heater consisted of 42 bayonet tubes designed to supply 440 KW of heat. Most of the NaK system was constructed of 316 stainless steel. The bed temperature was controlled by adjusting the NaK temperature which was controlled by adjusting the firing rate of the NaK furnace while maintaining a constant flow of NaK.

Numerous process and equipment changes were made during the testing program. The major process change was to send the fines from the primary cyclone to the solid storage facility rather than to return them to the calciner. In addition, a louvered baffle was installed to deflect solids away from the off-gas outlet, the cyclone was modified and the fluidizing velocity was decreased from 0.683 m/s to 0.31 m/s. These changes decreased the elutriation rate from approximately 68 kg/h to 11.4 kg/h (at a total solids production rate of 22.8 kg/h). The fines were routed to solid storage because pilot-plant studies conducted at the time indicated the fines were in general too small ($<10\ \mu m$) to act as new seed particles.[8] Modifications to the feed and transport system were also made during the testing program.

In general, the NaK heating system operated well. The bayonet type tubes were constructed of a core tube and an outer "duplex" tube (Figures 1 and 2). NaK entered through the core tube and left through the annulus between the core tube and the duplex tube. Helium gas at 25.8 kPag was introduced to the outermost tube. Should a leak have developed on the NaK side of the bayonet tube, the helium pressure would rise; a leak in the outer tube would cause a helium pressure drop as the helium was released to the calciner vessel. The latter type of leak occurred twice during one test run. A circumferential crack appeared around the bottom half of one outer tube approximately 2 cm from the base of the tube. The tube was repaired by welding a stainless steel sleeve over the crack. After only 5 days of operation, another crack developed on the same tube adjacent to the sleeve weld. The faulty tube was then completely encased in another tube. Vibration measurements of the bayonet tubes indicated that mechanical vibration had caused the failure of the tube. A tube support was installed and no more tube failures occurred. The primary and secondary coils on the NaK recirculating pump each failed; after replacement with coils of a different design, no further problems occurred. Two leaks occured in the NaK piping during the test program. Both, however, were caused by human error and did not result from weaknesses in the system. In one instance, threaded plugs were left out of a valve by the vendor; in the other instance, temporary wiring shorted and burned a hole in the NaK oxide removal system piping. In both instances, the damage was negligible.

4. Waste Calcining Facility Operation with the NaK Heating System

After testing, the Demonstration Waste Calcining Facility (DWCF) was renamed the Waste Calcining Facility (WCF).

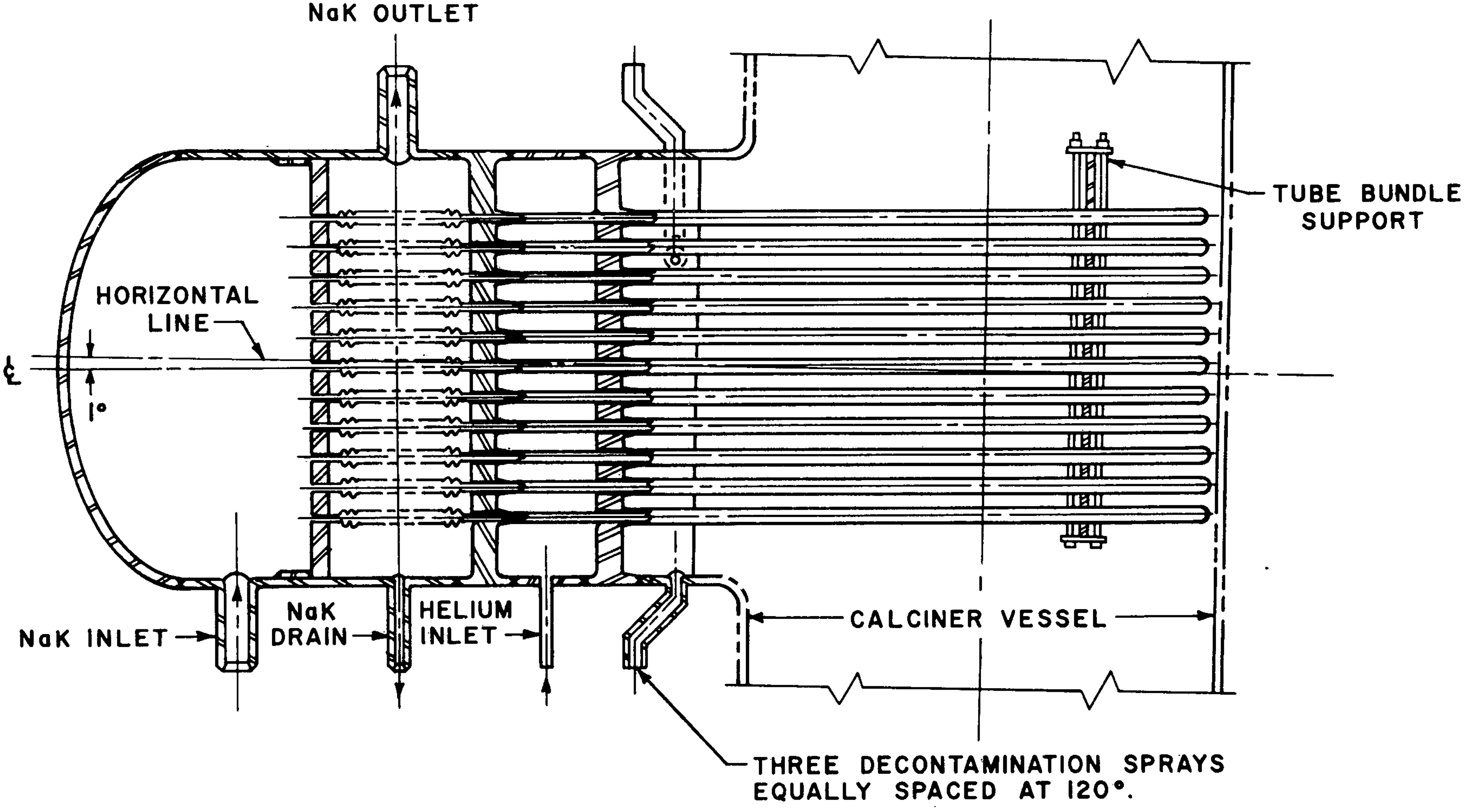

Figure 1. Fluidized-Bed Heat Exchanger

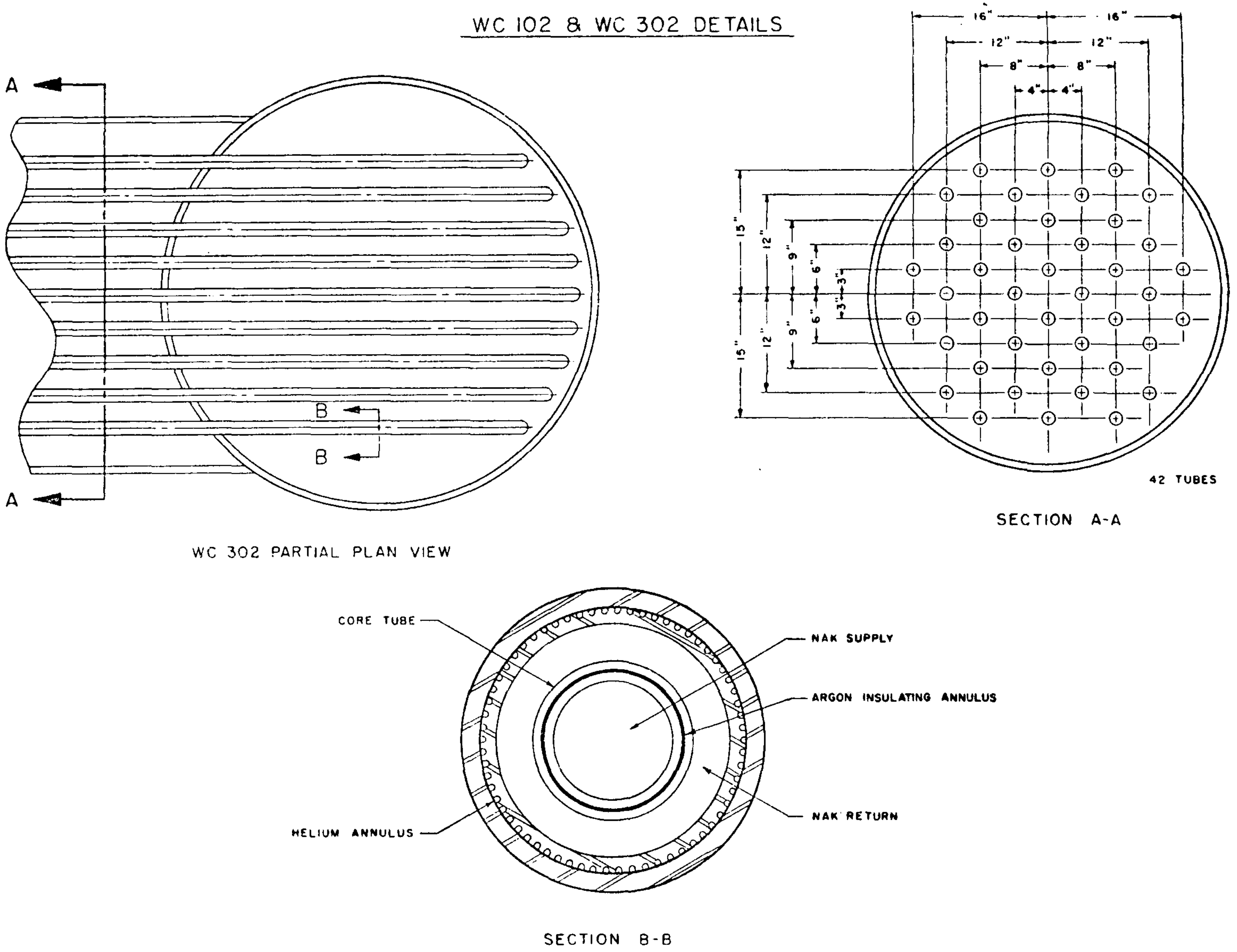

Figure 2. Details of Fluidized-Bed Heat Exchanger

4.1 WCF Campaign 1[10]

The first WCF processing campaign lasted ten months, from December 1963 to October 1964. Over 1.94 km^3 of aluminum nitrate waste was converted to 213 m^3 of solids. Total down time during the campaign was 57 hours, resulting from two NaK leaks and power outages. The feed rate was 349 L/h, 46L/h above the design rate; the net feed rate was 261 L/h. The average NaK flow was 20.4 Mg/h at furnace outlet temperatures of 690 to 750°C.

Two NaK leaks occurred at the same fitting on one of the NaK expansion tanks. After the second leak, the expansion tank was removed from the system and operation continued using one expansion tank. After removal of the NaK expansion tank, specimens of the tank nozzle, pipe nipple, and a small section of the tee were examined metallurgically to determine the cause of the leaks. The results of these tests are as follows:

(1) Visual examination of the specimens, in the "as received" condition, indicated that a circumferential crack had developed immediately above the nozzle-to-pipe connector transition weld. When NaK leaked from this crack, the reaction products and high temperatures cut a vertical groove in the pipe connector, which subsequently exposed a vertical crack in the pipe connector. This crack was probably the same crack through which the first NaK leak had occurred. (This had been repaired by "putty" welding and patching.) Additional vertical cracks found in both the pipe connector and tank nozzle had apparently formed as a result of excessive heat generation while welding the nozzle to the tank.

(2) Results of microscopic examination of the specimens were:

   (a) Numerous stress corrosion cracks, varying in depth and length, were found in the tank nozzle and pipe connector.

   (b) In general, cracks formed intergranularly at the inside surface, then propagated from there transgranularly.

   (c) Cracks were both circumferential and axial.

   (d) No evidence of cracking or corrosion of the tee was found.

   (e) There was no evidence of general corrosion of the inside surfaces of the nozzle, connector, or tee.

   (f) Chemical analyses of the specimens confirmed that all of the specimens were Type 316 stainless steel.

(g) Acidified copper sulfate corrosion tests indicated that the tank nozzle had become highly sensitized as a result of carbide precipitation. The pipe connector and tee showed essentially no attack during the corrosion tests.

(h) Microhardness surveys indicated that inside surfaces of the specimens were somewhat harder than the parent metal.

In addition to the above metallurgical examination, an analysis of the external stresses in the NaK piping system was conducted. A probable contributing cause of the stress corrosion cracking was that no provision was made for the expansion of the three-inch NaK line between the two expansion tanks. Thus, expansion forces may have resulted which exceeded the yield strength of the 1-1/2-inch pipe connector at the operating temperature of 760 °C. The review revealed that no other region of high external stress due to expansion forces should be present in the system.

4.2 WCF Campaign 2[11]

The second WCF processing campaign started in April 1966 and continued to March 1968. About 3.34 km^3 of aluminum nitrate waste and 413 m^3 of zirconium fluoride waste were calcined at net feed rates of 254 L/h and 180 L/h, respectively. Calcium nitrate solution was added to prevent fluoride volatility at 400°C when calcining zirconium fluoride waste, which reduced the net feed rate. During this campaign the NaK system was operated at essentially the same condition as in the first campaign, and another 16,000 hours of NaK operating time were accumulated. Most of the approximately 100 days of down time were caused by failures of the NaK heating system. The first of the NaK leaks occurred on August 9, 1966 at a welded "T" on one of the expansion tanks, and the "T" was replaced with a straight section of pipe eliminating the expansion tank from the system. The next leak on March 31, 1967 was in a reducer weld in the NaK dump tank line. The resulting fire and dense smoke necessitated the evacuation of the WCF except for those fighting the fire. The NaK pump was another source of trouble during the second campaign. Six failures of the NaK pump in the flow tube, pump electric coils or autotransformer resulted in about 300 hours of down time. The cold trap for collection of sodium oxide also caused some problems because the sodium oxide precipitated in different places causing line plugs in the cold trap loop. The WCF was shut down 36 hours to install cutoff valves in the cold trap inlet and outlet lines; plugs in the cold trap lines could then be cleared without draining the entire NaK loop.

The most serious problem with the NaK system resulted in more than seven weeks of down time, most of which was due to decontamination of the calciner cell. A leak was detected between the NaK system and the helium leak detection system on September 12, 1966. Repair of the tube bundle in the calciner would have taken six to twelve months; a replacement bundle would have taken even longer to acquire. A decision was made not to repair the NaK tube bundle but to operate with NaK in the helium leak detection system. The possibility of a NaK leak into the fluidized bed would have been greater; however, the consequences of such a leak would not be serious.[10] NaK tank level instrumentation was added to detect losses of NaK into the calciner vessel. Other modifications were made and processing continued on November 8.

4.3 WCF Campaign 3[12]

The third processing campaign in the WCF lasted from August 1968 to June 1969 during which 1.18 km^3 of zirconium fluoride waste and 64 m^3 of aluminum nitrate waste were calcined. The gross feed rate was 359 L/h with a net feed rate of 202 L/h for zirconium fluoride waste. The calciner was shut down during this period for 33 of 299 days for equipment repair. The longest period of down time resulted from failure of the scrub pumps because of excessive free fluorine in the scrub solution.

Particle size control was difficult during the third campaign. The maximum Mean Mass Particle Diameter (MMPD) was 1.2 mm. Water was added to the calciner to reduce the particle size by thermal shocking. Later, the feed was diluted with water to keep the particle size small. At one point, excessive calcium nitrate solution was added to the feed batches resulting in MMPD's around 0.6 mm without any other water addition. The aluminum nitrate waste was fed to the calciner late in the campaign to try to reduce the high solid elutriation rate.

The NaK heating system was operated in a manner similar to operations in the previous two campaigns. During the entire campaign the NaK heating system performed flawlessly; no process shutdowns occurred because of NaK system failures. The NaK system was replaced after this campaign by an in-bed combustion system rather than a new heat exchanger bundle. A new heat exchanger would have cost $500,000, but pilot-plant testing of the in-bed combustion method of heating indicated that a 50% increase in feed rate was possible and system operation would be simpler.

4.4 Final Evaluation of the NaK Heating System[13,14]

Stainless steel, Type 316, was selected as the material of construction for the vessels and lines in the NaK heat transfer system of the Waste Calcining Facility because of its tensile strength at elevated temperatures and its resistance to NaK and nitrate vapors at elevated temperatures. At the time this choice was made, there were no data on the net effect of long-term exposure of Type 316 stainless steel to NaK at 600 to 750°C. In general, the material performed very well although a specific limitation has been defined by experience. This is a susceptibility to failure by brittle fracture under applied stress. This dictates careful arrangement of vessels in the loop and requires thorough design analysis of the supporting structures.

4.41 Type 316 Stainless Steel

Service test examinations were conducted on three pieces of three-inch, Schedule 40, Type 316 stainless steel piping -- all of which had been in service conducting hot NaK from the heater to the calciner in the WCF. One piece of pipe was in service during the first 16,300 hours of operation with 1,120 hours below 600°C and 15,180 hours above 600°C and with 37 starts from room temperature. This pipe was replaced by another which was in service during the last 16,300 hours of operation with 300 hours below 600°C, 16,000 hours above 600°C, and with 15 starts from room temperature. The third piece of pipe was in use during the entire period of NaK loop service, i.e., for approximately 32,600 hours as enumerated above.

The principal effect shown on the Type 316 piping was carbon depletion at the NaK-pipe wall interface. The presence of sigma phase formation, as evidenced by metallographic examination and accompanying embrittlement, was indicative of a fundamental change in the microstructure of the alloy due to exposure at elevated temperatures. General corrosion damage was nil on all specimens.

The results suggest that sigma phase transformation in Type 316 stainless steel (when in NaK service at 700°C) increases with increasing service time; at the same time, the observed hardness values appeared to be quite constant through the 32,600 hours total exposure time. The impact strength of the alloy appears to decline to a minimum level within something less than 16,000 hours service and remains at that level for an indefinite time period. Although the general corrosion loss of Type 316 piping was nil, almost complete carbon depletion occurred at the NaK-piping interface.

The observed tensile and yield strength of the specimens exposed for the two different time periods compared favorably with the published values of unexposed Type 316 stainless steel at 500°C: 503 MPa and 317 MPa, respectively. When tested at 500°C in air, the elongation was 11% on pipe sections exposed to NaK during both periods, 75% lower than the average published percentage (43%) for the unexposed alloy. Izod impact tests showed that specimens of the pipe which had been in high temperature NaK service absorbed 66% less kinetic energy in breaking than similarly tested specimens from unexposed piping. A flattening test, "ASTM A 376 Seamless Austenitic Steel Pipe for High Temperature Central Station Service", showed that exposed pipe remained ductile. However, a pipe section that was exposed in NaK service at 700°C for 16,300 hours broke when flattening continued until the opposite walls of the pipe met.

Post-test microhardness surveys of the Type 316 pipe sections from the NaK loop had measured averaged diamond pyramid hardness (DPH) values of 158 and measured averaged Rockwell superficial 15-T scale (1/16-inch ball) values of 89 which correspond to Rockwell B-scale of 86.

4.42 Type 304 L Stainless Steel

An examination was conducted on a 3 x 3 x 3-inch, Schedule 80, Type 304 L stainless steel tee fitting which permitted the liquid metal to circulate through the loop and flow into the NaK expansion tank. The tee fitting was in service during the last 15,567 hours of the NaK loop operation of which 261 hours were below 600°C and 15,307 hours were above 600°C, with 13 starts from room temperature.

Evaluation of this Type 304 L stainless steel specimen showed carbon depletion at the NaK-metal interface; there were significant amounts of carbide precipitation at the grain boundaries and only trace quantities of sigma phase formation in the cross section of the tee. These observations suggest only minor changes in micro-structure of the alloy due to exposure at 700°C over 15,600 hours of service.

The post-service examination indicated that the general corrosion damage on the tee was nil. The concentration of sigma phase was estimated at less than 1% while carbide phases were present in concentration of about 2%. The band of decarburization found on the NaK side of the wall of the tee appeared to be about 2.5 μm thick.

The results of mechanical tests, at 760°C in air, for tensile and yield strength as well as elongation percentage of specimens from the pipe tee (158 MPa, 117 MPa, and 43%, respectively) compared favorably with published values of the unexposed alloy. Izod impact tests showed that specimens were ductile and not brittle. Sections of the Type 304 L stainless steel tee had averaged diamond pyramid hardness (DPH) values of 195 which corresponds to Rockwell B-scale of 90.

4.43 Type 318 Stainless Steel

The 1.27-cm thick, lower, semi-eliptical, Type 318 stainless steel head on the NaK expansion tank was examined after 32,600 hours of NaK loop operation of which 1,410 hours were below 600°C and 31,190 hours were above 600°C, with 52 starts from room temperature.

The most significant observed effect from the evaluation of the Type 318 stainless steel was almost complete absence of carbon depletion at the NaK-metal interface. Sigma phase formation, which was identified in cross sections of the columbium-molybdenum austenitic stainless steel alloy, and accompanying embrittlement are indicative of fundamental change in the microstructure of the alloy due to exposure at elevated temperatures. General corrosion damage was undetectable on the steel after 32,600 hours of service.

Mechanical tests at 500°C in air showed that the tensile and yield strengths of the type 318 stainless steel specimens (682 MPa and 482 MPa, respectively) were about 30% higher than published values for the unexposed alloy. The observed elongation percentage of the exposed sections was 5%, 88% lower than the average published percentages for unexposed alloy. The Izod impact test with a subsized specimen gave a relatively low result of 1.63 J, indicating brittleness.

4.44 Conclusions

The results of this work suggest that Types 304 L, 316, and 318 stainless steel alloys are suitable for materials of construction for nonisothemal loops containing NaK at 600 to 700°C. Because there appears to be a relationship between the failure of pipe fittings and applied stress on the components, applied stress should be minimized in the design of any future loops.

The presence of sigma phase in Type 316 or 318 stainless steel, which increases in concentration with increasing exposure time at temperatures above 600°C, does not appear to affect greatly the serviceability of the steel as long as the sigma particles are small and dispersed. Owing to significantly greater yield and ultimate tensile strengths after 32,666 hours of exposure, Types 316 and 318 stainless steels are favored for construction materials for NaK loop service. It should be noted, however, that embrittlement, which is usually associated with sigma phase formation, may cause failures in areas of high external stress. When sigma phase inhibition is desirable, the use of fully austenitic low-carbon stainless steels is suggested; Type 304 L is useful because it retains its impact strength and the lowest sigma phase concentration after 15,600 hours in NaK service. To inhibit decarburization with associated corrosion losses in NaK service, Type 318 (Mo, Cb) stainless steel is suggested because the alloy resists precipitation of carbides in the grain boundaries.

III. DEVELOPMENT AND OPERATION OF IN-BED COMBUSTION SYSTEMS

1. Pilot Plant Development of an In-Bed Combustion System

1.1 Preliminary Feasibility Testing of In-Bed Combustion

In-bed combustion for calciner heat input was investigated as a possible replacement for the NaK heating system to increase WCF feed throughput. The NaK heating system was limited in heat input to the calciner bed by heat transfer resistances at the in-bed heat exchanger surfaces and maximum NaK temperatures. In-bed combustion had the potential of achieving a higher heat input since there would not be any intermediate metal heat transfer surfaces.

Pilot-plant feasibility studies of in-bed combustion were started in 1967 and continued into 1968. The purpose of the program was to develop operating criteria for an in-bed combustion system. Initial studies indicated that stable operation could be achieved only at temperatures above 650°C.[13] Later studies in 1968 indicated stable combustion could be achieved at temperatures as low as 392°C.[15] A strong dependence of minimum operating temperature on nitrate concentration was reported (Figure 3).[15] The operating temperature of 392°C was achieved using air as the fuel atomizing gas and additional oxygen with the fluidizing gas. The use of oxygen in the fluidizing gas was necessary to supply sufficient oxygen for combustion at a fluidizing velocity under 0.31 m/s (1 ft/s). Other in-bed combustion processes had been reported in the literature using air for atomizing the fuel and fluidizing the bed; however, fluidizing velocities of several feet per second were necessary to obtain the required oxygen for combustion.[15]

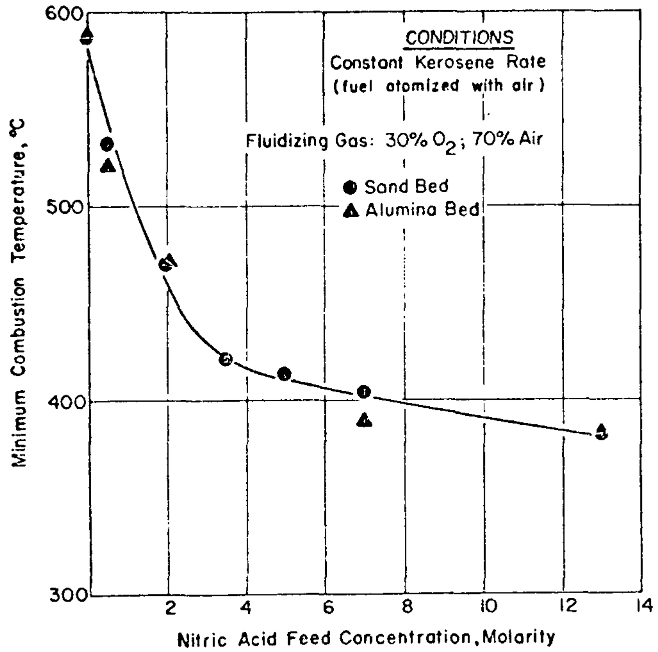

Figure 3. Effect of Nitric Acid Concentration on Minimum Operating Temperature

Typical operating conditions for indirect heating (electrical) and in-bed combustion heating while calcining aluminum nitrate and zirconium fluoride wastes are presented in Table I.[15] Operation with 145% theoretical oxygen yielded combustion efficiencies of 95%. (Based on studies in FY 1973 for determining combustion efficiencies from CO and CO_2 concentrations[16] and the CO and CO_2 concentrations reported.[15]) The percent theoretical oxygen was based on all oxygen from fluidizing and atomizing sources.

TABLE I

COMPARISON OF TYPICAL OPERATING PARAMETERS
(30-cm Diameter Calciner)

Feed	Operating Parameters	Conventional Indirect Heating	In-Bed Combustion
Aluminum Waste	Fluidizing Velocity (m/s)	∿0.31	∿0.37
	Waste Nozzle Air Ratio	500	325
	Fuel Nozzle Air Ratio	---	700
	Mass Median Particle Diameter (mm)	0.6	0.6
	Bed Temperature (°C)	400	480
	Feed Rate (L/h)	10	15
	Product Rate (kg/h)	∿2	∿1.1
	Fines Rate (kg/h)	∿0.09	∿0.23
Zirconium Waste	Fluidizing Velocity (m/s)	∿0.31	∿0.52
	Waste Nozzle Air Ratio	650	500
	Fuel Nozzle Air Ratio	---	700
	Mass Median Particle Diameter (mm)	0.65	0.8
	Bed Temperature (°C)	400	480
	Feed Rate (L/h)	16	30
	Product Rate (kg/h)	∿1.6	∿3
	Fines Rate (kg/h)	∿0.14	∿0.36

Lower operating temperatures were possible by using oxygen as the fuel atomizing gas. But during these tests, the atomizing oxygen was well below the stoichiometric O_2/fuel ratio of 2080. Part of the oxygen for combustion was supplied by excess oxygen in the fluidizing gas. Long term runs were made with oxygen as the atomizing gas since lower amounts of total oxygen were required for stable operation. Total operating time in the 30-cm--diameter calciner with the in-bed combustion system was 617 hours and formed the design basis for the WCF in-bed combustion system.

1.2 Summary of In-Bed Combustion Safety Studies Conducted in the 30-cm Diameter Calciner

A series of tests was conducted in a 30-cm-diameter pilot-plant calciner to provide information on any potential hazards from operation of an in-bed combustion system. During each test abrupt interruptions of waste feed or oxygen were made, and the effect of each interruption on the in-bed combustion system was recorded while all other process stream flows remained constant. Using simulated zirconium fluoride waste complexed with calcium nitrate, the tests were conducted in the pilot-plant calciner, shown schematically in Figure 4. Table II shows the nominal operating conditions used in the tests.

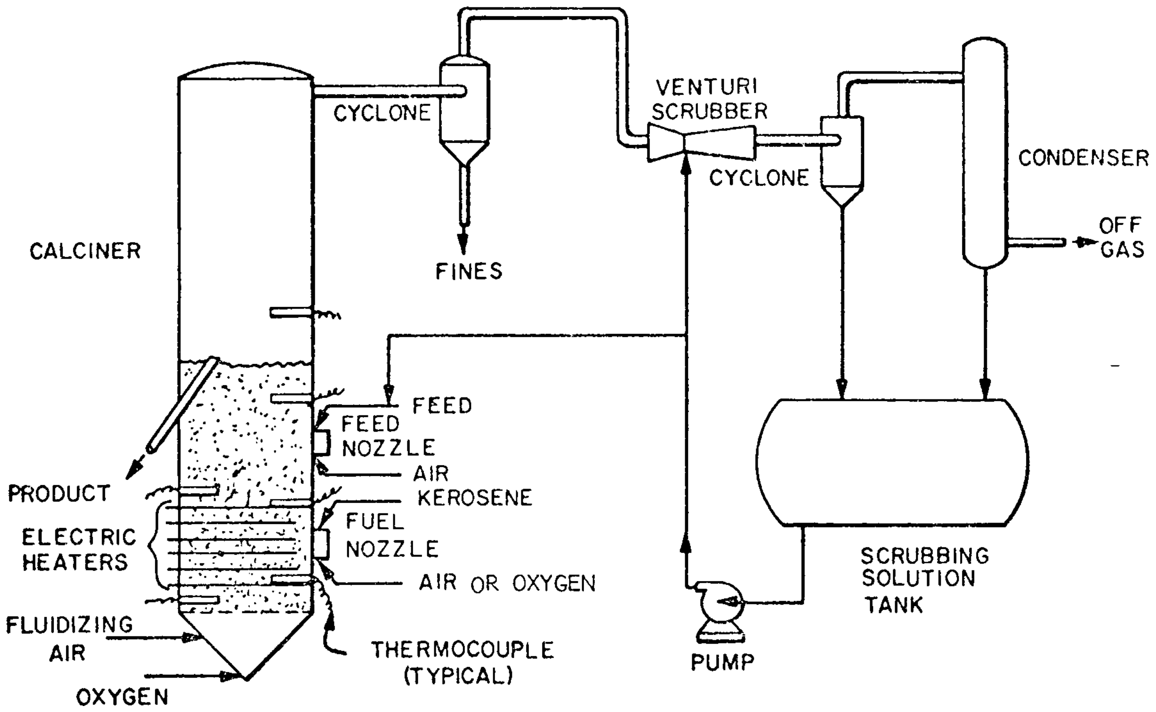

Figure 4. Schematic Diagram of 30-cm Pilot Plant Calciner

TABLE II

NOMINAL INITIAL OPERATING CONDITIONS

Bed Temperature	450°C
Bed Pressure	73.7 kPa
Waste Feed Rate	26.5 L/h
Waste NAR	500 (air-to-waste volume ratio)
Fuel Rate	5.7 L/hr (kerosene)
Starting Beds	Zirconia calcine
Fluidized Bed Height	50.8 cm above distributor plate
Nozzle Locations	Waste nozzle over fuel nozzle - same side of vessel

The results of each test are summarized in Table III and each test is discussed separately in the following paragraphs. In brief, the results of these tests amply demonstrated that temperature excursions in the calciner vessel resulting from abrupt interruptions of waste feed or oxygen streams could be controlled safely by restoring the interrupted stream or by manipulating other process streams; i.e., fuel, oxygen, or waste streams.

1.21 Tests 1 and 2 - Waste Feed Interruption

In the first two tests, waste feed to the calciner was shut off abruptly, and the effect of this on the vapor space and bed temperatures of the calciner was observed. (The recorded time-temperature relationships for Tests 1 and 2 are shown in Figures 5 and 6, respectively.) In both tests, the bed temperature began a rapid rise, 14 to 16°C/min, soon after the waste feed was halted. The rise continued at a steady rate in both tests until the fuel flow rate was reduced in Test 1 and the waste feed resumed in Test 2. Some above-bed burning was observed during Test 1, but none was observed in Test 2. Thus, these results indicate that fuel combustion generally was in the fluidized bed and that no explosion hazards were produced during the 20 minutes or more that the waste feed was halted.

TABLE III

SUMMARY OF FEED AND OXYGEN INTERRUPTION TESTS

Test Type	Figure	Perturbed Variable	Response	Corrective Action	General Comments
Waste Feed Interruption	5	Waste Feed Flow	Bed temperature excursion of $\sim 16^{\circ}$C/min with small amount of above bed burning for ~ 6 minutes.	Reduce fuel rate to control temperature excursion.	9-cm nozzle spacing.
Waste Feed Interruption	6	Waste Feed Flow	Bed temperature excursion of $\sim 14^{\circ}$C/min with no above bed burning.	Resume waste feed rate to control temperature excursion.	24-cm nozzle spacing.
Oxygen Interruption	7	Fuel Atomizing Oxygen	Above-bed burning accompanied by a decrease in bed temperature.	Reduce waste feed rate to increase bed temperature.	In-bed combustion resumed at $\sim 695^{\circ}$C.
Oxygen Interruption	8	Fuel Atomizing Oxygen	Above-bed burning accompanied by a decrease in bed temperature.	Resume fuel atomizing oxygen and temporarily reduce the waste feed rate.	Resumption of atomizing oxygen controlled above-bed burning at 620°C. Reducing the waste feed controlled the decreasing bed temperature.
Oxygen Interruption	9	Fluidizing Oxygen	Above-bed burning with decreasing bed and vapor temperature.	Resume fluidizing oxygen.	Total interruption of the fluidizing oxygen at 77 minutes extinguished the combustion reaction.
Oxygen Interruption	10	Total Oxygen-Fluidizing and Atomizing	Above-bed burning with bed and vapor temperatures decreasing at the same rate.	Resume atomizing and fluidizing oxygen.	In-bed combustion resumed at 495°C 8-½ minutes after resuming oxygen flow.
Oxygen Interruption	11	Total Oxygen-Fluidizing and Atomizing	Above-bed burning with vapor temperature increasing at $\sim 50^{\circ}$C/min and bed temperature decreasing at $\sim 15^{\circ}$C/min.	Resume oxygen and reduce feed rate.	In-bed combustion resumed at $\sim 590^{\circ}$C 27 minutes after resuming oxygen flow.

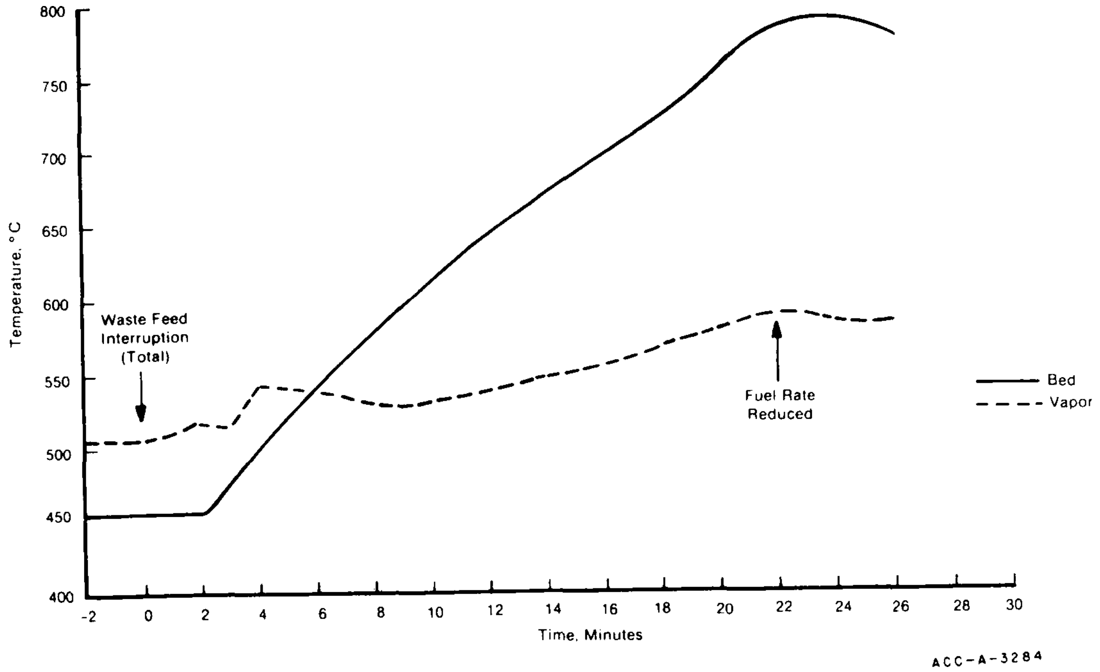

Figure 5. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of Waste Feed (9-cm Nozzle Spacing and 288 Percent Oxygen), Test 1

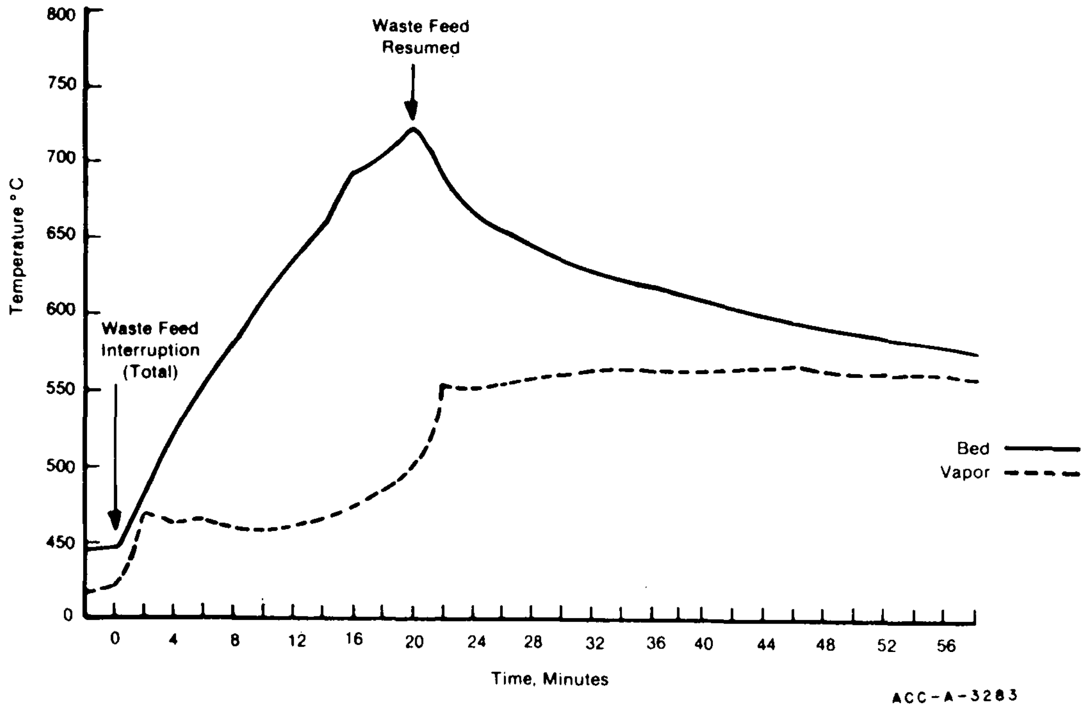

Figure 6. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of Waste Feed (24-cm Nozzle Spacing and 196 Percent Oxygen), Test 2

1.22 Tests 3 and 4 - Interruption of Fuel Atomizing Oxygen

In Tests 3 and 4, pure oxygen flow used to atomize fuel in the nozzles was abruptly halted and, as in Tests 1 and 2, the temperature effect was observed and recorded as shown in Figures 7 and 8. In Test 3, the above-bed temperature rose from 494 to 655°C within eight minutes while the bed temperature slowly decreased from 494 to 455°C. After the oxygen flow was halted for 15 minutes, the waste feed rate was reduced and the bed temperature began to rise while the above-bed temperature was nearly constant. Only when oxygen flow to the nozzle resumed did the above-bed temperature begin to decrease. In Test 4, oxygen flow rate to the nozzle was dropped to zero in two equal stages. Once oxygen flow was completely stopped, the calciner temperatures followed the same pattern as in Test 3. Three off-gas samples were taken during Test 3 at 9, 35, and 40 minutes after interruption of oxygen flow. The analysis results of each above sample as shown in Table IV, indicate that combustion of the fuel to CO or CO_2 was 99.9 percent complete. The concentration of unburned hydrocarbons in the calciner off-gas was less than 0.02 percent at all times during the test.

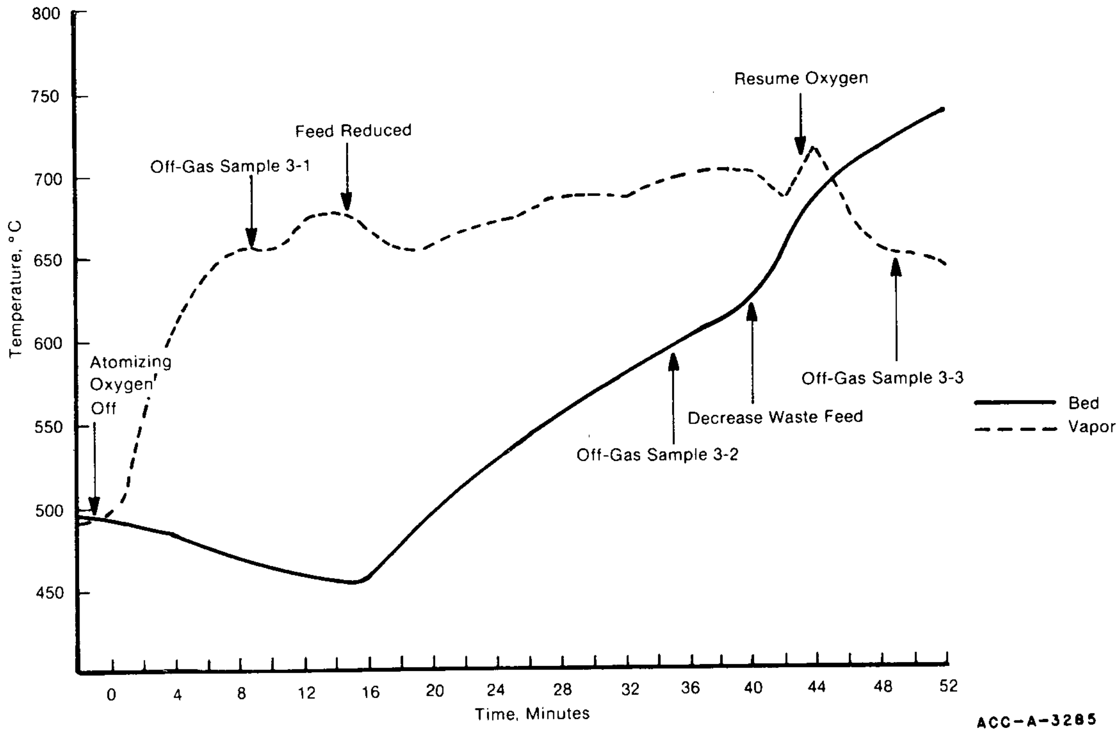

Figure 7. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of Fuel Atomizing Oxygen, Test 3

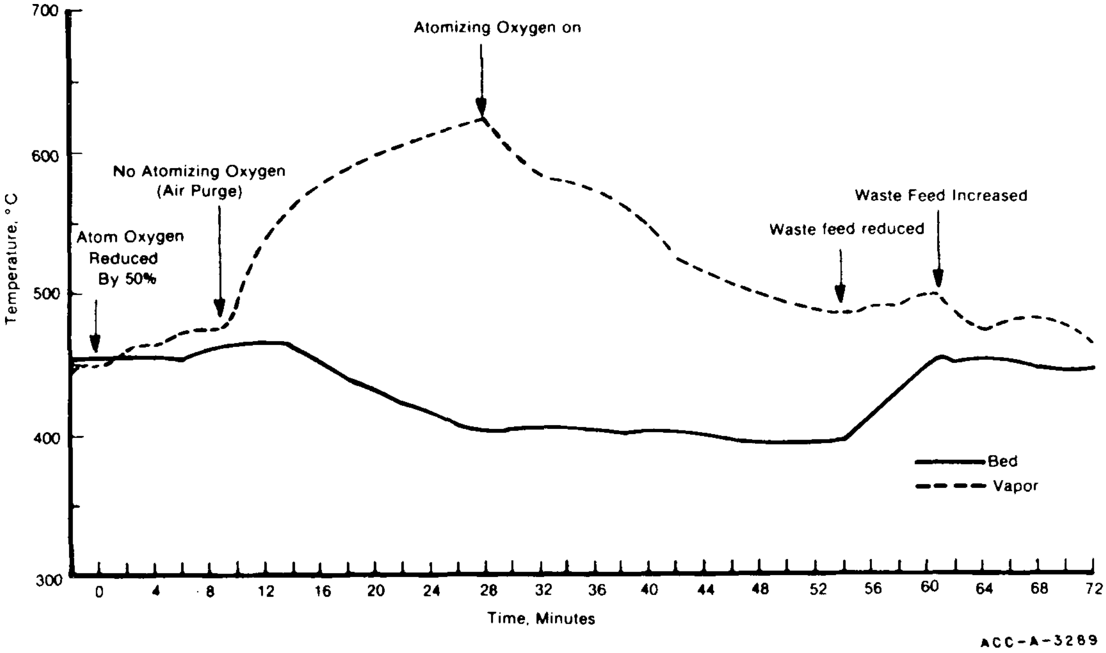

Figure 8. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of Fuel Atomizing Oxygen, Test 4

TABLE IV

OFF-GAS COMPOSITION AFTER ATOMIZING OXYGEN INTERRUPTION

Component (Mole Percent-Dry Basis)	Sample Number		
	3-1	3-2	3-3
H_2	0.04	0.02	0.01
N_2	67.9	70.5	68.7
CO	2.4	1.5	1.2
CO_2	16.3	14.7	13.8
O_2	12.2	12.2	15.3
Aliphatic Hydrocarbon	0.06	0.01	0.007
Aromatic Hydrocarbon	0.003 max.	0.002 max.	0.002 max.
Oxygen Inputs (Percent Theoretical Required for Complete Combustion)			
Fluidizing Gas	113.5	113.5	113.5
Atomizing Gas			
Fuel	2.8	2.8	2.8
Feed	10.4	10.4	12.8
as NO_3 in feed	33.4	13.0	-
TOTAL	160.1	139.7	156.5

1.23 Test 5 - Interruption of Fluidizing Oxygen

In Test 5 the flow of fluidizing oxygen, pure oxygen fed into the calciner with fluidizing air through the distributor plate, was reduced below normal levels; the temperature effects of the test are shown in Figure 9. Although above-bed burning resulted immediately after the flow rate of fluidizing oxygen was reduced only 20 percent, the vapor space temperatures were never above 505°C or never more than 75°C above the bed temperature even when the fluidizing oxygen flow was halted completely. Except for momentary periods, the vapor-space and bed temperatures rose and fell together as the flow rate of fluidizing oxygen was decreased or increased. After 77 minutes the fluidizing oxygen flow was halted and fuel combustion in the bed ceased. Seven samples of off-gas during the 90-minute test were taken, at 0, 30, 37, 40, 70, 76, and 82 minutes into the test. The analysis results are shown in Table V. The concentration of unburned hydrocarbons in the calciner off-gas did not rise above 0.14 percent until the fluidizing oxygen flow was halted. Five minutes after fuel combustion in the bed ceased, the unburned hydrocarbons concentration in the off-gas was measured at 0.32 percent; this indicates that the bed particles probably were adsorbing a considerable portion of the unburned fuel.

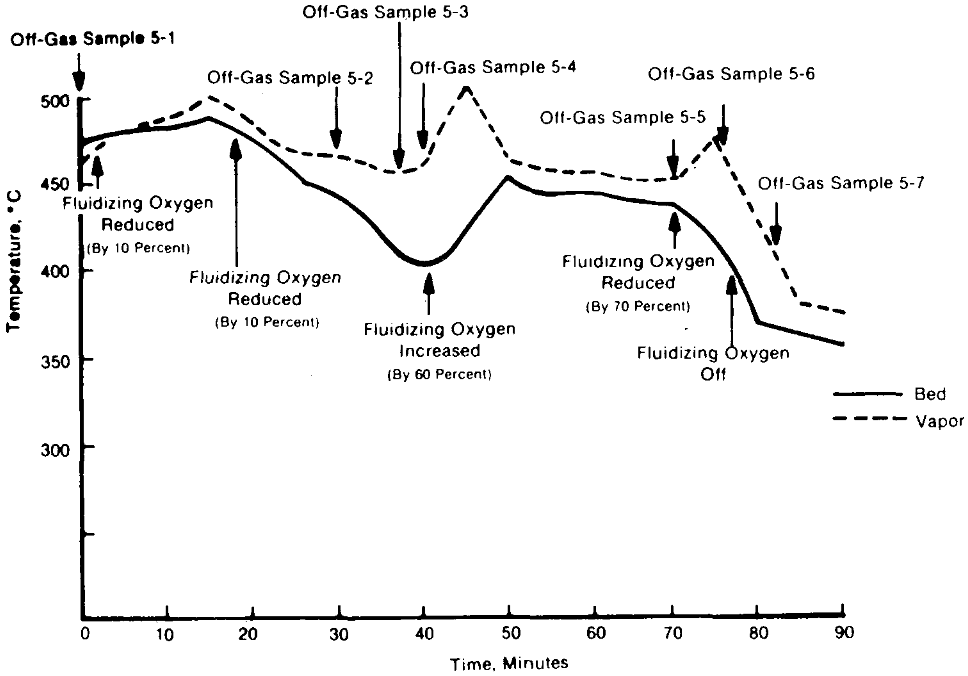

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Figure 9. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of Pure Oxygen to Fluidizing Air, Test 5

TABLE V

OFF-GAS COMPOSITION AFTER FLUIDIZED OXYGEN INTERRUPTION

Component (Mole Percent-Dry Basis)	Sample Number 5-1	5-2	5-3	5-4	5-5	5-6	5-7
H_2	0.68	0.76	0.69	0.67	0.60	1.1	0.11
N_2	53.1	56.8	56.7	57.4	48.7	63.4	76.7
CO	5.2	5.0	5.0	4.4	4.2	5.5	1.0
CO_2	16.0	14.9	14.3	13.3	14.5	13.5	4.0
O_2	23.8	21.3	22.1	23.1	31.0	15.1	16.8
Aliphatic Hydrocarbon	0.06	0.06	0.1	0.08	0.08	0.14	0.32
Aromatic Hydrocarbon	0.01	0.03	0.02	0.02	0.03	0.04	0.01
Oxygen Inputs (Percent Theoretical Required for Complete Combustion)							
Fluidizing gas	121.5	102.3	98.6	102.3	144.5	62.1	25.5
Atomizing Gas							
Fuel	25.0	25.0	24.1	25.0	24.1	24.1	2.3
Feed	11.1	11.1	10.7	11.1	10.7	10.7	20.0
as NO_3 in Feed	30.6	30.6	29.0	30.6	29.0	29.0	29.0
TOTAL	188.2	169.0	162.4	169.0	208.3	125.9	76.8

1.24 Tests 6 and 7 - Total Interruption of Pure Oxygen Streams

The total interruption of pure oxygen streams, atomizing and fluidizing oxygen, to the calciner produced differing effects on calciner temperatures in Tests 6 and 7. In Tests 6 the total loss of pure oxygen streams reduced the amount of available oxygen to less than stoichiometric amount required for complete combustion of fuel to CO_2 and H_2O. As a result, both vapor space and bed temperatures decreased steadily until flow of pure oxygen was resumed as shown in Figure 10. In Test 7 the amount of available oxygen after shut off of pure oxygen streams was greater than stoichiometric requirements, resulting in considerable above-bed burning and very high, up to 820°C, vapor space temperatures, as shown in Figure 11. However, vapor space temperature in Test 7 quickly decreased after pure oxygen flow returned. Analytical results, as shown in Table VI, of two off-gas samples taken during Test 6, again show that the concentration of unburned hydrocarbons in the calciner off-gas was less than 0.05 percent.

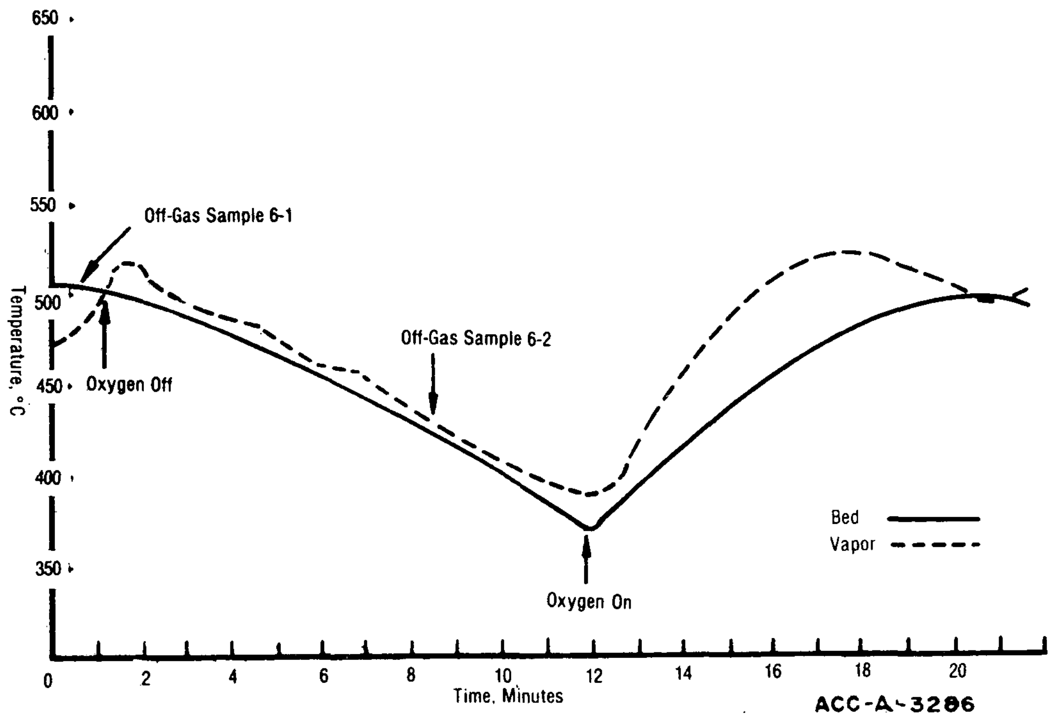

Figure 10. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of All Pure Oxygen Streams, Test 6

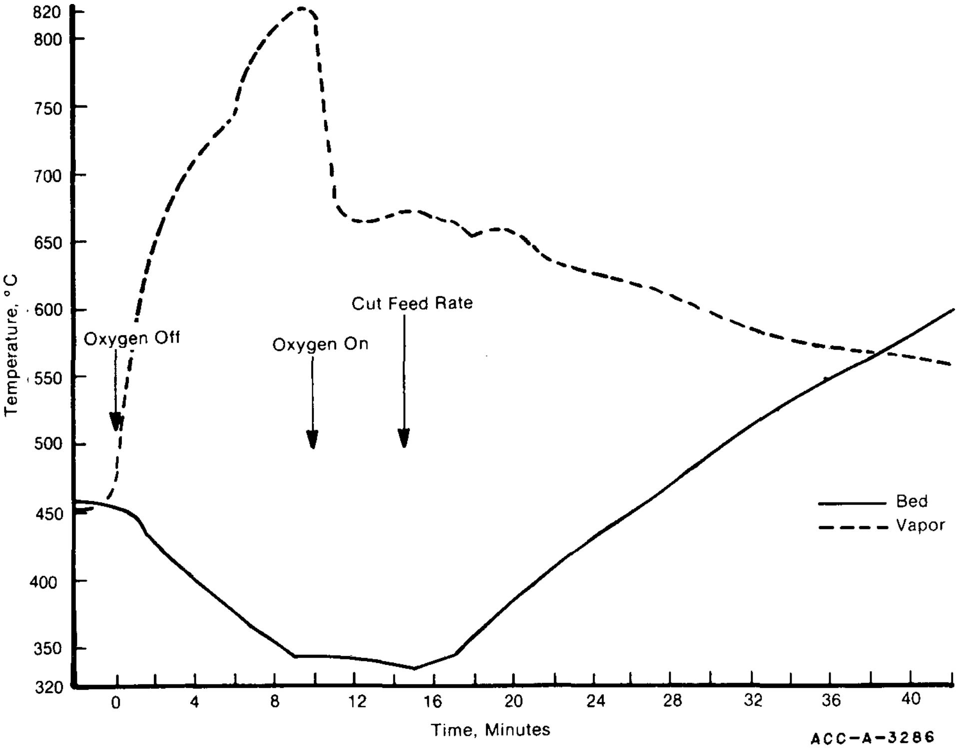

Figure 11. Time vs. Temperature Relationship of 30-cm Pilot-Plant Calciner after Interruption of All Pure Oxygen Streams, Test 7

TABLE VI

OFF-GAS COMPOSITION AFTER TOTAL OXYGEN INTERRUPTION

Component (Mole Percent-Dry Basis)	Sample Number 6-1	 6-2
H_2	0.66	0.22
N_2	54.7	77.5
CO	4.3	1.3
CO_2	14.9	5.3
O_2	24.3	14.3
Aliphatic Hydrocarbon	0.04	0.08
Aromatic Hydrocarbon	0.01	0.004 max.
Oxygen Inputs (Percent Theoretical Required for Complete Combustion)		
Fluidizing Gas	143.0	5.14
Atomizing Gas		
Fuel	14.0	2.8
Feed	10.4	10.4
as NO_3 in Feed	33.4	33.4
TOTAL	200.8	98.0

1.25 Conclusions

The important conclusions drawn from the results of these seven pilot-plant tests are as follows:

1.251 Hazardous conditions, i.e., formation of explosive fuel-air mixtures, do not result in an in-bed combustion system after major interruptions to waste feed or oxygen streams. Even during known conditions for poor combustion, the off-gas concentration of unburned hydrocarbons will be exceedingly low, less than 0.2 percent.

1.252 Temperature excursions in the calciner bed or vapor space after process flow interruptions can be controlled easily by resuming the interrupted flow or manipulating other process streams.

1.253 In all cases, ample time was available for operating personnel to perform corrective action after major upsets to process flow rates occurred.

2. Initial Operation of the WCF with In-Bed Combustion

2.1 Modification of the WCF for In-Bed Combustion

The WCF was modified for the in-bed combustion process in 1969 and 1970. The basic modifications were: (1) removal of the NaK heating system; (2) installation of three fuel nozzles; (3) modification of the NaK heating furnace to preheat the calciner to the 370°C kerosene autoignition temperature; and (4) installation of the flow control, interlock system, and storage facilities for the oxygen and fuel supplies. The maximum feed flow with in-bed combustion was estimated to be 570 L/h.[17] This value was determined from the expected off-gas system capacity and was possible because of the original 0.683 m/s fluidizing velocity designed into the WCF.[2] (Fluidizing velocities of 0.24 to 0.27 m/s have been used while operating with in-bed combustion.)[17,18] The fuel, oxygen, and fluidizing air flows required to calcine 570 L/h of zirconium fluoride waste were determined to be: 59.1 L/h of fuel, 35.7 standard m^3/h of fuel atomizing oxygen (O_2/fuel ratio of 600), 30.2 standard m^3/h of oxygen to the fluidizing air through the sparge ring and 304 standard m^3/h of fluidizing air. The fuel atomizing oxygen and additional oxygen supplied through the sparge ring were to provide 54% of the oxygen required to burn the fuel; the remainder of the oxygen required was to come from the fluidizing air.

2.2 Cold Testing of the In-Bed Combustion System in the WCF[17]

WCF campaign 4 was to be the first processing campaign to use the in-bed combustion system. Before calcining radioactive waste, the oxygen and fuel safety system was checked out and the complete system was checked out with a nonradioactive feed. Cold operation was started on May 27, 1970 with API No. 2 fuel oil atomized with external-mix type fuel nozzles (Figure 12). Fuel combustion after startup was extremely poor. Increasing the oxygen to the fluidizing air through the sparge ring did not improve the combustion while increasing the oxygen to the fuel nozzle provided some increase in performance. The calciner temperature was increased from 450 to 500°C to try to eliminate the carbon and unburned light hydrocarbons which were collecting on the silica gel adsorbers and final filters. Only a slight improvement was noted so the fuel was changed to kerosene; however, no improvement was observed. Tests conducted at the same time in the pilot-plant calciner with WCF sized nozzles (Spraying Systems Co. 1/2 J nozzles) confirmed the poor combustion performance of the external-mix nozzles.

Other nozzle types were tested in the 30-cm-diameter pilot-plant calciner to determine which type would provide good combustion efficiencies.[14] On July 9, 1970, the WCF was started using kerosene atomized in an internal-mix nozzle (Figure 13).

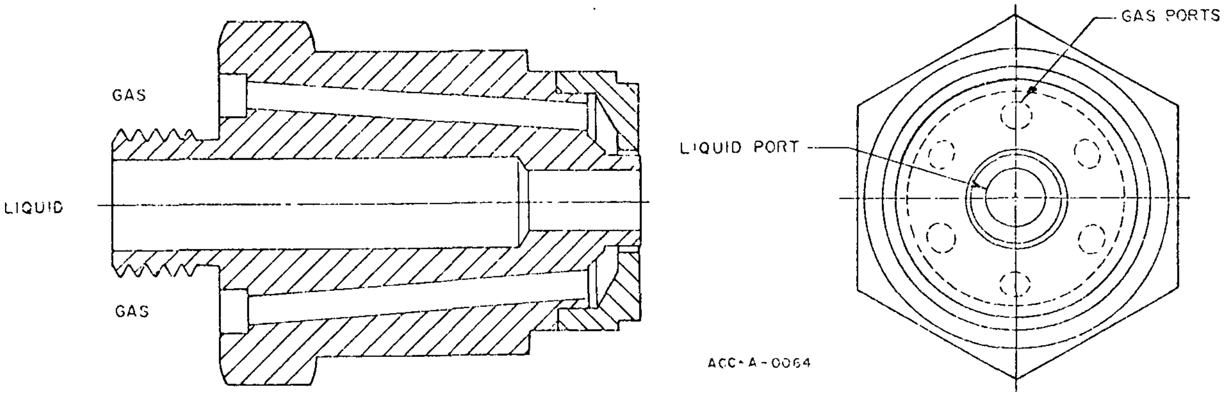

Figure 12. External Mixing Fuel Nozzle Detail

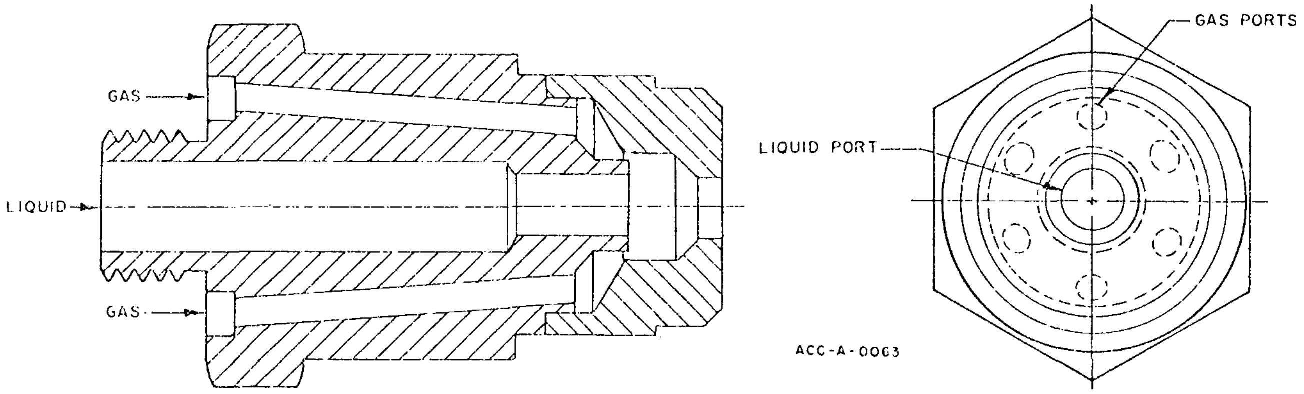

Figure 13. Internal Mixing Fuel Nozzle Detail

After startup, two of the nozzles were found to be igniting inside the fuel cap. A gasket leak allowing premature mixing of oxygen and fuel was suspected as the cause. A large fines carryover also occurred during this test, possibly because of the improper nozzle operation. On July 12, 1970, the calciner was shut down and the nozzles examined. The examination revealed that the gasket had leaked and the tips of the plungers had melted because of the preignition.

The next nozzle tested in the WCF was a modified external-mix type (Figure 14). During operation with this nozzle, excess carbon was found in the off-gas. Based on the results of the nozzle tests in the 30-cm-diameter pilot-plant calciner,[14] the oxygen was increased which reduced the amount of carbon and light hydrocarbons in the off-gas. After seven days of operation, the WCF was shut down to examine the fuel nozzles. Inspection of the nozzles revealed some loss of cap material due to abrasion, so the nozzles were replaced with wide angle internal-mix nozzles (Figure 15).

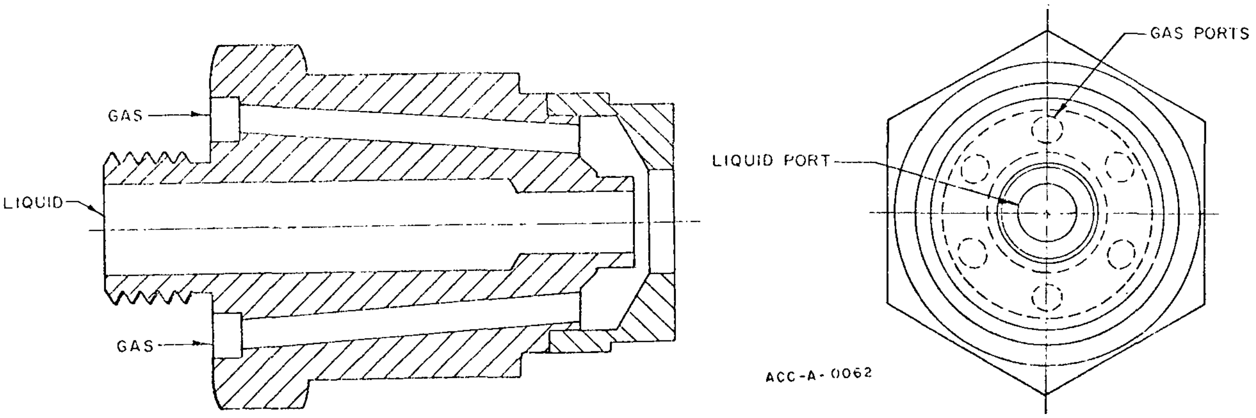

Figure 14. Modified External Mixing Fuel Nozzle Detail

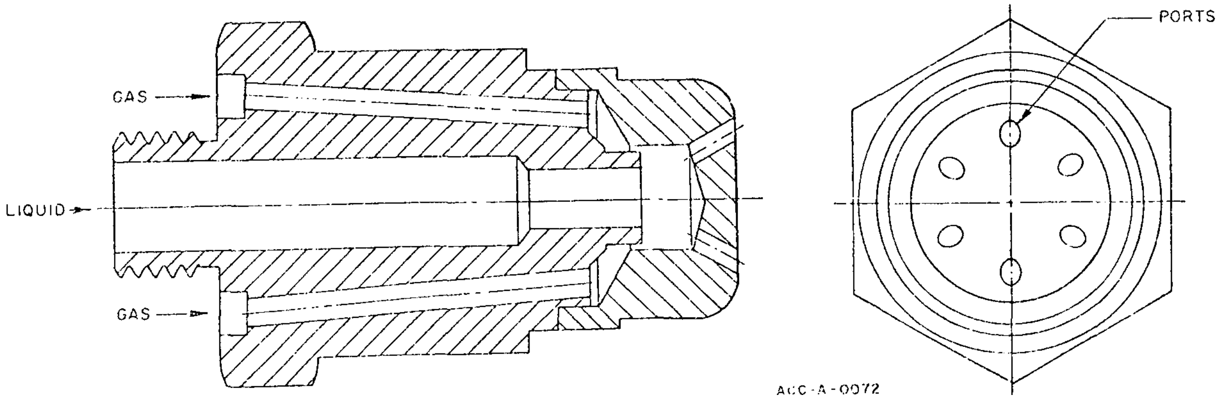

Figure 15. Wide Angle Internal-Mix Fuel Nozzle Detail

2.3 WCF Operation During Campaign 4[17]

Initial operation of the internal mix nozzles was erratic; however, by inserting the nozzle cleanout plungers, the combustion was stabilized. After six days of cold operation, hot waste was fed to the calciner. Excessive fines generation, indicated by decreasing bed height, was noted; to decrease attrition one fuel nozzle and one feed nozzle were turned off. To allow the use of all nozzles, the feed atomizing air was reduced, and the temperature was returned to 500°C to improve the combustion efficiency - no adverse effects were noted. Another attempt to increase the combustion efficiency was made by increasing the oxygen flow to the sparge ring from 34 m^3/h to 85 m^3/h (fluidizing air flow rate was 255 m^3/h). The increased oxygen in the fluidizing gas did not change the combustion efficiency.

During the campaign the net feed rate averaged 229 L/h for zirconium fluoride waste at a gross feed rate of 409 L/h. Approximately 822 m^3 of zirconium fluoride waste and 27 m^3 of aluminum nitrate waste were converted to 96 m^3 of solids. After calciner shutdown and decontamination, the fuel nozzle caps were examined. The caps of the fuel nozzles were damaged severely, as shown in Figure 16: whereas, the "liquid nozzles" were undamaged. The caps, which were fabricated from Armco 17-4PH steel hardened to H-900 condition, had been in service for 3,860 h. Metallurgical examination showed that the cylindrical portions of the caps were free of metallic deterioration, but that the spherical portions (faces of the caps in Figure 16) were carburized, with accompanying intergranular oxidation and detachment of grains (metal dusting). The examination suggests that the temperature on the faces reached at least the carburizing range (750 to 1000°C) and possibly reached the melting temperature (2500°C). (A similar deterioration of a pilot-plant nozzle showed dendritic structure in the face, which is prominent in "castings" but not found in wrought metal).

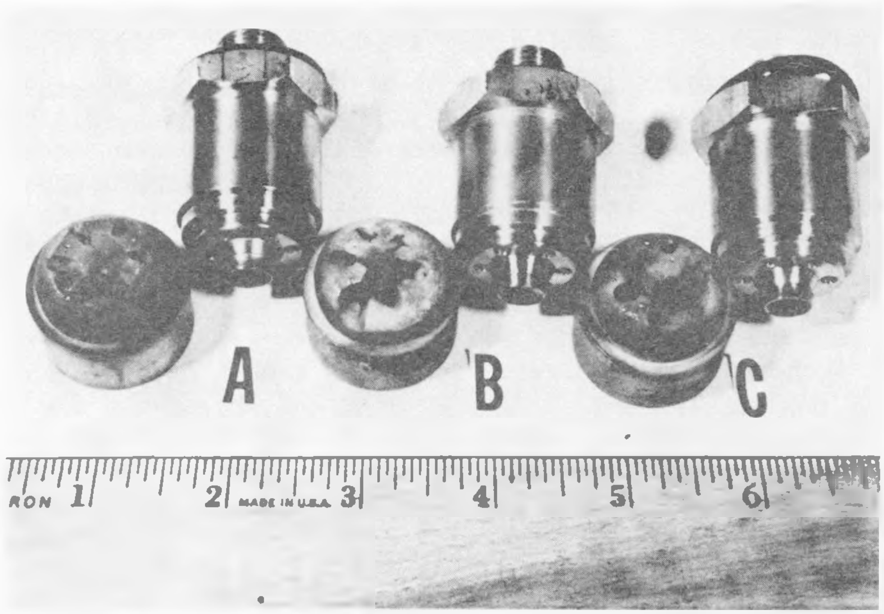

Figure 16. Damaged WCF Fuel Nozzle

3. Pilot-Plant Studies in Support of the WCF In-Bed Combustion System

3.1 Fuel Nozzle Performance Tests

During 1970 and 1971 extensive testing was done on the nozzle types to characterize their operation.[14] WCF sized nozzles were used in most of these tests rather than the 1/4 J (Spraying Systems Co. Designation) nozzles used in previous 30-cm-diameter calciner tests. The external-mix nozzle gave extremely poor performance with combustion efficiencies of only 80%. Combustion efficiencies as high as 98% were achieved with wide angle internal-mix nozzles and modified external-mix nozzles.[14] Nozzle performance was increased by operating at 500°C rather than 450°C and by using O_2 fuel ratios of 1800 rather than 1400.[14] The necessity of O_2/fuel ratios near stoichiometric (2080) was not anticipated. Previous pilot-plant operations with 1/4 J nozzles indicated a large portion of the oxygen needed for combustion could be supplied by the fluidizing gas. The operation of large WCF nozzles was completely different from the operation of small nozzles. There was also a difference in the combustion efficiencies of WCF nozzles in the 30-cm-diameter calciner and the WCF. Modified external-mix nozzle combustion efficiencies were 98% in the 30-cm-diameter calciner and less than 92% in the WCF. Modified external-mix nozzles were found to erode, so in 1970 the wide angle internal-mix nozzle was recommended for use in the WCF.

design. Tests conducted with the wide angle internal-mix nozzle caps indicated the problem was preignition of fuel and oxygen inside the caps at low oxygen and fuel flows.[19] The destruction of the caps was duplicated in an open air nozzle test stand by initiating combustion in the nozzle cap and then increasing oxygen and fuel flows to normal levels. Once burning in the cap is initiated, the flame can not be extinguished unless the fuel and oxygen are cut off and the nozzle restarted with proper flowrates.

The in-bed combustion method of heating in the WCF resulted in a substantial change in the method of operation with respect to the amount of feed atomizing air. The feed nozzle air ratios were decreased from approximately 700 to 200 to keep the particle size (MMPD) above 0.4 mm. This indicated that a substantial amount of the attrition to particles occurred at the fuel nozzles. Gas velocities at the fuel nozzles were determined to be 180 m/s to sonic.[16] To reduce these velocities, tests were conducted with Sonicore™ nozzles and Spraying Systems Co. nozzles mounted in a shroud. A wide angle internal-mix nozzle was mounted in a shroud and operated with only enough oxygen supplied to the nozzle to atomize the fuel. The remainder of the oxygen was supplied to the shroud to produce a low velocity flame the size of the shroud. The shrouded nozzle performed poorly because the flame impinged on the shroud resulting in rapid oxidation and melting of the shroud.[19]

Tests with the shrouded Sonicore™ nozzle (Figure 17) in the 30-cm-diameter calciner indicated that it could not be used to calcine ZrO_2-CaF_2 calcine.[16] Combustion efficiencies of 99% were achieved, ignition temperatures as low as 270°C were possible, and product-to-fines ratios with alumina calcine were increased by a factor of four because the nozzle gas velocities were reduced to 60 m/s. However, tests performed while calcining zirconium fluoride waste indicated the shroud and flame temperatures were too high. Most sintering seemed to have occurred when the calcine passed in front of the intensely hot flame of the Sonicore nozzle; some bed melting also occurred on the shroud.

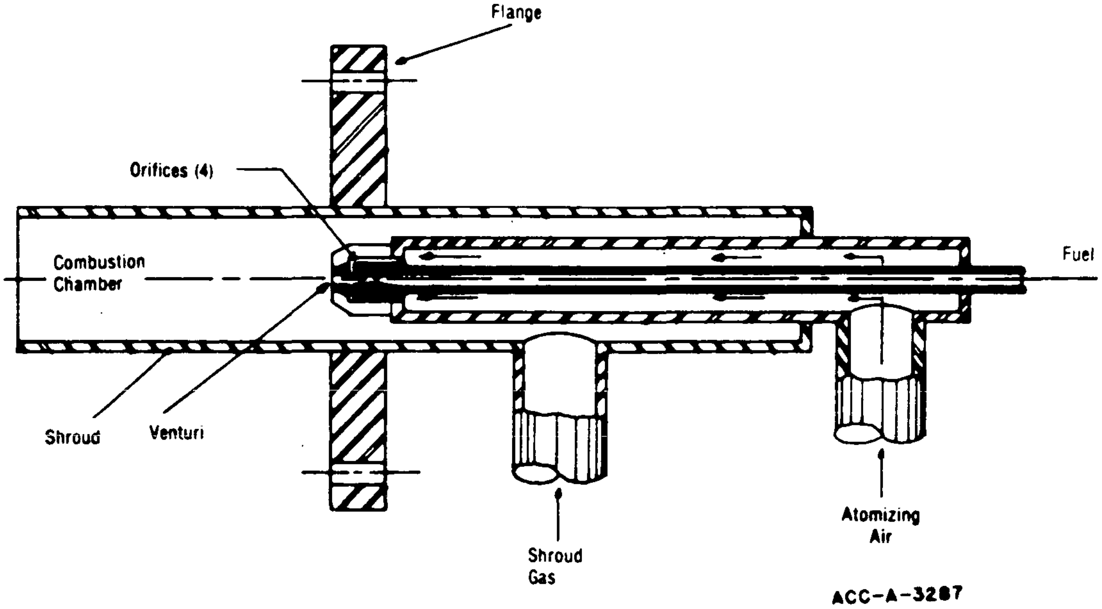

Figure 17. Shrouded Sonicore Fuel Nozzle

3.2 Determination of Combustion Efficiency from CO and CO_2 Analyses[16]

Work performed during 1973 produced a method for quick determination of combustion efficiencies. From gas-bomb sample analyses combustion efficiencies were determined for the WCF, and the 30-cm-diameter calciner used for pilot-plant nozzle testing. When these combustion efficiencies were plotted as a function of the $CO_2/(CO_2+CO)$ ratio, the result was a linear plot. Infrared CO and CO_2 analyzers could then be used for instant determination of combustion efficiencies during nozzle tests. The combustion efficiency measurements will also be useful in determining the condition of WCF nozzles during operation.

3.3 Nozzle Cap Material Tests

During the last part of WCF campaign 6 and during campaign 7, modified external-mix nozzle caps constructed of 440C stainless steel were installed. Their operation was satisfactory; however, during extensive decontamination, necessary for turnaround, the nozzle caps were destroyed. No determination of the extent of erosion or the effects of heat could be made. More importantly, decontamination solutions could not be brought into contact with the nozzles, which limited the extent of operations to dissolve restrictions in the calciner vessel or necessitated replacement of the caps after decontamination.

Some testing of nozzle cap materials has been made. The materials tested were Haynes 25, Haynes 188, 440C stainless steel, 304L stainless steel, Hastalloy X and three ceramics coated on 304L stainless steel. The 440C stainless steel was the most erosion resistant material; however, the decontamination solutions completely destroyed the 440C coupon. The ceramic coatings were rejected because they did not remain bonded to the base metal during the erosion tests. The Haynes alloys were fairly resistant to erosion and withstood the corrosion tests quite well. After completion of the tests, modified external-mix nozzle caps were fabricated of Haynes 25 and Haynes 188 alloys and installed in the WCF. Their performance during the first seven months of campaign 8 has been satisfactory.

4. WCF Operation From 1971 Through 1977

4.1 WCF Campaign 5[18]

WCF campaign 5 extended from September 23, 1971 to May 11, 1972. During this campaign 894 m^3 of zirconium fluoride waste, 220 m^3 of aluminum nitrate waste and 19 m^3 of stainless steel-sulfate waste were processed. Modified external-mix nozzles with 440C stainless steel caps were used to atomize the kerosene [19] (Figure 14). The gas passages in these nozzles were enlarged to yield a 30% increase in oxygen rate and thus, an increase in calcination capacity.[18] The gross feed rate during campaign 4 was 410 L/h[17] and was increased to 460 L/h during the fifth processing campaign.

Some of the increased capacity was due to the enlargement of the venturi scrubber and the use of an off-gas heater as a condenser to decrease the amount of off-gas reaching the blowers.[18]

The modified external-mix nozzles were operated at an O_2/fuel ratio of 1500 rather than stoichiometric (2080) to reduce the jet grinding effect on the bed from higher velocity gases. This produced a combustion efficiency of 85%. The kerosene rates were 16.3 to 23.9 L/h per nozzle. Oxygen was not used in the sparge ring since tests during campaign 4 indicated no improvement in combustion efficiency would result with up to 20% of the fluidizing gas made up of pure oxygen. (Section 2.3.)

The behavior of ruthenium during the fifth campaign was markedly different than the four previous campaigns. Ruthenium is released from the fluidized bed as both a gaseous (RuO_4) and particulate form (RuO_2). The two species are in equilibrium and driven to the particulate form by a reducing atmosphere. Decontamination of the calciner vessel and off-gas equipment was extremely difficult because ruthenium had plated out on the vessel walls. The plate-out of ruthenium may have been caused by the change in operation of the in-bed combustion system. The O_2/fuel ratio was less than stoichiometric and oxygen was not applied to the sparge ring, creating a reducing atmosphere at least near the fuel nozzles and possibly throughout the bed driving the RuO_4 and RuO_2 equilibrium to the ruthenium dioxide.

4.2 WCF Campaign 6 [20]

WCF Campaign 6 began on May 25, 1973 and continued to May 8, 1974 with several major shutdowns for repair of equipment. During this run 1.46 km^3 of waste were calcined. Wide angle internal-mix nozzles were selected for use during this campaign. (Figure 15.) The wide angle internal-mix nozzles used in campaign 4 were destroyed by heat so the nozzle caps for this campaign were constructed of tungsten. Operation with these nozzles was good through the first shutdown, after 2600 h, for repair of the feed control valves. Inspection of the A nozzle cap during this shutdown revealed a missing metal segment between two holes on the cap; the nozzle cap was reinstalled. After equipment repair had been completed, calciner startup was attempted. Oxygen and fuel flows to the B nozzle appeared to be restricted so the nozzle was removed for inspection. The shoulder of the cap was cracked where the cap seats against the calciner fuel nozzle port and a metal segment between two holes was missing. The cap was replaced with a modified external-mix nozzle cap (Figure 14) constructed of 440C stainless steel. Startup was then accomplished without incident.

After 2600 hours of operation the calciner was again shut down and extensive decontamination conducted to remove a primary cyclone restriction. During this shutdown all nozzle caps were replaced with modified external-mix caps. The two remaining tungsten, wide angle internal-mix caps were in good condition; however, they were replaced as a precaution. The 440C B nozzle cap was severely corroded by the decontamination solutions so it was also replaced. WCF campaign 6 was terminated after another 1100 hours of operation. The nozzle caps were examined after calciner decontamination. Extensive corrosion to two of the three fuel nozzle caps had occurred. No combustion efficiency data or O_2/fuel ratios are available for the sixth campaign.

4.3 WCF Campaign 7

WCF Campaign 7 lasted for eighteen months from June 1975 to December 1977 during which 845 m^3 of waste were calcined. Modified external-mix nozzles with 440C stainless steel caps were used with O_2/fuel ratios of 2000. No off-gas samples were taken for combustion analysis. Several calciner shutdowns occurred involving extensive decontamination, removal of primary cyclone restriction and repair of scrub pumps. During calciner decontamination the 440C fuel nozzle caps were destroyed and had to be replaced.

4.4 WCF Campaign 8

WCF Campaign 8 began on September 13, 1977;1.36 km^3 of zirconium fluoride waste and 85 m^3 of sodium-bearing waste have been calcined in 11 months with several shutdowns for equipment repair. Modified external-mix nozzles are being used with caps constructed of Haynes 25 or Haynes 188 alloys. CO and CO_2 analyzers have been installed for continuous measurements of combustion efficiency. O_2/fuel ratios have ranged from 1800 to 2400 and combustion efficiencies from 85 to 91%. The particle size has ranged from 0.39 to 0.46 mm while calcining zirconium fluoride waste and up to 0.75 mm while calcining the 3.5:1 blend of zirconium fluoride and sodium-bearing wastes.

5. Comparison of In-Bed Combustion Heating to Recirculating NaK Heating

Both NaK heating and in-bed combustion have distinct advantages. The following is a brief discussion of the advantages and disadvantages of each. Since WCF Campaign 4, bed attrition has been a problem requiring special attention. The high velocity flame from the fuel nozzles causes a higher attrition rate than that experienced during operation with the recirculating NaK system. The high attrition rates sometimes cause difficulty in maintaining the bed level To maintain bed levels, the oxygen rate to the fuel nozzle has been decreased; this sacrifices combustion efficiencies. High fines generation rates result in more fines carryover to the scrub system, necessitating higher scrub recycle rates than would otherwise be necessary. An increase in the fines also makes calcine retrieval from the storage bins more difficult and requires expensive bin space.

Burning a hydrocarbon fuel in the calciner bed yields combustion products (10% of total calciner off-gas) which must be cleaned of radioactive contaminants along with fluidizing gases, atomizing gases, and water vapor. A calciner using a recirculating NaK system for heat input does not produce any extra gases, but a larger diameter vessel (for the heat exchanger) is required to calcine waste at the same rate. A larger diameter vessel requires a larger volume of fluidizing air, and a NaK system requires higher waste nozzle atomizing air ratios. So the two systems produce nearly the same volume of gas for identical gross feed rates. The basic economic differences between a recirculating NaK heating system and an in-bed combustion system are a smaller calciner vessel for the in-bed combustion system and a NaK heating system vs. a kerosene and oxygen control and storage system.

Combustion efficiencies higher than 92% cannot be regularly achieved with the in-bed combustion system; therefore, light hydrocarbons are produced in the calciner. These unburned hydrocarbons may cause some of the plugging problems encountered in the WCF since in-bed combustion has been used.

The Sonicore nozzle tests (Section 3.1) showed that high nozzle performance with low attrition can be achieved while calcining aluminum nitrate waste. Zirconium fluoride waste, on the other hand, melted when passing through the intensely hot flame. Any other nozzle configuration, with a 99% combustion efficiency and a similar mix of oxygen and air, would also melt the calcine. Therefore, low flame temperatures are needed with in-bed combustion to calcine the present high level wastes at ICPP (zirconium fluoride waste); high combustion efficiency must be sacrificed. During pilot-plant calciner runs, melting of calcine has occurred while calcining blends of zirconium fluoride waste and sodium-bearing waste. This has made the development of flowsheets for sodium-bearing wastes even more difficult. During the latter part of Campaign 8, a flowsheet for calcination of sodium-bearing wastes blended with zirconium fluoride waste (1:3.5) has been tested. During the test the MMPD rose from 0.4 mm to 0.74 mm necessitating a fluidizing velocity of 0.4 m/s to reduce the sintering. Numerous sintered agglomerates have been found in bed samples but their presence has been tolerable. The calcine produce by this blend is extremely hard. To reduce the particle size, high feed nozzle air ratios have been used. Without the additional high attrition produced by the fuel nozzles this blend would be impossible to calcine.

IV. Selection of Fluidizing Velocity and Distributor Plate Design

1. Fluidizing Velocity

The fluidizing velocity in the six-inch-diameter calciner was selected to minimize electric heater burnout. A velocity of 0.61 to 0.76 m/s was selected as a rate which would not cause a large excess of elutriated fines and would prevent frequent heater burnouts.[4] Work in the 2-foot-square calciner showed that velocities as low as 0.21 m/s would give good heat transfer at the NaK heat exchanger bundle.[5] Fluidizing velocities of 0.18 m/s were determined to be the lowest acceptable rates without resulting in bed caking.

The Demonstration Waste Calcining Facility (DWCF) was designed to operate with a fluidizing velocity of 0.683 m/s based on the performance of the six-inch-diameter calciner.[2] The data from the two-foot-square calciner were not incorporated into the DWCF design. The initial test runs in the DWCF showed an excessive fines elutriation rate (maximum 68 kg/h). Further studies were conducted in the 2-foot-square calciner (Section II-2) to evaluate the problem. A fluidizing velocity of 0.31 m/s was selected as a safe value which would provide sufficient heat transfer coefficients and minimize solids elutriation. During the first three processing campaigns in the Waste Calcining Facility, fluidizing velocities of 0.21 to 0.31 m/s were used.[10,11,12]

With the in-bed combustion system, fluidizing velocities of 0.24 to 0.31 m/s are necessary to maintain adequate fluidization at the fuel nozzles.[17,18,20] If the fluidization is insufficient, the bed particles reside in the fuel nozzle flame too long and sintering occurs which leads to agglomeration and eventual melting of the entire bed. The fluidizing velocity at the WCF feed nozzles is approximately 0.43 m/s and 0.8 to 0.9 m/s at the top of the bed.

2. Distribution Plate Design

The development program for the two-foot-square calciner included development of distributor plates. Dependable operation of a fluidized-bed calciner required that the bed be thoroughly fluidized and that dead spaces be absent in order to promote high heat transfer rates and minimize the possibility of bed caking. To a large extent, this must be accomplished by proper introduction of the fluidizing medium into the bed, and hence, by proper design of the fluidizing gas distributor or bed support plate. Fluidizing gas can be distributed adequately by a number of different designs, but with any design, satisfactory uniform fluidization cannot be achieved unless the pressure drop across the bed support plate is at least 40 percent of the pressure drop across the bed.[21] When this provision is followed, rolling of the bed will not start preferential flow of gas through a portion of the bed.

The air distributor plate adopted after initial testing of several designs is shown in Figure 18. This plate, with its 23 capped openings, gave satisfactory service, and was used on Run 6 in the 2-foot-square calciner and subsequent runs. From 38 to 53 percent of the pressure drop across the fluidized bed was generated across this plate when using superficial fluidizing velocities from 0.24 to 0.31 m/s.

Other bed support plates tested were:

a. A flat bed support plate containing 38 air distributor caps positioned on a four-inch triangular pitch (Figure 19). This was the initial air distributor plate used in the calciner, and as far as could be determined, its operation was as good as that for the plate shown in Figure 18.

b. A plate similar to that shown in Figure 18, except that it did not have air distributor caps and was perforated with 3/16-inch-diameter holes centered on a 1 13/16-inch triangular pitch. Evaluation of this plate was inconclusive, because during the test run the plate warped away from the center drain pipe and allowed part of the fluidizing gas to enter the bed through this rather large opening. During the initial part of the run, bed fluidization seemed to be good; later in the run, bed fluidization was poor. No further tests were made using this plate, but there are no known reasons why it should not give satisfactory service if properly installed.

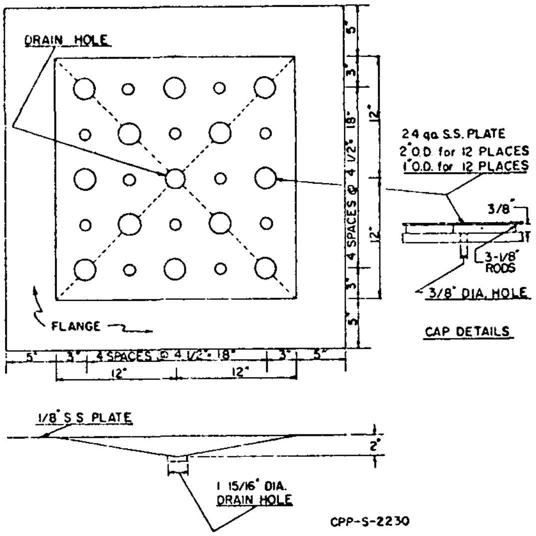

Figure 18. Air Distributor Plate Used Subsequent to Two-Foot-Square Calciner Run 6

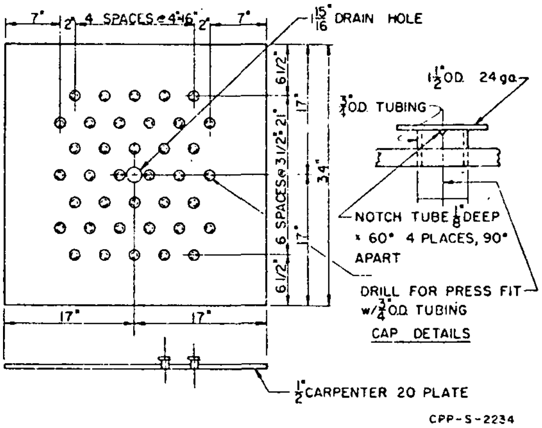

Figure 19. Two-Foot-Square Calciner Initial Air Distributor Plate

c. A plate similar to that shown in Figure 18, except that it had twelve air distributor caps, placed over 3/4-inch-diameter holes spaced on a nine-inch-square pitch, instead of 23 capped openings. The pressure drop across this plate was only 9 to 13 percent of that across the bed, and its use resulted in poor bed fluidization, which in turn frequently caused the bed to cake. Operation of the calciner, using this plate, was extremely unsatisfactory.

The WCF distributor plate is a 3/8-inch concave plate installed near the bottom tangent line of the calciner vessel. Fluidizing air is distributed to the bed through fourteen 3/4-inch-diameter holes located on a 9-inch triangular pitch; each hole is lined with a hard, tungsten-chrome-boron alloy to reduce erosion.

During DWCF testing the need for reducing the calciner elutriation losses and solids carryover into the scrubbing system became very evident by the end of the third run. As a partial answer to this problem, caps were installed over the air orifices in the plate to reduce the particle attrition resulting from direct impingement of the high-velocity fluidizing air into the bed. The caps installed for Run 4 were held in place by spring clips which proved inadequate, allowing several of the caps to slip out of place. For Run 5, the orifice insert and cap shown in Figure 20 were employed. The insert provided a more secure connection and by varying the insert thickness, the plate pressure drop could be held constant although fluidizing rates were changed from run to run. For Runs 5 through 10, the insert was sized to give a minimum pressure drop of at least 40 percent of the fluidized-bed pressure drop as recommended by Zenz and Othmer.[21] Another factor determining the design of the caps was the limited access to the air distributor plate. The top side of the plate could be reached only through an eight-inch nozzle in the calciner shell or from above the exchanger tubes, a distance of 1.5 meters. The bottom side of the plate could be reached only through an eight-inch nozzle in the calciner shell.

Inspections following Run 10 showed that severe erosion of the air distributor cap had occurred (Figure 21). A test program was then initiated from which a new cap design, less susceptible to erosion, was developed for radioactive operation.[22] The new nozzle cap was designed to prevent backflow of calcine through the distributor while maintaining a low attrition rate. The minimum velocity to prevent the backflow of calcine during operation was determined to be 49 m/s. The final cap was designed to produce gas velocities at the edge from 49 to 61 m/s. The attrition rate was determined to be low at these velocities. The cap was constructed with a cone shaped top to prevent dead spots above the cap and with three support legs to contact the distributor plate 4 inches from the center of the hole. The zone of high velocity particles, thus high erosion, extended 3.5 inches from the center of the hole. The final design for the WCF is shown in Figure 22.

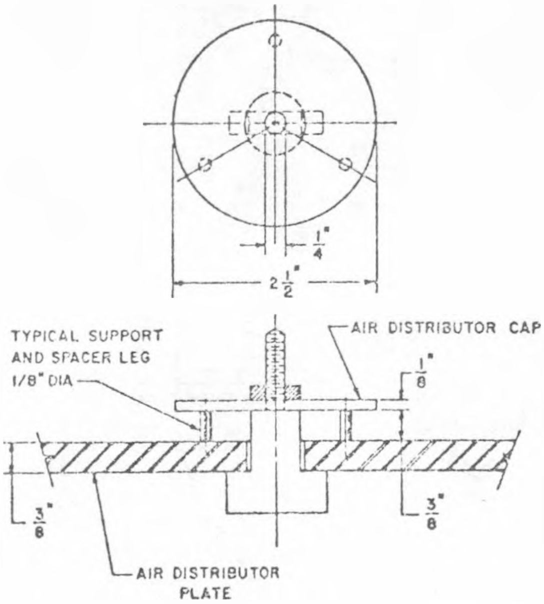

Figure 20. Air Distributor Cap Assembly Installed Prior to Run 5

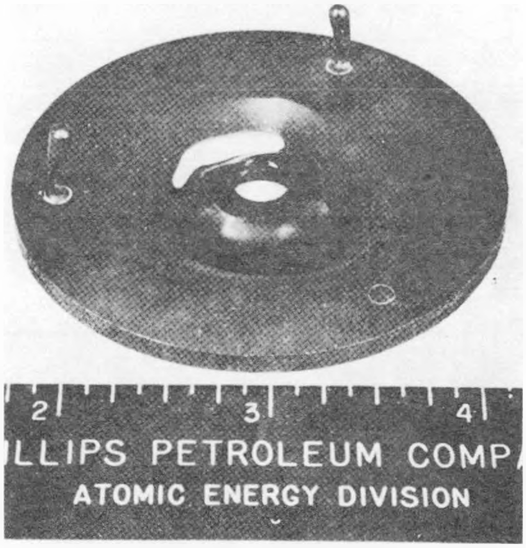

Figure 21. Erosion of Underside of Air Distributor Cap Removed from Calciner Vessel Following Run 10

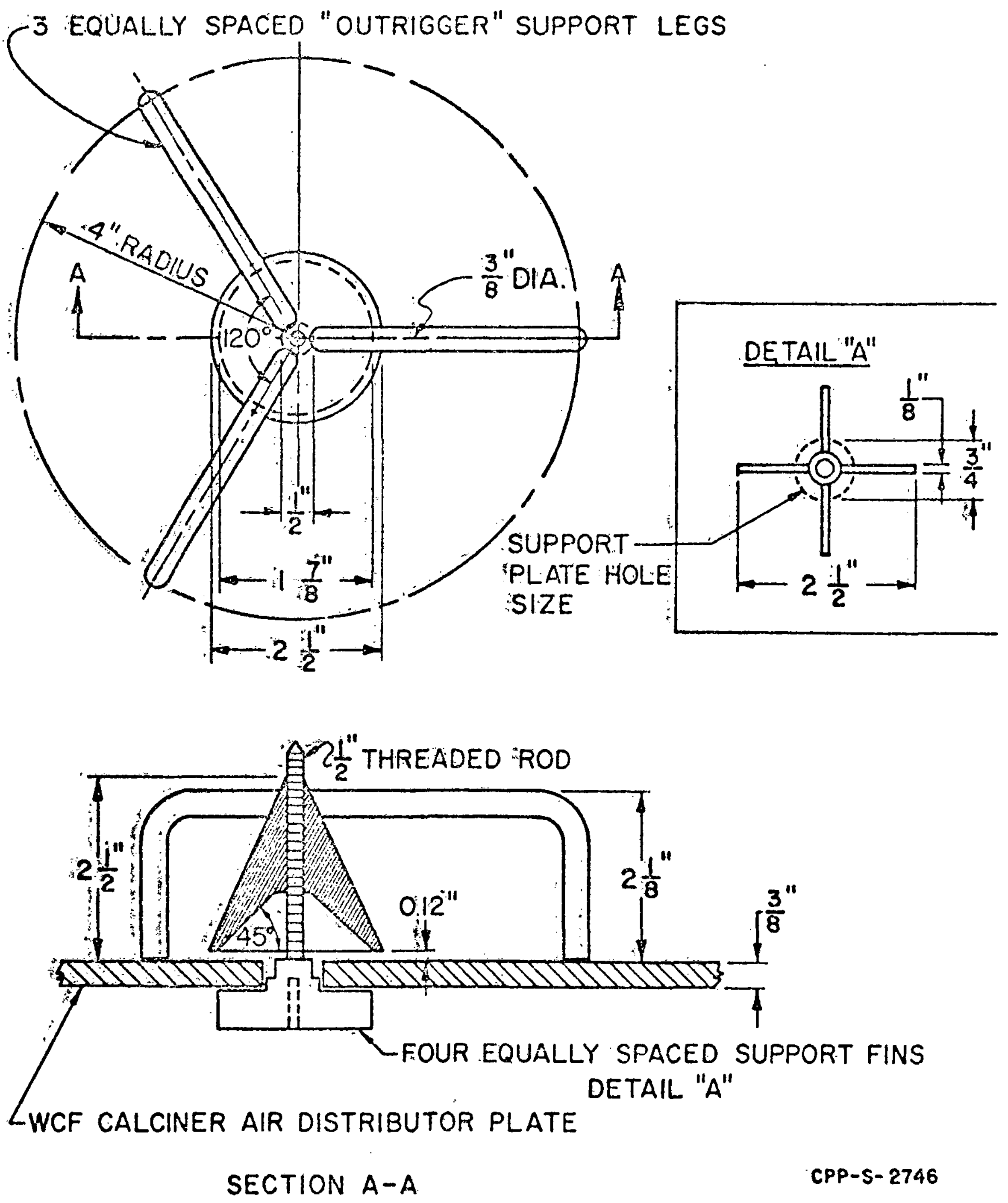

Figure 22. Modified Air Distributor Cap

V. Alternative Methods of Calciner Heat Input Investigated for the New Waste Calcining Facility

The conceptual design for the NWCF called for an in-bed combustion system as the primary heat source. A secondary heat source was proposed which could be used to calcine different wastes that might be produced in the future and not be possible to calcine with an in-bed combustion heat source. The investigation into alternate heating methods was conducted during 1973 and 1974.

Eight methods for indirectly heating the NWCF were evaluated on the basis of reliability, development required, cost, safety, and potential for environmental release. Electrical resistance heating offered a clear advantage in almost every respect as shown in Table VII. The combustion gas heat exchanger was considered second best. These two systems were recommended for further evaluation and pilot-plant verification. The reasons for investigating indirect heating and the evaluation of each alternative are:

1. Advantages and Disadvantages of Indirect Heating

1.1 Indirect heating has distinct advantages over in-bed combustion. Some of the advantages of indirect heating are:

1.11 Indirect heating would allow lower operating temperature and almost eliminate the potential for melting and agglomeration.

1.12 Indirect heating might reduce the amount of Ru plateout in the system (making decontamination easier), but since a reducing atmosphere would not be present, Ru volatility would probably be higher.

1.13 Indirect heating would eliminate unburned hydrocarbons and particulate carbon that can foul silica gel adsorbers and HEPA filters.

1.2 The disadvantages of indirect heating methods are:

1.21 Indirect heating is less efficient than in-bed combustion, requiring more energy.

1.22 Indirect heating is limited in the amount of additional heat that can be supplied for increased processing rates.

1.23 Indirect heating, in general, will have higher capital and operating costs than in-bed combustion.

TABLE VII

SUMMARY OF INDIRECT HEATING EVALUATION

Order of Ranking	Heating Method	Reliability	R&D Required	Cost (dollars)		Safety (Heating System)	Potential for Activity Release
				Capital	Operating		
1A	Electrical Resistance Finned Element	Good (5 yr design life)	Moderate (Pilot-Plant Studies)	100,000 (140 elements)	10,000/mo	Excellent	None
1B	Electrical Resistance Element in Finned Tube	Fair	Moderate (Pilot-Plant Studies)	142,000 (330 elements)	10,000/mo	Excellent	None
1C	Electrical Resistance Bare Element	Good	Moderate	150,000 (415 elements)	10,000/mo	Excellent	None
2	Combustion Gas in Finned Tube Exchanger	Good	Extensive (Pilot-Plant Studies)	440,000 (250 tubes)	8,500/mo	Good	Moderate
3	Fluidized Particle Heater Finned Tube Exchanger	Fair	Extensive	455,000 (200 tubes)	6,500/mo	Fair	Moderate
4	Helium Recirculation Finned Tube Exchanger	Good	Extensive	650,000	5,000/mo	Fair	Small
5	Electrical Induction Coil	Unknown	Extensive	Unknown	15,000/mo	Excellent	None
6	Heat Transfer Fluid Finned Tube Exchanger	(Eliminated since maximum temperature is 425^{o}C.)					
7	Heated Fluidizing Gas	(Required gas temperature or volume too high.)					
8	Heat Pipes	(Manufacturer could not be found to construct heat pipes containing Cd.)					

2. Explanation of Alternative Heating Methods

2.1 Electrical Heating with Resistance Elements

During recent years, electrical resistance elements have been developed for industrial and nuclear applications. These elements have high power densities, long life, and good reliability. Electrical resistance heaters were evaluated in three configurations -- finned element, bare element in finned tube, and bare element. In each case, calculations were made to determine the number of elements necessary to produce the necessary heat load. Costs and reliability of each design were obtained from the literature and from discussions with manufacturer's representatives. The best of the heating methods considered for the NWCF was electrical resistance elements with attached helical fins; see 1A in Table VII. This method required the least number of calciner vessel penetrations, had the lowest capital cost, has good reliability, and would have required only a moderate program of pilot-plant verification. In addition, there was no chance for any activity release (from heating system), and the safety features were excellent. With this approach, high quality elements are fabricated with a high power rating (10.8 kW/m) and a design life of at least five years. Helical fins would be welded to the outer stainless steel sheath of the element. This design allows for the highest heat flux while maintaining the lowest internal temperature. The problem of "hot spots" would be minimal because of the decreased resistance to heat transfer between the finned surface and the fluidized bed. For the above reasons, this method was recommended as the primary method for further evaluation and pilot-plant testing.

A second method of heating using electrical resistance heaters consisted of inserting the bare elements in finned tubes. The major problem with this design is the gap that remains between the element and the inside of the finned tube. This gap greatly reduces heat transfer, increases the internal temperature, and reduces the life of the element. It may be possible to fill the majority of the gap with a heat transfer media such as graphite. One advantage of this design is the reduced time required to replace a defective element. The element can be withdrawn and a new one installed, but a filler element in the gap could significantly increase the difficulty of removal.

Bare elements were the third possible variation on electrical resistance heating. The main drawback with this method is the low heat transfer rate between the surface of the element and the fluidized bed. This greatly increases the number of elements, since the power to each element must be reduced. In addition, this design is probably more susceptible to "hot spots" than the finned element but less than the element-in-tube design.

The tests with the finned heaters indicated heat densities as high as those achieved with in-bed combustion could not be achieved. Operation at 500°C was desired to keep ruthenium volatility as low as possible, which compounded the problem. A heat input rate as high as that produced by in-bed combustion was the criteria established for comparison and selection of a secondary heat supply. Based on the test results sufficient heat input could not be achieved.

2.2 In-Tube Combustion

In fluidized-bed heating, with a combustion gas heated exchanger, kerosene and air would be burned in a turbine type combustion unit. The hot gases would be diluted with air to reduce the temperature and then passed through an in-bed finned-tube exchanger. The exit gases would be used to preheat the combustion air and dilution air to improve efficiency and then discharged to the atmosphere. This method of heating was considered the second best after electrical resistance elements. The method would have good reliability, safety and a moderate potential for environmental release. The factors limiting the use of this system were the extensive development required and the high cost.

The performance of this type of unit is limited by the poor heat transfer between the hot gases inside the tubes and the walls of the tube. The obvious method to increase the inside heat transfer coefficient is to obtain tubes with internal fins. Several of the leading finned-tube manufacturers were contacted, and none could provide internal fins from a material (such as stainless steel) that could withstand the high gas temperatures. The only feasible suggestion was to place a spring (mechanical contact) inside the tubes, but this would only improve heat transfer rates by 10-15%. A combustion unit was ordered for testing in a 30-cm-diameter calciner; however, the project was cancelled before the burner arrived so no data were collected on this type of system.

2.3 Fluidized Particle Heater

The fluidized particle heater uses a separate fluidized bed with in-bed combustion heating to heat the bed particles to about 760°C. These particles would be transferred pneumatically through a U-shaped finned-tube exchanger in the calciner. The particles are then transferred back to the fluidized heater to complete the cycle. This method was not considered feasible because of the extensive development required, high cost, and only fair reliability. In addition, problems would exist with regard to erosion and plugging of the tubes.

2.4 Helium Recirculation

The helium recirculation method of heat input uses a fluidized-bed burner containing a heat exchanger through which the helium flows to a heat exchanger in the calciner and then back again. In this concept, a separate fluidized bed with in-bed combustion heating is used to heat high pressure helium within a finned-tube exchanger. The hot helium flows to another finned-tube exchanger in the calciner bed. The helium gas then passes through a recirculator and is returned to the heat exchanger in the heater. This method was not considered feasible because of the higher cost, extensive development required, and only fair safety aspects. The main drawbacks with this method were the high cost of the recirculators and the low temperature driving force in both the heater and the calciner. The high pressure, 3.45 MPa, of the helium in the piping presented a significant safety problem. Helium recirculators could be purchased; however, they would have been of an experimental design which the manufacturer could not guarantee.

2.5 Electrical Induction Heating

Induction heating is based on the principle that an eddy current is induced in an electric conductor that is subject to a changing magnetic field. This current flowing through the conductor will produce heat because of the I^2R losses. Over all efficiency associated with induction heating is about 50%, but it still has many important industrial applications. An induction heater for the calciner would require the installation of a large water cooled coil on the calciner and a capacitor bank within the calciner cell. The electronic control unit for the coil could be located within the control room. This method is not considered feasible because of the unknown reliability of such a large unit during continuous operation. No known unit in a similar size range has ever operated continuously for more than a few days. In addition, the power requirements are much higher than for resistance heating. No cost estimate was obtained since the manufacturer contacted thought the cost would be excessive.

2.6 Recirculating Heat Transfer Fluid

The heat transfer fluid concept would utilize a fluidized-bed heater with the synthetic organic fluid flowing from a heat exchanger in the heater to a heat exchanger in the calciner and then back again. This method was not feasible because there is no known synthetic organic fluid that could operate above 425°C. The use of sodium-potassium heat transfer fluid was not considered for use in the NWCF at this time.

2.7 Heated Fluidizing Gas

Another potential method of calciner heat input is to preheat the fluidizing air to provide the heat necessary for evaporation of the water and decomposition of the nitrates. This technique does not provide as much heat for the same size calciner as in-bed combustion. For instance, a calciner using preheated fluidizing gas and operating at present WCF temperatures, fluidizing velocity and feed rate (500°C, 0.31 m/s, and 455 L/h) would require a fluidizing air temperature of apporoximately 3200°C. A calciner using a practical gas temperature would require a higher fluidizing velocity and a larger diameter vessel. Higher capacity off-gas cleanup equipment would be necessary resulting in substantially higher capital costs.

2.8 Heat Pipes

Calciner heating could be accomplished using heat pipes if a suitable fluid could be found. Cadmium was a possible candidate since its boiling point is 767°C.

A crude calculation of the number of heat pipes necessary for the NWCF, based on heat transfer coefficients, indicated 56 8-foot, 1.5-inch pipes would be required. Evaporation and condensation rates were not accurately determined nor were the safety aspects of overheating and pressurizing the heat pipes addressed. A calciner system using heat pipes may have potential, but an experimental heat pipe would have to be constructed to determine the heat transfer rates.

VI. Conclusions

1. The NaK heating system provided good service during the three campaigns it was in operation. The major causes of WCF shutdown were NaK pump failures and NaK piping leaks. Eventually the NaK tube bundle failed causing a long shutdown, resulting in the development of an alternate method of calciner heating. In retrospect the 316 SS NaK loop performed well. Based on the knowledge gained from the 32,000 hours of operation of the NaK loop, a system could be designed with greater reliability by taking into consideration the mechanical stresses on such a loop and by selecting metals subsequently tested in sodium metal cooled reactors.

2. The in-bed combustion method of calciner heat input has the advantage of high calcination rates in a small calciner vessel. The combustion system does have problems though. Combustion efficiencies over 90% are rare, the high velocity flame causes high attrition, and the high flame temperature causes melting of the bed in some flowsheets attempted in the pilot plant calciners. The process of combustion in a fluidized bed is not well understood, indicating a need for further development work in this area.

3. Electric resistance heaters still have potential for high temperature fluidized bed calcination, but the state of the art cannot produce a reliable heater. The heaters are still subject to "hot spots" where fluidization is poor causing heater burnout.

4. A combustion gas indirect heat exchanger has potential; however, overall thermal efficiencies were low in the systems investigated. A system would have to be developed in which the high-temperature fluidized-bed heat exchanger exhaust gases could be used to preheat combustion air and dilution air.

VII. Recomendations

1. The present method of heat input to the WCF performs well for the type of waste currently processed; however, if a more flexible system is desirable to provide heat input for wastes with different properties, additional work should be done. The two areas where additional work is necessary are:

   a) Studies are needed on the basic combustion process in a fluidized bed such as autoignition, fuel types, effects of flame velocity, nozzle types, and combustion efficiency. Studies are needed on nozzle design to achieve the best design for the type of material being calcined. For example, zirconium fluoride waste produces a soft and a relatively low melting calcine; therefore, a fuel nozzle which does not produce an intensely hot flame that melts the calcine and which does not have a high velocity flame (thus producing high attrition) is necessary. With the zirconium fluoride and sodium-bearing waste blend, the high velocity flame produced by a modified external mix nozzle is absolutely necessary to control the particle size; however, the calcine produced is lower melting than that produced from zirconium fluoride waste; the calcine melting is barely tolerable in the WCF. Other feeds tested in the pilot plant produce calcine even softer than that produced by zirconium fluoride waste. For these, any nozzle design may produce excessive attrition. A study of nozzle types versus attrition rates will make it possible to determine whether these wastes could be calcined using in-bed combustion heating.

   b) The combustion gas heat exchanger should be investigated for heat input to a fluidized bed where low melting calcine might be produced. This method of heat input would be a possible choice where temperatures lower than those produced by in-bed combustion would be necessary.

2. Future facilities considering fluidized-bed calcination should investigate a recirculating NaK system for process heat input. A NaK heat exchanger should be able to provide enough heat for calcination at feed rates similar to those obtained through in-bed combustion by using a finned heat exchanger.

References

1. S. Lawroski, et al, Argonne National Laboratory Chemical Engineering Division Summary Report, July, August, September, 1955, ANC 5494 (Confidential).

2. L. T. Lakey, G. E. Lohse, and W. P. Palica, Development of Fluidized Bed Calcination of Aluminum-Nitrate Wastes in the Waste Calcining Facility, IDO-14608, (May 1965).

3. D. K. MacQueen and J. I. Stevens, Design Basis for ICPP Waste Calcination Facility, IDO-14462, (April 1959).

4. D. R. Evans, Pilot Plant Studies with a Six-Inch Diameter Fluidized-Bed Calciner, IDO-14539, (April 1961).

5. B. P. Brown, E. S. Grimmett, and J. A. Buckham, Development of a Fluidized-Bed Calcination Process for Aluminum-Nitrate Wastes in a Two-Foot-Square Pilot-Plant Calciner, Part I: Equipment Development and Initial Process Studies, IDO-14586, (June 1962).

6. B. R. Wheeler et al, Development of a Fluidized-Bed Calcination Process for Aluminum-Nitrate Wastes in a Two-Foot-Square Pilot-Plant Calciner, Part II: Factors Affecting the Intra-Particle Porosity of Alumina, IDO-14587, (July 1962).

7. B. P. Brown, et al, Development of a Fluidized-Bed Calcination Process for Aluminum-Nitrate Wastes in a Two-Foot-Square Pilot-Plant Calciner, Part III: Intermediate Process Studies - Runs 11 through 22, IDO-14618, (February 1964).

8. B. P. Brown, B. M. Legler, and L. T. Lakey, Development of a Fluidized-Bed Calcination Process for Aluminum-Nitrate Wastes in a Two-Foot-Square Pilot-Plant Calciner, Part IV: Final Process Studies - Run 23 through 37, IDO-14627, (June 1964).

9. L. T. Lakey and J. R. Bower, ICPP Waste Calcination Facility Safety Analysis Report, IDO-14620, (December 1963).

10. R. E. Commander, et al, Operation of the Waste Calcining Facility with Highly Radioactive Aqueous Waste, Report of the First Processing Campaign, IDO-14662, (June 1966).

11. G. E. Lohse and M. P. Hales, Second Processing Campaign in the Waste Calcining Facility, IN-1344, (March 1970).

12. C. L. Bendixsen, G. E. Lohse, and M. P. Hales, The Third Processing Campaign in the Waste Calcining Facility, IN-1474, (May 1971).

13. J. R. Bower, ed., Chemical Technology Branch Annual Report Fiscal Year 1967, USAEC Report IN-1987, pp. 45-46 (October 1967).

14. J. R. Bower, ed., Idaho Chemical Programs Annual Technical Report, Fiscal Year 1971, ICP-1006, (May 1972).

15. T. K. Thompson, Development of In-Bed Combustion Heating for Calcination of Radioactive Wastes, IN-1278, (July 1969).

16. J. R. Bower, ed., Idaho Chemical Programs Annual Technical Report, Fiscal Year 1973, ICP-1047, (June 1974).

17. J. A. Wielang, et al, The Fourth Processing Campaign in The Waste Calcining Facility FY-1971, ICP-1004, (March 1972).

18. J. A. Wielang and W. A. Freeby, The Fifth Processing Campaign in the Waste Calcining Facility FY-1972, ICP-1021, (June 1973).

19. J. R. Bower, ed., Idaho Chemical Programs Annual Technical Report, Fiscal Year 1972, ICP-1022, (April 1973).

20. G. W. Pelletier, The Sixth Processing Campaign in the Waste Calcining Facility, ICP-1140 (to be published).

21. F. A. Zenz and D. F. Othmer, Fluidization and Fluid-Particle Systems, 260, Reinhold Publishing Corporation, New York N.Y. (1960).

22. J. C. Petrie and D. E. Black, Development of Air Distributor Caps for a Fluidized Bed, IDO-14629, (April 1964).