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FLOWSHEET DEVELOPMENT FOR HTGR FUEL REPROCESSING

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INTRODUCTION

The General Atomic Company has been given the responsibility for pilot plant development for the demonstration of HTGR fuel reprocessing, as a part of the Thorium Utilization Program under the direction of the United States Energy Research & Development Administration (ERDA). Selection of the processes or operations to be used was discussed in an earlier paper in this session, "HTGR Fuel Reprocessing Technology," by L. H. Brooks, C. A. Heath and J. J. Shefcik.[1] The development of flowsheets and equipment items for pilot plant testing is the subject of this review.

The unit operations involved in this pilot plant development effort are prototypical fuel crushing, pneumatic transport, and fluidized-bed burning, followed by particle classification and reburning. The solvent extraction feed preparation, driers for insoluble material from the dissolver and the solvent extraction system are of engineering-scalable size. Plans are under way to add prototype-sized fuel particle dissolution and continuous centrifuge equipment to the pilot plant.

FUEL ELEMENT CRUSHING

The crushing of the fuel elements is accomplished via a three-stage crushing system consisting of two overhead eccentric jaw crushers, a double-roll crusher, and an oversize reduction system to ensure the complete reduction to the desired size.

The development studies directed toward the prototype crusher design were performed by modification of a standard surplus jaw crusher to provide an enclosed cavity. Guides were modified to provide both vertical and horizontal crushing. A secondary standard jaw crusher of smaller throat followed by a roll crusher was found to reliably produce a product of less than 3/16-in. size. A prototype crusher system was designed from the development data and while it will only crush unirradiated materials in the pilot plant, the design was specifically aimed at eventual hot cell operations.

The major equipment for the crushing system is mounted in a specially designed framework which replaces the jaw and roll crusher standard machine frames in an array which utilizes gravity flow, eliminates the requirement for material transport devices, and minimizes material holdup. The entire system has been designated UNIFRAME because of the integration of all the equipment into this specially designed structure (see Fig. 1).

The major equipment items are:

1. Primary Crusher: an overhead eccentric jaw crusher for reducing the elements to <6 in. ring-sized fragments.
2. Secondary Crusher: an overhead eccentric jaw crusher for further reduction of the fragments to <2 in. ring-sized fragments.
3. Tertiary Crusher: a double-roll crusher for final reduction of the fragments to <3/16 in. ring-sized product.
4. Screener: a vibratory screener-separator for separating the acceptable product from any oversized fragments.
5. Oversize Crusher: an eccentrically mounted single-roll crusher for reduction of oversize fragments to acceptable product size.

The components of the UNIFRAME system have been categorized into five subsystems to provide a logical plan for the design efforts. These subsystems are:

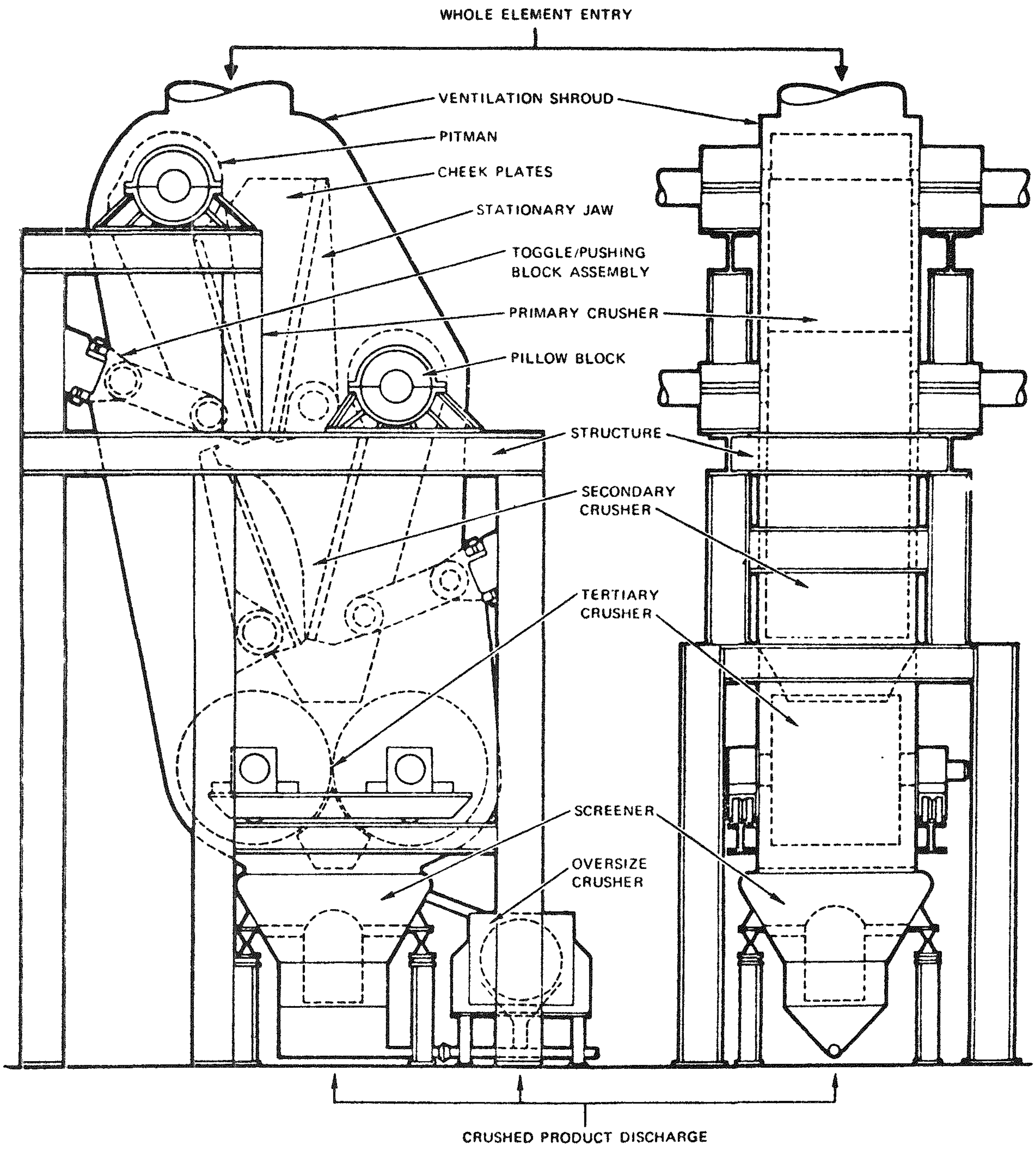

Fig. 1. UNIFRAME size reduction system

1. Structural: the special framework replacing standard machine frames to enable an efficient array of the equipment.
2. Ventilation: the enclosure that provides containment and collection of radioactive materials and dusts while minimizing the surfaces exposed.
3. Lubrication: the standard and special lubrication and bearings for equipment that make it more reliable and compatible with the radioactive environment and the remote operation requirements.
4. Drive: the standard and special drive components required to make the UNIFRAME system compatible with remote operation requirements and the radioactive environment.
5. Mechanical: the standard and special components required to make the major equipment items compatible with the structural, ventilation, and remote operation requirements.

Current status of the prototype fuel element crushing system is as described in the "time-activity chart" shown in Fig. 2.

FLUIDIZED-BED COMBUSTION

Two types of fluidized-bed combustion units are used: the primary burner for crushed fuel elements and the secondary burner for crushed fuel particles. Descriptive emphasis is placed on the primary burner, as its wide size distribution and density distribution bed material presents interesting fluidization and graphite fines recycle problems which have received the focus of fluidized-bed development.

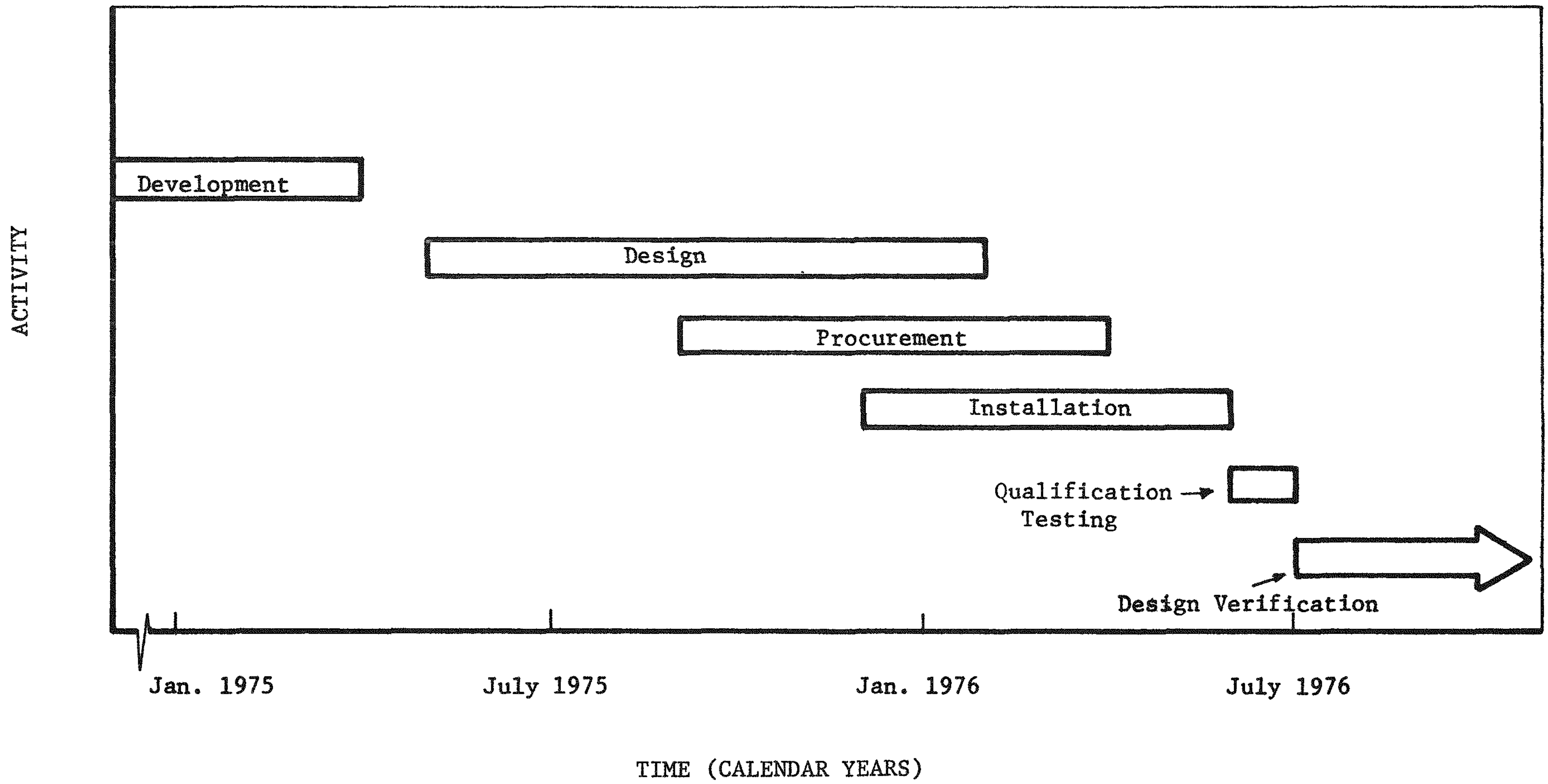

Fig. 2. Time-activity chart for development of prototype fuel element size reduction system

The primary crushed fuel element burner receives a feed stream of intact fuel particles and crushed graphite produced by the three-stage crushing system. Average properties of the burner feed, nominally minus 3/16 in., are shown in Table I. The primary burner must ignite and burn the fuel element graphite, the fuel rod pitch, and the fuel particle pyrolytic carbon producing a product of silicon carbide coated particles and exposed fuel kernel ash containing less than 5% burnable carbon (Table II). Adequate fluidization of the largest burning graphite requires superficial velocities of 3 to 4 ft/sec and a carefully designed gas distribution device. Graphite fines, generated both in the crushing process and in the fluidized-bed burning, elutriate before they are burned. This carry-over of fines is significant, amounting to over 20% of the carbon burn rate, and has been handled by external fines recycle back into the burner. The fines are ultimately consumed in multiple recycle passes. The technology developed has been verified to safely and reliably consume both the largest graphite and the smallest fines in the primary burner. The development highlights are presented below in the primary burner description.

The secondary crushed-particle burner receives the primary burner product after the silicon carbide coating is cracked open by a roll crusher. Residual carbon from the primary burner and pyrolytic carbon internal to the silicon carbide shell are consumed in the fluidized bed of the secondary burner. Heavy-metal carbides in the particle kernel are oxidized to a form readily dissolved in subsequent separation steps. The feed and product of the secondary burner are of a smaller and narrower size range (<400 microns) and contain a lower overall carbon content relative to the primary burner bed. These factors combine to allow a more easily handled medium in fluidized-bed combustion without an external fines recycle loop being required. The secondary burner development has progressed sufficiently to allow routine, automatically controlled operation.

TABLE I
AVERAGE PROPERTIES OF PRIMARY BURNER FEED AND STARTUP BED

Tap Density:	1.25 g/cm^3
Bulk Density:	1.08 g/cm^3
Angle of Repose:	35°
Average Burnable Carbon:	80%
Average Particle Size:	854 μ

Size	Wt % of Total Sample	% Burnable Carbon in Fraction
-3/16 in. + 869 μ	64.6	100
-869 μ + 550 μ	25.0	21
-550 μ + 420 μ	1.5	78
-420 μ + 375 μ	1.5	97
-375 μ + 250 μ	1.5	98
-250 μ	5.9	98

TABLE II
AVERAGE PROPERTIES OF PRIMARY BURNER FUEL PARTICLE PRODUCT

Density:	2 - 4 g/cm^3
Size:	200 - 870 μ
Burnable Carbon:	<5%

The development work described in primary and secondary burning has been accomplished in 8-in.- and 4-in.-diameter vessels.[2] The experiments to date have shown sufficient progress to allow completion of the final design for large-scale, prototype burner equipment. The 16-in.-diameter primary and 8-in.-diameter secondary prototype equipment will be operated in conjunction with the smaller vessels to verify long-term reliable operation, automatic control, and remote maintenance characteristics required for a successful long-term production operation.

THE PRIMARY CRUSHED FUEL ELEMENT BURNER

The primary burner process has been studied in 4-in.- and 8-in.-diameter vessels. Work has recently been concentrated in the 8-in. vessel due to excessive wall effects noted in the fluid beds of the smaller vessel. The prototype vessel presently under construction is 16 in. in diameter. The guidelines established for the burner are summarized in Table III.

The main problems which have been overcome in the primary burning process development are related to stagnation of the largest burning graphite in the lower fluid-bed region and carryover of the smallest fines graphite before combustion of this material is complete. Stagnant burning and resultant local hot spots have been eliminated by optimizing a unique gas distributor design. Completion of the fines combustion has been accomplished by using a graphite fines transport system capable of rapid external recycle of elutriated fines back into the burner. These designs are discussed below and are represented in Fig. 3.

GAS DISTRIBUTOR DESIGN IN PRIMARY BURNING

Conventional gas distributors such as perforated flat plates

TABLE III
OPERATING GUIDES - FLUIDIZED-BED BURNERS

	Crushed-Fuel-Element Burner (Primary)	Crushed-Particle Burner (Secondary)
a. Operating mode	Semicontinuous batch	Batch
b. Startup	Induction heater	Induction heater
c. Gas distributor	Perforated cone	Flat plate
d. Feed system	Gravity/rotary valve	Gravity/pneumatic
e. Product removal	Gravity/pneumatic	Gravity/pneumatic
f. Feed/product control	Metered feed/batched product	Batching system
g. Heat removal	Air cooling via annular shroud	Air cooling via annular shroud
h. Fines recycle	Pneumatic external recycle to burner via external cyclone/ filter system	Internal recycle to burner bed via internal filter system
i. Temperature	900 ± 50°C	900 ± 50°C
j. Pressure	Less than 15 psig at all vessel locations	Less than 15 psig at all vessel locations
k. Materials		
Vessel	Hastelloy X[a]	Hastelloy X[a]
Auxiliaries	304L SS	304L SS

[a] Product of Cabot Corporation.

have provided acceptable fluidized-bed combustion (isothermal bed temperature profile) with primary burner beds low in graphite content. Such is the case during the majority of the runs with semi-continuous operation, as the fresh feed (80% graphite) is fed into an existing bed of inert silicon carbide coated microspheres. However, the initial run of a customer lot involves combustion of an 80% graphite bed. The largest graphite segregates to the lower bed distributor region and causes local hot spots by burning statically. These hot spots could fuse the fuel particles into large agglomerates and burn holes through vessel materials at points of inherently poor circulation such as between perforations and around the periphery of flat distribution plates.

A gas distributor was designed to eliminate this stagnation and also allow maximum clean-out capability for product accountability. This distributor consists of a perforated cone with gas introduced through both the cone perforations and through an opening in the cone vertex. The distributor is shown in Fig. 3. The vertex opening diameter and vertex gas flow are such that bed material is levitated and well mixed during operation. The vertex gas flow is stopped and the cone perforation flow continued during product removal to allow rapid and complete product withdrawal through the vertex opening.

Testing of several cone angles has indicated that a 90° included angle cone operates optimally. A steeper 50° cone ran at over 150°C hotter surface temperatures than the 90° cone and displayed accelerated surface degradation. A shallower 120° cone ran at about the same temperature as the 90° cone, but the gently sloping surface allowed fuel particle agglomeration and fusion to the plate.[3]

FINES RECYCLE IN PRIMARY BURNING

A means of high capacity, rapid external recycle of fines back

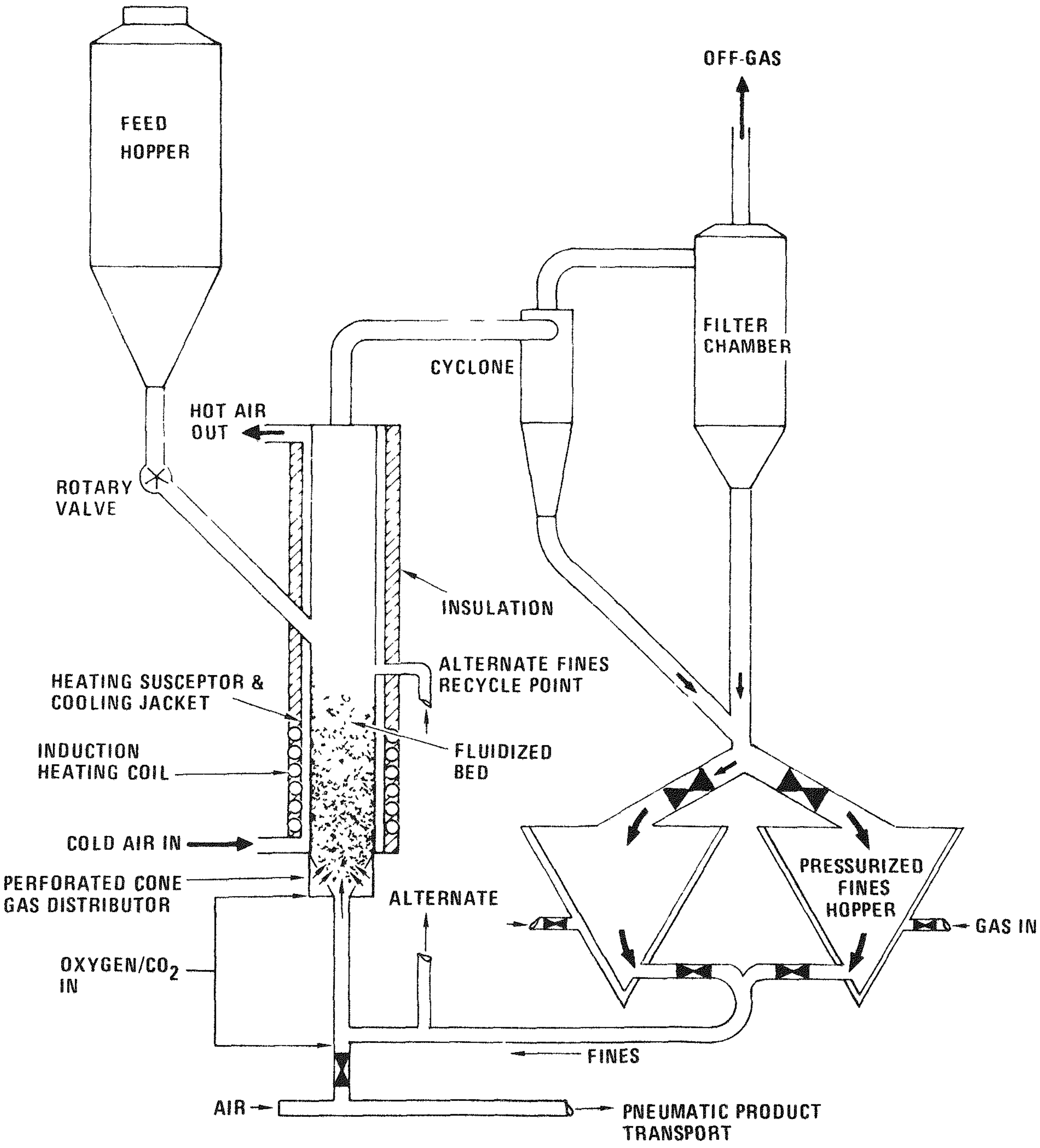

Fig. 3. Primary crushed-fuel-element burner configuration

into the burner is necessary to consume completely the large quantities of graphite fines elutriated. The system experimentally verified to accomplish this consists of parallel aerated hoppers which are alternatively pressurized by means of an air-lock system. The fines are pneumatically transported back into the burner in rapid dense-phase mass flow.[4] These hoppers are shown in Fig. 3.

Equivalent fines burning capacity has been noted with the fines recycle injected through the bed via the cone vertex gas inlet and with the recycling fines injected above the static bed into the bed solids disengaging height. The major differences between these two recycle modes are increases in the bed solids disengaging height and some lower bed temperature fluctuation when using the vertex recycle of fines through the bed.

HEAT TRANSFER IN PRIMARY BURNING

Because of nuclear criticality considerations, the cooling medium is limited to air which is forced through a clamshell annular to the finned burner wall. Figure 4 shows the heat balance for the 16-in.-diameter prototype primary burner.[5] The average overall heat transfer coefficient determined experimentally is 26 Btu/hr-ft^2-°F during steady-state combustion with a bed-to-wall coefficient of 95 Btu/hr-ft^2-°F. These coefficients decrease to 16 and 55, respectively, near the end of the burning period as the dense, low voidage fuel particle product accumulates.[6]

The nominal burn rate of the primary burner is about 33 g carbon/hr-ft^2 which corresponds to 0.2 kg carbon/min in the 8-in.-diameter vessel and 0.8 kg carbon/min in the 16-in. vessel.

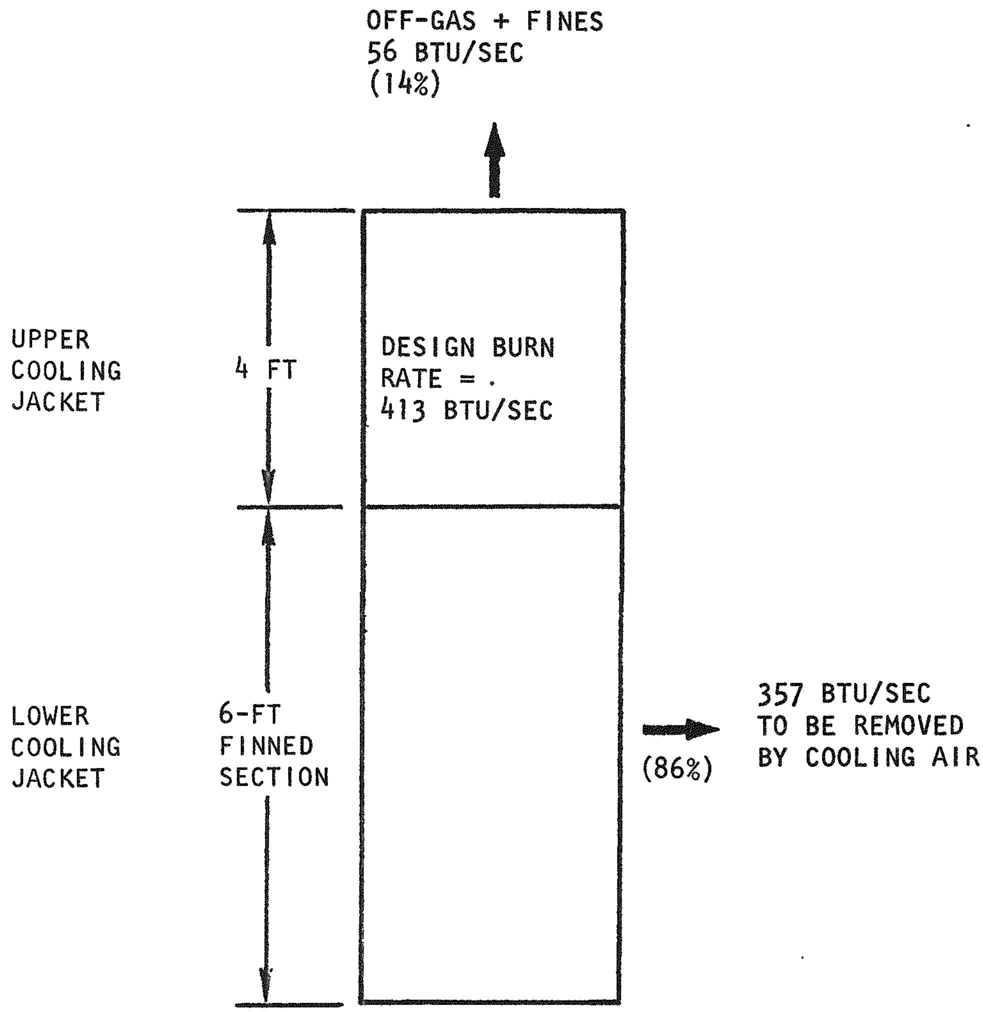

Fig. 4. Heat balance for 16-in.-diameter prototype primary burner with fins

THE SECONDARY CRUSHED PARTICLE BURNER

Figure 5 depicts the secondary fluidized-bed burner. The more easily fluidized nature and lower carbon content of the secondary burner bed material have allowed more of the development work to be concentrated in areas of reliable heating techniques and automatic control. Much of this experience is now being applied to the primary burner system.

The batch operation of the secondary burner consists of an automated induction heater temperature control loop and a burner control system. A series of repeating, programmed events is incorporated in the control philosophy. The bed of crushed fuel particles is batch fed into the burner and heated to ignition temperature by the induction system. External wall cooling air adjustments maintain the desired bed temperature during the equilibrium burning phase, while the gas velocity is held constant at 4-5 ft/sec. When most of the bed carbon is consumed and the bed temperature begins to drop, the gas velocity is reduced to <3 ft/sec, and the induction heater provides heat input to the bed to burn the remaining carbon. The product bed is then pneumatically removed in a batch.

GAS DISTRIBUTOR DESIGN IN SECONDARY BURNING

A flat perforated plate is used without difficulty in secondary burning. The powdery product is withdrawn through an opening in the vessel side wall just above the flat plate. A gas jet distributor sweep directs gas down on top of the plate during the pneumatic removal to clean off any residual product.

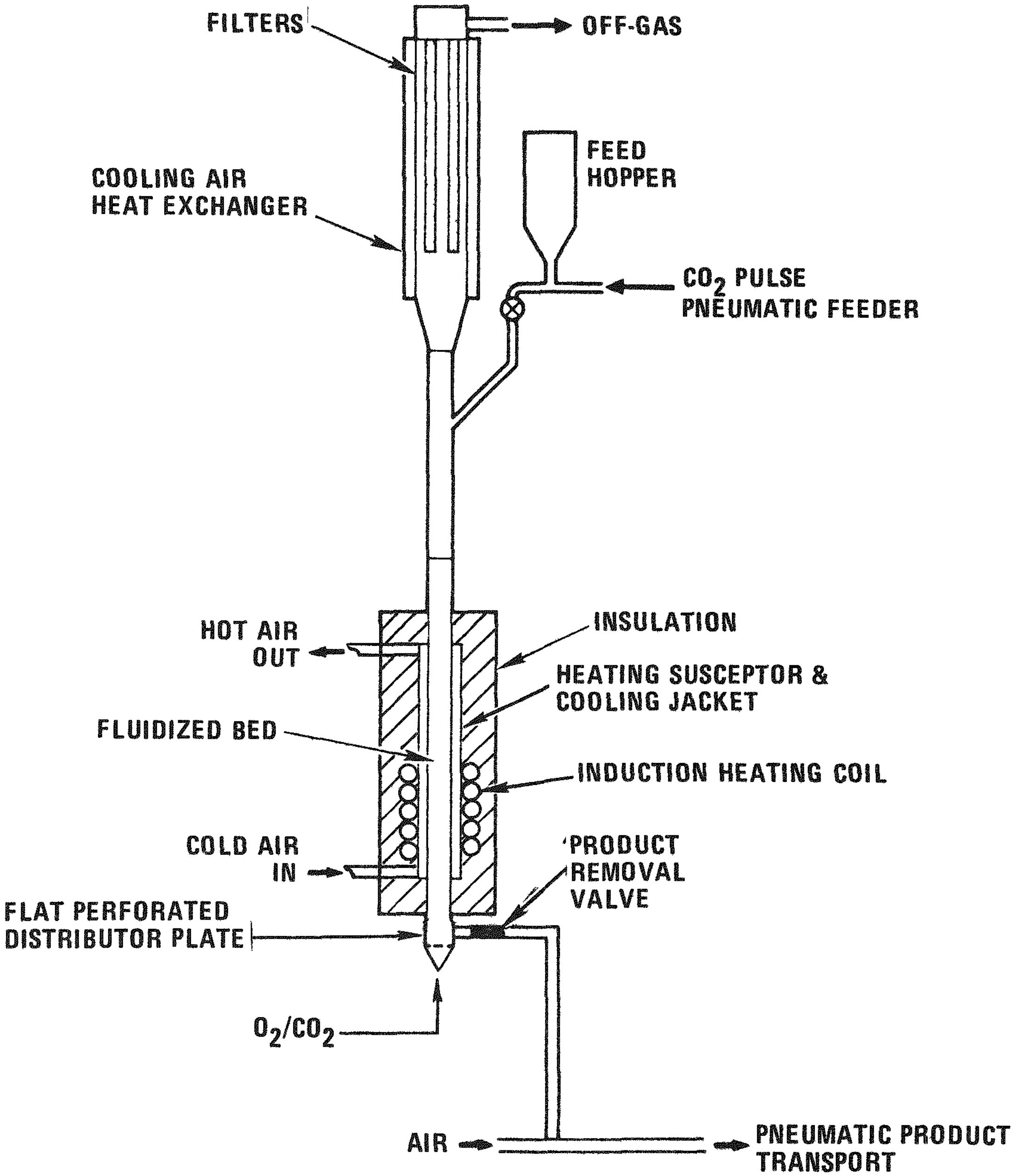

Fig. 5. Secondary crushed-particle burner

FINES RECYCLE IN SECONDARY BURNING

Sintered metal filters placed in an expanded section of the burner at a suitable height for disengaging flow entrainment are periodically blown back to return accumulated fines to the bed. The filter blow-back coupled with the reduced velocities near the end of the run allow internal recycle and combustion of the small amount of carbon in the secondary burner fines.

HEAT TRANSFER IN SECONDARY BURNING

The internal heat transfer coefficient for the secondary feed and product material at operating conditions is 80 and 70 Btu/ft^2-hr-°F, respectively.(7) The average burn rate is 20 to 25 g carbon/hr-ft^2.

Results indicate successful long-term operation of both the primary and secondary fluidized-bed combustion systems can be performed on equipment developed in this program.

AQUEOUS SEPARATIONS DEVELOPMENT

Engineering-scale development is under way in the solvent extraction feed preparation and processing unit operations. Studies include fuel dissolution, drying of insoluble dissolution residues for pneumatic transport, solvent extraction feed adjustment and solvent extraction design tests all on unirradiated materials. Prototype-sized dissolver and continuous centrifuge systems are planned.

A picture of the dissolver and feed adjustment equipment is shown in Fig. 6. Two dissolvers are used, one 13 cm and one 20 cm in diameter. The feed adjustment concentrator and acid stripper (20 cm) are shown in the foreground. The fluidized-bed insols

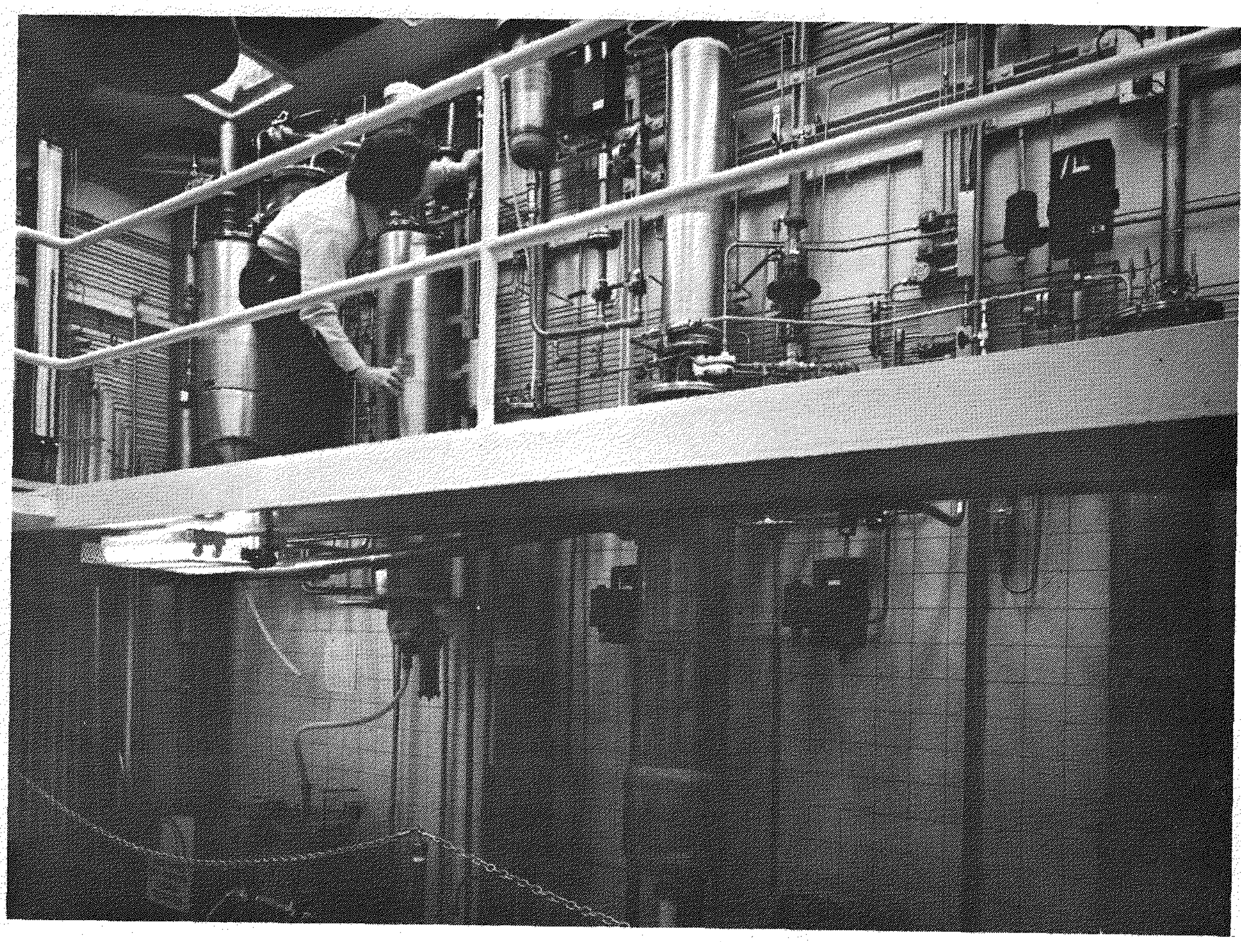

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Fig. 6. Dissolver - feed preparation area

dryer is shown in Fig. 7. The status of the dissolution development effort is shown in Table IV.[9] The design information studies for a larger (45 cm) dissolver have been completed. Steam jet transfer of dissolver slurries to the centrifuge has been extensively studied as part of this program. Operating data have been obtained for both ThO_2 from oxidizing ThC_2 fertile particles (Fort St. Vrain) and ThO_2 kernels (reference).

The status of the fluidized-bed insols dryer development is shown in Table V. The dryer is designed for direct coupling to a continuous centrifuge to allow transfer of centrifuged solids without a transfer step which would be required for batch centrifuge coupling. A poppet valve is opened to transfer dried insols. This transfer will be by pneumatic transport.

The status of the solvent extraction feed adjustment development is shown in Table VI.[10] Acid removal is needed for the dissolver solution which has an acidity too high for solvent extraction feed and also is being considered between the thorium cycles in order to make the second thorium cycle feed acid deficient. The solutions are evaporated to essentially molten hydrated salts and either steam or water is added to effect acid removal. Bench-scale studies have shown that formic acid will react rapidly with molten hydrated nitrate salts to produce acid deficiency. Continuous preparation of acid deficient thorium nitrate solution in simple equipment may require formic acid nitrate destruction.

Pictures of the solvent extraction system are shown in Figs. 8 and 9. The solvent extraction system contains five glass columns which are either 5 or 7.5 cm in diameter. These columns have been used to demonstrate one complete cycle of U and Th extraction, Zr fission product scrubbing, U-Th partitioning, and U strip. Solvent washing with sodium carbonate solution and product solution washing

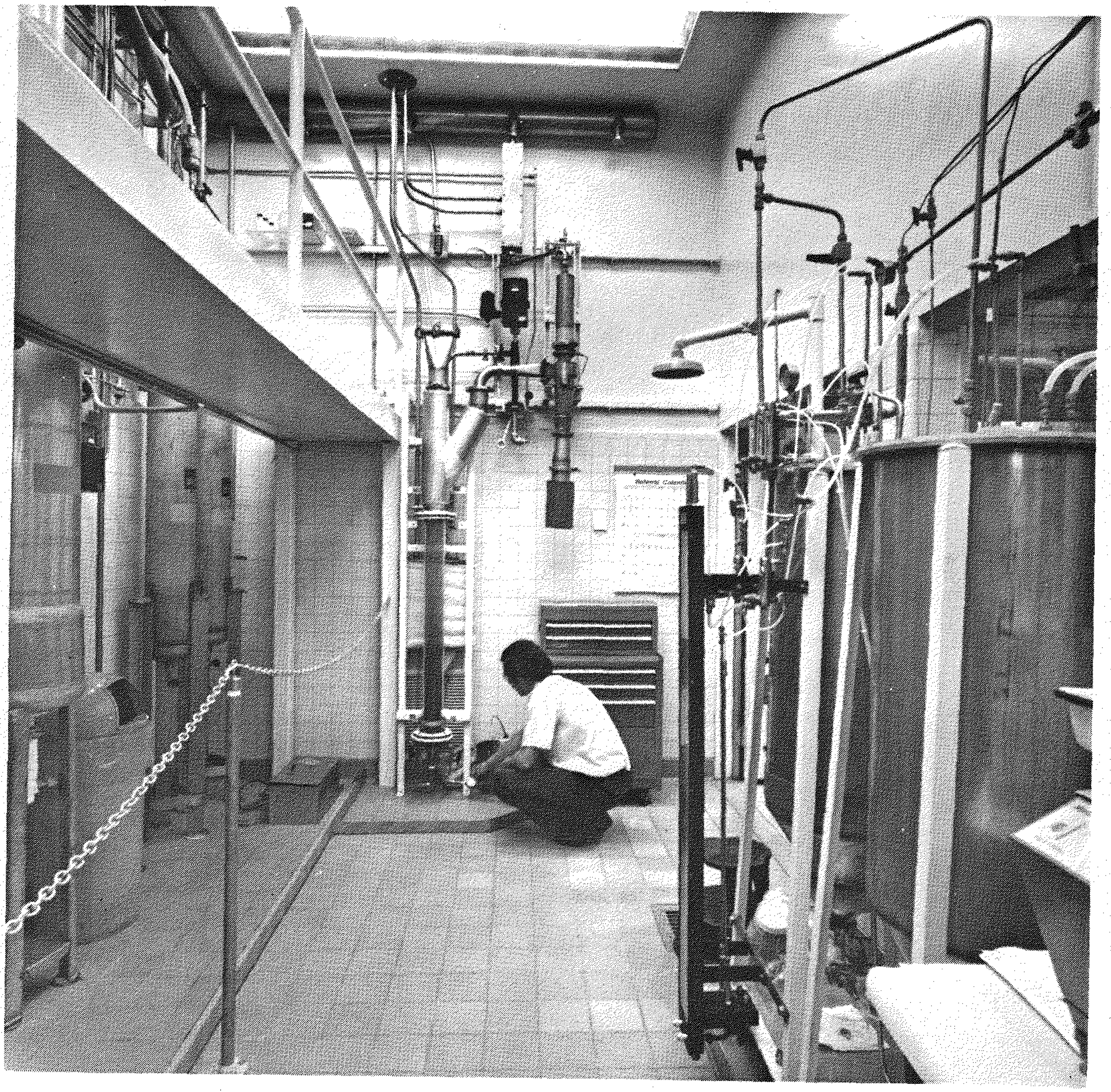

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Fig. 7. Insols dryer area

TABLE IV

HTGR Fuel Dissolver Development

Problem Area	Resolution or Status
Dissolver Design	Design information for batch prototype-sized leacher and continuous centrifuge system completed.
Heating Method	Steam jacket vessel bottom cone primary heating surface.
Agitation Method	Sparge dip tube plus bottom boiling.
Burner Ash Feed System	Hopper dump.
Product Removal	Submerged steam jet for dissolver solution slurry transfer to centrifuge.
Operating Cycle	Established for both unirradiated oxidized ThC_2 and burned back ThO_2 kernels.

TABLE V

Development of Dryers for HTGR Centrifuge Residues

Problem Area	Resolution or Status
Dryer Design	Fluidized-bed batch dryer direct coupled to continuous centrifuge discharge.
Drying Media	Dry heated air or nitrogen.
Heat Requirements	Established for unirradiated insols.
Dryer Efficiency	About 70% efficient.
Dried Solids Removal	Poppet valve - designed to connect to pneumatic transport system.

TABLE VI

Development of Feed Adjustment - Head-End and Intercycle

Problem Area	Resolution or Status
Feed Adjustment Equipment Design	Design demonstrated for batch system.
Acid Stripping Method	Water flash preferred over steam because of simplified control.
Product Removal	Dilution by water jet transfer or batch dilution followed by steam jet transfer.
Continuous Operation	Use of formic acid to strip acid as nitrogen oxide under study for continuous intercycle use.

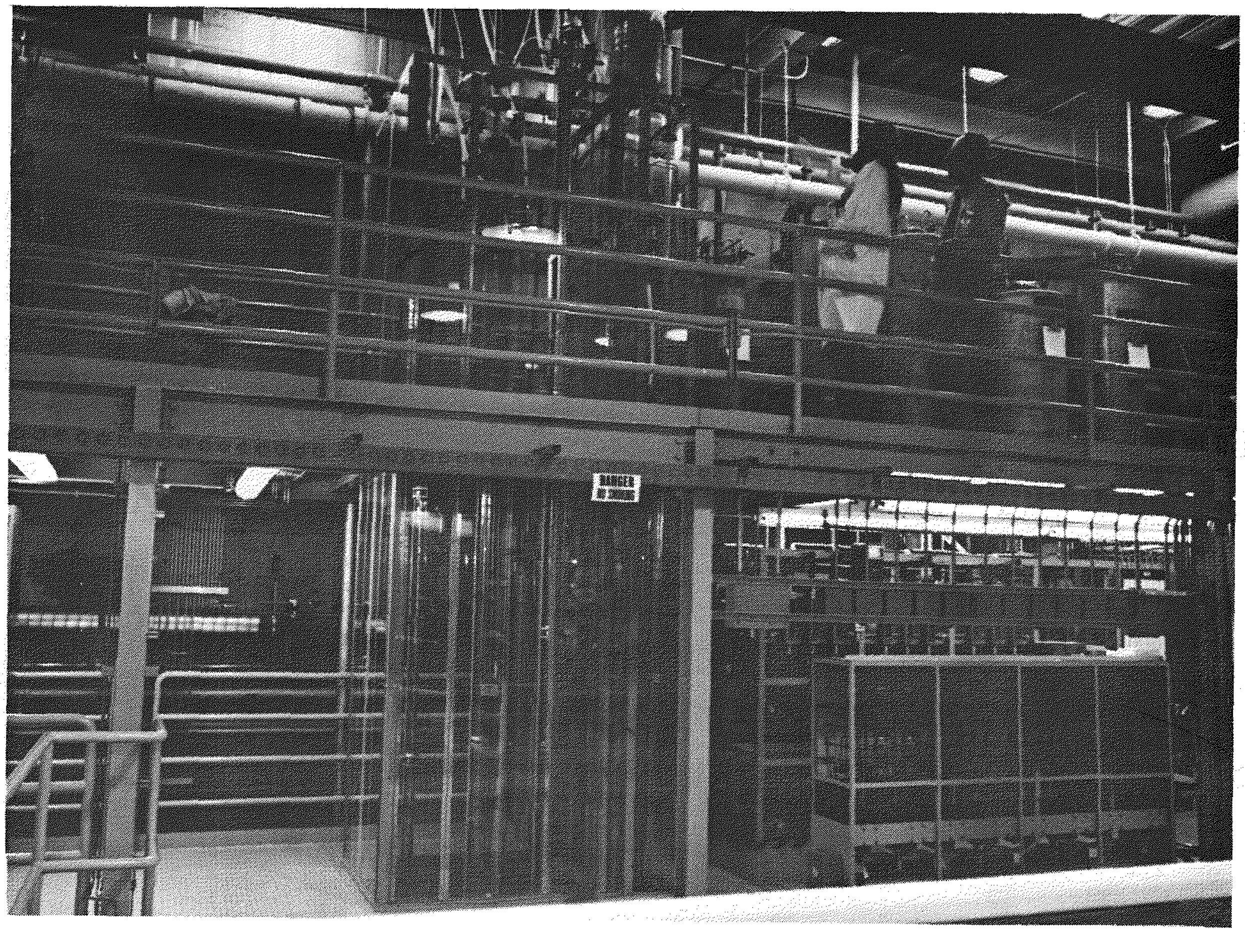

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Fig. 8. Solvent extraction area - second and third deck

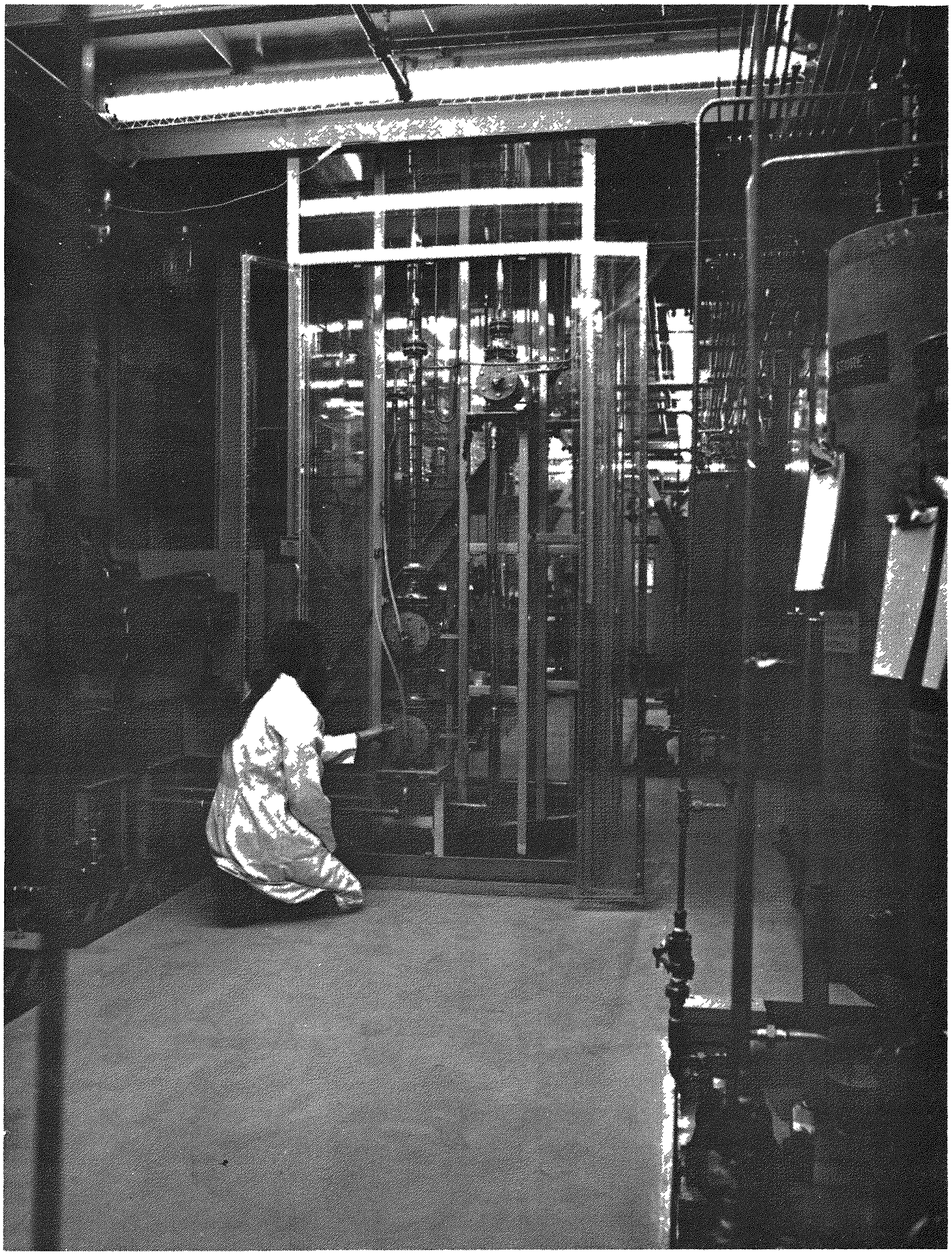

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Fig. 9. Lower level of the GA five-column solvent extraction pilot plant system

with high grade kerosene have also been demonstrated in this system. An eight-stage centrifugal contactor has been added which is sized compatible with the pulsed column system and can be substituted for any one of the five columns but is generally used to study extraction at short residence times. Short residence times may be important in processing very high burnup HTGR fuels, particularly the separated fissile fraction.

The results of the solvent extraction development work are summarized in Table VII.[11]

The preliminary design information for a pulsed column solvent extraction system suitable for HTGR reprocessing has been completed. Included are column heights, diameters, plate specifications, pulsing conditions, and interface positions. In the Thorex system, the thorium tributylphosphate complex is not soluble in the diluent at high thorium loadings. It has been demonstrated in this testing that operation of pulsed columns with the resultant two organic phases does not significantly affect column operation.

Solvent radiation damage has been simulated by addition of dibutylphosphate, the principal degradation product, to the extraction column. From these tests, it has been determined that the partition cycle should be the first cycle in an HTGR reprocessing plant. Low concentrations of fluoride added to the thorium partitioning solution improves separation of thorium even in the presence of dibutylphosphate and lowers carryover and precipitation of thorium dibutylphosphate in the uranium stripping column.

The HTGR solvent extraction feeds contain small amounts of solids which will pass normal centrifugation separation. These solids pass through the organic continuous extraction column to waste with no difficulty.

TABLE VII

HTGR Solvent Extraction Development

Problem Area	Resolution or Status
Pulsed Column Configuration	Preliminary column design information for HTGR reprocessing completed.
Pulsed Column Operation at High Thorium Solvent Loadings	Pulsed column not significantly affected by operating in region of two organic phases.
Effects of Solvent Radiation	Partition cycle selected for first cycle over co-extraction co-strip with dibutyl phosphate in solvent.
Damage Simulation	Fluoride addition to thorium partition solution lowers the effect of dibutyl phosphate on thorium-uranium partitioning and uranium stripping.
HTGR Solvent Extraction	No problems in handling typical feeds solids in pulsed columns.
Feed Requirements	Pilot plant feed lowers Zr separation from thorium and uranium - continuing study of feed effects.
Low Residence Contactors	Robatel centrifugal contactor added to pilot plant for feasibility study.

These solids and reaction products of carbon and nitric acid do cause a 2- to 5-fold lowering of Zr fission product separation from thorium. The feed effects on solvent extraction are continuing.

CONCLUSIONS

Development studies to date indicate that the HTGR fuel blocks can be effectively crushed with two stages of eccentric jaw crushing, followed by a double-roll crusher, a screener and an eccentrically mounted single-roll crusher for oversize particles.

Burner development results indicate successful long-term operation of both the primary and secondary fluidized-bed combustion systems can be performed with the equipment developed in this program.

Aqueous separation development activities have centered on adapting known Acid-Thorex processing technology to the HTGR reprocessing task. Significant progress has been made on dissolution of burner ash, solvent extraction feed preparation, slurry transfer, solids drying and solvent extraction equipment and flowsheet requirements.

REFERENCES

1. Brooks, L. H., C. A. Heath, and J. J. Shefcik," HTGR Fuel Reprocessing Technology," General Atomic Report GA-A13807, April 1976.
2. Baxter, B. J., *et al.*, "Fluidized-Bed Combustors Used in HTGR Reprocessing," General Atomic Report GA-A12285, October 1972.
3. Stula, R. T., D. T. Young and H. H. Yip, "Interim Development Report for Primary Burning," ERDA Report GA-A13546, General Atomic, January 5, 1976, p. 6-6.
4. Ibid., pp 4-4, 6-60 through 6-65.
5. Ibid., pp. 6-49.
6. Ibid., pp. 6-51 through 6-54.
7. "Thorium Utilization Program Quarterly Progress Report for the Period Ending August 31, 1975," ERDA Report GA-A13593, General Atomic, September 30, 1975, p. 4-51.
7. Rickman, W. S., "Interim Development Report for Secondary Burning," ERDA Report GA-A13540, General Atomic, December 25, 1975.
8. Hutton, A. E., "Dissolution of HTGR Fuel," ERDA Report GA-A13278, General Atomic, September 30, 1975.
9. Brown, C. A., "Solvent Extraction Feed Preparation for HTGR Reprocessing (Interim Report)," General Atomic Report, to be published.
10. Reddick, G. W., "Solvent Extraction Development for HTGR Reprocessing (Interim Report)," General Atomic Report, to be published.