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**CONSOLIDATED
REPROCESSING PROGRAM**

**QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING MAY 31, 1979**

Prepared under
Contract DE-AT03-76SF71053
for the San Francisco Operations Office
Department of Energy

DATE PUBLISHED: JUNE 1979

GENERAL ATOMIC COMPANY

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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 \$4.50; Microfiche \$3.00

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GENERAL ATOMIC COMPANY

QUARTERLY REPORT SERIES*

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GA-A13255 - September 1974 through November 1974
GA-A13366 - December 1974 through February 1975
GA-A13510 - March 1975 through May 1975
GA-A13593 - June 1975 through August 1975
GA-A13746 - September 1975 through November 1975
GA-A13833 - December 1975 through February 1976
GA-A13949 - March 1976 through May 1976
GA-A14085 - June 1976 through August 1976
GA-A14214 - September 1976 through November 1976
GA-A14304 - December 1976 through February 1977
GA-A14441 - March 1977 through May 1977
GA-A14583 - June 1977 through August 1977
GA-A14738 - September 1977 through November 1977
GA-A14878 - December 1977 through February 1978
GA-A15011 - March 1978 through May 1978
GA-A15105 - June 1978 through August 1978
GA-A15315 - September 1978 through February 1979

* Prior to GA-A13178, the Thorium Utilization Program was reported in the Base Program Quarterly Progress Report.

ABSTRACT

This publication continues the quarterly series presenting results of work performed under the Consolidated Reprocessing Program at General Atomic Company. Results of work on this program prior to June 1974 were included in a quarterly series on the HTGR Base Program.

The work reported includes the development of unit processes and equipment for reprocessing of High-Temperature Gas-Cooled Reactor (HTGR) fuel, the design and development of an integrated pilot line to demonstrate the head end of HTGR reprocessing using unirradiated fuel materials, and design work in support of Hot Engineering Tests (HET). Work is also described on trade-off studies concerning the required design of facilities and equipment for the large-scale recycle of HTGR fuels in order to guide the development activities for HTGR fuel recycle.

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1. SUMMARY

The first milestone was accomplished on the evaluation of GCFR fuel reprocessing, and the effects were summarized.

A User's Manual for the computerized cost data base for the HTGR commercial-scale recycle plant has been completed and will soon be issued.

A topical report describing the sequential operation of the dry head-end pilot plant equipment is now being reviewed for release.

Details of the proposed classification studies on the fuel produced by FRG were submitted for approval.

The off-gas system installation has been completed. A hydrogen compressor for the iodine bed regeneration has been ordered and RFQs for the burner off-gas (BOG) and dissolver off-gas (DOG) compressors have been sent out. All the preoperational system checks are progressing as planned.

A topical report describing the annular pulse column and its operating performance is in preparation. Data reduction and analysis are continuing for three alternative pulse column cartridges.

The Sharples Model P850 vertical continuous centrifuge has been installed in the pilot plant as part of the prototype dissolver-centrifuge system. The vertical centrifuge was selected because of its adaptability to remote hot cell operation and maintenance. The centrifuge will be tested for operability and solids-liquid efficiency under various operating conditions related to nuclear process applications.

2. STUDIES AND ANALYSIS - TASK 100

H. C. Carney

2.1 INTRODUCTION

The objectives of this task are to (1) define unique reprocessing development and facility requirements for spent GCFR fuel, compared to present LMFBR reprocessing plans and facility designs, (2) evaluate the impact of HTGR fuel design changes on reprocessing requirements and costs, and (3) confirm flowsheet requirements for HTGR reprocessing and waste streams, and prepare material balances as required.

2.2 ACTIVITY

2.2.1 Evaluation of GCFR fuel reprocessing (100.1)

V. H. Pierce

The first milestone was accomplished on schedule with the issue of a memorandum activity report for Studies and Analysis Task 100.1 to the CRP.²⁻¹ The activity report identified GCFR design features, the fuel cycle, and core and blanket assembly design aspects that would affect CRP process and facility development tasks. The anticipated effects were summarized.

2.2.2 Spent fuel storage (100.2)

N. D. Holder and R. M. Burgoyne

A report entitled "HTGR Spent Fuel Storage Study" is in preparation. A summary of the results has been accepted as a contributed paper for the American Nuclear Society annual meeting in June in Atlanta.

2.2.3 Recycle plant data base (100.2)

N. D. Holder and B. B. Haldy

A User's Manual for the computerized cost data base for the HTGR commercial-scale recycle plant has been completed and is undergoing internal review.

Design changes incorporated in the commercial-scale recycle plant as a result of the FY-78 data base update will be published as a supplement to Ref. 2-2.

2.2.4 Flowsheet and material balance (100.3)

N. D. Holder and B. B. Haldy

Processing requirements for all major HTGR reprocessing waste streams have been identified, and draft flowsheets (issued in FY-78) are being updated. Material balances are approximately 30% complete.

REFERENCES

- 2-1. J. W. Allen, "GCFR Fuel Reprocessing Development Requirements, Task 100.1," General Atomic Company, unpublished data, April 20, 1979.
- 2-2. "Conceptual Design Summary and Design Qualifications for HTGR Target Recycle Plant," ERDA Report GA-A13365, General Atomic Company, May 1975.

3. HEAD-END STUDIES - TASK 310

3.1 CRUSHED FUEL ELEMENT BURNING (SECONDARY SUBTASK 312)

J. M. McNair and D. E. Fields

The wiring changes required to accommodate 0.20-m burner automation were completed and checked out.

Hardware problems experienced with the Diogenes supervisory interface were repaired by Rosemount. Transmission rates of up to 9600 baud are now possible.

Actuators and positioners to control the cooling air flows by the Diogenes process control computer were installed.

A heat-up test performed on March 2 verified that the wiring changes were correct.

A new console was added in the control room to accommodate the automation equipment.

A 0.20-m burner combustion test was performed on March 12. The burner was brought on line and a burn rate of 200 g/min achieved. The cooling air modifications worked well. The cooling air control loops were tuned.

The gas flow transmitters are very sensitive and need additional work. It is mandatory to keep these signals from fluctuating excessively since they affect the burn rate setpoint calculation.

3.2 PARTICLE CLASSIFICATION, CRUSHING, AND CRUSHED PARTICLE BURNING (SECONDARY SUBTASK 313)

J. B. Strand

3.2.1 Pilot plant sequential operations

A topical report describing the sequential operation of the dry head-end pilot plant equipment has been prepared and is being reviewed for release.

3.2.2 US/Federal Republic of Germany cooperative program

Pacing research and development problems were outlined for primary burning for the US/FRG cooperative effort.

Details of the proposed classification studies on the fuel produced by FRG were submitted to FRG for approval.

Work packages were submitted for the conceptual design of a joint US/FRG cold prototype head-end test facility (JPHF).

3.2.3 Air classification

The design of advanced fuel types will affect the efficiency of separation by air classification proportionally to the differences in the densities and diameters of the fissile and fertile fuel particles. Studies to establish parameters for the separability of fuels to assist in advanced designs have been completed. Preparation of a complete report is underway.

3.2.4 Particle crushing

The present fuel particle crusher requires very close manufacturing tolerances, a high quality assurance follow up, and precision assembly. A new design that avoids these problems, provides increased bearing protection, and reduces sideplate wear has been completed. Preparations for its construction are underway.

3.2.5 Secondary burning

The initial gas distributor on the 0.10-m secondary burner was replaced by a remotely removable distributor. In addition to the remote features, the design located the flange connection outside of the high-temperature zone. The initial test of the distributor has been completed. No operating or process problems were observed.

3.3 DRY SOLIDS HANDLING (SECONDARY SUBTASK 314)

C. J. Everline, N. D. Holder, and J. M. McNair

3.3.1 Component testing

Component testing includes a recirculating pneumatic transport loop designed to wear test system components in long-term and/or cyclic tests. It also includes the selection of suitable remote coupling devices for solids handling piping.

Pneumatic transport component test loop. The test loop, which is computer-controlled, has not been operated this quarter due to use of the computer for other subtasks. The software is being modified to provide automatic shutdown of the test loop in the event of failure, so that tests can continue by overnight runs.

Remote coupling devices. A survey of national laboratories was performed to determine what types of remote couplers were in use or being developed that might be applicable to solids handling systems. A selection of couplers that appear promising were either purchased or borrowed, including Grayloc, Rocky Mountain Nuclear, and TRU disconnects. Aeroquip Marmon remote couplers require a minimum order of 5 and 36 weeks delivery time, and will not be included in this evaluation. Several inexpensive non-remote couplers were ordered for evaluation for possible modification to remote handling, including Victaulic, Unibolt, G&H, Marmon, and Rocky Mountain Nuclear. Handling characteristics of the connectors will be evaluated in the cold manipulator mockup station at the GA hot cell facility. Suitable candidate connectors can then be tested further in the component test loop.

3.3.2 Sampling plan and sampler criteria

A plan for obtaining samples for process data and accountability information in hot head-end operations is being prepared in order to establish additional development needs and sampler criteria as guidance for cold pilot plant sampler procurement. This is a continuation of the preliminary selection work.³⁻¹ The sampling plan is 90% complete. Sampler purchasing has been delayed to FY-80.

3.3.3 High-temperature rotary valve

Design of a high-temperature rotary feed valve is now complete. Materials are on order and fabrication can proceed soon. The valve design minimizes the possibility of leakage through the valve as well as to the environment. Alloy construction ensures operability at temperatures up to 650°C.

REFERENCES

- 3-1. E. J. Cook and P. C. Richards, "Selection and Testing of On-Line Samplers for Head-End Reprocessing," DOE Report GA-A14634, General Atomic Company, October 1977.

4. OFF-GAS TREATMENT - TASK 340

R. D. Zimmerman and U. S. Park

4.1 SYSTEM DESIGN AND INSTALLATION

N. G. Perreira

System installation has been completed. The last heat exchanger of the system, which is an addition to the system for the purpose of adsorption bed regeneration in the future, was delivered in February 1979, and has been installed. Some sample lines and gas supply lines have been heat-traced and insulated in order to prevent the condensation of moisture or low vapor pressure gases such as SO_2 and N_2O_4 .

A hydrogen compressor for the iodine bed regeneration has been ordered. RFQs for the burner off-gas (BOG) and dissolver off-gas (DOG) compressors needed for the system integration have been sent out. Due to the uncertainty of finding a DOG compressor that meets our specification, in-house detailed design and fabrication are still being considered.

4.2 PREOPERATIONAL SYSTEM CHECK

N. G. Perreira and R. D. Crabtree

The system leak checking has been completed. The total system leakage has been reduced to an acceptable level, i.e., less than 0.1% of the normal flow rate of $34 \text{ Nm}^3/\text{h}$ at 205 kPa (15 psig). The actual leakage will be even smaller considering the fact that all the vessels operate between 101 kPa (0 psig) and 170 kPa (10 psig). An additional leak check is planned after the system is fixed at a high temperature during the system shakedown period.

Flow tests were performed on both the BOG and DOG systems, at operating pressures and flows, i.e., 205 kPa (15 psig) at the system inlet for both systems and $34 \text{ Nm}^3/\text{h}$ and $17 \text{ Nm}^3/\text{h}$ for the BOG and DOG systems, respectively. The measured pressure drops for both systems were well within design values. Flow tests on all six sections of the CO/HT oxidizer heat exchanger confirmed the design flow.

Functional checks and calibration of system indicators and controls are continuing. Functional checking of the Diogenes process controller and all recorders except a multipoint recorder has been completed. All Diogenes control loops (control function matrices) have been prepared and incorporated into the control system.

The gas analyzer system has been functionally checked, and the output signals have been linearized jointly by GA and Beckman engineers. Calibration of the analyzers will be performed during the next report period.

4.3 SCHEDULES AND MILESTONES

System installation has been completed. The system functional check and calibration are progressing and are expected to be completed by June 30, 1979.

An activity plan for the off-gas treatment subtask has been released. The plan, shown in Fig. 4-1, describes the long-range planning (FY-79 to FY-87) as well as the short-range detailed planning (FY-79 and FY-80), under the assumption of the same funding level as FY-79 throughout the period. System documentation, including the system operating procedure and the maintenance manual, is continuing.

Fig. 4-1. Off-gas system development plan

5. SOLVENT EXTRACTION - TASK 350

R. D. Zimmerman, G. E. Benedict, and D. R. Engler

5.1 ANNULAR PULSE COLUMN EXTRACTION TESTS

The maximum size of critically safe plutonium or U-233 bearing cylindrical solvent extraction columns limits reprocessing plant capacity. The capacity of these columns can be increased by using larger columns that have an annular cross section. Preliminary testing of the pilot-scale annular pulse column has been completed. A topical report describing the column and its operating performance is in preparation.

5.2 CYLINDRICAL PULSE COLUMN PLATE TESTS

Data reduction and analysis are continuing for three alternative pulse column cartridges: (1) shielded slot plates, (2) the reference standard nozzle plates, and (3) the "zebra cartridge" (Hanford Purex stripping column configuration).

5.2.1 Shielded slot plates

Conclusions from work to date:

1. At a given pulse amplitude and frequency:
 - a. The capacity of shielded slot plates is less than that of standard nozzle plates.
 - b. When coated with an organic film, the capacity of shielded slot plates may increase by 100%, exceeding the capacity of standard nozzle plates.
 - c. Orientation of the slot (e.g., up or down) has no effect on capacity.
 - d. Variation of plate spacing has no effect on capacity.

2. Maximum throughput for uncoated shielded slot plates is no different from that for standard nozzle plates: 1450 gallons/hour/square foot. Coated shielded slot plates may have a slightly higher maximum throughput.
3. Both standard nozzle and shielded slot plates are comparable in efficiency. In the bottom 5 ft of the column, the height equivalent to a theoretical stage (HETS) is slightly less than 2 ft. For the bottom 10 ft, the HETS is about 2 ft.

5.2.2 Standard nozzle plates

Conclusions from work to date:

1. At a given pulse amplitude and frequency:
 - a. The capacity of standard nozzle plates is greater than that of shielded slot plates.
 - b. When coated with an organic film, the capacity of standard nozzle plates may increase by 30%.
2. The capacity at a pulse amplitude of 1/2 in. is 80% of the capacity at a pulse amplitude of 1 in.
3. The average height equivalent to a theoretical stage is about 1-1/2 ft at the 5-ft sample point, and about 2 ft at the 10-ft sample point.
4. Experimentally measured dispersed phase holdup ranges from about 9 to about 50 vol % within the stripping column cartridge. Holdup increases with increasing throughput and with increasing mixing, which is a function of pulse amplitude times pulse frequency.

5.2.3 Zebra cartridge (Hanford Purex plant stripping column configuration)

Significant improvement in capacity was noted. Other conclusions are pending complete data reduction.

5.3 ROBATEL CENTRIFUGAL CONTACTOR TESTS

These tests will determine the operability, efficiency, power requirements, and zirconium decontamination achieved in the eight-stage Robatel centrifugal contactor in the extraction mode. Figure 5-1 presents the flowsheet, showing the flow path, name, phase, typical concentration for uranium and nitric acid, and nominal flow rates for each of three throughputs.

In addition to the required piping changes, other modifications were made to the physical system. In the 1AS column, four profile samplers were installed in the scrub section at heights of 5, 10, 15, and 19 ft in preparation for measuring Zr profiles. Standard nozzle plates (23% free area, 3/16-in. dia. holes) were installed at 3-in. uniform spacing throughout the entire 22-ft height of the column.

Pumping was required for the uranium-bearing 1AP stream leaving the centrifugal contractor. To achieve this, a level transmitter, controller, and flow control valve were added to the 1AP tank.

The stripping column cartridge was shortened from 15 to 14 ft in length. Three new phase splitting samplers were installed at heights of 3, 6, and 9 ft from the bottom of the cartridge. The cartridge was also modified. Flat slot plates (23% free area) were installed.

In the shakedown run, using the Robatel contactor in the extraction mode, the unit was at least partially plugged at startup, but a flush with concentrated nitric acid restored aqueous flow capability.

Six additional runs have been completed, bringing the total operating time for the Robatel centrifugal contactor to 45 hr. Though balky in establishing phase separation on startup, the unit operated smoothly for the remainder at each run, even with intermittent flow stoppage. Uranium losses to the 1AW appear to be a function of the uranium in the 1AX. All phase splitting samplers worked well.

Zirconium tracers and chemical zirconium were added to the feed in each of the last two runs (five sets of data). Decontamination of Zr will be determined by gamma activity from sample aliquots counted using equivalent geometry. Two additional Zr runs are planned.

5-4

6. LABORATORY STUDIES - TASK 370

R. D. Zimmerman

6.1 VERTICAL CENTRIFUGE TESTING

L. J. Olguin

A Sharples Model P850 vertical continuous centrifuge has been installed in the General Atomic Company pilot plant as part of the prototype dissolver-centrifuge system. A vertical centrifuge was selected primarily because of its adaptability to remote hot cell operation and maintenance. The vertical centrifuge will be tested for operability and solids-liquid separation efficiency under various operating conditions related to nuclear process applications.

The solids-liquid separation efficiency of the Sharples vertical centrifuge was evaluated throughout a range of operating conditions which varied the slurry feed rate, the centrifuge g-force, the solids concentration, the solid particle diameter, and the liquid density. As shown in Table 6-1, separation efficiencies of 100% resulted for each of eight initial tests performed using dissolver slurries of glass beads and water or 7.4 M $\text{Ca}(\text{NO}_3)_2$ solutions to simulate separation of fuel particles. The estimated particle setting velocities for these tests ranged from 3.8 m/s to 472.0 m/s (12.5 to 1548.7 ft/sec respectively). The moisture content of the separated solids was found to increase as the slurry feed rate to the centrifuge was decreased. This appears to be a performance characteristic of the vertical centrifuge relating to its interior design.

Further tests will be aimed at evaluating the vertical centrifuge performance in separating simulated high level waste tank slurries.

6.2 DISSOLUTION TESTS

H. H. Yip

A 0.1-m glass dissolver has been used to investigate solids-liquid mixing during ThO_2 kernel dissolutions. The ThO_2 kernels used were from the FY-78 head-end sequential run, representing realistic prior process

Table 6-1. Initial vertical centrifuge test results

Run No.	Slurry feed rate (lpm)	Centrifuge g-force (g)	Solids concentration (wt %)	Liquid ^a density (g/cm ³)	Particle ^b diameter (μm)	Separation efficiency (%)	Settling velocity (ft/sec)	Separated solids moisture content (wt %)
B-1	10.3	1080	15	1.43	126	100	12.5	17.2
B-2	15.1	1080	5	1.0	526	100	1548.7	15.7
B-3	13.1	1080	5	1.43	126	100	12.5	3.2
B-4	10.0	1080	15	1.0	526	100	1548.7	41.8
B-5	15.0	529	15	1.0	126	100	43.5	11.1
B-6	9.8	529	5	1.0	126	100	43.5	39.0
B-7	9.6	529	5	1.43	526	100	106.7	30.5
B-8	14.0	529	15	1.43	526	100	106.7	17.4

^aLiquids tested are water and $\text{Ca}(\text{NO}_3)_2$

^bSolid particles tested are glass beads; density = 2.45 g/cm³

history. A series of reference 40% heel dissolutions were made to establish a baseline dissolution rate without any mixing method. The average dissolution time was 8-1/2 hours from startup to reach 1 M thorium concentration.

Two mixing methods were tried to date:

1. Pulsed-sparge technique. The experimental setup was described in the previous quarterly report. No improvement was observed in dissolution rate.
2. Liquid recirculation to solids bed. A metering pump loop (Fig. 6-1) was used to demonstrate the feasibility of recirculating liquid to the solids bed as a means to improve dissolution rate. Moreover, the pump loop serves to quantify and optimize the recirculation rate required to achieve a desired dissolution rate. Once the required recirculation rate is established, new liquid circulation designs more adaptable for hot cell operation (e.g., airlift, thermosiphon) can then be fabricated for further testing.

Preliminary results indicate approximately 50% reduction in dissolution time (4.3 hours from startup) can be achieved at a recirculation rate of 3% reactor volume per minute, as long as the solids bed temperature is maintained at a few degrees below the solution boiling point of 119°C. As indicated in Fig. 6-2, higher recirculation rates appear to have little effect on decreasing dissolution time further. Apparently, the dissolution rate is controlled by the solution temperature, and as long as there is sufficient liquid circulation to prevent a dry solids bed from forming, no further dissolution rate increase will be expected from higher flow rate.

6.3 BENCH-SCALE LABORATORY STUDIES

R. G. Wilbourn

6.3.1 Effect of thorium on hydrolysis of tributyl phosphate

TBP is the organic extractant used in the Acid-Thorex process. TBP has many inherent characteristics that make it highly suited for use with systems containing nitric acid. Among the desirable properties of TBP is

Fig. 6-1. 0.1-m glass dissolver recirculation loop

Fig. 6-2. Dissolution time versus pump recirculation rate in 0.1-m glass dissolver

its resistance to acid hydrolysis. However, while TBP is resistant to hydrolysis, it slowly decomposes in the presence of nitric acid to yield DBP and monobutylphosphate (MBP). The presence of DBP (and MBP) in solvent extraction streams is undesirable. Uranium, thorium, and zirconium complexes of DBP are more soluble in the TBP/NPH solvent than in aqueous solutions, and are thus responsible for the retention of those heavy metals in the organic phase. In addition, the thorium-DBP complex is not soluble in dilute acid and, therefore, tends to carry over and precipitate in the uranium stripping column (C column) causing a loss of efficiency and capacity.

Degradation of TBP is also influenced by the presence of heavy metals. Burger reported that the presence of UO_2^{2+} decreased the amount of solvent damage.⁶⁻¹ Other workers⁶⁻² found that the presence of zirconium complexes of DBP increased the TBP degradation.

In the reprocessing of fertile thorium fuels, thorium is the major element present. Determination of the effect of thorium nitrate on the degradation of solvent is the main purpose of this study.

The study of the effect of thorium on the rate of DBP formation continued during the reporting period. DBP formation rate data were obtained for sample sets at temperatures of -4°C , 35°C , and 52°C . The rate of DBP formation was found to be independent of the third phase characteristics associated with the thorium nitrate - TBP/NPH system.

The significant results obtained to date as functions of the indicated experimental parameters are summarized below:

1. Thorium nitrate concentration

The rate of DBP formation in 30% TBP/NPH was found to be directly proportional to the thorium nitrate content of the solvent. An example of this effect is shown in Fig. 6-3. Solvent samples containing 20 g/liter and 35 g/liter thorium (as the nitrate) produced 205 and 305 ppm DBP, respectively.

2. Aging time

As shown in Fig. 6-3, the rate of hydrolysis of TBP by thorium nitrate to produce DBP is linear with respect to time for contact intervals < 13 days.

3. Nitric acid

The presence of nitric acid in the thorium nitrate solvent system results in a decrease in the amount of thorium-DBP complex formed. This effect is shown graphically in Fig. 6-3. The mechanism for this effect is not fully understood. The retardation may be related to changes in the Th-TBP complex in the TBP/NPH system in the presence of nitric acid. Another possibility is that the thorium-DBP complex is less stable in the thorium nitrate solvent system as a function of acidity.

4. Temperature

As shown in Fig. 6-4, a small increase in the rate of DBP formation in the thorium nitrate solvent system was observed as a function of temperature in the 0 to 20°C range. The rate of DBP formation increased very rapidly with temperatures in the 20 to 50°C range. An example of the accelerated DBP formation rate at higher temperatures is given in Fig. 6-5.

In order to minimize the impact of DBP in solvent extraction operations, aqueous-organic contact times should be as short as possible. The scrub column should not be operated at low acidities. The extraction and partition operations should be conducted at the lowest possible temperature compatible with overall process performance.

6.3.2 Steam stripping TBP from thorium nitrate solutions

R. T. Stula

Bench-scale experiments have been initiated to produce data on steam stripping of soluble TBP from thorium nitrate solutions. Laboratory study of this separation is being done to evaluate whether this is a usable process. Simulated 1BT feed solutions containing typical amounts of TBP (or DBP) are fed to a column packed with glass cylinders and contacted with a countercurrent flow of steam. Effects of varying operating conditions will be evaluated. Also, measurement of TBP (or DBP) solubility in thorium nitrate solutions is part of this study.

Fig. 6-3. Effect of thorium concentration and time on DBP formation rate

Fig. 6-4. Effect of temperature on DBP formation rate

Fig. 6-5. Effect of temperature on DBP formation rate

6.3.3 Three-phase compositions in thorium, uranium, nitric acid, TBP diluent system

C. A. Kergis

The initial 18 solutions of the three-phase TBP-thorium nitrate-uranium nitrate-nitric acid system have been analyzed. Each phase has been analyzed for uranium and thorium concentration, TBP concentration, and acidity. All data have been reduced and correlation of this data is now underway. Findings will be summarized in the next report.

6.3.4 Dissolution tests on ThO₂/UO₂ fuel pellets

C. A. Kergis

Work has been started on 3/1-ThO₂/UO₂ dissolution tests. Fuel pellets have been ordered and equipment is being assembled.

REFERENCES

- 6-1 L. L. Burger and E. D. McClanahan, Nucl. Tech 50, 153 (1958).
- 6-2 A. J. Moffat and R. D. Thompson, "Basic Studies of Chemical Stability in Extraction Systems; the Effect of Zirconium and Nitric Acid on the Chemical Stability of Tributyl Phosphate," Phillips Petroleum Company, Atomic Energy Division Report IDO-14543 (1961).