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CHEMICAL TECHNOLOGY DIVISION

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ABSTRACT

A literature review is presented on mass transfer between two liquid phases. Vibratory compaction has been shown to be an acceptable method for fabricating fuel elements up to 85% theoretical power density. A correlation of data on the oxidation of carbon monoxide by copper oxide in helium was completed. The apparent induced underflow ratios for two multiclone units were 2.5 to 5.0 times the experimental and calculated values for single hydroclones of the same dimensions. The anion exchange uranium self-diffusion coefficients have been measured at several velocities using the submerged pump contactor and 1200 micron Dowex 21K resin. The instantaneous dissolution rates of UO_2-ThO_2 pellets in Thorex dissolvents distributed normally at both zero and 50% dissolution. The spread was higher for the 50% dissolved sample. The Sulfex dissolution rate appears to be independent of stainless steel loading. A 150 gal batch of solution was found to be essentially mixed in 6 min of air sparging in a packed tank. The dissolution rate of UO_2 in nitric acid is found to be a property of the source of the pellet. Pellets from the Davison Chemical Co. were found to dissolve at about 25% the rate of dissolution of FWR reject pellets. The dissolution of zirconium metal in molten fluoride baths is strongly influenced by the concentration of zirconium fluoride and only slightly affected by temperature. A waste calcination run using simulated Purex waste in a 6-in.-dia vessel tended to confirm the radial deposition model and the fact that density and thermal conductivity of the solids are not affected by different pot diameters.

CONTENTS

	<u>Page</u>
Abstract	2
Previous Reports in This Series	4
Summary	5
1.0 Chemical Engineering Research	8
2.0 Depleted Uranium Utilization	14
3.0 Fuel Cycle Development	15
4.0 GCR Coolant Cleanup Studies	17
5.0 HRP - Fuel and Thoria Blanket Studies	22
6.0 Ion Exchange	26
7.0 Power Reactor Fuel Processing	28
8.0 Volatility	50
9.0 Waste Treatment	81

PREVIOUS REPORTS IN THIS SERIES

CF Numbers for UNOP Monthly Reports

December 1954 (Part I-HR) 55-1-45
 December 1954 (Part II) 55-1-62

January 1955 55-1-194
 February 1955 55-2-185
 March 1955 55-3-190
 April 1955 55-4-164
 May 1955 55-5-179
 June 1955 55-6-180
 July 1955 55-7-138
 August 1955 55-8-157
 September 1955 55-9-150
 October 1955 55-10-110
 November 1955 55-11-176
 December 1955 55-12-154

January 1956 56-1-175
 February 1956 56-2-154
 March 1956 56-3-177
 April 1956 56-4-210
 May 1956 56-5-197
 June 1956 56-6-177
 July 1956 56-7-150
 August 1956 56-8-215
 September 1956 56-9-127
 October 1956 56-10-83
 November 1956 56-11-143
 December 1956 56-12-128

January 1958 58-1-137
 February 1958 58-2-139
 March 1958 58-3-71
 April 1958 58-4-123
 May 1958 58-5-50
 June 1958 58-6-85
 July 1958 58-7-126
 August 1958 58-8-59
 September 1958 58-9-62
 October 1958 58-10-90
 November 1958 58-11-93
 December 1958 58-12-35

January 1959 59-1-74
 February 1959 59-2-45
 March 1959 59-3-61
 April 1959 59-4-47
 May 1959 59-5-47
 June 1959 59-6-63
 July 1959 59-7-58
 August 1959 59-8-76
 September 1959 59-9-69
 October 1959 59-10-77
 November 1959 59-11-54
 December 1959 59-12-49

Chemical Technology Division Monthly Reports

January 1957 ORNO-2251
 February 1957 ORNL-2270
 March 1957 ORNL-2307
 April 1957 ORNL-2324
 May 1957 ORNL-2361
 June 1957 ORNL-2362
 July 1957 ORNL-2385
 August 1957 ORNL-2400
 September 1957 ORNL-2416
 October 1957 ORNL-2417
 November 1957 ORNL-2447
 December 1957 ORNL-2468

January 1960 60-1-49
 February 1960 60-2-56
 March 1960 60-3-61
 April 1960 60-4-37
 May 1960 60-5-58
 June 1960 60-6-11

SUMMARY

1.0 CHEMICAL ENGINEERING RESEARCH

A review of the literature has shown that since Whitman proposed two-film theory in 1923 there have been considerable refinements in the mathematical models for mass transfer. These include such things as the identification of the eddy penetration effect and the regimes where it is significant. Of particular interest in solvent extraction are the studies on the mass transfer from dispersed droplets. Rigorous solutions to the Navier-Stokes equations exist both for the case of no interfacial viscosity and for the presence of interfacial viscosity. It has now been established that surface active agents have the effect of inhibiting the circulation within a drop rather than "blocking" the interface. Among the more significant contributions in recent months is the mathematical analysis of the Marangoni effect in plane geometry.

2.0 DEPLETED URANIUM UTILIZATION

Two sub-contracts are active on development of non-nuclear uses for depleted uranium as petroleum refining catalysts and in the ceramic industry.

3.0 FUEL CYCLE DEVELOPMENT

The results for vibratory compaction of mixed oxides (ThO_2 - 3.4 wt % UO_2) using a single impact piston type pneumatic vibrator show densities of 8.77 g/cc in an 8 ft long 3/8-in. o.d., 35 mil wall stainless steel tube and 8.58 g/cc in a 2 ft long 3/8-in. o.d. aluminum tube. The effects of the tube length and the aluminum were not significant as compared to 2 ft stainless steel tubes. Mixed ThO_2 - UO_2 of 9.6 to 9.8 g/cc by toluene displacement were vibratorily compacted to 8.2 to 8.5 g/cc in 3/8-in. o.d. tubes. ThO_2 densified by a single treatment with concentrated HNO_3 followed by calcination to about 1050°C was vibratorily compacted to 8.37 g/cc.

4.0 GCR COOLANT CLEANUP STUDIES

A silver bed and charcoal adsorption system was sized for the EGCR experimental loops to be installed on a 1% bypass side stream.

Correlation of data on the oxidation of CO by copper oxide in helium was completed, which gives the effect of flow rate, temperature and inlet concentration on the degree of oxidation in a fixed bed.

5.0 HRP - FUEL AND THORIA BLANKET STUDIES

Apparent induced underflow ratios and efficiencies were measured for the new HRT multiclone and for a Dorr-Oliver TM stage modified to give 32 hydroclones in parallel on one induced underflow receiver. The apparent induced underflow ratios for the two multiclone units were 2.5 to 5.0 times the experimental and calculated values for single hydroclones of the same dimensions. The efficiencies for ThO_2 of about 1.6 μ dia, corrected for the underflow volume, were 80 to 90% for single hydroclones with continuous underflow, 50 to 60% for the multiclone with 5% of the feed flow as continuous underflow, and 16

to 22% for induced underflow operation of the multiclone. These results are believed due to unequal flows through the underflow ports of the parallel units.

6.0 ION EXCHANGE

Uranium self-diffusion runs have been made with the submerged pump contactor and 1200μ Dowex 21K under various solution flow rates. Twenty beads per sample were required to reduce the data scatter to an acceptable level. At the higher flow rates, particle diffusion appeared to be the rate controlling step. The uranium self-diffusion coefficient measured under these conditions was approximately $4.4 \times 10^{-8} \text{ cm}^2/\text{sec}$. This is slightly higher than the value of $3 \times 10^{-8} \text{ cm}^2/\text{sec}$ which had been estimated earlier from badly scattered single bead results.

7.0 POWER REACTOR FUEL PROCESSING

7.1 Darex-Thorex

In studying the reproducibility of instantaneous dissolution rates of $\text{UO}_2\text{-ThO}_2$ pellets in Thorex dissolvents, it was found that normal distributions were approximated by both 0 and ~50% dissolution with both the mean value of the dissolution rate (g/min-g) and its variability increasing with increasing dissolution.

7.2 Sulfex

Investigation of the instantaneous reaction rates of 304L stainless steel tubing in H_2SO_4 containing dissolved stainless steel was continued in an effort to explain the wide fluctuation in dissolution rates observed in the operation of the engineering scale equipment. The dissolvents investigated were 2-6 M H_2SO_4 containing 0-1.0 M dissolved stainless steel. The instantaneous reaction rates increased with increasing acidity for all stainless steel concentrations evaluated. No correlation of rate with stainless steel concentration at constant acidity was apparent; within the data scatter it must be concluded that reaction rate is independent of stainless steel loading.

7.3 Evaluation of Packed Process Tanks

Mixing of 75 and 150 gallon batches of solution in a packed tank, at air rates of 0.14 and 0.55 scfm/ft² of tank cross-section, demonstrated the sparge ring to be most effective, followed by the slotted draft tubes, and the conventional draft tubes. Time required to mix a 75-gallon batch ranged from 3 to 6 minutes; a 150-gallon batch required 4 to 20 minutes. No breakage and no change in the 77.4% void fraction were observed during these short term mixing tests.

7.4 Mechanical Processing

Leaching. Further studies of the instantaneous dissolution rates of several types of unirradiated UO_2 pellets in boiling nitric acid showed some wide variations dependent on some property of the pellets, other than density and chemical composition. Pellets used were of fairly uniform density and were all UO_2 ; no U^{+6} could be detected. PWR pellets (good grade) dissolved at slightly lower rates than found previously for PWR pellets (reject grade). Pellets from Davison Chemical Co. dissolved at considerably lower rates as did pellets reported on by Canadian experimenters. Typical instantaneous dissolution rates, in $\text{mg-cm}^{-2}\text{-min}^{-1}$, in boiling 10 M HNO_3 were 90 (PWR, reject), 62 (PWR, good), 23 (Davison) and 18 (Canadian).

7.5 SRE Dejacketing Studies

Tests with a cobalt 60 source showed that the 5 ft thick concrete shield walls of Cell A of the segmenting facility were free from voids.

8.0 VOLATILITY

8.1 Molten Salt Dissolution Studies

Data from a series of eleven runs indicate that dissolution rate is slightly temperature dependent and is strongly influenced by the concentration of zirconium fluoride in the fused salt; the maximum dissolution rate was at 700°C (maximum temperature) and 0% zirconium in the melt.

8.2 Moving Bed Absorber

Repeated tests demonstrated reliable mechanical functioning with loose pellets, caked pellet beds, and broken pellets.

9.0 WASTE TREATMENT

Study of pot calcination for high level liquid waste disposal was continued with emphasis on providing engineering design data for full scale plant design. A run (R-30) was carried out in a vessel 6-in. in dia and 84-in. long. Analysis of the mechanism of solid deposition showed that the data were best correlated assuming radial deposition. Comparison with a previous run in an 8-in. vessel showed that changing the vessel diameter did not affect the density and thermal conductivity of the solids, and that the average processing rate was independent of vessel diameter, as predicted by the solid deposition model.

Data of gasket assemblies were made in support of the study on remote connection and disconnection of flanges. A Goetze gasket (style 929) successfully passed the test program of thermal cycling, pressures testing at 60 psig, and remaking the flange.

1.0 CHEMICAL ENGINEERING RESEARCH

A. D. Ryon

1.1 Resistance to Mass Transfer at a Fluid Interface-A Review - C. V. Chester

Mass Transfer Models. One of the earliest successful attempts to provide a model for mass transfer between immiscible fluid phases was the "Two-Film Theory" proposed by Whitman in 1923.⁴⁵ This theory has been successful in explaining a large body of experimental data for both heat and mass transfer.²⁰ However under certain conditions, it was found that mass transfer was proportional to the square root of the diffusivity in the controlling film, rather than the first power as predicted by the film theory. Higbie²⁶ in 1935 showed that for short contact times the amount of solute penetrating an interface in short time, unsteady state diffusion was proportional to the 0.5 power of the diffusivity and time. In 1951 this penetration effect was incorporated into the eddy-penetration theory by Danckwerts.^{11,23} In this theory, the one-half power dependence on diffusivity would occur from transfer to or from transient eddies reaching the interface.

The two apparently diverse theories of mass transfer were reconciled in 1958 by Toor and Marchello⁴³ who showed the two theories were limiting cases of a more general solution to Fick's law for diffusion into a renewed interface. If fluid elements at the interface have a short life, the Danckwerts penetration theory applied and transfer is proportional to the half power of diffusivity. If fluid elements have a lifetime at the interface long compared with L^2/D , the long time approximation to Fick's law solution is valid, and transfer is dependent on diffusivity to the first power. In the expression L is the characteristic thickness of the eddy or surface fluid element and D is the solute diffusivity.

In all of the above theories, it is assumed that there is no resistance across the interface per se, i.e., the two phases are in equilibrium. This is apparently a good assumption for most cases of simple mass transfer. However calculations have been made on the effect on column profile¹ and HTU,³⁸ and a modest resistance at the interface (equivalent to 0.1 mm film or greater) will produce a detectable effect on column performance.

Hydrodynamic Resistances. Since many of the changes in apparent resistance to mass transfer can be accounted for by hydrodynamic effects, it will be necessary to review some of the pertinent work in the hydrodynamics of single drop experiments.

If a single drop of a liquid is permitted to fall through another immiscible liquid, circulation of the liquid in the drop can be observed.^{2,33,14} In 1911, Hadamard²¹ solved the Navier-Stokes equations for the circulation in the drop for a spherical drop at low Reynolds numbers, and no interfacial viscosity. Boussinesq^{3,4,5} in 1913 proposed the existence of an interfacial viscosity, and took it into account for solution of equations of motion of a falling drop. This interfacial viscosity is quite important, and as will be shown later, is the factor through which many surface active agents retard mass transfer. This viscosity has been considered at length by Joly,³⁰ Harkins, and others.

Naturally the circulation in the drops will increase mass transfer over simple diffusion. Kronig and Brink³¹ in 1950 solved the diffusion equations for a falling drop using Hadamard's solution for the circulation, and were able to show that the transfer to a circulating drop should be 2.5 times that for a noncirculating drop. This was confirmed experimentally by Calderbank and Korchinski,⁸ among others, in 1956.

However, the smooth laminar flows analyzed in the previous cases are not always the role in solvent extraction equipment. If a drop is large and interfacial tension low, it will deform from spherical, and even oscillate. This problem was treated by Hu, Shengen, and Kinter²⁷ in 1955. The effect of oscillation on mass transfer was treated by Handlos and Baron²² in 1957.

Droplet oscillation can also be caused by local changes in interfacial tension during mass transfer. This situation is by far the more important cause. The motion of drops or interfaces during and due to mass transfer have been reported by Lewis and Pratt,³² Sigwart and Nassenstein,⁴⁰ Sherwood and Wei,³⁹ and Garner et al.¹⁶ In all these cases motion was produced in the interface by local reduction in surface tension either due to concentration of the solute, or increase in temperature due to heat of reaction.³⁶ Analytical treatment of this phenomenon, called the "Marengoni Effect," was carried out for drying paint films by Pearson³⁷ in 1958. An elegant analysis of the conditions for stability of a plane interface in the presence of the Marengoni effect was done by Sternling and Scriven⁴² in 1959. In this work, the Navier-Stokes equations were solved for a simplified two-dimensional system in the vicinity of a plane interface across which solute was diffusing. The conditions for the production of "roll cells" (or convection cells) driven by the changes in interfacial tension were determined. Many simplifying assumptions were made in order to get a system of equations which would yield to analytical treatment. However it was a brilliant attack on a problem which will require much subsequent work, probably requiring machine calculations to analyze experimental observations.

The recoil of single drops exposed to a jet of solute, reducing interfacial tension (e.g., acetone in the toluene-water system) was analyzed by Haydon.^{24,25,12} A simplified model was used, and the assumption was made of a single roll cell of modulus on the order of drop diameter. The concentration changes considered were much greater than those normally encountered in typical differential mass transfer operations, and the phenomena analyzed are probably much more violent than might be expected in a commercial solvent extraction. But the situation considered is very likely a limiting case of the actual situation in many systems, and is important.

In systems where drop oscillation is observed, the rate of mass transfer is almost always greater than that expected for a simple spherical drop with internal circulation. Transfer coefficients as high as 30 times those expected for a noncirculating drop (compared with 2.5 for a circulating drop) have been observed.^{17,42,28,29} This can only be attributed to interfacial turbulence somewhere between the gross oscillations analyzed by Haydon and the interfacial network of small convection cells analyzed by Sternling and Scriven.

The Role of Surface Active Agents. Surface active agents are important in mass transfer systems, occurring usually as an impurity and occasionally deliberately introduced in an attempt to increase transfer rates by increasing interfacial area. Unfortunately most surface active agents reduce transfer rates. This has been observed by Chu et al.⁹ among others in packed columns, and in a great host of single drop experiments by Coulson and Skinner,¹⁰ West, Herrman and Chong,⁴⁴ and Terjesen and his co-workers.^{34,35,6} The means by which the transfer rate was lowered was a subject of controversy for some time, one school holding that a membrane was formed at the interface, blocking molecular diffusion, the other holding that the agent altered only the hydrodynamics of the system, reducing turbulence, and hence the eddy diffusivity of the transferring solute. Although the former hypothesis may be more appealing to some for its simplicity, a preponderance of evidence has gradually accumulated to support the latter, or hydrodynamic, mechanism.

Surface active agents do more than merely reduce surface tension. It turns out they also increase the two-dimensional viscosity of the interface treated by Boussinesq and Joly, and in sufficient quantity can make the interface quite rigid. This will not only reduce interfacial turbulence, but also drop circulation in a falling drop. This reduction of drop oscillation and circulation has been observed by Terjesen⁷ and Garner^{18,13,19} and their co-workers. The mass transfer rates have also been observed to decrease, but in no case to less than that expected for diffusion into a rigid sphere, which is only approached. The excellent systematic study of surface active agents by Garner and Skelland¹⁹ published in 1956 showed that there was in many cases a preliminary increase in mass transfer coefficient for drops with concentration of surface active agent before the subsequent decrease toward the case of the rigid sphere. This is attributable to the decrease in surface tension of the drop and its consequent enhanced susceptibility to deformation during fall, before the viscosity of the interface has risen very far.

Another factor at low concentrations of surface active agents is the time one phase is exposed to the other, or "age" of the interface. It takes a little time for surface active agents to migrate to and penetrate the interface and build up an equilibrium concentration. This time was measured and correlated with structure of the agent by Garner and Mina¹⁵ with a very elegant falling jet technique. It might be injected parenthetically that the nebulous term "age" can also include the decay of Marangoni turbulence if it is present.

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2.0 DEPLETED URANIUM UTILIZATION

P. A. Haas

Development of non-nuclear uses for depleted uranium produced as gaseous diffusion plant "bottoms" is an objective of two ORNL sub-contract studies and of a number of U. S. Bureau of Mines studies.

2.1 Trip Report: U. S. Bureau of Mines-AEC Sponsored Meeting to Review Depleted Uranium Studies* - P. A. Haas

Studies reported by U. S. Bureau of Mines personnel at Reno, Nevada, on April 12-13, 1960, show promising properties of uranium oxides as petroleum refining catalysts, of uranium steels, and of Sn-U as a bearing metal alloy. Results were also reported for use of uranium as automobile afterburner catalysts, in cathodic protection and in heavy media separations, and for electrowinning, electrorefining, and alkali metal reduction preparation of uranium. Other reviews applicable to non-nuclear uses of uranium were presented by AEC and Bureau of Mines personnel.

2.2 Possible Uses of Depleted Uranium by the Ceramic Industry - As reported by G. C. Robinson, Clemson College, for sub-contract No. 1484

Literature searches of the publications and abstracts of the American Ceramic Society and of British ceramic publications were completed. Experimental equipment was set-up, UO_2 was received, and experimental studies were started for several applications suggested by the literature searches.

2.3 Uranium Catalyst Investigations - As reported by R. L. Nickelson, Montana State College, for sub-contract No. 1483

Test of uranium compounds as promoters for cobalt-molybdate catalysts show a decrease in catalytic activity for desulfurization of a diesel fraction as compared to an unpromoted catalyst. These tests were run at 700°F with 1.885% sulfur in the feed, 200 psig, 1000 SCF H_2 /bbl, 0 to 2 wt % U and 5.0 ml feed/hr-ml catalyst. Initial results for uranium oxides and sulfides deposited directly on an inert carrier as desulfurization catalysts appear more promising.

*Abstracted from CF 60-5-47.

3.0 FUEL CYCLE DEVELOPMENT

P. A. Haas

Studies are being conducted on fuel element fabrication procedures economically adaptable to remote operation for recycle of the fissile and fertile materials used in power reactors. The initial emphasis is on vibratory compaction of high density particles of ThO_2 or $\text{ThO}_2\text{-UO}_2$ of controlled size distributions. This has included studies of the compaction of arc-fused ThO_2 and $\text{ThO}_2\text{-UO}_2$ by both pneumatic and electronic vibrators and preliminary consideration of chemical methods of densifying ThO_2 .

3.1 Vibratory Compaction Studies - S. D. Clinton, J. W. Snider, R. D. Arthur

Two vibratory compaction runs were made with fused $\text{ThO}_2\text{-UO}_2$ (3.4 wt % UO_2) to explore the effect of tube properties on the vibrated bulk oxide density. Using a BH-1-1/4-in. single impact type pneumatic vibrator, 950 g of mixed fused oxide was compacted in an 8 ft long, stainless steel tube (3/8-in. o.d. and 35 mil wall thickness) to a bulk density of 8.77 g/cc. This result was essentially identical to vibrated densities obtained previously in 2 ft tubes (see CF 60-4-37). Since the properties of a tube material should influence the manner in which a particular vibration is translated along the tube length, a single run was made with a 2 ft aluminum tube. The Young's Modulus of aluminum is approximately one-third that of 300 series stainless steel. After screening and blending the fused mixed oxide to the following: 58 wt % -10 +16 mesh, 15 wt % -70 +100 mesh, and 27 wt % -200 mesh; the oxide was vibrated to a bulk density of 8.58 g/cc in the 3/8-in. aluminum tubing. For this one run, the aluminum tube under the influence of pneumatic vibration did not significantly effect the powder compaction as compared to a similar stainless steel tube.

Four vibratory compaction runs were made with three mixed oxide feed powders prepared by Chemical Development Section A using a "hydrothermal denitration technique". The $\text{ThO}_2\text{-UO}_2$ (5.0 wt % UO_2) was fired between 1200 and 1300°C, blended to the standard size distribution (see percentages in preceding paragraph), and pneumatically vibrated in 2 ft, stainless steel tubes. The mixed oxide powder was vibrated to a bulk density of 8.3 ± 0.1 g/cc with the BH-1-1/4-in. vibrator. By employing a load to the surface of one of the powders, a compacted bulk density of 8.5 g/cc was obtained. A lead brick weighing 25 lbs served as the load source, and the downward force was transmitted to the powder surface through a 1/4-in. steel rod. Toluene displacement densities on the mixed oxide particles prepared by Chemical Development varied between 9.6 and 9.8 g/cc.

Five ThO_2 powders were densified using varying preparation procedures in an effort to obtain a material suitable for vibratory compaction. The following general conditions would be desirable of an oxide feed material for compaction: a. the preparation procedure should be adaptable to remote operation, b. at least 60 wt % of the oxide should be between 10 and 16 mesh, c. the particles should possess sufficient strength to minimize size degradation during vibration, and d. the individual particles should closely approximate the theoretical oxide density. Of the five ThO_2 powders prepared,

the highest vibrated density obtained (with no load on the powder surface) was 8.37 g/cc. This particular oxide preparation was made by initially treating 650°C fired, oxalate precipitated thorium oxide with 6.1 M nitric acid (Th to NO_3 mol ratio of 2). After digesting at room temperature for 2 to 4 hours, the paste-like oxide was evaporated to dryness at 80 to 90°C. The dried cake was heated for 2 hrs at 500°C and then fired between 1000 and 1100°C for approximately 8 hrs. The ThO_2 produced by this procedure was glass-like in appearance, and the bulk of the oxide particles were larger than 10 mesh (2000 microns). After crushing, screening, and blending to the standard size distribution; the oxide was vibrated to the previously mentioned density of 8.37 g/cc. From screen analysis before and after vibration approximately 15 wt % of the coarse and mid size fractions degraded enough to pass through the 16 and 100 mesh screens, respectively. Some apparent particle breakage would be indicated if the feed material was simply re-screened without being subjected to compaction.

4.0 GCR COOLANT CLEANUP STUDIES

J. C. Suddath

Contamination of coolant gases by chemical impurities and release of fission products from fuel elements is a major problem in gas cooled reactors and in-pile experimental loops. Investigations are being made to determine the best methods to reduce the impurities, both radioactive and non-radioactive, with emphasis on chemical impurities in the EGCR coolant and radioactive impurities in the EGCR experimental loops.

4.1 EGCR Experimental Loops - J. C. Suddath

A silver bed iodine trap and a charcoal adsorption bed system was sized for the EGCR loops to be installed on a 1% side stream. The silver bed will have 99.9% efficiency for iodine removal from the side stream and the charcoal bed will allow a one day and one hour delay time for the xenon and krypton, respectively.

A literature search is underway to determine the feasibility of employing a light scattering technique to the circulating coolant for the determination of size distribution and concentration of aerosols.

4.2 Evaluation of a Fixed-Bed CuO Oxidizer - C. D. Scott

CuO is being tested as an oxidizing agent for H₂, CO and CH₄ in helium as the first processing step in removing these gases from helium. The initial tests have been made with analytical grade CuO wire 0.017-in.-dia with an average length of 0.034-in. Tests for the kinetics of the reaction of CuO with H₂, CO, and CH₄, are being conducted at anticipated reactor coolant conditions (300 psia and 400-600°C) in 2-in.-dia oxidizing vessels with CuO bed depths of 1/4-in. to 6-in. The operating procedures for these tests were outlined in April 1960 Unit Operations monthly progress report.

Oxidation of CO. A total of 12 tests were made with 1/4-in. CuO bed depths in the 2-in. oxidizers for oxidizing CO to CO₂ ($\text{CO} + \text{CuO} \rightarrow \text{CO}_2 + \text{Cu}$) in a flowing stream of He. In these tests, CO concentrations of 1.1% to 3.43% at bed temperatures of 388 to 572°C and mass flow rates of 0.068 to 0.167 g-mols/cm²-min were used (Table 4.1).

It was found that the apparent reaction rate could be expressed by,

$$r = KG^{+0.5} p_{\text{CO}}^{0.5} \quad (1)$$

where

r = reaction rate, g-mols/cc-min

G = mass flow rate, g-mols/cm²-min

p_{CO} = partial pressure of CO at any point in the oxidizer, atm

Table 4.1. Experimental Results from 14 Runs on Oxidation of CO in a Flowing Stream of Helium by a Fixed-Bed CuO Oxidizer

Run No.	Maximum Bed Temperature °C	Total mass flow rate, g-mols/cm ² -min	Initial CO concentration, vol %	Maximum Conversion of CO to CO ₂ , %
1	472	0.0678	2.73	99.7
2	418	0.0678	2.73	98.5
3	388	0.0678	2.73	97.3
4	421	0.0683	3.43	94.3
5	510	0.0683	3.43	96.7
6	452	0.0683	3.43	96.0
7	555	0.0683	3.43	97.4
8	450	0.1670	1.10	99.7
9	465	0.1640	1.85	95.3
10	573	0.1630	1.94	95.6
11	453	0.1153	1.62	98.9
12	535	0.1153	1.62	99.1

Table 4.2. Experimental Results of 6 Runs on Oxidation of CH₄ in a Flowing Stream of Helium by a CuO, Fixed-Bed Oxidizer

Run No.	Bed Depth, inches	Maximum Bed Temperature, °C	Total mass flow rate, g-mols/cm ² -min	Initial CH ₄ concentration, vol %	Maximum conversion of CH ₄ , %
1	0.25	402	0.0662	0.52	2.6
2	0.25	535	0.0662	0.50	5.0
3	1.0	403	0.0662	0.45	1.7
4*	1.0	565	0.0662	0.44	8.1
		552	0.1650	0.25	3.8
		550	0.0263	0.46	13.4
5	1.0	597	0.0662	0.43	14.4
6	1.0	608	0.0662	0.20	7.6

*Three different tests on the same bed without regeneration.

Correlation of Data. The same basic assumptions and methods were used in this correlation as were used in the correlation of the data from oxidation of H_2 by CuO (May 1960 Unit Operations monthly progress report).

The two main assumptions were (1) mass transfer within the 0.017-in.-dia CuO is not the rate controlling step, and (2) the reaction occurs essentially in a very narrow band which progresses up the bed as bed depletion occurs according to the stoichiometry of the reaction $CO + CuO \rightarrow Cu + CO_2$.

By use of the flow reactor design equation,

$$V/F = - \int_{y_0}^{y_1} \frac{dy}{r} \quad (2)$$

and equation (1), after integration the following equation results,

$$V/F = \frac{2}{K G^{+0.5} \pi^{0.5}} \left[y_0^{0.5} - (y_1)^{0.5} \right] \quad (3)$$

or

$$K = \frac{2}{(V/F) G^{+0.5} \pi^{0.5}} \left[y_0^{0.5} - (y_1)^{0.5} \right] \quad (4)$$

where

V = effective reacting volume of the reactor, cc

F = total feed rate of the gas to the reactor, g-mols/min

y = mol fraction of CO at any point in reactor

π = total pressure, atm

y_1 = mol fraction of CO at exit of reactor

y_0 = mol fraction of CO in feed to reactor

The function, $G^{+0.5}$, represents the effect of resistance to mass transfer by a gas film around the individual particles. This effect can also be described mathematically by the conventional two film theory and put into the reaction rate equation, however, good experimental correlations which would lead to values of the mass transfer coefficient are lacking for the small-sized particle used and the mass transfer coefficient is very dependent on particle size in this size range. Correlating the data for the 12 tests by the above-mentioned method resulted in good agreement for initial CO concentrations of 1.1 to 3.4% and at all of the temperatures and mass flow rates used (Figure 4.1). It was found that K was slightly temperature dependent and could be described by the equation,

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Fig. 4.1. Effect of temperature on the reaction rate constant for the oxidation of CO in a flowing stream of helium by a fixed-bed, CuO oxidizer.

$$K = 0.0541 \exp \left(\frac{-487}{T} \right) \quad (5)$$

The resulting design equation for fixed-bed CuO oxidizers using the 0.017-in.-dia CuO wire (0.034-in. long) is equation (3) with K being described by equation (5).

Oxidation of CH₄. Six tests made with the CuO oxidizer from oxidizing CH₄ indicate that the CH₄ is much more difficult to oxidize than H₂ or CO.

In these tests (Table 4.2) at temperatures of 403 to 608°C, CH₄ concentrations of 0.20 to 0.52%, and mass flow rates of 0.026 to 0.165 g-mole/cm²-min the conversion of CH₄ varied from 1.7% to 14.4%. In general, conversion increased with increasing CH₄ concentration and bed length, while it decreased with increasing mass flow rate.

5.0 HRF - FUEL AND THORIA BLANKET STUDIES

P. A. Haas

Development studies were continued as necessary for processing and preparation of aqueous homogeneous reactor fuel and blanket fluids. Tests with multiple hydroclones in parallel on one induced underflow receiver were conducted along with calibrations of a new HRT multiclone. These results will permit more valid interpretations of results from operation of the multiclone as part of the reactor system. Flame calcination studies were directed toward obtaining 5 to 10 μ dia thoria-alumina particles with the properties previously obtained for 1 to 2 μ dia material.

5.1 CPP Multiple Hydroclone Studies - P. A. Haas, V. L. Fowler

Studies of operation of a number of hydroclones in parallel on one induced underflow receiver were continued using a modified Dorr-Oliver TM stage and using the new multiclone fabricated for installation in the HRT reactor cell. The results confirm the higher apparent induced underflow rates and the lower efficiencies for the multiclone units which are believed to indicate unequal flows through the parallel underflow ports. Flow rate versus pressure drop calibrations of the new HRT multiclone were also obtained and the unit was sent to the HRT to be prepared for installation.

The apparent induced underflow rates for the HRT multiclone were 3.3 to 3.9% of the feed flow rate as compared to 1.3 or 1.4% for single hydroclones of the same dimensions (Table 5.1). These values along with an experimental value of 1.8% for a single 2.64-in. long Bakelite hydroclone confirm apparent induced underflow rates of the multiclones of 2.5 to 5 times the values for single hydroclones of the same dimensions.

The feed flow versus feed to overflow pressure drop for the new HRT multiclone agree with the values previously obtained for CPP prototype hydroclones of the same dimensions (Figure 5.1). The empirical capacity correlation* for this unit would be:

$$F = 18 \left(\frac{P_F - P_O}{235} \right)^{0.44}$$

At 100 ft pressure drop, this gives a flow of 12.4 gpm as compared to 13.4 gpm from the experimental curve of Figure 5.1. The $P_F - P_O$ versus flow values were not significantly affected by B/F ratios of up to 0.08 or by the recirculation rate through the underflow receiver while the $P_F - P_U$ values were slightly changed. The efficiencies of the HRT multiclone for ThO₂ in water at room temperature confirm the variation with underflow rate observed for a TM multiclone (May 1960 Unit Operations monthly report). The efficiencies for B/F = 0.10 were close to those of single hydroclones with either continuous or induced underflow. As the underflow rates were decreased, the efficiencies decreased from within 40 to 75% for B/F = 0.10 to within 10 to 25% for B/F = 0 or 0.007 (Table 5.2).

* ORNL-2876, equation 15, p. 10.

Table 5.1. Multiclone and Single Hydroclone Induced Underflow Ratios

Hydroclone: 0.40-in.-dia, modified Dorr-Oliver TM unit had 32 Bakelite hydroclones in parallel in a 6-in.-dia chamber, the HRT multiclone had 18 titanium hydroclones in parallel as shown on drawing D-34004.

Conditions: Water at room temperature, $P_F - P_O$ of 63 ft except as noted.

Underflow Receiver Agitation: Induced underflow plus external recirculation by a pump at the rates tabulated. Tangential return line of 3/8-in. o.d. tubing for TM unit and special mixing jets as shown on D-34004 for the HRT multiclone.

Unit	Hydroclone Length, in.	Underflow Port dia, in.	External Recirculation Rate, gpm	B/F for a Single Hydroclone, %		B/F for the Multiclones, %	
				Calculated ^a	Experimental	From $\left(\frac{C_O}{C_P}\right)_O$	From Receiver Volume ^c
Modified TM Unit	2.64	0.132	0	1.6	1.8 ^d	6.2	6.8 ^e
Modified TM Unit	2.64	0.132	0.8	1.6	1.8	5.1	5.0
Modified TM Unit	3.14	0.090	0	0.5	0.6	1.5	- ^f
Modified TM Unit	3.14	0.090	0.8	0.5	0.6	1.7	1.6
HRT Multiclone	2.40	0.104	0	1.3	1.4 ^g	3.4, 3.6	- ^f
HRT Multiclone	2.40	0.104	1.3	1.3	1.4	3.9	2.9
HRT Multiclone	2.40	0.104	0	1.3	1.4	3.3 ^h	- ^f
HRT Multiclone	2.40	0.104	0.5	1.3	1.4	3.6	9.9 ^e

^aAs in ORNL-2876, Equation 18, p. 13.

^gFor $P_F - P_O = 100$ feet.

^b $\frac{B}{F} = \left(\frac{C_O}{C_P}\right)_{\text{time} = 0}$ as given in ORNL-2876.

^hFor $P_F - P_O = 41$ feet.

^c $\frac{B}{F} = \frac{0.6V_p}{F(t_2 - t_1)} \ln \frac{C_{O2}}{C_{O1}}$

^dFor $P_F - P_O = 80$ feet.

^eThese values are high because recirculation did not give adequate mixing of the underflow receiver.

^fValues were not calculated because lack of mixing in the underflow receiver would make them meaningless.

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Fig. 5.1. Capacity calibration for the new HRT multicclone.

Table 5.2. Measurement of New HRT Multiclone Efficiencies

Hydroclone: HRT Multiclone as fabricated from drawing D-34004 with 18 0.40-in.-dia hydroclones in parallel on one induced underflow receiver.
 ThO₂ Slurry: Pilot Plant ThO₂ dispersed in 0.001 M Na₄P₂O₇.

Underflow rate, % of feed flow	P _F -P _O	ThO ₂ mean dia, μ	Calculated efficiency, % ^a	Experimental Efficiencies, E _O , %	
				From C _F ^b and C _O	From C _U ^c and C _O
10	63	1.6	65	75	75
5	63	1.6	65	54	57
2.4	63	1.6	65	28,42	33,41
0.7	63	1.6	65	12	- ^d
0	63	1.6	65	29,26,34	- ^e
0 ^b	63	1.6	65	23,22 ^b	- ^e
10	28	1.6	55	41	44
5	28	1.6	55	19	12
0	28	1.6	55	10,20,26	- ^e
5	63	1.1 ^c	40	28,16	19,22,22
2.4	63	1.1 ^c	40	~10	~18
0	63	1.1	40	~10	~12

^aFrom empirical correlations in ORNL-2876.

$$^b E_O = (C_F - C_O) / C_F$$

$$^c E_1 = \frac{C_U}{C_F}, E_O = \frac{E_1 - B/F}{1 - B/F}$$

^dRepresentative underflow samples not obtained.

^eNo underflow stream and representative underflow receiver sample not taken.

6.0 ION EXCHANGE

J. C. Suddath

6.1 Uranium Anion Exchange Kinetics Studies - J. S. Watson

Attempts have been made to use the submerged pump contactor to obtain a value for the self-diffusion coefficient of uranium in uranyl sulfate loaded 1200 μ Dowex 21K. Earlier measurements using the single bead technique resulted in badly scattered data because of nonuniformity of individual beads of Dowex 21K. The best estimate of the coefficient in 1200 μ Dowex 21K which could be obtained from the earlier single bead data was 3×10^{-8} cm²/sec.

The submerged pump runs were made with resin which had been equilibrated with a 0.005 M enriched uranyl sulfate solution 0.15 M in total sulfate. Twenty-four hours or more were allowed for equilibration. A sample of equilibrated resin was then rinsed rapidly with water and contacted for a specified period of time with a natural uranyl sulfate solution with the same composition as the equilibrating solution. Finally the resin sample was again rapidly rinsed with water and counted in a gamma spectrometer for its U-235 content. An initial run was made using 10 beads per sample, but 20 beads per sample proved to be required to reduce the data scatter to an acceptable level.

The results of these runs made with solution flow rates of 13.4, 16.6, and 19.2 cm/sec are shown in Figure 6.1. The diffusion coefficient for each sample was calculated, and the resulting coefficients for each run were averaged. The respective runs gave coefficients of 4.78 ± 0.91 , 4.46 ± 0.77 , and $4.04 \pm 1.23 \times 10^{-8}$ cm²/sec. Within the scatter of the data, these results are identical. This is an indication that at these flow rates particle diffusion is the rate controlling step. If this were not the case, the average coefficient measured in this manner should be an increasing function of the flow rate. The conclusion then is that the uranium self-diffusion coefficient in 1200 μ Dowex 21K is approximately 4.4×10^{-8} cm²/sec.

Two other runs were made with lower solution flow rates. These are shown in Figure 6.1. The resulting average diffusion coefficients calculated were lower than those observed at higher flow rates. This is an indication that under these conditions film diffusion is becoming significant. However, there is an indication that the equilibration and contact solutions may not have had identical concentrations. This could have arisen because of the gradual depletion of the equilibrating solution.

Fig. 6.1. Uranium self-diffusion from 1200 μ Dowex 21K

7.0 POWER REACTOR FUEL PROCESSING

C. D. Watson

7.1 Darex-Thorex - F. G. Kitts

The purpose of the Darex process is to convert stainless steel-containing fuels into chloride-free nitrate solutions suitable for processing in existing stainless steel equipment. Chloride is necessary to effect dissolution but it must be removed to avoid corrosion of subsequent processing equipment. Presently Darex-Thorex is being evaluated for the processing of stainless steel clad $\text{UO}_2\text{-ThO}_2$ fuels such as Consolidated Edison. After decladding with 5 M HNO_3 - 2 M HCl the ceramic core material is dissolved in fluoride catalyzed nitric acid. In the current investigation the reproducibility of instantaneous dissolution rates is being studied while determining the relationship between rate and per cent dissolution.

Two groups of pellets representing initial condition and ~50% (by wt) dissolution were contacted with Thorex dissolvent (12 M HNO_3 , 0.04 M NaF , 0.1 M $\text{Al}(\text{NO}_3)_3$, 0.2 M Th with $\text{Th/U} = 20$) under identical conditions in order to show the distribution of the instantaneous dissolution rates obtained and to show the effect of the increased surface/weight ratio produced by partial dissolution. The data are presented in Table 7.1. Plots of the two distributions are shown in Figures 7.1 and 7.2.

Table 7.1. Distributions of Dissolution Rates at Different Stages of Dissolution

No. of Pellets*	% Dissolution (by wt)	Dissolution Rates (mg/g-min)	Mean Rate	Standard Deviation	Mean σ
51	0	0.280-0.372	0.325	0.022	14.8
55	33-61	0.543-1.17	0.772	0.164	4.7

* From Universal Match Co. 95.6% ThO_2 , $\text{O/U} = 2.0$, density ≈ 9.5 g/cc weight 5.0-5.5 g, diameter = 0.264-in., length = 0.60-0.65-in.

Although normal distributions are approximated in both cases, much greater variability is evident in the rates for partially dissolved pellets since the standard deviation (σ) increases by a factor of 8 while the mean value changes by 2-1/2 (see Table 7.1).

In order to further explore the relationship of dissolution rate and per cent dissolution, rates were obtained for 32 pellets ~1% dissolved and a group of 52 pellets 47-70% dissolved. The data for these pellets combined with the data from Table 7.1 are presented in Table 7.2. This shows a sharp rise in rate from 0 to 1% dissolution and then a gradual increase in rate with % dissolution; a band width of about a factor of 2 is evident from 1 to 70% dissolution. Addition data covering 1 to 40 and >70% dissolution will be obtained.

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Fig. 7.1. Distribution of instantaneous dissolution rates of "as sintered" $\text{UO}_2\text{-ThO}_2$ pellets in 12 M HNO_3 - 0.2 M Th.

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Fig. 7.2. Distribution of instantaneous dissolution rates in 12 M HNO₃ - 0.2 M Th of UO₂-ThO₂ pellets 40 - 57% dissolved.

Table 7.2. Dissolution Rate Ranges as a Function of Per Cent Dissolution

% Dissolution	No. of Pellets	Diss. Rates mg/g-min	Rates
			Mean rate at 0% diss.
0	51	0.28-0.37	0.86-1.14
~1	32	0.41-0.80	1.26-2.46
40-58	71	0.54-1.17	1.66-3.60
58-70	33	0.84-1.75	2.58-5.38

7.2 Sulfex - B. C. Finney, T. D. Napier

Stainless steel clad $\text{UO}_2\text{-ThO}_2$ and UO_2 power reactor fuels may be de jacketed by the Sulfex process. The clad metal is dissolved in boiling 4-6 M H_2SO_4 ; the core in boiling nitric acid (for UO_2) or fluoride catalyzed nitric acid (for $\text{UO}_2\text{-ThO}_2$ mixtures). The application of the Sulfex process to the NMSR and Consolidated Edison fuels is being investigated.

Drastic variations in the instantaneous hydrogen evolution rate over relatively short periods of time were encountered during the semi-continuous decladding of prototype Consolidated Edison fuel assemblies. There is a direct relationship between the hydrogen evolution rate and stainless steel dissolution rate (1.1 - 1.2 g-mols of H_2 are generated per g-mol of stainless steel dissolved). Figure 7.3 is a plot of the instantaneous hydrogen evolution rate as a function of time for semi-continuous declad run SX-32 (decladding prototype Consolidated Edison fuel assemblies in 4 M H_2SO_4). In this run a 6-14 fold increase in the instantaneous hydrogen evolution rate was observed within a 15-30 min period. The reason for the wide fluctuations in the instantaneous hydrogen evolution rate (indicative of an erratic dissolution rate) is not fully understood at this time. Although the fluctuations are probably attributable to the preferential dissolution of stainless steel tubing (February 1960 Unit Operations monthly progress report, CF 60-2-56), there has been no indication why some tubes are attacked more readily than others.

A laboratory scale investigation was made to study the effect of acidity and stainless steel loading on the instantaneous reaction rate. Small pieces of 304L stainless steel tubing (5/16-in. o.d. x 0.020-in. wall thickness x ~1-1/4-in. long) were batch dissolved for 5 min in 250 ml of dissolvents varying from 2-6 M H_2SO_4 and 0-1 M stainless steel. The data are summarized in Table 7.3. Instantaneous reaction rates were calculated according to the equation

$$R = \frac{W}{At}$$

where

Fig. 7.3. Instantaneous hydrogen evolution rate as a function of elapsed time for the semi-continuous Sulfex dejacketing of prototype Consolidated Edison fuel assemblies (304 L - 5/16 in. o.d. stainless steel clad, $\text{UO}_2\text{-ThO}_2$ pellets).

Table 7.3. Instantaneous Reaction Rate, mg/cm²-min,
of 5/16-in. o.d. 304L Stainless Steel Tubing in Various
Concentrations of H₂SO₄ and Stainless Steel Loadings

Stainless Steel Loading <u>M</u>	0	0.1	0.3	0.5	1.0
H ₂ SO ₄ <u>M</u>					
2	0.91 0.67	0.68 0.67	0.31) 0.30) 1 0.32) 0.65) 2 0.66)	0.58 0.66 0.49 0.58	0.42
3	1.44 1.12 1.21	0.87 0.97	0.70) 0.66) 1 0.69) 1.12) 2 1.14)	1.16 1.12	0.97
4	2.14 1.41 1.36 1.65	1.40 1.25	1.52) 1.43) 1 1.36) 2.01) 2 1.91)	1.64 1.73	1.72
5	2.40 2.48	1.82 1.97	3.07) 2.87) 1 2.91) 2.50) 2	2.87 2.66	2.68
6	3.54 2.43 4.79 4.77	2.85 2.60	6.70) 5.53) 1 5.72) 3.70) 2 5.50)	4.82 4.08	5.74 3.85

1. Rates attained using same dissolvent.
2. Rates attained using fresh dissolvent.

R = instantaneous reaction rate, mg/cm²-min

W = weight loss, mg

A = initial surface area, cm²

t = time, min

The assumptions were made that within the dissolution time (5 min) the area of the specimen did not change and the dissolution occurring did not alter the composition of the dissolvent.

At the lower acidities (2-3 M H₂SO₄) and stainless steel loadings (0-0.3 M) the reproducibility was good but at higher acidities the rates varied as much as an order of magnitude. The average rates for a given stainless steel loading increased with increasing acidity and a smooth curve was obtained when the rates were plotted as a function of acidity (Figure 7.4). When comparing the rates as a function of acidity for various stainless steel loadings there appears to be no correlation with stainless steel concentration (Figure 7.5). The curves cross and no trends are established. The data scatter probably represents the precision of the rate determinations and the data could best be presented as a single line with a "width" of plus or minus 30-50% expressing the instantaneous reaction rate as a function of acidity and independent of stainless steel loading.

The scatter in rates apparently is caused by some solution variability which is as yet undefined. A given solution will yield reproducible rates but a second solution made up using identical procedures will not reproduce the rates of the first solution although it will yield reproducible rates itself. This phenomenon was encountered when attempting to reproduce the rates for the solutions loaded to 0.3 M stainless steel (Table 7.3). After storage in a closed container for approximately 24 hrs following the first test, the fresh dissolvent 5 M H₂SO₄ - 0.3 M SS had turned green (originally all dissolvents were definite bluish-green) and it was found that the tubing specimens were passive to the solution. Analysis showed that 26% of the iron in the green solution was in the ferric state compared to the usual ~ 2%. Varying degrees of oxidation may be responsible for the observed scatter in the rate data.

7.3 Evaluation of Packed Process Tanks - B. A. Hannaford

Large capacity tanks, planned for critically-safe storage of fissile material, may incorporate a nuclear poison of randomly packed raschig rings of borosilicate glass. Satisfactory methods for solution mixing, liquid level determination, and removal of particulate solids must be demonstrated for such a packed vessel. In addition, observations must be made on attrition of the glass, change in void fraction, and leaching of boron.

Experiments* to compare three different devices for mixing 75 and 150 gal batches of solution in a 32-in.-dia tank packed with 1.5-in.-dia x 1.75-in.-long glass rings demonstrated that a sparge ring near the tank

*W. R. Alcorn, J. D. Mottley, "Use of Packed Tanks for Safe Storage of Fissile Solutions," KT-534 (May 26, 1960).

Fig. 7.4. The effect of acidity on the instantaneous reaction rate of 304 L - 5/16 in. o.d. stainless steel tubing at a constant dissolvent metal loading of .3 M stainless steel.

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Fig. 7.5. Instantaneous reaction rate as a function of acidity and dissolvent metal loading for the dissolution of 304L - 5/16 in. o.d. stainless steel tubing in Sulfex type dissolvents (H_2SO_4 plus dissolved stainless steel).

bottom was somewhat more effective than a set of three 1-in.-dia slotted draft tubes. A set of three conventional draft tubes was least effective.

Table 7.4 summarizes results of the mixing experiments. Difference in effectiveness among the three devices is most apparent for the 150 gal batch size; for the smaller batch neither air rate nor mixing device appear to have an important effect. The sparge ring is the best mixing device, for the test conditions, on the basis of efficiency and mechanical simplicity.

Void fraction in the packed tank remained constant, at 77.4%, during the course of one week's mixing tests. No breakage was observed.

Table 7.4. Comparison of Devices for Mixing Dilute
NaNO₃ Solutions at 17-23°C

Mixing Device	Liquid Level gals	Time to Achieve 90% Homogeneity, ^d minutes	
		Air Rate = 0.14 scfm/ft ²	Air Rate = 0.55 scfm/ft ²
Conventional Draft tubes ^a	150	19	16-1/2
	75	(e)	4
Slotted Draft tubes ^b	150	12-1/2	9
	75	5-1/4	4-1/4
Sparge Ring ^c	150	8-1/2	3-3/4
	75	6	3

^aThree tubes, 1-in.-dia x 52-in.-long, equally spaced on a 20-in.-dia circle.

^bSame as (a), except two 1/4-in.-wide slots cut into upper 28-in. of each tube.

^cA 28-in.-dia ring, fabricated from 3/8-in.-dia tubing, containing 12 equally-spaced 1/16-in.-dia holes. Entire ring supported approximately 1-in. from tank bottom.

^dDefined as the time when all (2 or 3) sample points are at concentration $C_f \pm 0.10 (C_f - C_i)$, where

C_f = final bulk concentration

C_i = initial bulk concentration

^eNo flow of liquid through draft tube at these conditions.

7.4 Mechanical Processing - G. K. Ellis, J. B. Adams, G. B. Dinsmore

Alternate Methods of Exposing Ceramic Core Elements. Alternate methods of exposing the irradiated ceramic core of tubular assemblies for leaching are being investigated in conjunction with the main line development of methods of shearing entire assemblies. A constricted arc direct-current powered underwater cutting torch was operated at a current of 100 amperes and a speed of 30-in./min to consistently expose porcelain cores of single layers of 0.5-in.-dia tubes with little marring of porcelain surfaces (Figure 7.6). Precise positioning of the torch, which would be difficult in a remote operation with different shaped bundles, was, however, required to remove the stainless steel supporting structure without seriously marring the ceramic. At the various conditions tried in determining the optimum current and torch speed 2.3% of the total porcelain available was enveloped or alloyed in the characteristically porous spherical slag material. Other preliminary tests using the same technique but operating in an air atmosphere were not successful. There was excessive melting and apparently appreciable ceramic envelopment and alloying at any of the several combinations of current and torch speed.

It may be possible with this underwater cutting technique to reduce an entire assembly to a suitable feed for the HNO_3 leachers being considered in this program. This, however, as a remote operation must preclude precise torch positioning and will therefore probably produce an appreciably fractured and surface glazed UO_2 product partially enveloped and alloyed in stainless steel. The feasibility of this technique, in one aspect, depends upon the accessibility of this enveloped UO_2 to nitric acid in the subsequent leaching operation. Two stainless clad prototype sections (3 x 6 array of 35 mil wall tubes containing 5 kg UO_2) have been fabricated and will be cut by a constricted arc for nitric acid leaching.

Leaching. Modifications of the PRFR Cell 4A leacher-condenser-scrubber system have been completed (Figure 7.7). Hydraulic tests of the system were made, and conditions were selected for making 8 batch leaching runs (Table 7.5), each at approximately 7 kg UO_2 loading. The effect on leaching rate of varying reactant concentrations (Table 7.5) and changing the liquid velocity through the packed UO_2 bed will be determined. The effect on removal of nitrogen oxides in the condenser and scrubber using either air or oxygen as a purge gas will be considered.

Hydraulic tests were run boiling water in the Cell 4A batch leacher. Condensate rates in the heating jacket, water boil-up rates from the leacher, and estimates of axial velocities were obtained as a function of steam pressure in the heating jacket. The volumetric flow rate from natural convection transfer at a total liquid volume of 18 liters varied from 6.5 to 9.5 gpm for heat inputs through the steam heating jacket of approximately 400 and 800 Btu/min, respectively (Figure 7.8). The qualitative effect on volumetric flow rate at constant heat input from changing either the liquid level or the void density in the packed bed (such as will occur leaching out the ceramic core) may be observed from Figure 7.9. Probably no significant difference should be shown between the two parameters of ceramic core and leached core cylinders considering the inexactness of velocity measurements used in estimating the volumetric flow rate. However, it is observed that

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Conditions: Current, 300 amp
Speed of Torch, 30 in./min

Fig. 7.6. Exposition of ceramic core by underwater cutting of stainless steel clad (35 mil wall 0.5-in. dia tubes) with constricted arc torch.

Fig. 7.7. PRFR, mechanical phase, leacher-condenser-scrubber system.

Table 7.5. Proposed Operating Conditions for 8 Leaching Runs
in Cell 4A Intermediate Size Leacher

Run	Uranium loading	<u>HNO₃</u>		UO ₂ , kg	Al, mols	<u>Final Concentrations (M)</u>			<u>Purge Gas</u>	
		<u>Conc.</u> M	<u>Volume</u> ℓ ¹			<u>HNO₃</u>	<u>U</u>	<u>HNO₃</u>	<u>Kind</u>	<u>CFM</u>
2	mol U/0.590 & HNO ₃	13.0	16.35	7.48	1	8.6	1.70	12.0	20% excess O ₂ as oxygen	0.93
3	mol U/0.590 & HNO ₃	10.5	16.75	7.67	1	6.09	1.70	9.5	20% excess O ₂ as oxygen	0.636
4	mol U/0.590 & HNO ₃	8.0	17.05	7.81	1	3.59	1.70	7.0	20% excess O ₂ as oxygen	0.355
5	mol U/0.690 & HNO ₃	13.0	18.35	7.19	1	9.27	1.45	12.19	20% excess O ₂ as air	4.23
6	mol U/0.690 & HNO ₃	10.5	17.95	7.02	1	6.72	1.45	9.6	20% excess O ₂ as air	2.76
7	mol U/0.690 & HNO ₃	8.0	18.10	7.07	1	4.22	1.45	7.12	20% excess O ₂ as air	1.535
8	mol U/0.690 & HNO ₃	13.0	18.10	7.06	1	9.2	1.45	12.1	20% excess O ₂ as air	4.18
9	mol U/0.690 & HNO ₃	13.0	15.75	7.21	1	8.55	1.70	12.0	20% excess O ₂ as oxygen	0.897

¹ Assuming $\frac{2.5 \text{ mols HNO}_3}{\text{mol U}}$ required

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Fig. 7.8. Volumetric flow rate from boiling water natural convection transfer in intermediate size Cell 4A batch leacher vs steam pressure in heating jacket. Conditions: 18-1 liquid volume, leach bucket full of 0.5-in. dia x 1-in. long steel cylinders.

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Fig. 7.9. Volumetric flow rate from boiling water natural convection transfer in intermediate size Cell 4A batch leacher vs liquid volume in leacher. A-flow rate starts as liquid level comes up to middle cross-over. B-pumping starts of liquid over top cross-over. C-bulk liquid level up to top cross-over location.

flow rate will not change significantly if the liquid level is kept below "B" the point at which pumping of liquid over the top cross-over begins. The runs in Table 7.5 are all in this lower flow rate range, except run 9 where the effect of a 2.5 factor increase in volumetric flow rate will be observed. This increase will be obtained by displacing the liquid level upwards to point "C". At point "C" the liquid level is about mid-way up in the top 4-in.-dia cross-over leaving only the top half of the cross-over for a vapor outlet. This is the highest practical operating level and the level at which there is maximum volumetric flow.

The flow rate appears to be a linear function of the steam pressure in the heating jacket from 15 to 55 psig with the leach bucket charged with 0.5-in.-dia solid steel cylinders (Figure 7.8). The total heat input, and the per cent heat utilization measured by the water boil-up rate is shown in Figure 7.10. The boil-up rate vs total heat input was independent of liquid volume in other tests at 15.5 and 23.5 liters total liquid volume. This information will be used in later runs to estimate the heating contribution from the UO_2 -acid exothermic reaction.

Leaching- UO_2 . Further studies of the instantaneous dissolution rates of two additional types of UO_2 pellets in boiling nitric acid showed some wide variations dependent on some property of the pellets, other than density and chemical composition. Pellets used were of fairly uniform density and were all UO_2 ; no U^{+6} could be detected. PWR pellets (good grade) dissolved at slightly lower rates than found previously for PWR pellets (reject grade). Pellets from Davison Chemical Co. dissolved at considerably lower rates as did pellets reported on by Canadian experimenters. **Typical instantaneous dissolution rates, in $\text{mg-cm}^{-2}\text{-min}^{-1}$, in boiling 10 M HNO_3 were 80 (PWR reject), 62 (PWR, good), 23 (Davison) and 18 (Canadian).

All data reported are summarized in Figure 7.11. Each data point is the average of from two to five replicates using nominally identical pellets. Data on each type of pellet are summarized separately in Figure 7.12, A, B, C and D. The spread of data points indicated in Figure 7.12 is three times the standard error of the mean* which is an estimate of the limits in which the average of instantaneous dissolution rates from several pellets would fall with a 99.7% probability if the experiment were duplicated under identical conditions.

It is concluded that not only is there a wide variability in dissolution rates between samples of the same type of pellets but also between pellets manufactured in different ways to very similar specifications. Design of dissolution systems, particularly for continuous operation, will have to take this factor into account.

*This was calculated from the original data with the standard deviation,

$$s = \sqrt{\frac{\sum (R - \bar{R})^2}{N-1}} \text{ and standard error of the mean, } S_{\bar{R}} = \frac{s}{\sqrt{N}} \text{ at each point where}$$

N is the number of pellets, R the dissolution rate of a single pellet and $\bar{R}$ the average value of R calculated from N pellets.

**CRDC-822.

Fig. 7.10. Total heat input and percent heat utilization vs steam pressure in intermediate size Cell 4A batch leacher. Conditions: boiling water, leach bucket full of 0.5-in. dia x 1-in. long solid steel cylinders.

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ORNL-LR-DWG 50423 Fig. 7.11. Dissolution rates of UO_2 pellets in nitric acid.

Fig. 7.12. Dissolution rates of UO₂ pellets in nitric acid.

7.5 SRE De Jacketing Studies - G. A. West

Radiation Beam-Hole Test. The shield walls of the segmenting facility, Cell A, Bldg. 3026-D, are sufficiently void free to prevent over exposure of operating personnel. This was determined by scanning the outside of the cell to detect radiation from a 10 curie Co^{60} source located inside the cell. The only radiation beam detected was at the manipulator mounting holes where 12 mrep/hr was recorded when the source was held by the manipulator and raised up to a position almost in horizontal alignment with the holes and 16 ft from the cell face. A known void existing under the cell door is to be sealed by placing lead brick on the cell floor at the door opening.

Hydraulic De Jacketing. Reproducibility tests were conducted to determine the total expansion of the SRE type tubular jackets, 10 mil wall 304L S/S, at various hydraulic pressures. Total expansions of 28 and 36 mils were produced by pressure of 1400 and 1500 psig, respectively. This was ~20% less than was obtained previously on a different shipment of identical size tubing (Figure 7.13).

Multipurpose Saw. Alteration of the drain system and repairs to two Vickers hydraulic motors were made to correct the malfunction of the Vickers hydraulic system. A Vickers hydraulic supply pump was repaired by the Vickers Co. but installation was not completed due to delay in shipment. Operability tests of the hydraulic system and saw are to be continued after the alterations are completed.

Lubricants. In tests to demonstrate the NaK reaction with lubricants in mineral oil, there was no observed reaction with Molykote (molybdenum disulfide) grease or powder. Tricresyl phosphate, a lubricant additive to the mineral oil, caused a slow reaction producing an oxide coating on the NaK which would result in difficult transfer and possibly plugging of the small 1/4-in. o.d. 35 mil wall, stainless steel tubing transfer lines. It was concluded from the tests that molybdenum disulfide lubricants would be used to lubricate the operating parts of the de jacketing equipment.

7.6 Radiation Damage - G. A. West

Sealing compounds of Duxseal, Q-Calk and Novoid-X, considered for sealing the electrical conduit lines inside the segmenting cell were irradiated to 1×10^5 and 5×10^5 r, γ by a Co^{60} source at 140 to 230°F and an intensity of 2.4×10^5 r/hr to determine the leak-tightness of conduit boxes sealed with these materials after irradiation. The Duxseal was satisfactory after 1×10^5 r exposure but was hardened and exhibited a cellular structure at 5×10^5 r. The "Q-Calk" calking compound was expanded and exhibited a cellular structure at 1×10^5 r. The Novoid-X high voltage insulating compound by the G and W Electric Specialty Co. was expanded and exhibited a charring of the surface which increased in depth as the radiation dosage was increased to 5×10^5 r.

Leak tightness tests showed that (1) the Duxseal alone (unirradiated) will leak at 1 to 2 psig pressure, (2) the Q-Calk calking compound backed with Duxseal (unirradiated) will hold ~20 psig pressure, however, after 1×10^5 r irradiation, it allows air leakage at less than 5 psig pressure. Due to the radiation effect on the calking compounds it is recommended that a secondary seal be made at the conduit junction boxes located on the outside of the cell.

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Fig. 7.13. Expansion of SRE tubular jackets with internally applied hydraulic pressure. Jacket: 304-L stainless steel, 10-mil wall, 0.790" o.d.; Fluid: No. 6 White Mineral Oil, 0.8097 gms/cc at 100°F.

8.0 VOLATILITY

R. W. Horton

8.1 Molten Salt Dissolution Studies - S. H. Stainker

The dissolution of zirconium metal in molten salt baths of sodium fluoride-lithium fluoride or sodium fluoride-zirconium fluoride using anhydrous HF is a proposed head-end step for the reprocessing of zirconium matrix power reactor fuels. Dissolution studies are being made using 2 in. by 2 in. dummy elements of the plate type fabricated from Zircaloy-2. The purpose of this program is to study the dissolution rates in order to construct a rate predicting formula. The complete set of proposed conditions for this series of tests were given last month (see Table 7.1, May 1960 Unit Operations monthly progress report). The unique feature of this series is that the salt volume was chosen to allow a maximum change in zirconium concentration of 2 mol per cent in 43/57 sodium fluoride-lithium fluoride melts in a given run. The copper lined dissolver, Mark II, will be used as the dissolution vessel to avoid melt contamination from the iron, nickel, and chrome corrosion products.

Eleven runs are reported in this series. Data from these runs show a small effect of temperature and a larger effect of zirconium concentration in the bulk of the melt. The magnitude of these effects depends on the absolute zirconium concentration in the melt. The range of the averaged dissolution rates was 0.053 to 0.269 lb/hr; the maximum "instantaneous" dissolution rate, 0.8 lb/hr, occurred during DS-1 at 700°C and zero ZrF_4 concentration.

The mechanism for this reaction is thought to be diffusion of HF through a thin layer of molten salt clinging to the surface of the element, then through a second layer of partially hydrated or partially hydrofluorinated zirconium to react with the zirconium base metal. There is a subsequent release of product by cracking, scaling, and diffusion of the ZrF_4 out to some point in this metallic interfacial network at which the product is absorbed or dissolved in the fused salt solvent. The HF must be supplied to the reacting surface through the molten salt. It is apparent, however, that the reaction rate is quite sensitive to the proximity of the gaseous HF phase. This effect may be explained by either the increased turbulence caused by the rising gas bubbles, or the proximity of a replenishing source of HF, or both. The reaction rates obtained in the INOR-8 runs were generally low by factors of 20 compared with those obtained during laboratory runs with higher agitation and HF supply. The INOR-8 rates were, in fact, similar to those obtained in an experiment where HF saturated fused salt without gaseous HF present was passed over a zirconium plate.

The most difficult aspect in predicting gross dissolution rates is the geometrical distribution of local rate. The gross effects of temperature, and ZrF_4 concentration in the melt have been previously investigated (CF 57-8-101). Significant differences in dissolution rate with changes in both of these parameters were exhibited. The rate increased as the temperature increased and decreased as the ZrF_4 concentration in the melt increased. The application of these and other available rate data to

prediction of total rate in the INOR-8 geometry is one of determining the point rate distribution function and surface area as a function of that distribution and time. Since the hydrogen evolution cannot be segregated to give us this information, one alternative is to measure differential penetration rates experimentally over the surface of the element to yield the distribution function directly. This is a very involved and difficult approach considering the system.

There is another way of predicting dissolution behavior which is based on utilizing the total H_2 evolution. This is the pragmatic approach of assuming a mechanism, predicting a point rate distribution function based on that mechanism for one plate or a pair of plates, computing the surface area remaining at a point in time, then computing the total H_2 evolution at that time. A surface integration of the dissolution rate-reaction area product using a transverse distribution function corresponding to the observed HF flow pattern in an element, in addition to the longitudinal distribution computed for a single plate should yield an approximation to the true H_2 generation rate.

These inferred functions might then yield to correlation with chemical engineering parameters such as Reynold's number, Schmidt's number, Sherwood's number, etc. to allow design calculations for plant dissolvers.

Equipment. The equipment used in these tests has been described previously in the May 1960 Unit Operations monthly progress report. The various surface and flow areas used in computations are given in Table 8.1. Fused salt used in these tests was obtained from the molten salt production facility at Y-12. The HF gas used was commercially obtained and used as received.

Experimental Procedure. The method of conducting these experiments was as follows: the weight of the particular composition salt required to produce a volume of 0.148 ft^3 at temperature was charged into the dissolver in crushed form, dry and at room temperature. An argon purge was established on the salt dissolver system and the salt temperature raised to the melting point. When the salt had melted, the system was raised to the operating temperature and allowed to soak at temperature for one to two hours.

In the hour preceding the start of the run, an HF purge of 1 lb per hour was directed into the vapor space of the system to remove inert materials such as nitrogen, argon or air from the system. This method of purging was effective in clearing the system down to the exit of the hydrogen fluoride condensers. There was a hold-up of gas in the absorber bed, and in the 3/8-in. copper tubing which extended from the condenser outlet to the wet test meter exit. When the purge had been completed (which was determined by following the exponential decay of the output on the wet test meter) the HF was directed into the normal feed line which extended into the bottom of the dissolver to a distributor plate. Hydrogen evolution was counted from this point in time.

Temperatures of the outside of the vessel, the sodium fluoride final absorber for HF, the HF feed-condensing system, were recorded. These temperatures were monitored to establish normal operation of the system. The pressure

Table 8.1. Areas - DS Series

Description	in ²	ft ²
Element surface area	-	0.563
Draft tube cross sectional area	6.491	0.04508
Total face area of element and channels	3.562	0.02475
Flow area outside element, inside draft tube	2.929	0.02068
Metal area facing HF flow	2.190	0.01521
Channel area	1.372	0.00952
Perimeter area immediately adjacent to element perimeter assuming width of 3/32-in. i.e. one channel width around 4 sides	0.709	0.00492
Probable area of HF flow from which HF can "reach" a metal surface = channel area + perimeter area =	2.081	0.01446
Area used to compute HF flow rate as lb/hr-ft ² = draft tube area minus metal area facing flow =	4.301	0.02988

of the entering HF upstream from the feed rotameter (that is the cylinder pressure), the pressure drop across the dissolver vessel, and the pressure at the hydrogen wet test meter were recorded. These measurements were used to indicate that no plugs were occurring in the system. The total hydrogen evolution was recorded at 10 min intervals throughout the entire run. The gas pressure and temperature at the wet test meter were also recorded to permit correction of these data to standard temperature and pressure.

The run was terminated when one of two events occurred. Either hydrogen evolution stopped completely or it decayed to a low rate and remained constant for one-half to one hour. On completion of the run, the system was purged with HF to recover any hydrogen contained in the vapor space of the dissolver. An argon purge was then used to eliminate some of the residual HF from the molten salt. The resistance heated, salt transfer lines were then raised to temperature, the dissolver pressurized, and the fused salt transferred by this pressure. The salt was examined and sampled to determine the major components. The inside of the dissolver was examined for build-up of slags, and any element remains (Figure 8.1) were retrieved, cleaned and weighed to determine the exact weight of zirconium dissolved.

The solids knockout drum atop the dissolver was flushed with water and the water occasionally analyzed to determine the approximate amounts of material leaving the system via this route. Samples of the salt product, salt feed, and, on occasion, element slags were submitted for analyses.

It was necessary in several of the runs to reuse the salt product because of its unique composition. This was done prior to analytical knowledge of composition as far as contaminants were concerned; however, it was shown by the analytical results that this reuse was justified.

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Fig. 8.1. Element remains after DS-9.

The HF cylinder and the salt feed and products were weighed before and after each run. These weights together with the analytical results were used to compute material balances for each run.

Experimental Problems. Experimental difficulties encountered in obtaining these data were: 1) the high ratio of the volume of inerts contained at the start of a run within the dissolver system to the total hydrogen evolution; this problem was eliminated by using an HF purge to remove inert gases from the system before and after the dissolution run; 2) temperature control of the salt in the dissolver which was finally achieved within $\pm 10^\circ\text{C}$ in spite of the 25 degree controller differential which existed on the outside of the dissolver wall; and 3) control of the HF flow rate. Runs 1 and 4 were made using the rotameter originally in the system from the INOR-8 runs, and it was found that control at 1 lb/hr HF feed was not possible with this rotameter. It was replaced with a second lower ranged rotameter and much closer control was achieved. The maximum variation of the flow rate was from 38-1/2 to 47-1/2 lb/hr-ft². The variation of the flow rate in those runs deemed consistent was from 38-1/2 to 42-1/2 lb/hr-ft², a deviation of 10%.

Noncondensable Gas Holdup of the System. The gas holdup of the off-gas system was established by purge measurements and rough calculations to be 1.62 SCF. About 1.26 SCF of H₂ was recoverable by using an HF purge of the vapor spaces up to the HF condensers. The volume of the system after the condensers represents the nondisplaceable H₂ volume and is primarily the void space of the NaF HF trap which is about 0.36 SCF (see Table 8.2).

The averaged rate of gas evolution during the purge was used to "correct" the data of unpurged run DS 1 to the purged basis. This is a significant correction to the total H₂ evolution charged to metal dissolution.

Analytical Results. The summary of analytical data for DS 1 through 9 is given in Table 8.3. The average initial metallic contaminant concentration was 1435 ppm (0.14 wt %). The largest contributors to this average were Fe and Sn which were present initially in average concentrations of 329 and 744 ppm, respectively (see Table 8.4).

The Na/Li ratio was to have been fixed at 43/57; however, the difficulties of salt production yielded melts which had 5 mol % variation in the Na, Li content (see Table 8.5). This resulted in the salts having Na/Li ratios which ranged from 0.57 to 0.95 instead of the expected ratio 0.755.

Off-gas solids recovered from atop the baffle just below the dissolver gas outlet contained high concentrations of all metallic contaminants, particularly Ni, Fe, and Sn. The nickel and tin contents of the salts generally show removal of these materials by the off-gas, but the iron content was not lowered by this loss.

Material Balances. Material balances for zirconium show a range of 84 to 110 per cent. The averaged recovery was 98.8 per cent (see Table 8.6).

The comparison of theoretical H₂ evolution based on the weight of Zircaloy-2 dissolved compared to the experimental evolution yields an average deviation of 2.9% (see Table 8.7). The range of deviations was from -5.7 to +8.1 per cent.

Table 8.2. Displacement Data for Determination of Noncondensable Gas Holdup of Copper Lined Dissolver System

Run No.	DS-1A	DS-3	DS-3A	DS-6	DS-7	DS-8	
HF Rate (lb/hr)	1.25	1.14	1.17	1.17	1.27	1.18	
Displacement rate (cu ft argon/10 min interval)							
Time (min)							Average for 6 runs
10	0.596	0.700	0.477	0.626	0.508	0.424	0.555
20	0.224	0.477	0.385	0.254	0.327	0.285	0.325
30	0.288	0.140	0.252	0.150	0.313	0.071	0.228
40	0.144	0.211	0.211	0.205	0.135	0.179	0.181
50	0.074	0.114	0.125	0.127	0.103	0.094	0.106
60	0.057	0.091	0.092	0.087	0.081	0.067	0.079
Total (cu ft)	1.383	1.733	1.542	1.449	1.507	1.120	1.456

Using an average correction to STP of 0.868, the system volume up to condensers = $(1.456)(0.868) = 1.264 \text{ ft}^3$.

Volume of System after Condensers - Holdup of NaF trap $\approx \pi/4 (1/2)^2(3) = 3\pi/16 = 0.6 \text{ ft}^3$ including porosity: $(0.6 \text{ ft}^3)(0.6) = 0.36 \text{ ft}^3$ gas holdup.

Table 8.3. Summary of Analytical Results for DS 1 through 9

Run DS-	Weight %				ppm						
	Na	Li	Zr	F	Ni	Cr	Fe	Mo	Sn	S	
1-Feed	30.0	10.8	0.3	54.3	620	25	300	<35	200	80	
Product	26.7	9.6	6.6	53.1	265	25	390	<35	200	<10	
1A-Feed	29.5	11.7	<0.4	58.8	220	370	2500	180	<250	240	
Product	26.9	10.2	8.0	56.4	300	420	3400	130	1200	<10	
Off-gas Solids	22.5	8.5	12.6	53.0	9150	1900	1100	700	5100	90	
Metallic Slag from Top of Product	28.1	10.8	6.5	55.1	4540	725	3900	570	950	170	
2-Feed	17.6	5.68	26.4	50.3	75	559	1300	48	<250	<10	
Product	16.0	5.56	26.6	51.2	<40	562	1200	32	400	<10	
Off-gas Solids	11.3	3.82	16.9	48.8	920	677	4200	<10	5400	202	
Solid Deposit from Draft Tube	9.49	8.00	11.7	60.9	<100	230	800	48	18000	88	
3-Feed	8.31	4.33	37.3	48.5	236	205	229	-	<250	13	
Product	7.76	4.14	39.0	48.2	100	235	361	-	<250	<10	
Off-gas Solids	6.65	2.38	17.2	45.3	67900	7700	1600	-	7500	482	
3A-Feed	No analysis available										
Product	7.19	3.84	39.3	48.2	8	12	300	<10	620	19	
Off-gas Solids	0.42	<0.01	<0.9	14.1	31900	264	81200	<10	3000	113	
4-Feed	7.10	2.17	42.4	47.1	<50	95	970	<10	123	<10	
Product	6.40	2.01	43.2	47.5	<50	90	780	<10	196	<10	
	Cu was 50 ppm in feed, 30 ppm in product.										
4A-Feed	6.83	2.11	44.0	46.6	35	128	900	35	<100	<10	
Product	6.51	2.00	44.6	47.2	110	128	10300	30	700	20	
Off-gas Solids	3.36	0.79	46.6	44.7	18900	661	29500	25	5300	<10	
6-Feed	Used 3A product salt as feed.										
Product	6.77	3.54	40.4	48.1	38	13	290	<10	1100	<10	
7-Feed	6.70	2.12	43.7	47.7	147	102	55	37	<250	22	
Product	6.28	1.97	45.0	47.9	55	113	20	40	<250	23	
Black Residue in Product	5.96	1.80	43.4	46.9	1900	1400	3800	20	3300	<10	
Off-gas Solids	5.52	1.55	44.5	42.4	3500	5200	3800	42	14300	<10	
8-Feed	Used 6 product salt as feed.										
Product	6.38	3.36	39.4	47.8	38	13	340	<10	1500	17	
9-Feed	6.80	2.15	44.3	46.6	110	115	400	15	<250	<25	
Product	6.37	2.06	44.9	47.3	45	100	400	15	584	<25	
Slag from Bottom of Dissolver	5.04	1.51	46.7	44.4	2200	715	2500	45	3520	625	
Off-gas Solids	5.87	1.61	34.8	45.8	44700	4200	6900	30	69400	400	

Table 8.4. Concentrations of Metallic Contaminants in Feed Salts
for Runs DS 1 through 9

DS Run	Initial Analysis					Total
	Sn	Ni	Cr	Fe	Mo	
	ppm					
1	200	620	25	300	<35	1180
1A	<250	220	370	2500	180	3520
2	<250	75	559	1300	48	2232
3	<250	236	205	229	-	968
3A (1)	-	-	-	-	-	-
4	123	<50	95	970	<10	1268
4A	<100	35	128	900	35	1198
6	620	8	12	300	<10	950
7	<250	147	102	55	37	591
8	1100	38	13	290	<10	1451
9	<250	110	115	400	15	890
Averages	329	109	188	744	48	1435

Average initial contaminant level = 1435 ppm
= 0.14 wt %

Range from 0.35 to 0.059

(1) Analysis not available.

Table 8.5. Comparison of Actual Initial Salt Compositions with
Expected Compositions for DS 1 through 9

DS	Initial Mol Per Cent					
	From Analytical			Expected (1)		
	Na	Li	Zr	Na	Li	Zr
1	45.7	54.2	0	43.0	57.0	0
1A	43.5	56.6	0	43.0	57.0	0
2	41.0	43.5	15.5	36.3	48.2	15.5
3	26.0	44.5	29.4	30.0	40.6	29.4
3A (2)	24.2	42.5	33.4	28.6	38.0	33.4
4	28.6	28.7	42.7	24.6	32.7	42.7
4A	27.5	27.9	44.6	23.8	31.6	44.6
6	24.2	42.5	33.4	28.6	38.0	33.4
7	27.1	28.5	44.3	23.9	31.8	44.3
8	23.7	40.8	35.5	27.7	36.8	35.5
9	27.2	28.3	44.5	23.8	31.7	44.5

(1) Based on 43/57 Na/Li ratio and analytical result for Zr.

(2) Final analysis.

Table 8.6. Zirconium Material Balances for Runs DS 1 through 9

DS Run	Zr Weight, lbs			
	In Initial Salt	Added by Dissolution	Recovered	% Unaccounted
1	0.057	1.166	1.345	+10
1A	0.057	1.081	1.672	+4.7
2	6.075	1.145	6.920	-15.8
3	9.520	1.134	10.85	+1.9
3A (1)	-	-	-	-
4	11.45	1.059	12.87	+2.1
4A	11.62	1.123	12.30	-3.5
6	10.53	1.124	11.55	-0.9
7	12.67	1.022	13.54	-1.1
8	11.23	1.097	11.54	-6.4
9	13.96	1.046	13.96	-2.7
				$\Sigma = -11.7$

(1) Initial analysis not available.

Arithmetic average recovery = 98.8%.

Table 8.7. Percentage of Theoretical H₂ Evolved

Run	Theoretical H ₂ SCF	Experimental H ₂ SCF	Deviation Experimental minus Theoretical SCF	Deviation %
1	9.06	9.10	+0.04	+0.5
1A	8.38	9.00	+0.62	+7.40
2	8.80	8.54	-0.26	-2.95
3	8.80	8.86	+0.06	+0.68
3A	8.84	8.65	+0.01	+0.11
4	8.20	7.54	+0.66	+8.05
4A	8.71	9.12	+0.41	+4.71
6	8.72	8.68	-0.04	-0.46
7	7.93	7.48	-0.45	-5.67
8	8.51	8.57	+0.06	+0.71
9	7.76	7.80	+0.04	+0.52
				$ \Sigma = 31.76$

Average per cent deviation = 2.9%.

Results. Dissolution rate data were obtained which exhibited the effects of salt temperature and composition on both the transient and overall dissolution rates. These data are presented in Tables 8.8 and 8.9 through 8.19. The run summary (Table 8.8) shows those conditions necessary to characterize a given run according to temperature, flow rate, composition and Zr recovery. The trend to longer dissolution time at higher ZrF_4 concentrations and lower temperatures is exhibited. Three runs did not achieve complete metal dissolution.

Tables 8.9 through 8.19 give the detailed H_2 evolution data, experimental and computed values, required to start the mathematical procedure to define a rate equation. The entry, R' , is the actual reading of the wet test meter, corrected from the HF purge, and is the basis of calculation. Certain time intervals have been expanded from the original 10 min period (to reduce calculations) to a 60 or 90 min period when the rate was constant or oscillatory over that longer interval. The dissolution rates presented as a function of the fraction dissolved (Figure 8.2) were averaged over the dissolution interval immediately preceding the fraction with which they are associated. The fraction dissolved was computed from the cumulative H_2 evolution. Overall averaged rates were directly computed from weight loss and time measurements.

The effect of the zirconium concentration in the salt on averaged dissolution rate seemed to increase as the salt temperature was lowered. The effect of a 43 mol % change at $700^\circ C$ was not great, but the effect of a 10 mol % increase at $500-525^\circ C$ was to reduce the rate from 0.103 to 0.053 lb/hr (Figure 8.3).

The effect of temperature at a fixed ZrF_4 concentration was also dependent on the value of the ZrF_4 concentration (Figure 8.4). At 33 mol % ZrF_4 , there was no effect of increasing the salt temperature from 525 to $700^\circ C$. However, at 44 mol % ZrF_4 , the rate increased (perhaps linearly) with increasing salt temperature.

The widely varying temporal behavior of the dissolution rate is shown in Figures 8.5 and 8.6. The data used in Figure 8.5 are from a group of runs in which the ZrF_4 concentration varied from 29 to 36 mol %. The parameter was the temperature, which ranged from 525 to $700^\circ C$. The data in Figure 8.6 are for a constant temperature of $700^\circ C$, ZrF_4 concentrations from zero to 44 mol %.

The plots of rate vs time do not follow a single form, but maxima and knees occur at different points in time. In fact, for the runs plotted on Figures 8.5 and 8.6, there are different times when each of the runs shows the highest rate.

Discussion of Results. Certain of these data concerning parametric effects are questionable because both the averaged rates and the time variation of rates do not fit a rational pattern. The temporal behavior of the rates are not consistent either expressed as a function of time or as a function of per cent dissolution.

Table 8.8. Data Summary for Runs IS 1 through 9

- Conditions:
1. Element Description:
10 plates: 2-in. x 2-in. x 3/32-in.
16 spacers: 3/16-in. x 3/32-in. x 2-in.
 2. Initial surface area of element = 0.563 ft²
Initial area on bottom of element exposed to HF flow = 0.01521 ft²
Draft tube cross-sectional HF flow area = 0.04508 ft²
Actual flow area = 0.04508 - 0.01521 = 0.02987 ft²
 3. Probable value of (usable HF flow/total HF flow) defined as ratio of channel cross-sectional area to draft tube cross-sectional area = 0.321.
 4. Salt volume = 0.148 cu ft, minimum salt level is 3-in. above draft tube.

	1	1A	2	3	3A	4	4A	6	7	8	9
Salt Compositions: mol % NaF (initial)	45.7	43.5	41.0	26.0	-	28.6	27.5	24.2	27.1	23.7	27.2
(final)	44.6	43.1	39.1	24.7	24.2	26.9	26.7	23.7	26.2	23.4	26.1
mol % LiF (initial)	54.2	56.6	43.5	44.5	-	28.7	27.9	42.5	28.5	40.8	28.3
(final)	52.6	53.7	44.6	43.3	42.5	27.8	27.0	40.8	27.0	40.5	27.8
mol % ZrF ₄ (initial)	0	0	15.5	29.4	-	42.7	44.6	33.4	44.3	35.5	44.5
(final)	2.8	3.2	16.4	31.3	33.4	45.4	46.3	35.3	46.9	36.1	46.1
Weight of initial salt charge, lbs	19.0	19.0	23.0	25.5	27.6	28.2	26.4	26.8	29.0	27.8	30.0
Salt temperature, °C ± 10°C	680	700	700	700	700	690	700	600	600	525	500
HF feed rate, lbs/hr ft ² flow area ⁽¹⁾	47-1/2	42	39	39	39-1/2	46	41-1/2	39-1/2	43	40-1/2	38-1/2
Original weight element, lbs	1.167	1.081	1.145	1.134	1.139	1.126	1.123	1.124	1.099	1.097	1.123
Weight loss of element, lbs	1.167	1.081	1.145	1.134	1.139	1.059	1.123	1.124	1.022	1.097	1.046
Calculated H ₂ off-gas SCF ⁽²⁾	9.06	8.38	8.80	8.80	8.84	8.20	8.71	8.72	7.93	8.51	7.76
Experimental H ₂ off-gas SCF ⁽³⁾	9.10	9.00	8.54	8.86	8.85	7.54	9.12	8.68	7.48	8.57	7.80
Averaged dissolution rate, lb/hr ⁽⁴⁾	0.269	0.138	0.118	0.084	0.113	0.153	0.112	0.104	0.089	0.103	0.053
Zirconium recovery, per cent ⁽⁵⁾	110	105	84	102	-	102	96	99	99	93	97
Run time, hr ⁽⁶⁾	4.33	7.83	9.67	13.50	10.09	6.92	10.00	10.83	11.50	10.67	19.83

1. By cylinder weight loss and computed flow area of 0.02987 ft².
2. By weight loss of element, 7.759 SCF H₂ per lb Zr-2 dissolved.
3. Corrected for moisture content, temperature and pressure.
4. Element weight loss/run time.
5. By element weight loss and feed and product analysis.
6. Run terminated at zero H₂ evolution or after long period of low evolution.

Table 8.9. Run Data from DS-1

	H'	$\Delta H'$	H	G	f	R	Y_{HF}		
Time Interval min	Meter Temperature °F	Meter Volume Correction	Meter Reading, Total H ₂ , ft ³	Change in Meter Reading, H ₂ rate, ($\frac{ft^3}{interval}$)	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved	Dissoln Rate ($\frac{lb\ Zr-2}{hr}$)	Concentration of HF in gas leaving dissolver
0-10	78°	0.8607	0.63	0.63	0.54	3.24	5.93	0.420	
20			1.45	0.82	1.24	4.20	13.61	0.544	
30			2.27	0.82	1.94	4.20	21.30	0.544	
40			2.92	0.65	2.50	3.63	27.45	0.435	
50			3.52	0.60	3.01	3.06	33.05	0.397	
60			4.08	0.56	3.49	2.88	38.32	0.378	
70			4.65	0.57	3.98	2.94	43.70	0.379	0.618
80			5.16	0.51	4.42	2.64	48.53	0.339	0.651
90			5.65	0.49	4.84	2.62	53.14	0.326	0.653
100			6.11	0.46	5.24	2.40	57.54	0.306	0.679
110			6.53	0.42	5.60	2.16	61.49	0.279	0.706
120			6.94	0.41	5.95	2.10	65.33	0.273	0.711
130			7.78	0.84	6.67	4.32	73.23	0.559	0.487
140			8.11	0.33	6.95	1.68	76.31	0.220	0.756
150			8.47	0.36	7.26	1.86	79.71	0.240	0.742
160			8.81	0.34	7.55	1.74	82.90	0.226	0.757
170			9.14	0.33	7.83	1.68	85.97	0.220	0.764
180			9.42	0.28	8.03	1.44	88.17	0.186	0.794
190			9.62	0.20	8.23	1.02	90.37	0.133	0.851
200			9.82	0.20	8.43	1.02	92.56	0.133	0.851
200-220			10.30	0.48	8.91	1.23	97.83	0.160	0.822
220-250			10.49	0.19	9.10	0.43	99.92	0.042	0.902
250-260				0.0	9.10	0.0	100.00	0.0	1.00

Table 8.10. Run Data from DS-1A

	H'	$\Delta H'$	H	G	f	R	Y_{HF}		
Time Interval min	Meter Temperature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ , ft ³	Change in Meter Reading, H ₂ rate, $\frac{ft^3}{interval}$	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved	Dissoln Rate $\left(\frac{lb\ Zr-2}{hr}\right)$	Concentration of HF in gas leaving dissolver
0-10	83	0.848	1.00	1.00	0.848	5.088	9.41	0.655	0.377
10-20	83	0.848	1.94	0.94	1.645	4.782	18.26	0.616	0.406
20-30	84	0.845	2.92	0.98	2.473	4.968	27.45	0.640	0.388
30-40	84	0.845	3.84	0.92	3.250	4.662	36.07	0.600	
40-50	84	0.845	4.80	0.96	4.061	4.866	45.08	0.627	0.397
50-60	85	0.843	5.66	0.86	4.785	4.344	53.11	0.560	
60-70	85	0.843	6.38	0.72	5.392	3.642	59.85	0.469	0.512
70-80	86	0.840	7.05	0.67	5.955	3.378	66.10	0.435	
80-90	86	0.840	7.68	0.63	6.484	3.174	71.97	0.409	0.561
90-110	87	0.837	8.82	1.14	7.437	2.859	82.55	0.368	0.595
110-140	88	0.834	10.10	1.28	8.504	2.134	94.39	0.275	0.681
140-150	89	0.831	10.34	0.24	8.702	1.188	96.59	0.153	
150-160	89	0.831	10.39	0.05	8.744	0.252	97.06	0.032	
160-170	89	0.831	10.42	0.03	8.769	0.150	97.34	0.019	
170-180	90	0.828	10.44	0.02	8.786	0.102	97.52	0.013	
180-190	90	0.828	10.460	0.02	8.803	0.102	97.71	0.013	
190-220	90	0.828	10.507	0.047	8.842	0.078	98.15	0.010	
220-280	92	0.823	10.588	0.081	8.909	0.067	98.89	0.009	
280-340	93	0.820	10.647	0.059	8.957	0.048	99.42	0.006	
340-360	94	0.817	10.666	0.019	8.973	0.048	99.60	0.006	
360-390	94	0.817	10.686	0.020	8.989	0.032	99.78	0.004	
390-450	94	0.817	10.701	0.015	9.001	0.012	99.91	0.0015	
450-460	94	0.817	10.703	0.002	9.003	0.012	100.00	0.0015	
460-470	94	0.817	10.703	0.000	9.003	0.000	100.00	0.0000	100.000

Table 8.11. Run Data from D8-2

	H'	$\Delta H'$	H	G	f	R		
			Change in Meter Reading, H ₂ rate. ($\frac{\text{ft}^3}{\text{interval}}$)					
Time Interval min	Meter Temper- ature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ , ft ³	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved.	Dissolvn Rate ($\frac{\text{lb Zn-2}}{\text{hr}}$)	
0-10	77	0.8632	0.207	0.207	0.179	1.074	2.10	0.138
10-20	77	0.8632	0.805	0.598	0.695	3.096	8.15	0.399
20-30	77	0.8632	1.332	0.527	1.150	2.730	13.48	0.352
30-40	77	0.8632	1.792	0.460	1.547	2.382	18.13	0.307
40-50	77	0.8632	2.132	0.340	1.840	1.758	21.57	0.226
50-60	77	0.8632	2.532	0.400	2.185	2.070	25.61	0.267
60-90	77	0.8632	3.583	1.051	3.092	1.814	36.24	0.234
90-100	77	0.8632	3.911	0.328	3.375	1.698	39.56	0.219
100-110	77	0.8632	4.214	0.303	3.637	1.572	42.63	0.202
110-140	77	0.8632	5.092	0.878	4.395	1.516	51.51	0.195
140-150	78	0.8607	5.362	0.270	4.627	1.392	54.23	0.179
150-160	78	0.8607	5.612	0.250	4.842	1.290	56.75	0.166
160-180	78	0.8607	6.087	0.475	5.251	1.227	61.54	0.158
180-210	78	0.8607	6.742	0.655	5.815	1.128	68.15	0.145
210-230	78	0.8607	7.140	0.398	6.158	1.029	72.17	0.133
230-260	78	0.8607	7.677	0.537	6.620	0.928	77.59	0.120
260-290	78	0.8607	8.122	0.445	7.003	0.766	82.08	0.099
290-310	78	0.8607	8.393	0.271	7.236	0.699	84.81	0.090
310-330	78	0.8607	8.645	0.252	7.453	0.434	87.35	0.056
330-350	78	0.8607	8.873	0.228	7.649	0.392	89.65	0.050
350-370	78	0.8607	9.085	0.212	7.831	0.364	91.78	0.047
370-380	78	0.8607	9.235	0.150	7.960	0.774	93.29	0.100
380-390	78	0.8607	9.362	0.127	8.069	0.654	94.57	0.084
390-400	78	0.8607	9.470	0.108	8.162	0.558	95.66	0.072
400-410	78	0.8607	9.572	0.102	8.250	0.528	96.69	0.068
410-420	78	0.8607	9.662	0.090	8.327	0.462	97.59	0.060
420-440	78	0.8607	9.795	0.133	8.441	0.342	98.93	0.044
440-450	78	0.8607	9.848	0.053	8.487	0.276	99.46	0.036
460	80	0.8555	9.865	0.017	8.502	0.090		0.012
470	80	0.8555	9.873	0.008	8.509	0.042		0.005
480	80	0.8555	9.878	0.005	8.513	0.024	99.77	0.003
490	80	0.8555	9.882	0.004	8.516	0.018		0.002
500	80	0.8555	9.886	0.004	8.519	0.018		0.002
500-560	80	0.8555	9.901	0.015	9.532	0.013		0.002
560-570	80	0.8555	9.905	0.004	8.535	0.018	100.00	0.002
570-580	80	0.8555	9.905	0.000	8.535	0.000		0.000

1.14 lb = 8.80 SCF H₂

1.14 lb = 8.80 SCF H₂

Table A.12. Run Data from DS-3

	H'	ΔH'	H	G	r	R	Y _{HF}

Table 8.13. Run Data from DS-3A

	H'	$\Delta H'$	H	G	f	R

Table B.14. Run Data from DS-4

	H'		$\Delta H'$		H	G	F	R
				Change in Meter Reading, H ₂ rate, ft ³ (interval)	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved.	Dissoln Rate ($\frac{lb\ Zn-2}{hr}$)
Time Interval min	Meter Temper- ature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ , ft ³					
0-10	69	0.8832	0.210	0.715	0.186	1.116	2.47	0.144
20	70	0.8808	0.485	0.385	0.428	1.452	5.68	0.187
30	70	0.8808	0.785	0.252	0.692	1.584	9.18	0.204
40	71	0.8782	1.308	0.211	1.151	2.754	15.26	0.355
50	71	0.8782	1.724	0.125	1.516	2.190	20.10	0.282
60	72	0.8759	2.230	0.094	1.959	2.658	25.97	0.343
70	72	0.8759	2.733	0.503	2.400	2.646	31.82	0.341
80	73	0.8734	3.207	0.474	2.814	2.484	37.31	0.320
90	73	0.8734	3.659	0.452	3.209	2.370	42.55	0.305
100	75	0.8684	4.073	0.414	3.573	2.184	47.37	0.281
110	75	0.8684	4.467	0.394	3.919	2.076	51.97	0.267
120	75	0.8684	4.842	0.375	4.248	1.974	56.33	0.254
130	75	0.8684	5.175	0.333	4.541	1.758	60.21	0.226
140	80	0.8555	5.500	0.325	4.819	1.668		0.215
150	81	0.8529	5.797	0.297	5.072	1.518	67.25	0.196
160	81	0.8529	6.084	0.287	5.317	1.470	70.50	0.189
170	82	0.8503	6.342	0.258	5.536	1.314		0.169
180	83	0.8476	6.586	0.244	5.743	1.242	76.15	0.160
190	83	0.8476	6.817	0.231	5.939	1.176		0.151
200	83	0.8476	7.032	0.215	6.121	1.092	81.16	0.141
210	83	0.8476	7.207	0.175	6.269	0.888		0.114
220	83	0.8476	7.352	0.145	6.392	0.738	84.76	0.0950
230	83	0.8476	7.462	0.110	6.485	0.558		0.0719
240	83	0.8476	7.562	0.100	6.570	0.510	87.19	0.0657
250	83	0.8476	7.690	0.128	6.678	0.648		0.083
260	83	0.8476	7.797	0.107	6.769	0.546	89.77	0.073
270	83	0.8476	7.910	0.113	6.865	0.576		0.074
280	83	0.8476	8.002	0.092	6.943	0.468	92.06	0.060
290	83	0.8476	8.081	0.079	7.010	0.402		0.052
300	83	0.8476	8.157	0.076	7.074	0.384	93.80	0.050
310	83	0.8476	8.237	0.080	7.142	0.408		0.053
310-330	83	0.8476	8.368	0.131	7.252	0.330	95.43	0.043
340	83	0.8476	8.432	0.064	7.306	0.324		0.042
350	82	0.8503	8.487	0.055	7.353	0.282	96.77	0.036
360	82	0.8503	8.576	0.089	7.429	0.456		0.059
370	82	0.8503	8.618	0.042	7.465	0.216	98.26	0.028
380	82	0.8503	8.654	0.036	7.496	0.186		0.024
390	82	0.8503	8.683	0.029	7.521	0.150	99.00	0.019
400	82	0.8503	8.713	0.030	7.557	0.156		0.020
410	82	0.8503	8.760	0.047	7.587	0.240	99.87	0.031
415	82	0.8503	8.767	0.007	7.593	0.036	100.00	0.005

Table 8.15. Run Data from DS-4A

	H'	$\Delta H'$	H	f	R		
			Change in Meter Reading, H ₂ rate. $\left(\frac{\text{ft}^3}{\text{interval}}\right)$				
Time Interval min	Meter Temper- ature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ . ft ³	Total H ₂ Evolution SCF	Fraction of Total H ₂ Evolved.	Dissoln Rate $\left(\frac{\text{lb Zr-2}}{\text{hr}}\right)$	
0-10	79	0.8881	0.414	0.414	0.355	3.89	0.275
20	79	0.8881	0.903	0.489	0.775	8.49	0.325
30	79	0.8881	1.377	0.474	1.182	12.95	0.315
40	79	0.8881	1.787	0.410	1.534	16.31	0.272
50	79	0.8881	2.187	0.400	1.877	20.57	0.266
50-80	79	0.8881	3.197	1.010	2.744	30.07	0.226
80-110	79	0.8881	4.172	0.975	3.581	39.25	0.216
110-140	79	0.8881	5.077	0.905	4.358	47.76	0.201
140-170	79	0.8881	5.887	1.810	5.053	55.38	0.179
170-200	79	0.8881	6.722	0.835	5.770	63.24	0.185
210	79	0.8881	6.987	0.265	5.997	65.72	0.176
220	79	0.8881	7.252	0.265	6.224	68.22	0.176
230	79	0.8881	7.492	0.240	6.430	70.47	0.159
230-260	79	0.8881	8.147	0.655	6.992	76.63	0.145
260-290	78	0.8609	8.784	0.637	7.540	82.64	0.137
300	78	0.8609	8.974	1.190	7.704	84.44	0.126
310	78	0.8609	9.139	0.165	7.846		0.110
320	78	0.8609	9.278	0.139	7.966	87.31	0.093
330	78	0.8609	9.407	0.129	8.077		0.086
340	78	0.8609	9.524	0.117	8.178	89.63	0.078
350	77	0.8632	9.630	0.106	8.270		0.071
360	77	0.8632	9.722	0.092	8.349	91.51	0.061
370	77	0.8632	9.811	0.089	8.426		0.059
380	77	0.8632	9.890	0.079	8.494	93.09	0.053
380-410	77	0.8632	10.129	0.239	8.700	95.35	0.053
410-440	76	0.8659	10.311	0.182	8.858		0.040
450	76	0.8659	10.355	0.044	8.896	97.50	0.030
460	76	0.8659	10.390	0.035	8.926		0.023
470	75	0.8684	10.416	0.026	8.949		0.017
480	75	0.8684	10.440	0.024	8.970		0.016
490	75	0.8684	10.461	0.021	8.988	98.50	0.014
500	75	0.8684	10.481	0.020	9.005		0.013
510	75	0.8684	10.499	0.018	9.021		0.012
520	75	0.8684	10.515	0.016	9.035	99.02	0.011
530	75	0.8684	10.529	0.014	9.047		0.009
530-590	75	0.8684	10.604	0.075	9.112	99.87	0.009
600	75	0.8684	10.611	0.007	9.118		0.005

Table 8.16. Run Data from DS-6

	H'	$\Delta H'$	H	G	f	R		
Time Interval min	Meter Temperature °F	Meter Volume Correction	Meter Reading, Total H ₂ , ft ³	Change in Meter Reading, H ₂ rate, $\frac{ft^3}{(interval)}$	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved.	Dissoln Rate $\left(\frac{lb\ Zr-2}{hr}\right)$
0-10	70	0.8808	0.300	0.300	0.264	1.584	3.04	0.204
20	71	0.8782	0.664	0.364	0.582	1.908	6.70	0.246
30	71	0.8782	1.054	0.390	0.922	2.040	10.61	0.263
40	72	0.8759	1.456	0.402	1.274	2.112	14.66	0.272
50	73	0.8734	1.851	0.395	1.619	2.070	18.63	0.267
60	73	0.8734	2.251	0.400	1.968	2.094	22.65	0.270
70	73	0.8734	2.653	0.402	2.319	2.106	26.69	0.271
80	73	0.8734	3.046	0.393	2.662	2.058	30.63	0.265
90	73	0.8734	3.421	0.375	2.990	1.968	34.41	0.253
100	73	0.8734	3.783	0.362	3.306	1.896	38.05	0.244
110	73	0.8734	4.138	0.355	3.616	1.860	41.62	0.240
110-130	73	0.8734	4.817	0.679	4.209	1.779	48.45	0.229
140	72	0.8759	5.139	0.322	4.491	1.692	51.69	0.218
150	72	0.8759	5.447	0.308	4.761	1.620	54.80	0.209
160	72	0.8759	5.728	0.281	5.007	1.476	57.63	0.190
170	72	0.8759	6.041	0.313	5.281	1.644	60.78	0.212
180	72	0.8759	6.297	0.256	5.505	1.344	63.36	0.173
180-200	72	0.8759	6.773	0.476	5.922	1.251	68.16	0.161
210	72	0.8759	6.955	0.182	6.081	0.954	70.00	0.123
220	81	0.8529	7.171	0.216	6.265	1.104	72.11	0.142
230	81	0.8529	7.445	0.274	6.499	1.404	74.80	0.180
240	81	0.8529	7.505	0.060	6.550	1.306		0.039
250	81	0.8529	7.662	0.157	6.684	1.084	76.93	0.104
250-270	81	0.8529	7.949	0.287	6.929	1.735	79.75	0.095
280	81	0.8529	8.088	0.139	7.048	1.714		0.092
290	81	0.8529	8.228	0.140	7.167	1.714	82.49	0.092
300	81	0.8529	8.377	0.149	7.294	1.762		0.098
310	81	0.8529	8.497	0.120	7.396	1.612	85.13	0.079
310-330	81	0.8629	8.709	0.212	7.577	1.543	87.21	0.070
330-390	81	0.8529	9.223	0.574	8.067	1.490	92.85	0.063
390-410	81	0.8529	9.399	0.176	8.217	1.450	94.58	0.058
410-430	83	0.8476	9.546	0.147	8.342	1.375	96.02	0.048
440	83	0.8476	9.607	0.061	8.394	1.312		0.040
450	83	0.8476	9.652	0.045	8.432	1.228	97.05	0.029
450-480	83	0.8476	9.729	0.077	8.497	1.130		0.017
480-510	83	0.8476	9.791	0.062	8.550	1.106	98.41	0.014
510-540	83	0.8476	9.839	0.048	8.591	1.082		0.011
540-570	83	0.8476	9.901	0.062	8.644	1.106		0.014
580	83	0.8476	9.915	0.014	8.656	1.072	99.63	0.009
590	83	0.8476	9.925	0.010	8.664	0.048		0.006
590-620	83	0.8476	9.942	0.017	8.678	1.028		0.004
630	83	0.8476	9.944	0.002	8.680	1.012	99.91	0.002
640	83	0.8476	9.945	0.001	8.681	1.006		0.001
650	83	0.8476	9.945	0.000	8.681	0.000		0.000

Table 8.17 Run Data for DS-7

	H'	$\Delta H'$	H	G	f	R		
Time Interval min	Meter Temper- ature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ . ft ³	Change in Meter Reading, H ₂ rate. $\left(\frac{\text{ft}^3}{\text{interval}}\right)$	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved.	Dissoln Rate $\left(\frac{\text{lb Zn-2}}{\text{hr}}\right)$
0-10	76	0.8659	0.278	0.278	0.241	1.446	3.21	0.186
20	76	0.8659	0.578	0.300	0.501	1.560	6.69	0.201
30	80	0.8555	0.881	0.303	0.761	1.560	10.2	0.201
40	80	0.8555	1.159	0.278	0.999	1.428	13.3	0.184
50	80	0.8555	1.453	0.294	1.251	1.512	16.7	0.195
60	81	0.8529	1.686	0.233	1.450	1.194	19.4	0.154
70	81	0.8529	1.939	0.253	1.666	1.296	22.3	0.167
80	81	0.8529	2.154	0.215	1.849	1.098	24.7	0.141
90	81	0.8529	2.368	0.214	2.032	1.098	27.1	0.141
90-110	81	0.8529	2.804	0.436	2.404	1.116	32.1	0.144
120	82	0.8503	3.009	0.205	2.578	1.044		0.134
130	82	0.8503	3.251	0.242	2.784	1.236	37.2	0.159
130-150	82	0.8503	3.653	0.402	3.126	1.026	41.8	0.132
160	82	0.8503	3.849	0.196	3.293	1.002	44.0	0.129
170	82	0.8503	4.066	0.217	3.478	1.110	46.5	0.143
170-200	83	0.8476	4.683	0.617	4.001	1.046	53.5	0.135
200-230	84	0.8449	5.186	0.503	4.426	0.950	59.1	0.122
230-260	86	0.8395	5.660	0.474	4.824	0.796	64.5	0.103
260-320	86	0.8395	6.533	0.873	5.557	0.733	74.2	0.094
320-380	87	0.8367	7.365	0.832	6.253	0.696	83.5	0.090
380-440	87	0.8367	8.128	0.763	6.891	0.638	92.1	0.082
440-460	87	0.8367	8.332	0.204	7.062	0.513	94.3	0.066
470	87	0.8367	8.411	0.079	7.128	0.396	95.2	0.051
470-490	87	0.8367	8.484	0.073	7.189	0.183		0.024
490-520	87	0.8367	8.565	0.081	7.257	0.204	97.0	0.026
520-580	87	0.8367	8.684	0.119	7.357	0.100		0.013
580-610	86	0.8395	8.743	0.059	7.407	0.100	99.0	0.013
610-640	86	0.8395	8.794	0.051	7.450	0.086		0.011
640-670	85	0.8428	8.829	0.035	7.479	0.058	99.9	0.007
680	85	0.8428	8.834	0.005	7.483	0.024	100.0	0.003
690	85	0.8428	8.834	0.000	7.483	0.000		0.000

Table 8.18. Run Data from DS-8

	H'	$\Delta H'$	H	G	F	R	
		Change in Meter Reading, H ₂ rate. ($\frac{\text{ft}^3}{\text{interval}}$)					
Time Interval min	Meter Temper- ature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ . ft ³	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved.	Dissolv Rate ($\frac{\text{lb Zr-2}}{\text{hr}}$)
0-10	72	0.8759	0.085	0.075	0.450	0.88	0.058
20	72	0.8759	0.180	0.095	0.498	1.84	0.064
30	72	0.8759	0.283	0.103	0.540	2.89	0.070
40	74	0.8684	0.438	0.155	0.810		0.104
50	74	0.8684	0.620	0.182	0.948	6.31	0.122
60	77	0.8632	0.830	0.210	1.086		0.140
70	77	0.8632	1.065	0.235	1.218	10.79	0.157
80	77	0.8632	1.272	0.207	1.104	12.88	0.138
80-100	78	0.8607	1.761	0.489	1.525	17.79	0.163
100-120	78	0.8607	2.260	0.499	1.954	22.80	0.166
120-140	78	0.8607	2.812	0.552	2.429	28.34	0.182
140-160	78	0.8607	3.340	0.528	2.883	33.64	0.175
160-180	78	0.8607	3.845	0.505	3.318	38.72	0.168
180-200	81	0.8529	4.365	0.520	3.762	43.90	0.172
210	83	0.8476	4.636	0.271	3.992	46.59	0.178
210-240	84	0.8449	5.408	0.772	4.644	54.20	0.155
240-270	84	0.8449	6.072	0.664	5.201	60.70	0.145
270-290	84	0.8449	6.498	0.426	5.565	64.94	0.139
290-350	84	0.8449	7.755	1.257	6.627	77.34	0.137
360	84	0.8449	7.928	1.173	6.773		0.113
360-390	84	0.8449	8.399	1.471	7.171	83.68	0.103
390-410	84	0.8449	8.720	0.321	7.442	86.84	0.105
410-440	84	0.8449	9.123	0.403	7.782	90.82	0.088
440-460	84	0.8449	9.408	0.285	8.023		0.093
460-520	84	0.8449	9.816	0.408	8.368	97.65	0.044
530	84	0.8449	9.872	0.056	8.415		0.036
540	84	0.8449	9.920	0.048	8.456	98.68	0.032
540-560	84	0.8449	9.988	0.068	8.513		0.022
560-580	84	0.8449	10.023	0.035	8.543	99.70	0.012
580-600	84	0.8449	10.042	0.019	8.559		0.006
600-630	84	0.8449	10.053	0.011	8.568		0.002
640	84	0.8449	10.053	0.000	8.568	100.00	0.000

Table 8.19. Run Data from DS-9

	H'	ΔH'	H	G	F	R	
		Change in Meter Reading, H ₂ rate, ft ³ (interval)					
Time Interval min	Meter Temper- ature °F	Meter Volume Correc- tion	Meter Reading, Total H ₂ , ft ³	Total H ₂ Evolution SCF	H ₂ Rate SCFH	Fraction of Total H ₂ Evolved.	Dissoln Rate (lb 2r-2 hr)
0-10	83	0.8476	0.045	0.045	0.038	0.228	0.029
20	83	0.8476	0.152	0.107	0.129	0.546	0.070
20-40	83	0.8476	0.462	0.310	0.392	1.578	0.203
50	83	0.8476	0.588	0.126	0.499	0.642	0.083
60	83	0.8476	0.697	0.109	0.591	0.552	0.071
60-90	83	0.8476	1.012	0.315	0.858	0.534	0.069
90-120	83	0.8476	1.333	0.321	1.130	0.544	0.070
120-150	83	0.8476	1.650	0.317	1.399	0.538	0.069
150-180	83	0.8476	1.995	0.345	1.691	0.584	0.075
180-200	83	0.8476	2.193	0.198	1.859	0.504	0.064
200-220	83	0.8476	2.397	0.204	2.032	0.519	0.067
220-280	84	0.8449	3.020	0.623	2.558	0.526	0.068
280-340	84	0.8449	3.641	0.621	3.083	0.525	0.068
340-400	84	0.8449	4.222	0.581	3.574	0.491	0.063
400-410	84	0.8449	4.318	0.096	3.655	0.486	0.063
410-440	84	0.8449	4.604	0.286	3.897	0.484	0.062
440-470	84	0.8449	4.864	0.260	4.117	0.440	0.057
470-500	84	0.8449	5.129	0.265	4.341	0.448	0.058
500-520	84	0.8449	5.304	0.175	4.489	0.444	0.057
520-580	81	0.8529	5.772	0.468	4.888	0.399	0.051
580-640	81	0.8529	6.239	0.467	5.286	0.398	0.051
640-700	81	0.8529	6.662	0.423	5.647	0.361	0.046
700-730	81	0.8529	6.857	0.195	5.813	0.332	0.043
730-790	78	0.8607	7.317	0.460	6.209	0.396	0.051
790-850	79	0.8581	7.705	0.388	6.542	0.333	0.043
850-910	79	0.8581	8.265	0.560	7.023	0.481	0.062
920	79	0.8581	8.265	0.000	7.023	0.000	0.000
930	79	0.8581	8.265	0.000	7.023	0.000	0.000
930-990	79	0.8581	8.537	0.272	7.256	0.233	0.030
990-1010	79	0.8581	8.633	0.096	7.338	0.246	0.032
1010-1070	83	0.8476	8.981	0.348	7.633	0.295	0.038
1070-1130	83	0.8476	9.123	0.153	7.763	0.130	0.017
1130-1160	83	0.8476	9.164	0.030	7.788	0.050	0.006
1160-1180	83	0.8476	9.181	0.017	7.802	0.042	0.005
1190	83	0.8476	9.181	0.000	7.802	0.000	0.000

Fig 82 Transient behavior of Zr-2 dissolution rates, DS series. Data points are located by a number which is the DS run having rates at fraction of dissolution indicated

Fig. 8.3. The effect of ZrF_4 concentration on dissolution rate of Zr-2. Numbers circled are run designations.

Fig. 8.4. The effect of salt temperature on Zr-2 dissolution rate. Numbers circled are run designation in DS series. Others are HF rate in lb/hr-ft² for that run.

Fig. 8.5. Temporal behavior of the dissolution rate of Zr-2 in the ZrF_4 concentration range 29 to 36 mole % at various temperatures.

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Fig. 8.6. Temporal behavior of the dissolution rate of Zr-2 at 700°C and various ZrF_4 concentrations.

It was expected that decreased temperature and increased ZrF_4 concentration would decrease the dissolution rate. The predicted order of rates for the series was: $(1 > 2 > 3 > 4)$, $(3 > 6 > 8)$ and $(4 > 7 > 9)$. It was necessary to use three expressions to describe the order because of the conflicting effects of temperature and concentration. The observed order of rates was: $(1 > 4 > 1A > 2 > 3A > 4A > 3)$, $(3A > 6 > 8 > 3)$ and $(4 > 4A > 7 > 9)$.

The first of these ordered groups suggests that runs 4 and 3 are in error; the second group again suggests that run 3 does not fit. Because the rates did not fit the predicted behavior, DS-4 was rejected in preparing the figures showing the effects of temperature and concentration. However, the shape of the rate vs. fraction dissolved curve for DS-3 is closer to the expected shape than DS-3A which exhibits a pronounced knee from 60 to 90% dissolution. Also DS-3A follows DS-3 closely up to 60% volume dissolution as discussed below. Thus, DS-4 remains as the only run which exhibited completely unusual rates.

Seven of the rate-time curves (Figures 8.4 and 8.5) were integrated (Table 8.20) as a check of the calculational and plotting procedure used to process the H_2 evolution data. The integrations to obtain total weight dissolved agreed within 0.06 lbs with the weights obtained by direct weighing.

Table 8.20. Integration of Rate-time Curves

DS Run	Weight Dissolved	
	by integration	by experiment
1A	1.144	1.081
2	1.082	1.145
3A	1.114	1.139
4	1.158	1.123
3	1.124	1.134
6	1.095	1.124
8	1.067	1.097

The only true duplicate run was DS-3A. Runs 1A and 4A were made for the purposes of achieving closer control of HF flow rate, and salt temperature and to incorporate the HF purge of the vapor space into the experimental technique. The maximum variation of the two dissolution rates (3A vs. 3) obtained at equal fractions of total H_2 evolved was 0.056 lb Zr-2/hr. Most of the rates reproduced with 0.030 lb/hr. This absolute variation represents a range of percentage variation over a run of from 9% at the beginning to 70% at the end.

The high final variation is thought to be caused by the highly variable dissolution rate of metallic impurities in the salt.

Run DS-1 exhibited an average rate which was twice the rate obtained from DS-1A. The temperature of DS-1 was 20°C less than in DS-1A, but the HF feed rate was 13% greater in DS-1. The compositions of salt differed by no more than 2 mol %. The metallic contaminants in run DS-1 totaled 1180 ppm, the contaminant in run DS-1A totaled 3520 ppm, the difference being mostly the iron concentrations (2500 compared with 300 ppm). It is believed that both the higher HF rate and the lower contamination level contributed to the higher rate of DS-1.

Discussion. The stepwise nature of the dissolution of a multiplate element is clearly shown in Figures 8.4 and 8.5. This repetitive, interrupted rate curve may indicate the reaction on, and the subsequent destruction of plates or, more probably, pairs of plates. There appear to be four interruptions in slope on each curve, except in DS-1A which had a rapid rate. This number of distinct interruptions suggests the dissolution of pairs of plates. Dissolution by pairs would require two of the original 10 plates to be responsible for the long tail of the rate-time curve.

8.2 Moving Bed Absorber - R. J. McNamee, J. Beams, F. N. McLain

The "moving bed" or "temperature zoned" sorption device combines the functions of the existing Volatility Pilot Plant fixed sodium fluoride sorption beds and the disposable pellet CRP trap used to collect entrained particulates and the volatile fluorides from certain corrosion and fission products which can be retained by sodium fluoride at 400°C. In this device, the UF_6 sorption bed is incrementally renewed by fresh sorbent as the oldest (bottom) increment is dropped into the high temperature trapping zone. The spent trap section is periodically discharged to the fluorinator where it is melted and disposed of with the waste salt.

Final testing of the movable pellet bed unit was carried out, and the unit released to the pilot plant for installation. The purpose of this last phase of the Unit Operations testing program was to demonstrate repeated operation. It was not known to what extent disintegrated pellets would work into the annular space between the piston and cylinder, or what effect this would have on operation. Furthermore, it was desired to determine the effect of caking on the problem, due to the resulting higher discharge stresses involved and possibly greater attrition. No adverse effects were encountered. The piston rod gas seal was successful in preventing HF leakage and the piston power was adequate for all discharge loads developed.

Repeated tests demonstrated reliable functioning with pellets alone, with pellets fused together in a solid cake (by sorption of HF), and with pellets degraded in size distribution by crushing a part of the charge in an effort to exceed the worst case which might be obtained in practice. No discharge pressure build-up with successive runs, which would have indicated increasing friction due to particle accumulation, was observed in any of the series. Pressures were slightly less in the series containing fines, suggesting a possible lubricating effect.

The tests are summarized in Table 8.21. The method employed to form each bed has been previously described.⁽¹⁾ Sodium bifluoride pellets (1/8-in. right

Table 8.21. Summary - Repetitive Tests

Vertical section initially filled with sodium biferuoride 1/8-in. right cylindrical pellets (6 horizontal beds formed per filling).
Initial temperature: ~90°F.

Pellets Only			Pellets Exposed to HF for 30 min			Degraded Pellets ^(a)		
Run No.	Discharge Pressure, psig		Run No.	Maximum Discharge Pressure, psig		Run No.	Discharge Pressure, psig	
	Ave.	Max.		~3 lb/hr HF	~1-1/3 lb/hr HF		Ave.	Max.
1	43	65	1	140		1	37	50
2	41	60	2	140		2	37	50
3	41	60	3	140		3	37	51
4	40	60	4	140		4	36	47
5	39	55	5(b)	125		5	38	52
6	39	50	6(b)	50		6	36	50
7	40	55	7		140			
8	40	57	8		100			
9	37	50	9		138			
10	39	55	10		140			
			11(b)		140			
			12		83			

(a) Contained 25 wt % pellets crushed in jaw crusher, to give broken pellets and fines.

(b) Vertical section plugged with caked pellets. (Not >65% HF injected in series sorbed in horizontal section.)

cylinders) were used in these tests instead of sodium fluoride pellets. The physical properties of the two materials are nearly identical, and no bias in results was noted.

Following all 28 runs, the piston was removed for examination of the cylinder. There was a thin layer of fines over most of the surface, as well as a small accumulation in the rear of the cylinder and some inside the piston. A small cluster of caked pellets was located on the bottom of the cylinder directly below the vertical section. The dimensions of the cylinder and piston were checked and found to be unchanged.

(1) Unit Operations Section Monthly Progress Report, Chemical Technology Division, March 1960, CF 60-3-61, p. 54.

9.0 WASTE TREATMENT

J. C. Suddath

Study of pot calcination for high level liquid waste disposal was continued. A run (R-30) was carried out in a 6-in. dia vessel. An analysis of the mechanism of solid deposition was made. Tests of gasket assemblies were made in support of the study on remote connection and disconnection of flanges.

9.1 Waste Calcination Test R-30 - C. W. Hancher

Run R-30 was a waste calcination test using Purex waste in a 6-in. i.d. x 84-in. long calciner vessel (Figure 9.1). Calcium oxide was added to the waste (0.8 M as in R-27 and R-29) to reduce the sulfate volatility.

The starting procedure for this test was to pump water into the calciner vessel, which was at 900°C, until the level was up to thermocouple No. 5 (19-in. or 9 liters vol.). The reason for the water addition was to keep the initial Purex feed from flashing and causing entrainment of solids out of the vessel.

A purged liquid level probe attached to differential pressure cell was used to sense and control the liquid level. The liquid level control point was 1 in. above No. 1 thermocouple (73-in. or 35 liters vol.). The liquid level control system functioned properly until the last part of the test, when the purged probe (3/8-in. tubing) tended to plug with calcined solids which could not be washed out with water.

The feed rate decreased from 53 liters/hr at the start of the run to 0.5 liters/hr at the end, and the average feed rate over the feeding period was 11 liters/hr. The condensate rate varied from 44 liters/hr to 0.1 liters/hr, averaging 9 liters/hr (Table 9.1).

Chromium-51 tracer (1 mc) was injected at the end of the third hour of test (Figure 9.2). The only solid deposited at that time extended 6-in. from the bottom and was less than 1/2-in. thick on the walls.

Five per cent of the total sulfate in the feed and 84 per cent of the nitrate reported to the condensate (Table 9.2). The remaining nitrate is assumed to have been vented with the off-gas or NO-NO₂ mixture.

The solid calcined waste had a bulk density of 1.5 g/cc (Table 9.2). The calcined solids from this test, like that in R-27 and R-29, was very dense and hard extending inward from the wall of the vessel from 1 to 2 inches and was soft and porous in the center of the vessel.

One reason for dense layers of solid near the outside diameter of calciner vessel and a porous center section may be that outer layer due to high flux denitrated and calcined simultaneously allowing the gas to escape and resulting in dense solid free void spaces. The center section due to low heat flux forms solid (or semi-solid-gas) metal nitrate salt, then denitrates slowly leaving a less dense solid full of voids due to gas bubbles.

Fig. 9.1. Six-inch-dia calciner vessel for test R-30.

Table 9.1. Test R-30 Operating Data

Time	Feed Vol (liters)	Cond. Vol (liters)	Acid Conc. M	Furnace Power KWH	Center Line Thermocouples - °C						Furnace at 900°C
					Top A-1	A-2	A-3	A-4	A-5	Bottom A-6	
5-5-60					°C	°C	°C	°C	°C	°C	
9:00 A.M.	-	-	-	-	680	770	790	730	360	110	Feed start
10:00	53	44	6.6	46	230	210	130	130	130	130	
11:00	31	33	12.1	46	125	130	130	130	130	130	
12:00	33	28	6.5	40	125	130	130	130	130	160	
1:00 P.M.	33	24	5.1	32	130	130	130	130	140	200*	Cr ⁵¹ tracer
2:00	23	19	6.0	27	120	125	125	140	290*	385	
3:00	5	13	10.0	19	110	120	125	170	575	750	
4:00	8	13	5.1	15	130	135	135	330*	815	845	
5:00	12	7	5.8	15	160	135	135	475	870	880	
6:00	5	6	9.0	15	190	135	140	635	900	900	
7:00	8	5	7.0	15	140	135	160	790	910	910	
8:00	3	4	7.9	12	150	130	205*	860	915	910	
9:00	7	4	6.8	11	145	135	455	890	920	910	
10:00	2	3	8.6	12	150	140	780	905	920	910	
11:00	5	3	10.3	13	140	145	865	910	920	910	
12:00	3	2	7.9	11	135	145	895	915	925	910	
1:00 A.M.	5	3	5.6	12	140	175	905	910	925	910	
2:00	7	2	5.0	12	140	245*	910	910	915	900	
3:00	0.5	2	5.7	12	140	460	915	910	910	900	
4:00	0.5	2	6.6	8	140	650	915	910	910	900	
5:00	0	2	8.1	11	150	750	915	910	910	900	
6:00	0	1	7.7	11	170	820	920	910	910	900	
7:00	0.5	1	6.2	10	195	875	920	910	910	900	Feed stopped
8:00		1	8.6	10	330*	900	920	915	915	905	
9:00		0.3	13.9	10	555	910	920	915	915	905	
10:00		0.1	14.5	6	665	915	920	915	915	905	Heat cut-off
	Total 246	Total 223		Max 53							

*Time which contents changed from liquid to solid.

Fig. 9.2. Profile of Cr⁵¹ tracer injected into test R-30.

Table 9.2. Test R-30 Material and Heat Balance
and Solid Compositions

		Na	Ca	SO ₄	NO ₃	
Feed	Molar %	1.3 100	0.6 100	0.9 100	6.0 100	
Condensate	Molar %	0 0	0 0	0.05 5	5.5 84	
Solid	Wt %	14 94	15 122	36 83	300 ppm Low	Bulk Density 1.5 g/cc
Heat in = 453 KWH		155,000 Btu				
Heat out - Condensate 223L at 1300 Btu/lb at 75 lb/ft ³		77,000 Btu (50%)				

9.2 Analysis of Solid Deposition in R-30 - J. J. Perona

In deriving mathematical expressions relating the experimental variables in pot calcination, simplified models were hypothesized and examined for their closeness of fit to experimental data. For simulated Purex waste, both radial and vertical deposition appeared to take place in R-27 while only radial deposition occurred in R-29. Mathematical models were derived for these two cases (February and May 1960 Unit Operations Section monthly reports). The data for R-30 were found to best represented by the equation developed for radial growth alone.

The equation for equal radial and vertical deposition was shown to be

$$t = \frac{3\alpha_p \lambda R^2}{4k(\Delta T)} \left[1 - \left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^2 \ln \frac{r}{R} \right] \quad (1)$$

and the equation for radial growth alone was:

$$t = \frac{\alpha_p \lambda R^2}{4k(\Delta T)} \left[1 - \left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^2 \ln \frac{r}{R} \right] \quad (2)$$

From the equation it may be seen that the effect of vertical deposition is to increase the filling time by a factor of 3 over radial deposition alone, due to the decrease in heat transfer surface caused by the vertical deposition. For each equation, a plot of the term in brackets versus time should yield a straight line with a slope having the value of the reciprocal of the grouping of constants. By assuming a series of values for r between 0 and R , values for the term in brackets in (1) and (2) were calculated. Using these same values of r , the volume of deposited solid was calculated for the two models as a function of time which was converted to the volume of condensate produced

as a function of time using the experimental ratio of condensate to solid, α . For radial deposition alone the volume of condensate corresponding to a value of r is

$$V = \alpha\pi(R^2 - r^2)H = \alpha\pi R^2 H (1 - x^2) \quad (3)$$

where H = height of cylindrical calcination vessel

$$x = \frac{r}{R}$$

For equal radial and vertical deposition, where $r/R = h/H$, the volume of condensate is

$$V = \alpha\pi(R^2 - r^2)H + \alpha\pi r^2(H - h) = \alpha\pi R^2 H (1 - x^3) \quad (4)$$

where h = distance between horizontal surface of solid and top of vessel. From the experimental data giving condensate as a function of time, the term in brackets in (1) and (2) was plotted against time for the two solid deposition models (Figures 9.3 and 9.4). The equation for radial growth alone appears to represent the data best over the whole feeding period of the run, which lasted 22 hours. The fit assuming radial growth alone is especially better during the first 4 hours of the feeding period, in which 60% of the feed was introduced. From the analysis of run 27, in which equal radial and vertical deposition is known to have occurred from tracer deposition patterns, and from run 29, in which radial deposition alone is known to have occurred from tracer and thermocouple data, the average thermal conductivity of the solids during deposition was determined for both runs to be 0.27 Btu/hr-ft-°F. Thus the value of 0.22 Btu/hr-ft-°F calculated for run 30 from the slope of Figure 9.4, assuming radial growth alone, is reasonable, while the calculated values for radial plus vertical deposition of 0.50 Btu/hr-ft-°F is unreasonably high.

9.3 Effect of Vessel Diameter on Processing Rate - J. J. Perona

The time to fill a calcination vessel with solids, assuming radial deposition, is obtained from equation (2) letting $r \rightarrow 0$. The resultant expression is

$$t = \frac{\alpha\rho\lambda R^2}{4k(\Delta T)} \quad (5)$$

Therefore, R^2/t is equal to a grouping of constants not affected by vessel diameter, and the processing rate should be independent of diameter. Plots of cumulative feed volume versus run time for R-29 and R-30, in which vessel diameters of 6 and 8 inches were used, is shown in Figure 9.5. In R-29, 460 liters were converted to solid in 47.5 hours, yielding an average processing rate of 9.7 liters/hr. In R-30, 275 liters were converted in 22 hours, yielding an average rate of 12.0 liters/hr. While these rates differ by over 20%, it should be pointed out that the rates are very small during the last hours of the run and the decision as to when the vessel is full is not easy to make. Thus the value of the average processing rate is subject to some error. This error can be reduced by comparing the average rates to fill 90% of the vessel volume. For this case the average rate for R-29 was 21.2 liters/hr and for R-30 19.8 liters/hr. Thus the proposition that processing rate is independent of vessel diameter is confirmed.

Fig. 9.3. Fit of mathematical model assuming both vertical and radial deposition to experimental data.

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Fig. 9.4. Fit of mathematical model assuming radial growth alone to experimental data.

Fig. 9.5. Cumulative feed volumes vs time for Runs 29 and 30.

9.4 Remote Disconnection of Calciner Flange - C. W. Hancher

The reason for the study was to demonstrate the feasibility of remotely disconnecting, sealing and removing filled containers of calciner solids to an ultimate storage site. The details are outlined in CF 60-5-58 (Unit Operations Section monthly progress report, May 1960).

The procedure briefly is to lower a calciner vessel (pot) into the cell with a blank flange as cover and with the gasket connected to the pot flange. Remove the blank flange remotely. Move the pot to feed flange, connect, and operate. The procedure would be reversed to remove the pot from the calcining cell.

There will be two or three lines into or out of the calciner vessel:

1. Feed line
2. Off-gas
3. Liquid level probe (problematical)(Figure 9.6)(Feed flange - Unit Operations Section monthly progress report, May 1960).

For the convenience of only having one flange to make and break, it was attempted to use a set of blank flanges with 3 holes and a multihole gasket. The following are the requirements for the system:

1. 3 lines
 - A. 3/8-in. dia feed line
 - B. 3/8-in. dia liquid level probe
 - C. 1-1/2-in. dia off-gas line or larger.
2. Each line pressure sealed from each other and exterior for 20 psig and 100-in. H₂O vac.
3. Withstand one temperature cycle to 200°C.
4. Gasket must seal twice
 - A. Feed flange for operation
 - B. Blind flange for storage

A feed flange and calciner pot flange was fabricated (Figures 9.7 and 9.8) using a 347 SS - 150 lb blind flange with facing finished to 32 micro-inches.

SECTION A-A

FIG. 9.6 REMOTE FLANGE
SCALE: ONE-HALF SIZE

ELEVATION

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Fig. 9.7. Feed Flange for Calciner Vessel.

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-93-

Fig. 9.8. Calciner vessel sealing flange.

Two types of gasket assemblies were used:

1. Style 929 (Goetze Gasket), Figure 9.9, one 3-in. dia with two 1/2-in. dia located inside of 3-in. gasket
2. Style 913 (Goetze Gasket), Figure 9.10, (Same layout as 1).

Both these gaskets were tested on the flange set-up using the remote tools described last month. The remote tools operated very satisfactorily.

The temperature limitation maximum of 200°C was adopted after the thermocouple attached to a nut and bolt on the flange of test R-29 had maximum temperature of 90°C. The flange and gasket itself may get twice as hot as the bolt maximum.

Two No. 1 gasket assemblies were tested using the following procedure:

1. Sealed using 80 ft torque.
2. Tested 60 psig (air) - each section.
3. Heated (pot section of equipment to 900°C as if in normal operation).
4. Tested 60 psig (air).
5. Cooled.
6. Seal broke.
7. Resealed.
8. Tested 60 psig.

Each of the No. 1 assemblies passed the test. Kel-F grease was used to lubricate the gasket surfaces.

One No. 2 gasket assembly was satisfactorily tested using 20 psig air pressure at room temperature. The feed flange face was damaged after this test and will be refinished.

These tests concluded the preliminary testing of the remote tools and calciner feed and sealing flange assemblies. Further testing should be deferred until a firm design on this hardware has been approved. These preliminary tests should give the engineering designer enough information for pilot plant test model.

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Fig. 9.9. Gasket assembly No. 1, corrugated stainless steel.

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Fig. 9.10. Gasket assembly No. 2, spiral wound (stainless steel and asbestos).

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