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CHEMICAL ENGINEERING DIVISION**FUEL CYCLE PROGRAMS
QUARTERLY PROGRESS REPORT****July—September 1978****by**

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M. J. Steindler, Milton Ader, R. E. Barletta, J. K. Bates,
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CHEMICAL ENGINEERING DIVISION

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ABSTRACT

Fuel cycle work reported for this period includes testing of hydraulic performance and extraction efficiency of eight-stage centrifugal contactors, testing of a flowsheet for the Aralex process, evaluation of ruthenium and zirconium extraction in a miniature centrifugal contactor, study of zirconium aging in the organic phase and its effect on zirconium extraction and hydraulic testing of the 9-cm-ID contactor.

Work to develop information for predicting accident consequences in LWR fuel processing facilities consisted of work to show the relationship between energy input (to subdivide a solid) and the modes of particle size frequency distribution.

In the program on pyrochemical and dry processing of nuclear fuel, a facility for corrosion-testing materials for containment vessels is complete and equipment for studying carbide reactions in bismuth is under construction. Analytical studies have been made of salt-transport processes to suggest the direction of the experimental programs; efforts to spin tungsten crucibles 13-cm in diameter continue, and other information on tungsten fabrication is being assembled; the process steps of the chloride volatility process have been demonstrated on a laboratory scale and the thorium powder product was used to produce oxide pellets; the solubility of uranium dioxide, plutonium dioxide, and selected fission product elements in molten alkali nitrates is being investigated; work was continued on the development of a flowsheet for reprocessing actinide oxides by extracting the actinides into ammonium chloroaluminate from a bismuth solution; the preparation of thorium-uranium carbide from the oxide is being studied as a means of improving the oxide reactivity; studies are in progress to elucidate the chemistry and kinetics involved in producing

uranium metal and decontaminated ThO_2 by the reaction of $(\text{Th,U})\text{O}_2$ solid solution in molten salts containing ThCl_4 and thorium metal chips. Since in the molten tin process, no basic thermodynamic or kinetic factors have been found that may limit process development, development studies continue.

In work on the encapsulation of radioactive waste in metal, leach rates of granules, pulverized granules, and granules encapsulated in a lead matrix have been studied. Also, a literature search was done on the impact resistance of glass and metal-matrix forms of waste.

Work on the transport properties of nuclear waste in geologic media consisted of the development of experimental techniques (1) for using a solid waste form as a source of radionuclides for migration studies and (2) for preparing solutions having compositions typical of those expected in deep geological formations. Also, column filtration experiments were performed to study the migration of cesium and iodine in kaolinite.

SUMMARY

Development of Advanced Solvent Extraction Techniques

A program is under way to develop advanced solvent extraction techniques for Purex reprocessing of LWR fuel. Testing of hydraulic performance and extraction efficiency of two eight-stage 2-cm-ID centrifugal contactors has been completed, as was report earlier. In that work, extraction efficiencies decreased from about 94% for single-stage operation to about 85% for multistage operation under similar operating conditions. Disk bases, used initially in the second eight-stage contactor, produced lower extraction efficiencies than did the vane bases used in the first contactor. The second unit has been converted to vane bases, making the two contactors identical. A new rotor design was developed that has a significantly higher flow capacity at low organic-to-aqueous flow ratios than had been observed with the rotor of earlier design.

A flowsheet was tested for a process (Aralex) developed to recover actinides from neutralized high level waste solutions. In this process, dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid (H_2MBP) are extracted from the reprocessing aqueous salt waste streams with 2-ethyl-hexanol (2-EHOH), leaving the actinides in the aqueous raffinate. After being scrubbed with acid, the 2-EHOH is stripped successively with water and dilute sodium carbonate to remove all HDBP, H_2MBP , and zirconium, and is then stripped with acid before being recycled. All operations were successfully carried out in an eight-stage miniature contactor which served first as an extraction/scrub bank and then as a strip/wash bank.

At the end of FY 1978, funding of the program to construct and test a large (25-cm-ID rotor) annular centrifugal contactor for processing LWR fuel at a rate of 10 Mg/d was terminated. At that time, fabrication of the contactor was about 50% complete.

Extraction behavior of ruthenium and zirconium was studied, using the Argonne miniature annular centrifugal contactor. A primary objective in undertaking the studies was to determine whether a short-residence-time contactor of the annular type would yield a significantly higher decontamination of uranium and plutonium (say, fivefold) than would longer-residence-time contactors, based on the extraction rates of these two elements differing from the extraction rates of fission products. Extraction and scrubbing coefficients were measured for ruthenium and zirconium as a function of residence time and nitric acid concentration. Multistage extraction and scrubbing tests with uranium present were carried out in the Argonne eight-stage miniature contactor (with four extraction and four scrub stages). Results obtained in the kinetic tests imply that the residence times achievable in the annular centrifugal contactor under plant operating conditions are too long for decontamination to be significantly improved.

Tests were made on zirconium aging in the organic phase and its effect on back extraction. They showed that the distribution coefficients of zirconium for back extraction (1) were higher at lower initial concentrations of this element in the 30% tri-n-butyl phosphate (TBP)/n-dodecane (nDD) phase and (2) increased at a constant rate with time. The effect was especially pronounced at higher nitric acid concentrations; more zirconium was retained in the organic phase when it was contacted with more concentrated nitric acid solutions.

Hydraulic testing of the 9-cm-ID (0.5 Mg/d) annular centrifugal contactor is essentially complete. Increasing the rotor speed above 1800 rpm yields only a slight increase in throughput. As much as 35% of the separating zone volume of the rotor can be filled with interfacial particles (simulating interfacial crud) and hydraulic performance remain good. The height of liquid in the mixing annulus was measured under various operating conditions, allowing the residence time in the mixing zone to be calculated. Regions of organic-to-aqueous ratios for organic-continuous and aqueous-continuous operation were determined. In nine months of intermittent operation of the motorized spindle, there was no evidence of mechanical wear.

A series of experiments was performed to determine the effect on zirconium extraction of the hydrolysis of TBP in nDD. However, preliminary experiments showed that the effect of hydrolysis on zirconium extraction cannot be duplicated by the simple addition of monobutyl phosphoric acid to 10^{-3} M di-n-butyl phosphoric acid/30% TBP/70%nDD.

Environmental Effects

The purpose of this program is to develop a systematic and coherent body of knowledge as a basis for predicting accident consequences in LWR fuel processing facilities, for estimating source terms of radioactive releases, and

generally for assembling information useful as a means of further reducing the consequences of accidents, if such be needed. The objectives and scope encompass (1) determination of source terms for postulated accidents in reprocessing plants, including physical and chemical properties of materials airborne in primary dispersion; (2) identification of property modifications of airborne materials under the conditions of transport to the first stage of an air-cleaning system; (3) estimation of the quantitative penetration of radio-nuclides through the confinement and air-cleaning systems; and (4) identification of the properties of airborne products of accidents as released into the atmosphere at the stack or into the environment at the boundary of the plant.

In the preceding progress report, methods of estimating small particle sizes from experimental explosive test data were described. The methods that were identified and compared were based on log-normal and semilog distributions. During this report period, another distribution, the self-preserving distribution, is analyzed and compared with the semilog distribution.

The self-preserving particle size distribution has the characteristic that, whether based on particle number, surface area, or volume, the differential frequency (dN/dr for particle number, dA/dr for surface area, or dV/dr for volume) is high for low values of r and decreases as r is increased. The semilog distribution has the same characteristic when based on particle number. When based on surface area and volume, the differential frequencies for the semilog distribution are dissimilar to those of the self-preserving distribution, each displaying a distinct maximum (mode) at a value of r and decreasing as r is either increased or decreased from that value.

The energy needed to subdivide a solid by brittle rupture was considered in the previous report. This work has been extended to show the relationship between energy input and the predicted modes (maximums) of particle size frequency distributions, assuming that the semilog distribution is applicable. The mode of a distribution based on surface area or volume was found to be proportional to the volume of the material impacted and its rupture modulus and to be inversely proportional to the energy applied.

Pyrochemical and Dry Processing Methods Program

A Pyrochemical and Dry Processing Methods (PDPM) Program was established at the beginning of FY 1978 in the Fuel Cycle Section of the Chemical Engineering Division (CEN) at Argonne National Laboratory (ANL). This program is an extension of the National Fuel Cycle Program for reprocessing fuel by processes that will reduce the risk of proliferation of nuclear weapons. Argonne has been designated by the United States Department of Energy (DOE) as the lead laboratory for PDPM, with various reprocessing developments being performed at other DOE laboratories and by industrial contractors.

The program has been administratively divided into individual work packages, four of which are being done at ANL. Each work package is being managed for conformance to established statements of work, program objectives, a cost

plan, a milestone plan, and a management plan in accordance with Uniform Contractor Reporting Guidelines (UCRG) as required by DOE.

Program Evaluation. The ANL PDPM Program management was requested by DOE-HQ to assist Oak Ridge National Laboratory (ORNL) in conducting a study to analyze the potential of PDPM reprocessing vis-a-vis comparable aqueous methods to meet the requirements of an "exportable technology." A preliminary pyrochemical flow sheet was submitted for ORNL review. ANL is to provide ORNL with a more detailed "reference" flow sheet based on the preliminary flow sheet. The process and proliferation criteria prepared by ANL were identified by DOE-Nuclear Power Development as reference criteria to be applied to the ORNL study.

Program Management. All contractors were visited during August to review technical progress, to discuss FY 1979 program plans and management plans, and to introduce the CEN Division Project Quality Engineer (PQE) to contractor personnel who are responsible for implementing quality assurance. Preliminary analyses and literature surveys required for flow sheet preparation are completed or near completion by all contractors. Except for those contractors that did not receive authorization to start work until the third quarter of FY 1978, contractors have in-place and operable facilities and equipment needed to perform laboratory-scale experiments.

The molten bismuth process separates actinides from fission products on the basis of reaction or dissolution of some of the carbides to form bismuthides. While laboratory renovations are under way, the effort has been directed to a literature search on the properties of carbides.

Quality assurance policies and procedures and quality assurance plans were reviewed. A quality assurance plan is required for each work package for FY 1979.

Notification by DOE-NPD of a reduction of funding for PDPM in FY 1979 led to redirection and reduction of effort. It was decided to terminate "Aluminum-Alloy Processing of Thorium- and Uranium-Based Fuels" and "Reprocessing of Thoria-Urania Fuel in Molten Salts Containing ThCl_4 ." Two other programs, "AIROX Processing" and "Chloride Volatility," are also to be terminated. The contractors will be assigned other tasks.

Materials Development for PDPM. The design for the PDPM Environmental Test Facility is complete. A prototype pump was fabricated of Type 304 SS and was tested in a mixture of molten zinc and a molten salt consisting of MgCl_2 -25 mol % KCl -25 % NaCl . The pump functioned well until the lower impeller dissolved in molten zinc. The actual pump is to be fabricated of tantalum.

Metallic materials are being gathered for corrosion testing.

Small crucibles of highly dense ceramic with adherent crack-free tungsten coatings have been fabricated by air brushing, then sintering. Current

investigations have yielded two coated specimens of relatively high tungsten density. The use of consolidated plasma spraying for tungsten coating is also being investigated.

Carbide Fuel Reprocessing. Laboratory renovations are under way prior to evaluation of a molten bismuth process (to separate actinides from fission products on the basis of reaction or dissolution of some of the carbides to form bismuthides). Effort has been directed to a literature search on the properties of the carbides.

The equipment for molten cadmium/salt reprocessing is being assembled and tested. The initial experiments will investigate the rate of reaction of UC or ThC with CdCl_2 as a function of temperature and CdCl_2 concentration in 50 mol % MgCl_2 -30 mol % NaCl -20 mol % KCl .

Thorium-Uranium Salt-Transport Processing. A rough draft of a topical report describing the reduction, solubility, and hydriding aspects of the thorium-uranium salt-transport process has been completed. An analytical study based on available data was made to estimate plutonium hydride solubility in zinc-magnesium for a range of compositions. The data indicate that for recovery of at least 75% of the plutonium before recycling, an alloy containing at least 75 at. % magnesium would be required.

Electrolysis of CaO in CaCl_2 - CaF_2 will be examined experimentally as a technique for removing CaO from the fused salt, permitting continued recycle of the salt. Literature data suggest that electrolytic reduction of CaO to metal is feasible.

Uranium-Plutonium Salt-Transport Processing. A rough draft of the topical report summarizing the literature search on the salt-transport pyrochemical process has been completed. A material balance was completed around the Pyro-redox process.

A change in program direction has resulted in immediate selection of a flow sheet for coprocessing uranium and plutonium by the salt-transport method. Work is being started on a defensive engineering analysis of the flow sheet and a conceptual design of a full-scale plant based on the flow sheet.

Pyrochemical partitioning of metals, vacuum distillation, corrosion considerations, and reduction salt recycle are discussed.

A presentation of the computer program for use in modeling selected flow sheets is given. The work to be done on the copper-magnesium-uranium ternary phase diagram in FY 1979 is outlined. The preparations for operation of the salt purification laboratory and for proof-of-principle experiments are discussed.

Fabrication of Process-Size Refractory Metal Vessels. The topical report summarizing the literature search on tungsten fabrication has been written and typed for final editing. Four tungsten blanks have been drawn and will be spun

into crucibles. Conversations with tungsten suppliers have provided valuable information regarding the production of crucibles, transfer lines, and molten metal pumps.

Chloride Volatility Processing of Thorium-Based Fuels. Identifying satisfactory materials of construction is the greatest challenge to establishing the feasibility of the chloride volatility coprocess in which high temperature is combined with extremely aggressive reagents.

Decladding of Zircaloy cladding has been demonstrated on a laboratory scale. Yet to be determined are the relative volatilities of thorium and uranium at decladding conditions.

Vaporization of thorium and uranium was demonstrated by chlorination of 80/20 ThO_2/UO_2 pellets with a mixture of carbon tetrachloride and chlorine at approximately 800°C.

The additional process steps of fuel dechlorination and ash oxidation were demonstrated on a laboratory scale. Thoria powder that had been prepared in dechlorination experiments was used to produce pellets, and a sintered density as high as 9.04 g/cm³ was achieved.

Preliminary corrosion tests in a dry chlorine atmosphere indicated the following to be candidate materials of construction: Nickel 201, Inconel 600, Inconel 601, and Incoloy 800.

Molten Nitrate Salt Oxidation Processes. In equimolar sodium nitrate-potassium nitrate, uranium dioxide reacts to form uranates; plutonium dioxide does not react. Analysis of the reaction products indicates that a diuranate species is present and that sodium is the favored cation in the compound.

The behavior of fission product elements in the melt was studied. Based on tests to date, cerium, cesium, iodine, molybdenum, and possibly ruthenium may be found as soluble species to some extent in the equimolar sodium nitrate-potassium nitrate melt.

Uranyl chloride and uranyl fluoride have negligible solubility in halide-nitrate melt systems. Upon the addition of carbonate ion, no soluble uranium is produced in equimolar sodium nitrate-potassium nitrate, but the temperature and the time for reaction of uranium dioxide with alkali nitrates to yield diuranates ($\text{Na}_2\text{U}_2\text{O}_7$) are decreased.

Molten Salt Processes Applied to Nuclear Fuels. In one step of the molten salt process under consideration, fissile and fertile materials are transferred from molten lithium chloride into molten bismuth-lithium reductant after which the two phases are separated. Detailed analyses are needed of the temperature

dependencies of the redox distribution coefficients of various solutes in the LiCl/Bi-Li solvent pair so that the optimum temperature for the critical separations step can be determined. Much of this information is available and has been assembled in a draft report.

After the fissile and fertile materials are isolated in bismuth, they are transferred into ammonium chloroaluminate (NH_4AlCl_4). Scouting experiments indicate that uranium and thorium can be extracted from bismuth into molten ammonium chloroaluminate. Other experiments demonstrated that actinides could then be recovered by distilling away the ammonium chloroaluminate and collecting the actinides in the bottoms.

Reprocessing of Thoria-Urania Fuel. In order to increase the reactivity of $(\text{Th},\text{U})\text{O}_2$, it is converted by heating with carbon to the dicarbide at about 2400°C . During this conversion, the barium and strontium fission products are removed. After electron beam melting which followed conversion to carbide, significant decreases in the lanthanum, neodymium, praseodymium, and yttrium contents were noted. However, significant amounts of actinides were also lost. The melting point of $(\text{Th},\text{U})\text{C}_2$ -C eutectic containing the fission product additions was determined as $2420 \pm 25^\circ\text{C}$, which is about 75 Celsius degrees lower than the melting point of the $(\text{Th}-10\% \text{U})\text{C}_2$ -C eutectic reported in the literature.

A major problem in this or any other scheme for reprocessing nuclear fuels is containment and storage of nuclear waste. Fractionation of the fission product elements vaporized during the conversion to carbide may alleviate this problem. Such a separation has been demonstrated on a laboratory scale and may be suitable.

Molten Tin Process for Reactor Fuels. A literature search was made for thermodynamic data relevant to the molten tin process. This initial effort revealed no basic thermodynamic or kinetic factors that limit the development of the molten tin process. However, calculations do not suffice to define the quantitative behavior of the process steps, and so experimentation will be done as an essential part of the process evaluation. A flow diagram has been developed for the process and has been revised once. A batch process with an input of 965 kg of UO_2 was assumed; and it was calculated that approximately 4000 kg of charge would have to be handled in the major high-temperature process steps, i.e., the carbothermic reduction and the nitriding steps.

Several carbothermic reductions of UO_2 have been conducted in the induction furnace. The reduction of pure UO_2 is quite slow at 1900 K,--only 10% reacted in 3 h.

Encapsulation of Radioactive Waste in Metal

Leach Rate Determination in Simulated Waste Forms. Leaching characteristics of solid simulated radioactive waste forms are being investigated to

establish the resistance of the waste materials to dispersal by hydraulic means. These studies have been based exclusively on neutron activation analysis techniques.

The leach rates of a sintered waste material (PW-7a) in three different physical forms have been compared. These forms are granules, pulverized granules, and granules encapsulated in a lead matrix. The results indicated that: (1) determination of surface area is a recurring problem in the interpretation of leach rate data, (2) pulverizing waste in preparation for Soxhlet extraction can significantly change the leaching characteristics of the waste form, and (3) incorporating a very porous waste form into a small metal-matrix ingot with no protective lead envelope did not reduce the surface area exposed to the leaching medium (i.e., the leach rates were comparable to leach rates of the unencapsulated forms).

Leach testing of a relatively leach-resistant simulated waste glass using a variety of leaching media is in progress. The tests involve varying the temperature, pH, and salinity of the leaching medium in order to determine the effects of these variables on the leach rate.

Experiments are also in progress to determine the effect of decreased porosity of the waste form on the overall leaching characteristics of metal-encapsulated composites. Preliminary experiments indicate that neutron-activated commercial Pyrex (borosilicate) glass beads may not be the most desirable material for this purpose because of the activatable chemical elements in the glass.

Comparative Evaluation of Impact Resistance of Metal-Matrix Waste Forms.

A literature search has been made for information relevant to evaluation of the impact resistance of waste forms, including glass and metal-matrix forms. Although no general theory was formed allowing quantitative predictions of impact deformations in particular cases, approximate engineering methods were found for stress and deformation analysis and for measurements of impacts of models, which may be scaled so that the small models deform similarly to larger prototypes. These methods are quite effective for modeling of metals and metal composites, and large-scale demonstrations have been made of successful resistance to impact of transportation casks.

Because brittle glass and ceramics are fragmented by impacts, impact resistance of these materials is more difficult to measure. The energy of impact was found to be proportional to the surface area of particles formed. Various methods of characterizing particle sizes and surfaces of fragmented specimens are under development. A variety of metal-matrix forms are being examined.

Establishment of Tentative Criteria for Hulls Treatment

Draft copies of Development of Criteria for the Handling of Waste Cladding Hulls and Associated Metal Wastes were distributed to reviewers. Comments from the reviewers indicate that a number of sections of the draft will need revision. Revision is currently under way.

Transport Properties of Nuclear Waste in Geologic Media

The experimental program was formulated to develop quantitative data describing the interactions of nuclides with solutions and rocks; such interactions control the transport of radionuclides in geologic media.

During this quarter progress has been made by the development of experimental techniques that improve our ability to conduct specific types of experiments. Two new experimental techniques have been tested. The first, termed leach-migration, uses a solid waste form as a source of radionuclides for migration studies. Preliminary results from experiments indicate that the migration behavior of a radionuclide of cesium leached from irradiated glass differs from that of a radionuclide added to solutions as cesium chloride.

The second technique is a method of lowering the dissolved-oxygen concentrations in solutions to the concentrations at the stability limit of water. By this technique, oxygen levels are produced that may be expected in waters in deep geologic formations.

Trace-Element Transport in Lithic Material by Fluid Flow at High Temperatures

Column-infiltration experiments were performed to study the migration of cesium and iodine in kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] by fluid flow. Kaolinite is a nonexpanding common clay that has a low exchange capacity, and there are radioactive isotopes of cesium and iodine that are important in nuclear waste disposal. The temperature and the composition of the aqueous solution were varied in these experiments.

A strong selectivity of kaolinite for Cs^+ over Na^+ diminishes by about two orders of magnitude when the temperature is increased from 25°C to 170°C . In the experiments, cesium is eluted in broad, nearly symmetrical peaks. The peak elution volume changes only about 10% with a doubling of flow rate. In NaHCO_3 solutions, the elution volume is theoretically inversely proportional to NaHCO_3 concentration. This relation was observed over a twofold concentration range.

At room temperature, iodine moves through columns of kaolinite in as many as three peaks in near-neutral dilute solutions; but the results are time-dependent, with a peak prominent in one experiment and absent in another experiment. The various peaks are due to different chemical species. Iodide (I^-) and periodate (IO_4^-) have been detected in the solution by paper chromatography.

Iodide and iodate (IO_3^-) are not absorbed on kaolinite in near-neutral dilute solutions. Therefore, each of the three peaks may be attributed to a species other than iodide or iodate, such as IO_4^- or possibly HOI . Alternatively, any of the three peaks may be caused by iodide in solution reacting with impurities (such as iron oxides from the apparatus) deposited on the clay. The former possibility is the more likely, but neither explanation can be eliminated.

I. DEVELOPMENT OF ADVANCED SOLVENT EXTRACTION TECHNIQUES

(G. J. Bernstein, R. E. Barletta, C. A. Blomquist,*
E. P. Horwitz,† R. A. Leonard, G. W. Mason,†
R. H. Pelto, B. B. Saunders, A. A. Siczek,
J. H. Meisenhelder, A. A. Ziegler, and C. S. Sabou†)

A. Developments for the Reprocessing of Light Water Reactor (LWR) Fuel

1. Introduction

A program has been conducted in cooperation with the Savannah River Laboratory to develop advanced solvent extraction techniques for Purex reprocessing of LWR fuel. Specific elements of the program are: (1) design, construction, and testing of single-stage and multistage miniature annular centrifugal contactors;† (2) design and construction of a large annular centrifugal contactor having a reprocessing capacity of 10 Mg/d of LWR fuel; (3) study of the chemistry and kinetics of the solvent extraction of ruthenium and zirconium for the purpose of achieving enhanced decontamination of uranium and plutonium in short-residence contactors; (4) investigation of uranium-plutonium partition in short-residence or other types of contactors; and (5) investigation of alternative aqueous processes for recovery of thorium-based fuel, including causes and effects of solvent damage.

2. Development of a 10-Mg/d Centrifugal Contactor

(G. J. Bernstein and R. A. Leonard)

A large annular centrifugal contactor (25-cm-ID rotor) designed for Purex processing of LWR fuel at a rate of 10 Mg/d has been under fabrication. At the end of FY 1978, funding for this program was terminated. At that time, fabrication was about 50% complete.

3. Development of Mini-Contactors

(R. A. Leonard, R. H. Pelto, A. A. Ziegler, and G. J. Bernstein)

Work continued on the development and testing of 2-cm-ID annular centrifugal contactors. These units are being used to develop flow sheets for nuclear fuel reprocessing, for solvent cleanup, and for actinide

*Energy and Environmental Systems Division.

†Chemistry Division.

‡In an annular centrifugal contactor (ANL-78-68, p.10) aqueous and organic phases are fed into the annulus between a hollow rotor and a casing. Here, they are mixed by skin friction as they flow down the annulus and then inward to an orifice in the bottom of the rotor. The organic and aqueous phases enter the rotor and are separated by centrifugal force, and the separated phases are directed over weirs to appropriate discharge ports.

recovery from waste solutions. With hydraulic testing of these contactors completed, efforts were focused on completing the measurements of mass transfer efficiency. Alternative contactor designs were tested to develop a unit that can be operated at low O/A ratios.

a. Mass Transfer Efficiency

Earlier mass transfer efficiency measurements [STEINDLER-1978D] showed lower mass transfer efficiencies for multistage tests ($85 \pm 2\%$) than for single-stage tests ($91 \pm 1\%$). Because of some differences in flow rates and equipment, further single-stage tests were made to determine whether the loss in mass transfer efficiency was specifically an effect of multistage operation. At the same time, the effects of specific changes in flow rates, equipment design, and equipment operation were evaluated to determine which factors affect mass transfer efficiency.

Extraction tests were made on the single-stage 2-cm-ID centrifugal contactor, using Rotor II (rotor types are described below), and on single stages from both of the eight-stage contactors, which use Rotor III. Variables that were studied in these tests are the type of contactor base, the separating zone length inside the rotor, the annular gap in the mixing zone, the rotor speed, the throughput, the O/A ratio, and presaturation of organic phase with HNO_3 . Extraction efficiency was calculated using:

$$E_a = \frac{(1 + RK)(K_{\text{eff}} - S)}{K - S + RK(K_{\text{eff}} - S)} \quad (1)$$

where E_a is the extraction efficiency of the aqueous phase (that is, the amount of uranium extracted from the aqueous phase divided by the amount that would be extracted at equilibrium); K is the distribution coefficient (that is, the uranium concentration in the organic phase divided by its concentration in the aqueous phase at equilibrium); K_{eff} is the apparent distribution coefficient based on the actual uranium concentrations in the exiting organic and aqueous streams; R is the organic-to-aqueous flow ratio; and S is the ratio of the uranium concentration entering the stage in the organic stream divided by its concentration in the aqueous stream leaving the unit. The organic feed stream contains no uranium and so Eq. 1 reduces to

$$E_a = \frac{(1 + RK) K_{\text{eff}}}{(1 + RK_{\text{eff}})K} \quad (2)$$

At low uranium concentrations (where K is relatively large), the effects of analytical errors in measuring K and K_{eff} are minimized when E_a is calculated.

Stripping tests were made in a fashion similar to extraction tests. In these tests, the aqueous feed stream contained no uranium and so the organic phase stripping efficiency, E_o , was calculated using:

$$E_o = \frac{(1 + R'K')K'_{eff}}{(1 + R'K'_{eff})K'} \quad (3)$$

where all primed symbols are the reciprocals of the unprimed symbols.

Results of the extraction efficiency tests are listed in Table 1. Single-stage Test 1 with an E_a of $94.4 \pm 0.5\%$ was performed under conditions that were the same as in the earlier multistage test which had an E_a of $85 \pm 2\%$. This shows that stage mass transfer efficiencies can be significantly lower in a multistage test.

Results with a disk base installed (Tests 7-12) are erratic and generally much lower than vane-base extraction efficiencies.* This is attributed to reduced mixing of the emulsion when the emulsion flows below the disk prior to entering the rotor. With a disk base installed, extraction efficiency is thus much more dependent on the liquid height in the annular region. The latter is erratic and increases as O/A ratio decreases. Hence, the highest extraction efficiency with a disk base installed occurs at the lowest O/A ratio.

Variables such as separating-zone length, annular gap, rotor speed, total flow rate, and O/A ratio had only small effects on the efficiency of vane-base units. Those changes that favored increased mixing produced some improvement in extraction efficiency.

Stripping tests with vane-base units showed efficiencies greater than 95%; efficiencies with disk-base units were only $58 \pm 8\%$.

Among the variables tested was type of contactor base. The use of the vane base produced extraction efficiencies consistently above 90%, while the disk base produced efficiencies that were generally lower. Therefore, the second eight-stage contactor (originally built with disk bases to achieve higher throughput) has been converted to vane bases.

Extraction efficiencies in a limited number of multistage tests were lower than efficiencies observed for individual stages. This may be due to the multistage tests having been made at near-maximum throughputs so that any hydraulic upsets tended to propagate through all stages and thus disturb the overall stability of operation. It is thought that at lower flow rates, higher overall efficiencies would be reached.

*In the disk design, a horizontal disk is supported above the casing bottom slightly below the rotor bottom. In the vane design, radial vanes project up from the casing bottom.

Table 1. Single-Stage Extraction Efficiency Tests

Organic Phase: 30% TBP in nDD
 Washed with 2.5 wt % Na_2CO_3
 Presaturated with 3.0M HNO_3

Aqueous Phase: 0.0499M Uranyl nitrate in 3.06M HNO_3
 Rotor OD: 2.19 cm

Test	Contactor Base	Separating-Zone Length, cm	Annular Gap, cm	Rotor Speed, rpm	Total Flow Rate, mL/min	O/A Ratio	K_{eff}	K	Efficiency, E_a , %	Rotor ^a	Notes
1	Vane	3.25	0.50	6000	98	2.5	5.38	24.8	94.4 $\pm$ 0.5	III ^b	c
2	Vane	3.25	0.50	7500	98	2.5	7.67	24.8	96.6	III ^b	
3	Vane	3.25	0.50	6000	49	2.5	3.11	24.8	90.7 $\pm$ 0.7	III ^b	d
4	Vane	3.25	0.50	6000	40	1.0	13.21	26.3	96.8	III ^b	e
5	Vane	2.31	0.50	6000	98	2.5	3.80	24.8	92.1	II	
6	Vane	2.31	0.34	6000	98	2.5	7.22	24.8	96.7	II	d
7	Disk	3.25	0.50	6000	98	2.5	1.228	24.8	76.4 $\pm$ 0.3	III ^b	
8	Disk	3.25	0.50	7500	98	2.5	1.406	24.8	79.9	III ^b	d
9	Disk	3.25	0.50	6000	49	2.5	1.492	24.8	80.4	III ^b	d
10	Disk	3.25	0.50	6000	40	1.0	8.69	26.3	93.0	III ^b	d,f
11	Disk	2.31	0.50	6000	98	2.5	1.186	24.8	76.5	II	
12	Disk	2.31	0.34	6000	98	2.5	1.450	24.8	80.0	II	

^aRotor designs are described in Table 2.

^bUsed in eight-stage minicontactor.

^cConditions identical to eight-stage test in which extraction efficiency was 85 $\pm$ 2%.

^dMaterial balance for uranium off by more than 5%.

^eEarly test with Rotor II and 0.34-cm annular gap gives a slightly lower E_a , 90 $\pm$ 1%.

b. New Contactor Designs

For the current vane-base and disk-base contactors, the hydraulic capacity is sharply reduced when the O/A ratio falls below 1.0 [STEINDLER-1978D]. This has also been observed in multistage contactors. A different design is needed to test flow sheets having O/A ratios significantly below 1. New designs intended to have this capability were tested, and the results are reported here.

Some of the most important alternative design details are listed in Table 2. Vanes were made deeper, and the annular gap was increased to reduce the shear rate in the annular mixing zone. Rotor IV differs from Rotor II in three respects. It has a longer separating zone, a larger aqueous weir diameter, and a diverter disk just inside the rotor inlet port. Results of tests with these units are shown in Table 3.

Table 2. Alternative Design Details for Single-Stage 2-cm-ID Annular Centrifugal Contactor

Contactor Design	Rotor Code	Aqueous Weir Dia, ^a cm	Separating-Zone Length, cm	Rotor Diverter Disk Present	Height of Vanes, ^b cm	Annular Gap, ^c cm
1 ^d	II	0.928	2.15	No	0.24	0.34
2	II	0.928	2.15	No	0.79	0.34
3	II	0.928	2.15	No	0.79	0.50
4	IV	0.946	3.26	Yes	0.24	0.34
f	III	0.852 ^e	3.26	No	0.24	0.50

^aOrganic weir diameter is 0.801 cm except where noted otherwise.

^bEach base has eight vanes with a gap of 0.08 cm.

^cRotor OD is 2.19 cm in all cases.

^dThis is the best of the earlier designs in which the vane base is used [STEINDLER-1978A].

^eOrganic weir diameter is 0.723 cm.

^fIncluded for reference. This is the current design for individual stages in multistage contactors.

In tests in which the same rotor design (Rotor II) was used, other modifications of the contactor had only a slight effect on the hydraulic performance of the unit. The deep-vane base of contactor design 2 produced a very slight improvement over the former standard, contactor design 1. However, the existence of a condition where the unit runs well at 80 mL/min but not at 40 mL/min is very unusual and makes this design of questionable

value. In design 3, the larger zone below the rotor is matched by a wider annulus. Performance of design 3 is a little better than performance of design 1 at an O/A of 0.5 but is a little worse at an O/A of 0.2.

Table 3. Acceptable Rotor Speeds for New Contactor Designs at Low O/A Ratios.

Rotor Speeds: 3600, 4800, 6000, 7500, and 8400 rpm
 Organic Phase: 30% TBP in nDD
 Aqueous Phase: 3.0M HNO₃
 Acceptable Performance: <1% contamination in each phase

Contactor Design ^a	Total Flow Rate, mL/min	Acceptable Rotor Speeds, rpm			
		Organic Phase		Aqueous Phase	
		Initially Continuous		Initially Continuous	
		0.2 O/A	0.5 O/A	0.2 O/A	0.5 O/A
1	40	NG ^b	NG ^b	3600, 7500	3600-6000
	80	NG ^b	NG ^b	NG ^b	6000
	120				
2	40	NG ^b	8400 ^{b,c}	4800, 7500	3600-4800, 8400
	80	NG ^b	7500-8400 ^b	NG ^b	7500-8400
	120		NG ^{b,c}		NG
3	40	NG ^b	4800-8400	NG ^b	4800-8400
	80		8400		8400
	120				
4	40	d	d	d	d
	80	4800	4800-7500	3600-8400	4800-7500 ^b
	120	NG	6000	4800-8400	4800-6000

^aSee Table 2.

^bFull range of rotor speeds not tested.

^cNot acceptable at 7500 rpm.

^dNot tested. Acceptable range should be at least as broad as that at 80 mL/min.

Design 4 showed satisfactory performance at total throughputs of 80 to 120 mL/min at an O/A ratio of 0.2. None of the other designs could handle more than 40 mL/min at this O/A ratio.

Although not shown in Table 3, further tests with design 4 showed high throughput (>100 mL/min) over the range of O/A ratios from 0.1 to 10 as long as the unit was operated with the aqueous phase initially continuous. This is the manner in which a multistage contactor is normally operated; i.e., the flow of aqueous phase through all stages is established before flow of organic phase is started. The organic-continuous mode could be reached under two operating conditions: (1) when the process flow sheet stipulates that the O/A ratio be above about 0.5; (under these conditions a total throughput above 100 mL/min can be maintained), or (2) if a hydraulic upset were to temporarily cut off flow of the aqueous phase to one or more stages.

At present, there are no plans to modify the rotors in the existing eight-stage contactors to change them to the Rotor IV type. The rotor design (Rotor III) is suitable for operation with Purex flow sheets and has been used successfully on other flow sheet tests (see Section 4 below).

4. Separation of Selected Actinides and Fission Products from HLLW

(M. J. Steindler, E. P. Horwitz,* G. W. Mason,* C. A. Blomquist,†
G. J. Bernstein, R. A. Leonard, and A. A. Ziegler)

A flow sheet (Aralex) has been developed by a Chemistry Division group associated with the Fuel Cycle Section. In the Aralex (Actinide Recovery Alcohol Extraction) process, tri-n-butyl phosphate (TBP) degradation products, dibutylphosphoric acid (HDBP) and monobutylphosphoric acid (H_2MBP), are extracted from the actinides in the reprocessing aqueous salt waste streams with 2-ethyl-1-hexanol (2-EHOH). The actinides remain in the aqueous raffinate. The loaded organic phase, 2-EHOH, is scrubbed with acid to remove all actinides; it is stripped successively with water and dilute Na_2CO_3 to remove all HDBP, H_2MBP , and zirconium; and finally it is washed with acid and recycled.

The flow sheet is now being tested by the Aqueous Fuel Reprocessing Group of the Fuel Cycle Section. Preliminary tests on a single-stage 2-cm-ID contactor were followed by full flow sheet tests in an eight-stage mini-contactor. Details of the extraction/scrub flow sheet test are shown in Fig. 1, while those for the two stripping sections and the wash section are shown in Fig. 2.

*Chemistry Division.

†Energy and Environmental Systems Division.

Fig. 1. Extraction and Scrub Steps of the Aralex Flow Sheet. Tests in the Eight-Stage 2-cm-ID Contactor. Rotor speed: 6000 rpm. Vane base. Rotor-to-vane gap: 0.025 cm.

*Organic phase is acid-washed organic solvent, as shown in Fig. 2, and contains about 0.8M HNO₃.

†The aqueous salt feed, F, was injected with a stainless steel capillary tube directly into the mixing annulus of Stage 4 through the organic port. The feed composition is 0.21M Na₂CO₃, 0.038M NaHCO₃, 0.038M NaNO₃, 0.020M HDBP, 0.0067M H₂MBP, 0.01M UO₂²⁺, 0.0002M Zr⁴⁺.

‡Organic feed for the flow sheet shown in Fig. 2.

a. Preliminary Tests

Before the Aralex flow sheet tests were run, preliminary tests were made to investigate and resolve any potentially troublesome aspects. The tests considered the effects of the viscosity of the 2-EHOH organic phase (higher than the viscosity of 30% TBP in normal dodecane), the hydraulic performance of each section of the flow sheet, and the use of the feed stage to acidify the aqueous feed. In addition, test tube emulsification experiments were evaluated for their ability to predict contactor performance.

Viscosity was considered to be important since it affects the rate at which the phases of the emulsion can move and so can limit contactor throughput. The viscosity of 2-EHOH was measured and was found to be 8.0 mPa·s (8.0 cP), which is 4.6 times that of 30% tributyl phosphate (TBP)

Fig. 2. Strip and Wash Steps of the Aralex Flow Sheet as Tested in the Eight-Stage 2-cm-ID Contactor. Rotor speed: 3000 rpm. Vane base. Rotor-to-vane gap: 0.025 cm.

*Organic phase from flow sheet in Fig. 1. Contains some HNO₃, HDBP, H₂MBP, and Zr.

†Organic feed for flow sheet shown in Fig. 1. Contains about 0.8M HNO₃.

in normal dodecane (nDD), the solvent normally used in Purex tests performed in the mini-contactors. However, numerous tests with 2-EHOH showed the hydraulic performance with 2-EHOH was comparable to that with 30% TBP in nDD.

Hydraulic performance of each section of the Aralex flow sheet was checked in a single-stage 2-cm-ID centrifugal contactor having a transparent plastic housing. Flow rates were three times those planned for the eight-stage unit, to verify that no problems of hydraulic stability would be encountered in the multistage unit. For hydraulic performance to be acceptable, it was required that less than 1% of either phase be in the exit stream of the other phase.

Hydraulic performance in the extraction, scrub, and first strip sections was good. The acid wash section performed satisfactorily when the exit phases were not recycled to the acid wash stage. The second strip section (using sodium carbonate) proved to be very sensitive to the compositions of the process streams; operation appeared to be borderline due to emulsions forming that were difficult to handle. Test results indicated that to avoid overmixing of the phases, the multistage test should be made at rotor speeds of 3000 rpm instead of the intended 6000 rpm.

The original Aralex flow sheet calls for acidification of the feed before it enters the extractor. However, unless this is done with 2-EHOH present, a whitish third phase forms that is difficult to dissolve. To simplify the operation and the feed preparation step, the flow sheet was changed to provide for the acidification of the feed in the annular mixing zone of the feed stage (Fig. 1). In the improved configuration, the acid entered the feed stage with the aqueous stream from the scrub section. The aqueous feed was injected directly into the mixing zone through a capillary tube installed in the organic feed port. This method of operating the feed stage eliminated any third-phase formation, gave good hydraulic performance, and was used in the eight-stage extraction/scrub flow sheet test.

Various qualitative observations suggest that the rate at which an emulsion breaks in a shaken test tube can be used to predict performance in the centrifugal contactor. In two tests, after equal durations of mixing in a vortex mixer, the times required for phase separation from dilute sodium carbonate of two different samples of 2-EHOH were measured. The first sample required 200 s for complete separation in the test tube and also showed good hydraulic performance in the single-stage contactor. The second 2-EHOH sample (containing small amounts of HNO_3 , U^{6+} , and Zr^{4+}) required 600-1200 s for complete separation in the test tube and showed very poor hydraulic performance in the contactor. (Both samples also contained small amounts of HDBP and H_2MBP .)

b. Flow Sheet Tests

The information from the preliminary single-stage tests was used in Aralex flow sheet tests with an eight-stage mini-contactor. Hydraulic performance was good. When chemical analysis of the collected samples is completed, stage efficiency and overall separation factors will be evaluated.

To adapt the Aralex flow sheet to a single eight-stage contactor, the extraction/scrub test was run first, followed by the strip/wash test. In each test, six holdup volume throughputs were allowed so that the unit would reach steady state. During a run, hydraulic performance was evaluated by observing the height of the liquid in the transparent PVC inter-stage lines and by monitoring the contamination of each exiting stream. Exit samples are collected to check the approach to steady state. At the end of a run, the aqueous and organic phases inside each rotor were isolated and collected for use as samples so that exit compositions from each stage could be measured.

The extraction/scrub flow sheet (Fig. 1) was tested first. To fit the operation to an eight-stage contactor, only four stages were used in each section rather than the six stages preferred. Hydraulic performance was excellent.

The strip/wash flow sheet (Fig. 2) was then tested. An overall view of the apparatus setup for the strip/wash test is shown in Fig. 3.

Fig. 3. Eight-stage Mini-Contactor Setup for Aralex Strip/Wash Flow Sheet Tests. ANL Neg. No. 308-78-598.

Hydraulic performance in the dilute Na_2CO_3 strip section was adequate. Hydraulic performance of the water strip and the acid wash sections was excellent. In the Na_2CO_3 section, organic phase backed halfway up the inter-stage lines so that aqueous phase had to sink through this liquid to reach the next stage. Operation in this fashion was quite stable. The organic phase from these four Na_2CO_3 strip stages was cloudy; the organic phase from the final acid wash stage was clear.

c. Acknowledgments

Chemical analyses of stage samples (used to determine extraction efficiency) were done by M. Bouchard and A. Essling of the Analytical Group of the Chemical Engineering Division, under the direction of K. Jensen.

5. Extraction of Ruthenium and Zirconium in Centrifugal Contactors in the Purex Process
(A. A. Siczek and J. H. Meisenhelder)

Additional multistage extraction/scrubbing runs were conducted in an eight-stage miniature contactor to measure the effect of multistage short-residence-time extraction upon the separation of uranium from ruthenium and zirconium. It was desired to learn whether separation would be enhanced because of the differing rates of extraction. Extent of extraction of the zirconium and ruthenium fission products was measured in these tests and in previous tests with a single-stage contactor [STEINDLER-1978D].

a. Extraction/Scrub Tests

Studies of the kinetic behavior of ruthenium and zirconium in the presence of uranium in a multistage extraction process have been conducted. Extraction/scrub tests were performed in the eight-stage 2-cm-ID centrifugal contactor. Three different sets of flow rates (each with approximately the same ratio of organic phase to aqueous phase) were used which produced three different residence times (see Table 4). The experiment was described in [STEINDLER-1978C]. The results of the tests are shown in Tables 5-7.

Table 4. Estimated Residence Times in the Mixing Zone and Separation Zone of the Argonne Centrifugal Contactor. The total holdup volume in the separation zone is about 8 mL (about 6 mL of aqueous phase and about 2 mL of organic phase). (See also comments in text.)

Test	Contactor Section	Residence Time, s/stage				
		Flow Rate, mL min ⁻¹		Mixing Zone Total	Separation Zone	
		Organic (AX)	Aqueous (AF+AS)		Organic	Aqueous
1	Extraction	56	32	2	2	11
	Scrub	56	12	2	2	30
2	Extraction	20	11.2	4	6	32
	Scrub	20	3.7	4	6	97
3	Extraction	7.3	4.6	7	16	78
	Scrub	7.3	1.7	7	16	212

Table 5. Extraction/Scrub Test 1 in an Eight-Stage Miniature Contactor. Distribution of Uranium, Ruthenium, and Zirconium.

Extraction section: Stages 1-4 The feed entered stage 4
 Scrub section: Stages 5-8 Rotor Speed: about 7000 rpm

Stream		Flow Rate, mL/min	
AF - 1.2M U, 2M HNO ₃ , 0.02M Ru and Zr		20	
AX - 30% TBP/nDD		56	
AS - 3M HNO ₃		12	

Stream Leaving Stage	Uranium, mg/mL		Ruthenium, μg/mL		Zirconium, μg/mL		H ⁺ , meq/mL, Aqueous
	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	
1	1.1	37.4	1334	249	790	23	2.1
2	28.4	88.2	1645	69	813	26	2.8
3	129.6	112.9	1318	5	748	4	2.4
4	157.0	116.1	1245	5	738	5	2.4
5	72.9	112.3	12	5	11	4	2.6
6	51.8	107.3	4	5	7	5	2.7
7	39.0	103.6	<1	5	4	4	2.8
8	23.7	97.6	<1	3	2	2	2.9
Initial (AF)	283.0		2117		1342		1.7

Both ruthenium and zirconium showed consistent behavior in all three tests. The agreement for ruthenium and zirconium data was excellent in tests 2 and 3 (when the same aqueous feed solution was used) and very close to the results obtained in test 1. In the extraction section, zirconium transferred into the organic phase to a very small degree. The distribution coefficient (D_{Zr} about 0.01) was the same as that obtained in single-stage extraction tests ($D_{Zr} = 0.01$) for the same nitric acid concentration (about 2M). This indicates that no advantage due to kinetics of zirconium extraction has been realized in the multistage operation. Ruthenium was extracted into the organic phase in the extraction section (stages 1, 2, and 3) to a greater degree than was zirconium; the value of the distribution coefficient of ruthenium

Table 6. Extraction/Scrub Test 2 in an Eight-Stage Miniature Contactor.
Distribution of Uranium, Ruthenium, and Zirconium.

Extraction section: Stages 1-4. The feed entered stage 4
Scrub section: Stages 5-8. Rotor Speed: about 7000 rpm

Stream		Flow Rate, mL/min	
AF - 1.2M U, 0.02M Ru and Zr, 2M HNO ₃		7.5	
AX - 30% TBP/nDD		20.0	
AS - 3M HNO ₃		3.7	

Stream Leaving Stage	Uranium, mg/mL		Ruthenium, μg/mL		Zirconium, μg/mL		H ⁺ , meq/mL, Aqueous
	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	
1	0.5	1.4	1676	190	2235	22	1.7
2	1	4	2586	387	2449	20	2.2
3	9	37	2605	311	2383	29	2.7
4	99	105	2344	18	2321	18	2.6
5	48	104	406	17	354	10	
6	42	102	116	10	73	7	2.8
7	34	98	42	10	29	2	2.9
8	23	95	14	18	10	2	2.9
Initial (AF)	308		1983		2851		

(D_{Ru} about 0.12 to about 0.14) obtained in the multistage tests was slightly higher than that previously observed in single-stage experiments (D_{Ru} about 0.11) and was about equal to the value for 5-min phase equilibration. This may be due to the total contact time of the two phases being quite long even though

Table 7. Extraction/Scrub Test 3 in an Eight-Stage Miniature Contactor.
Distribution of Uranium, Ruthenium, and Zirconium.

Extraction section: Stages 1-4.

The feed entered stage 4

Scrub section: Stages 5-8.

Rotor Speed: about 7000 rpm

Stream		Flow Rate, mL/min	
AF - 1.2M U, 0.02M Ru and Zr, 2M HNO ₃		2.9	
AX - 30% TBP/nDD		7.3	
AS - 3M HNO ₃		1.7	

Stream Leaving Stage	Uranium, mg/mL		Ruthenium, μg/mL		Zirconium, μg/mL		H ⁺ , meq/mL,
	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	
1	0.05	0.1	1598	181	2517	20	1.3
2	0.4	2	2043	356	2220	26	2.2
3	5	26	2523	371	2249	20	2.8
4	73	101	2592	33	2303	8	2.6
5	--	99	--	18	--	4	--
6	30	97	84	12	73	<1	2.8
7	30	99	26	10	28	<1	2.8
8	23	95	5	10	8	2	2.8
Initial (AF)	308		1983		2851		

residence time in the mixing zone of each stage was only about 10 s.* The total residence time in the multistage extraction section was probably long

*There is also contact in the separation zone. Phase separation in the rotor is not instantaneous, and even the separated phases have a significant interfacial area. It is difficult to estimate mass transfer in the separating zone, but it should not be more than 10-20% of the mass transfer that takes place under vigorous agitation in the mixing zone.

enough (about 5-10 min) to reestablish partially an equilibrium of the different ruthenium nitrosyl species, and thus regenerate the concentrations of the form of ruthenium that is most extractable into the organic phase.

Ruthenium and zirconium concentrations in the solvent entering the scrub section were very low (about 5-10 $\mu\text{g/mL}$) and at the limit of analytical detection, which makes evaluation of the effectiveness of scrubbing difficult. However, the increase in ruthenium and zirconium concentrations in the aqueous phase as it moved through the scrub section suggests that some scrubbing took place and was equally effective for both elements.

The decontamination factor* for zirconium (DF_{Zr}) was 230 in test 1 and >400 in tests 2 and 3. The decontamination factor for ruthenium (DF_{Ru}) was 240 in test 1, but smaller in the other two tests. Calculating the DF values is difficult since the error in analysis of both fission products in the organic phase at concentrations of about 10 $\mu\text{g/mL}$ can be quite high ($\pm 100\%$).

The uranium extraction profile for the extraction section in test 1 differed somewhat from those obtained in tests 2 and 3. This may be due to difficulties which had been encountered in test 1 in sampling the aqueous phase in stages 2 and 3 (the older burette sampling system was used in test 1), or to slight fluctuations in the ratio of the organic-to-aqueous flow rates at the high throughput employed in test 1.

The extraction/scrub tests showed that the modest kinetic effects in ruthenium and zirconium extraction measured in the single-stage miniature annular contactor were not enhanced by multistage operation. Thus, decontamination of uranium and plutonium from zirconium and ruthenium based on differences in the extraction rates is not likely to be improved at the residence times achievable in the annular centrifugal contactor under plant operating conditions.

b. Zirconium Studies

Forward Extraction. Martin's method [MARTIN] was applied to forward extraction of zirconium from 3M HNO_3 with 30% TBP/nDD to determine the amount of nonextractable zirconium in a one-day-old solution. The method is based on the fact that the true equilibrium distribution coefficients (called here, K) are independent of the relative phase volumes. When there is more

$$* \text{DF}_M = \frac{[\text{M}]/[\text{U}] \text{ in the feed}}{[\text{M}]/[\text{U}] \text{ in the product}}$$

than a single species involved, however, the observed values (called here, D) are dependent on the phase volume ratio. Under the latter condition, the concentration of the element in the solvent (C_o) plotted against its concentration in the aqueous phase (C_a), would give a line whose slope is equal to the K value, and the intersection with the ordinate indicates the concentration of the nonextractable form, C'_a , since

$$K = \frac{C_o}{C_a} \quad \text{and} \quad D = \frac{C_o}{C_a + C'_a}$$

The results, reported in Table 8, indicate that the distribution coefficient is independent of the phase volume ratio and thus represents the true equilibrium extraction coefficient. It can be concluded that in the solutions used in these tests (all one-day-old solutions), zirconium was present only in the extractable form.

Back Extraction. During the course of studies of zirconium back extraction, it was observed that the distribution of zirconium between the organic phase [30% tri-n-butyl phosphate (TBP)/nDD] and aqueous phase (nitric acid solution) depends on the age of the zirconium-containing solvent and the initial concentration of the zirconium. To determine the cause of the "irreproducibility" of previous back-extraction tests, a systematic study was performed of zirconium aging in the 30% TBP/nDD solutions at two different concentrations of zirconium. The initial organic solution, A, was prepared by contacting 30% TBP/nDD with concentrated zirconium solution in about 4M nitric acid. A less concentrated organic solution, B, was obtained by diluting some of solution A with TBP/nDD (previously preequilibrated with 4M HNO_3) at a volume ratio of 2:1. The back extraction of zirconium into 1, 2, 3, and 4M nitric acid solutions was carried out on the same day and also 1, 6, 16, and 34 days later. Additionally, on the sixth day, solution A (already 6 days old) was diluted again in the proportion 2:1 (solution C) to check whether the aging effect depends on zirconium concentration.

The results of the tests are presented in Table 9 and are also illustrated in Figs. 4-7. The results as reported here reproduce very well the results obtained earlier in independent tests and reported in [STEINDLER-1978C]. The recent tests show that the distribution coefficients of zirconium in back extraction, D_{Zr} , depend on the initial zirconium concentration in the organic phase. The D_{Zr} values were found to be higher at lower zirconium concentrations; for solution B, with 1.20 mg Zr/mL in the organic phase, the distribution coefficients were approximately twice as high as for solution A containing, 3.71 mg Zr/mL in the organic phase (Table 9, Fig. 6). The distribution coefficient values for solution C are close to those for solution B.

It has been found that the rate of "aging" is approximately constant, as measured by the change in the D_{Zr} value with the age of the organic solution. In the back extraction into nitric acid solutions (Figs. 4 and 5), the dependence of the distribution coefficient on the acidity of

Table 8. Martin's Method Applied to Forward Extraction of Zirconium from $3M$ HNO_3 with 30% TBP/nDD.

Contact Time: 5 min

Initial Solutions: 0.02M zirconium in $3M$ HNO_3
(1.91 mg Zr/mL), 30% TBP/nDD
preequilibrated with $3M$ HNO_3

Sample No. FM-	O/A mL	Volume Ratio	mg Zr/mL	D_{Zr}	H^+ , meq/mL	Mass Balance
1-0			0.16		0.66	
1-A	$\frac{15}{75}$	0.2	1.84	0.087	3.06	98%
2-0			0.16		0.65	
2-A	$\frac{15}{30}$	0.5	1.81	0.088	3.02	99%
3-0			0.15		0.65	
3-A	$\frac{15}{20}$	0.75	1.87	0.080	3.00	104%
4-0			0.15		0.65	
4-A	$\frac{15}{15}$	1.0	1.80	0.083	2.96	103%
5-0			0.15		0.65	
5-A	$\frac{15}{15}$	1.0	1.78	0.084	2.95	101%
6-0			0.14		0.64	
6-A	$\frac{30}{15}$	2.0	1.67	0.084	2.88	102%
7-0			0.11		0.61	
7-A	$\frac{75}{15}$	5.0	1.35	0.081	2.79	99%

Table 9. Zirconium Distribution Coefficients, $D_{Zr} = [Zr]_{\text{organic}}/[Zr]_{\text{aqueous}}$ for Back Extraction into Aqueous Nitric Acid Solutions of Zirconium Aged in 30% TBP/nDD Solutions

Volume ratio, organic: aqueous = 1.1

Initial Organic Solutions: (A) 3710 μg Zr/mL, 0.8M HNO_3
 (B) 1200 μg Zr/mL, 0.8M HNO_3
 (C) 1250 μg Zr/mL, 0.8M HNO_3

Solution	Age of the Zirconium Solution, days	Final Nitric Acid Concentration, M, Organic/Aqueous			
		0.3/1.5	0.5/2.3	0.6/3.1	0.8/4.0
A	Fresh	$\frac{72}{3690} = 0.019$	$\frac{155}{3500} = 0.044$	$\frac{338}{3420} = 0.099$	$\frac{747}{3040} = 0.246$
	1	$\frac{191}{3580} = 0.053$	$\frac{287}{3500} = 0.082$	$\frac{432}{3350} = 0.129$	$\frac{822}{2950} = 0.279$
	6	$\frac{372}{3130} = 0.119$	$\frac{781}{2960} = 0.264$	$\frac{970}{2640} = 0.367$	$\frac{1390}{2300} = 0.604$
	14	$\frac{759}{2500} = 0.304$	$\frac{1320}{2350} = 0.562$	$\frac{1600}{2060} = 0.77$	$\frac{1620}{1560} = 1.04$
	26	—	—	$\frac{2120}{1530} = 1.39$	—
	34 ^a	$\frac{876}{1637} = 0.535$	$\frac{1441}{1431} = 1.01$	$\frac{2455}{1183} = 2.07$	—
B	Fresh	$\frac{51}{1160} = 0.044$	$\frac{90}{1130} = 0.080$	$\frac{154}{1150} = 0.134$	$\frac{335}{890} = 0.376$
	1	$\frac{97}{1150} = 0.084$	$\frac{136}{1080} = 0.126$	$\frac{213}{970} = 0.220$	$\frac{376}{830} = 0.453$
	6	$\frac{298}{967} = 0.308^a$	$\frac{385}{907} = 0.424^a$	$\frac{393}{845} = 0.460$	$\frac{524}{656} = 0.799$
	14	$\frac{301}{746} = 0.403$	$\frac{518}{738} = 0.702$	$\frac{608}{620} = 0.981$	$\frac{688}{487} = 1.41$
	34 ^a	$\frac{311}{440} = 0.705$	$\frac{466}{397} = 1.174$	$\frac{904}{327} = 2.76$	$\frac{1022}{292} = 3.49$
C	6	$\frac{254}{971} = 0.262$	$\frac{295}{963} = 0.31$	$\frac{397}{865} = 0.46$	$\frac{496}{729} = 0.68$

^aThe samples precipitated while awaiting analysis. There is a deficiency in the mass balance.

Fig. 4. Changes in Zirconium Distribution Coefficients in Back Extraction with Time. Solution A of 3.7 mg Zr/mL, 0.8M HNO_3 in 30% TBP/nDD. The curves are labeled according to initial nitric acid concentrations in the aqueous solutions.

the aqueous solution for A and B solutions is about the same (as is also shown in Fig. 6 for 14-day-old solutions). This dependence of D_{Zr} on the acidity of the aqueous phase in back extraction becomes stronger with the age of the solution; *i.e.* as aging progresses, there is a greater increase in the amount of retained zirconium with an increase in the acidity of the aqueous phase (Fig. 7).

To determine the amount of zirconium in nonscrubbable form in the organic solution (30% TBP/nDD), Martin's method was applied to back extraction of zirconium from the organic phase into aqueous nitric acid solutions. The following equations apply in this case:

$$K = \frac{C_o}{C_a} \text{ and } D = C_o + \frac{C_o'}{C_a}$$

and the intersection of the line, $C_o + C_o' = DC_a$ with the y axis ($C_a = 0$) gives a value of C_o' , *i.e.*, a concentration of zirconium in nonscrubbable

Fig. 5. Changes in Zirconium Distribution Coefficients in Back Extraction with Time. Solution B of 1.2 mg Zr/mL, 0.8M HNO₃ in 30% TBP/nDD. The curves are labeled according to initial nitric acid concentrations in the aqueous solutions.

form. The initial organic solution used in these tests (Table 10) was prepared one day in advance of extraction and was a duplicate of solution A (Table 9) used in the zirconium-aging studies. When the solution was 14 days old, Martin's test was repeated on the remainder of the zirconium solution (Table 11). The results of these tests are given in Tables 10 and 11 and in Fig. 8. The observed D_{Zr} values agree with those previously obtained in the aging studies (Table 9). The true extraction coefficient K_{Zr} is about 0.083, as determined from the slopes of the curves where the concentration of zirconium in the organic phase is plotted against the concentration of zirconium in the aqueous phase (Fig. 8). The fact that this value of K_{Zr} is equal to the forward extraction coefficients for zirconium obtained at the same nitric acid concentration (Table 8) confirms that the value determined corresponds to the true equilibrium value for extractable-scrubbable species.

The intersection points of these lines (Fig. 8) indicate that about 30% of the zirconium present is in nonscrubbable form after 14 days of aging, as compared with only about 6% of nonscrubbable species in one-day-old organic solution.

Fig. 6. Zirconium Distribution Coefficients in Back Extraction from 14-Day-Old Solutions A and B vs. Initial Nitric Acid Concentration in the Aqueous Phase.

At present, the form of the retained species is unknown; some light may be shed on their structure by recently initiated infrared studies of zirconium aging in the organic phase. Preliminary spectra of the chemical components of the organic phase have been accumulated as a basis for study of zirconium aging in the organic phase. Three peaks which may be characteristic of the formation of zirconium nonscrubbable species are being followed.

Aging of zirconium in the aqueous phase has had no observable effects. Values of D_{Zr} obtained in forward extraction tests did not change during a period of 3.5 months. Since the observed distribution coefficients have shown an inverse relation to initial concentration of zirconium in the organic phase, there is a possibility that zirconium is retained in the organic phase due to the formation of complexes with di-n-butyl phosphate. Since the concentration of formed di-butyl phosphate can be expected to be constant in solutions of the same acidity, the amount of retained zirconium in the solvent will be constant. However, depending on the percent zirconium, the retention will appear to be higher in solutions of lower concentrations of zirconium, and these solutions will be characterized by higher D_{Zr} values for back extraction, as has been observed.

Fig. 7. Changes in Zirconium Distribution Coefficients in Back Extraction with Time and Initial Acidity of Aqueous Phase.

B. Development of Techniques for Reprocessing of Fast Breeder Reactor (FBR) Fuel

1. Introduction

Work is continuing in the program to develop improved solvent extraction techniques for Purex reprocessing of fast breeder reactor (FBR) fuels. This program is being carried out in cooperation with Oak Ridge National Laboratory (ORNL). The main objectives of the ANL program are: (1) design, construction, and testing of an annular centrifugal contactor to reprocess FBR fuel at a rate of 0.5 Mg/d in a unit that is critically safe for high plutonium concentrations; (2) adaptation of a Purex flow sheet for use in short-residence-time centrifugal contactors; and (3) a study of solvent clean-up techniques which may involve use of short-residence-time centrifugal contactors aimed at improving the cleanup process and reducing the impact of solvent cleanup upon waste handling.

Table 10. Martin's Method Applied to Back Extraction of 1-Day-Aged Zirconium from the Organic Phase (30% TBP/nDD) with 3M HNO_3 .

Contact time: 5 min

Initial Solution: 3245 $\mu\text{g Zr/mL}$, $[\text{H}^+] = 0.81 \text{ meq/mL}$ in the organic phase.

Sample No. MZB-	O/A, mL/min	Volume Ratio	$\mu\text{g Zr/mL}$	D_{Zr}	H^+ , meq/mL	Mass Balance
1-0	$\frac{15}{75}$	0.2	219		0.66	
1-A			630	0.348	3.09	104%
2-0	$\frac{15}{30}$	0.5	289		0.67	
2-A			1 510	0.191	3.11	102%
3-0	$\frac{15}{20}$	0.75	380		0.67	
3-A			2 250	0.169	3.13	104%
4-0	$\frac{15}{15}$	1.0	372		0.68	
4-A			2 952	0.126	3.18	102%
5-0	$\frac{15}{15}$	1.0	409		0.68	
5-A			2 966	0.138	3.20	104%
6-0	$\frac{30}{15}$	2	497		0.72	
6-A			5 539	0.093	3.28	100%
7-0	$\frac{75}{15}$	5	860		0.74	
7-A			12 400	0.069	3.44	103%

Table 11. Martin's Method Applied to Back Extraction of 14-Day-Aged Zirconium from Organic Phase (30% TBP/nDD) with $3M$ HNO_3 .

Contact time: 5 min

Initial Solution: 3.29 mg Zr/mL, $[H^+] = 0.83$ meq/mL

Sample No. 14MZB-	O/A mL min	Volume Ratio	mg Zr/mL	D_{Zr}	H^+ , meq/mL	Mass Balance
1-0	$\frac{15}{75}$	0.2	1.33	3.41	0.65	
1-A			0.39		3.07	101%
2-0	$\frac{15}{30}$	0.5	1.49	1.62	0.67	
2-A			0.92		3.14	101%
3-0	$\frac{15}{20}$	0.75	1.54	1.13	0.67	
3-A			1.37		3.16	102%
4-0	$\frac{15}{15}$	1.0	1.60	0.95	0.68	
4-A			1.68		3.17	99%
5-0	$\frac{15}{15}$	1.0	1.59	0.93	0.68	
5-A			1.71		3.16	100%
6-0	$\frac{30}{15}$	2.0	1.80	0.57	0.69	
6-A			3.18		3.31	103%
7-0	$\frac{75}{15}$	5.0	2.05	0.33	0.73	
7-A			6.13		3.47	100%

2. Development of a 0.5-Mg/d Centrifugal Contactor

(R. A. Leonard, R. H. Peltz, A. A. Ziegler, and C. J. Bernstein)

Laboratory testing of the 9-cm-ID (0.5 Mg/d) annular centrifugal contactor is continuing. Hydraulic tests are essentially complete, including measurements of the effect of rotor speed and of solid particles at the O/A interface. Mixing zone residence time, determination of dispersed phase, and mechanical wear measurements were made. Preparations have been completed for mass transfer efficiency tests using uranium and thorium.

a. Effect of Rotor Speed

As a means of increasing the throughput of the 9-cm-ID contactor, the rotor speed was increased above the standard motorized spindle

Fig. 8. Martin's Method Applied to Back Extraction of Zirconium from the Organic Phase (30% TBP/nDD) with 3M HNO_3 . Contact time, 5 min. (A) 1-day-old solution: (B) 14-day-old solution.

C_O^T = concentration of zirconium in the solvent phase, mg/mL, $C_O^T = C_O + C_O'$

C_a = concentration of zirconium in the aqueous phase, mg/mL.

speed of about 1765 rpm. The results showed that throughput increased about 20% at a rotor speed of 2500 rpm but dropped about 20% at a rotor speed of 3000 rpm. The drop in throughput at 3000 rpm is attributed to the relatively narrow annular gap (used in this design) inhibiting the flow of intensively mixed emulsion. The small annular gap (0.635 cm) was selected at a time when the design was directed toward achieving minimum residence time in the mixing zone. Since short residence time did not provide the anticipated improvement in ruthenium and zirconium decontamination (see Section 5 above), an improved design of the 0.5-Mg/d contactor will have a larger annular gap and a somewhat larger rotor. To avoid the higher bearing loads and wear rates likely to be encountered at higher speeds, rotor speed will be held to about 1765 rpm.

b. Tests with Particles at Organic/Aqueous Interface

The 9-cm-ID centrifugal contactor feed system was modified to permit testing of contactor operation with high-density polypropylene powder simulating interfacial crud. These polymeric solids have a density

between those of the organic and aqueous phases. They apparently collect at the O/A interface inside the rotor, but have no effect on the hydraulic performance of the contactor. In earlier tests [BERNSTEIN] finely divided manganese dioxide was used. That material, which is denser than either of the liquid phases, collected along the rotor wall until a steady state amount had accumulated. The recent tests more nearly represent the effect of interfacial solids in an operating contactor.

In order to avoid contaminating the existing solution supply system with the particles, a modified feed system was used that reduced each circulating phase to about 0.5 L. In the modified system, each exiting stream flows to a small feed reservoir where it spills over a 90° V-notched weir and flows by gravity back to the contactor inlet. The organic feed reservoir is shown in Fig. 9. Flow rate is measured by correlating the flow rate with the diameter of the jet from the weir. Flow rate is controlled by adjusting the total liquid volume.

Polymeric solids for these tests were polypropylene (PP) with a density of 892.5 kg/m³. This density is between the 1015 kg/m³ density of 0.5M HNO₃ and the 818 kg/m³ density of 30% tri-n-butyl phosphate (TBP) in n-dodecane (nDD). The powder size ranged from 15 to 150 μm.

During contactor tests under normal flow conditions, PP powder was added to the organic feed stream in the organic feed reservoir. The total flow rate was 4.0 L/min (2.3 L/min organic phase and 1.7 L/min aqueous phase). The particles were added in increments until 390 mL (bulk volume) was collected in the rotor without affecting hydraulic performance. This volume represents 35% of the total volume in the separating zone of the rotor.

c. Determination of Residence Time

The extraction efficiency of an annular centrifugal contactor depends on the degree of mixing of the two liquid phases and the time available for diffusion while they are highly intermixed. The residence time in the annular mixing zone has some effect upon the extent of mixing and a direct effect upon available diffusion time and is therefore an important factor in achieving high extraction efficiency. Measurements were made to allow calculation of the residence time in the annular mixing zone.

Liquid height in the annular mixing zone was measured with a 1.6-mm (1/16-in) ID stainless steel probe which was introduced into the annular region through a sliding seal in the bottom of the housing. The probe was initially positioned with its opening above the level of liquid in the annulus. With a vacuum on the probe, the probe was lowered until liquid appeared in the probe line.

Liquid heights in the annulus for a range of total throughputs are plotted in Fig. 10. The increase in height with flow rate is linear above 1.0 L/min. The height for aqueous-continuous operation is slightly lower

Fig. 9. Organic-Phase Feed Reservoir (stainless steel beaker) for Particle Tests. ANL Neg. No. 308-78-601.

than that for organic-continuous operation. This may be a result of (1) the lower viscosity of the aqueous-continuous mixture and (2) its greater average density requiring less total height to provide the pressure needed for flow into the rotor orifice.

Residence time is calculated to be the liquid volume in the mixing zone divided by the flow rate. The volume in the mixing zone is divided into two portions. The portion below the rotor bottom of the 9-cm-ID contactor is 109.8 cm^3 (based on the 1.2-cm clearance above the housing bottom). The portion in the annulus is $20.2 \text{ cm}^3/\text{cm}$ of height measured above the rotor bottom. For a flow rate of 8 L/min with the organic phase continuous, the residence time is 2.3 s. It should be noted that the volume measurement does not make allowance for the volume of any air that might be entrained in the liquid emulsion. Accordingly, a residence time determined by the above type of measurement would be the theoretical maximum at given flow rate.

Fig. 10. Effect of Flow Rate on Liquid Height in the Annular Mixing Zone. 9-cm-ID Contactor. Diverter Disk. 1765 rpm

d. Regions of Aqueous-Continuous and Organic-Continuous Operation

When extraction tests are made in the 9-cm-ID contactor, it may be important to know whether the material is being transferred from the continuous to the dispersed phase or vice versa. For this reason, continuous-phase tests have been completed at selected flow rates and organic-to-aqueous flow ratios.

The continuous phase was determined by drawing a 100-mL sample from the bottom drain in the contactor housing. Visual inspection of the emulsion during its coalescence revealed which phase was continuous. It was found that at organic-to-aqueous ratios (O/A) of 1.0 or greater, the system operates organic-continuous. At an O/A smaller than 0.2, the system operates aqueous-continuous. With an O/A of 0.5, the system can be made to

operate with either phase continuous. In the region where O/A is about 0.5, the maximum total throughput is significantly greater for an aqueous-continuous system. The time for aqueous-continuous emulsions to coalesce is about one-half that for organic-continuous emulsions. The shorter coalescence times for aqueous-continuous emulsions may explain the higher throughputs possible with aqueous-continuous operation of a contactor.

e. Vibration Measurements

To monitor the mechanical wear on the Whitnon motorized spindle that drives the 9-cm-ID rotor, the vibration level was measured at nine points on the surface of the spindle over a period of time. (The rotor is suspended from the motorized spindle and has no bottom bearing. Consequently, an unbalanced condition in the rotor could cause excessive vibration in the spindle with attendant wear of its bearings.) The results of these measurements (Table 12) show some variation with time, but no trend of increased vibration levels which would indicate mechanical wear. Vibration levels at 1765 rpm are approximately those specified for precision grinders (0.04-mil displacement) and well below that for precision machine tools (0.20-mil displacement).

Table 12. Vibration Levels in the Spindle of the 9-cm-ID Contactor

Whitnon^a motorized spindle, 0.75 kW (1 hp).
Vibration measured at nine locations on the
surface of the spindle with a Vibropac-I^b meter.
Rotor speed: 1765 rpm.
Empty rotor, no-flow conditions.

Date	Average Displacement, mils (peak-to-peak)
Jan 1978	0.030
Jun 1978	0.051
7-5-78	0.031
7-30-78	0.024
9-29-78	0.041
9-29-78	0.046 ^c

^aProduct of Whitnon Spindle Division of Mite Corporation.

^bProduct of Balance Technology, Inc.

^cRotor under flow conditions of 8 L/min at O/A of 1.0.

3. Solvent Cleanup

(B. B. Saunders, R. E. Barletta, and J. H. Meisenhelder)

A series of experiments was performed (Fig. 11) to determine the effect on zirconium extraction of the hydrolysis of tri-n-butyl phosphate in n-dodecane (TBP/nDD). Preliminary analytical results for zirconium have been obtained.

In the first experiment, equal volumes of 30% TBP/70% nDD/ 10^{-3}M di-n-butyl phosphoric acid (HDBP)* and 3M HNO_3 solutions were stirred for approximately 24 h at 60°C . The two solutions were then separated. The organic layer and a solution of 0.001M $\text{Zr}(\text{NO}_3)_4$ in 3M HNO_3 (volume ratio, 2:1) were then stirred for 1 h at 60°C . No precipitates formed. The various solutions were analyzed for zirconium by the Analytical Chemistry Group of this Division, using a colorimetric method.

In the second experiment, instead of purified HDBP being mixed with 30% TBP/70% nDD, a mixture of 55% HDBP and 45% monobutyl phosphoric acid (H_2MBP) supplied by Eastman was used (approximately 10^{-3}M HDBP and 10^{-3}M H_2MBP in final solution). The organic solution was divided into two parts.

The first part of the organic solution was stirred with 0.001M $\text{Zr}(\text{NO}_3)_4$ in 3M HNO_3 (volume ratio, organic: aqueous = 2:1) for 1 h at 60°C . The two layers were separated; after a period of several days, a precipitate formed in the organic layer. The organic layer was analyzed for zirconium.

The second half of the HDBP- and H_2MBP -containing organic solution was stirred with an equal volume of 3M HNO_3 for 24 h at 60°C . The two layers were separated, and the organic layer was stirred with 0.001M $\text{Zr}(\text{NO}_3)_4$ in 3M HNO_3 as above. After several days, a precipitate formed in the organic phase. The solutions were analyzed for zirconium.

Unfortunately, the zirconium analyses were not performed for several months and the organic solutions in particular had probably deteriorated, thus complicating the zirconium determinations. Some of the zirconium might have been bound up in a polymerized form in the precipitate.

*HDBP, a major product of solvent damage, forms strong complexes with zirconium, thorium, plutonium, and uranium which are somewhat soluble in the organic phase.

Fig. 11. Zirconium Hydrolysis Experiments

The results of the zirconium analyses are shown schematically in Fig. 11. After the hydrolysis of 10^{-3}M HDBP/30% TBP/70% nDD, the distribution ratio for zirconium (organic/aqueous) was 24.5, and 76% of the zirconium was detected. In the absence of hydrolysis other than that caused by $\text{Zr}(\text{NO}_3)_4$ in 3M HNO_3 , the zirconium O/A distribution was 0.59 and only 54% of the zirconium was detected after the zirconium solution was stirred with 10^{-3}M H_2MBP / 10^{-3}M HDBP/30% TBP/70% nDD. When hydrolysis of the H_2MBP - and HDBP-containing solution preceded stirring of the aqueous zirconium-containing solution and the organic solution, the zirconium O/A distribution was 15.7 and only 49% of the zirconium was detected.

These experiments were originally intended to be the beginning of a series of hydrolysis experiments including a study of the effect of zirconium on hydrolysis. Analytical results for HDBP and H_2MBP are still to be obtained. However, these preliminary results show that the effect of hydrolysis of 10^{-3}M HDBP/30% TBP/70% nDD on zirconium extraction cannot be duplicated by the simple addition of H_2MBP to the solution.

II. ENVIRONMENTAL EFFECTS (W. Seefeldt and W. Mecham)

A. Introduction

The purpose of this program is to develop a systematic and coherent body of knowledge as a basis for predicting accident consequences in LWR fuel processing facilities, for estimating source terms of radioactive releases, and generally for assembling information useful as a means of further reducing the consequences of accidents, if such be needed. The objectives and scope encompass (1) determination of source terms for postulated accidents in reprocessing plants, including the physical and chemical properties of materials made airborne during primary dispersion; (2) identification of modifications of the properties of airborne materials under the conditions of transport to the first stage of an air-cleaning system; (3) estimation of the quantitative penetration of radionuclides through the confinement and air-cleaning systems; and (4) identification of the properties of the airborne products of accidents as released into the atmosphere at the stack or into the environment at the boundary of the plant. In this work interest is principally in particle sizes that are inhalable (generally smaller than 10 μm).

The principal types of accidents identified for this study are explosions, fires, and criticality. Explosions were given initial emphasis because of the relative difficulty of obtaining results in this area consistent with program objectives.

In the preceding quarterly report [STEINDLER-1978D], methods of estimating the quantities of small particles from empirical test data were described. The empirical data showed that the sizes of most of the fragmentation particles were much larger than are of interest for environmental effects. Two methods of extrapolation to include the small particle size ranges were based on the use of two different particle-size distributions, the log normal and the semilog. The relative quantities of small particles predicted by the two distributions were found to be very different, although the absolute quantities for both were low.

During this report period, another alternative distribution, the self-preserving distribution, is analyzed and compared with the semilog distribution.

In the preceding quarterly report, the energy needed to subdivide a solid by brittle rupture was considered. This work has been extended to show the relationship between energy input and the predicted modes (maximums) of particle size frequency distributions, assuming that the semilog distribution is applicable.

B. The Self-Preserving Particle-Size Distribution

The log normal and semilog particle-size distributions of airborne materials were analyzed and compared in the preceding quarterly report [STEINDLER-1978D]. Another distribution, the self-preserving distribution, is analyzed with the semilog distribution.

The semilog distribution is defined in terms of particle number as follows:

$$\frac{dN}{dD} = Ke^{-mD}, \quad (1)$$

where N = the number of particles, D = particle diameter, dN = the number of particles in the size interval D to $D + dD$, and m and K are constants. This particle number distribution may be normalized by integrating dN over the full range of diameters, from 0 to ∞ , to yield the total number of particles, N_T^* .

$$N_T = \frac{K}{m} \quad (2)$$

Thus

$$\frac{dN}{dD} = mN_T e^{-mD} \quad (3)$$

or

$$\begin{aligned} \frac{dN/N_T}{dD} &= \frac{dF_n}{dD} \\ &= me^{-mD} \end{aligned} \quad (4)$$

where dF_n is the fraction of total particles in the size interval, D to $D + dD$. Converting to logarithmic form

$$\begin{aligned} \frac{dF_n}{d(\ln D)} &= D \left(\frac{dF_n}{dD} \right) \\ &= mDe^{-mD} \end{aligned} \quad (5)$$

*The subscript, T , on a symbol refers to the total of the items represented by the symbol.

By taking the derivative of Eq. 5 and equating it to zero, we find that the mode occurs at

$$\bar{D}_n = \frac{1}{m} \quad (6)$$

Equation 1 can be converted to reflect the distributions based on surface area, A, and volume, V.*

Surface Area

$$A = \pi D^2 \cdot N \quad (7)$$

$$dA = \pi D^2 dN \quad (8)$$

$$\frac{dA}{dD} = \pi K D^2 e^{-mD} \quad (9)$$

$$A_T = \frac{2\pi K}{m^3} \quad (10)$$

$$\frac{dF_A}{d(\ln D)} = \frac{(mD)^3 e^{-mD}}{2} \quad (11)$$

$$\bar{D}_A = \frac{3}{m} \quad (12)$$

Volume

$$\bar{V} = \frac{\pi}{6} D^3 \cdot N \quad (13)$$

$$dV = \frac{\pi}{6} D^3 dN \quad (14)$$

$$\frac{dV}{dD} = \frac{\pi K}{6} D^3 e^{-mD} \quad (15)$$

$$V_T = \frac{\pi K}{m^4} \quad (16)$$

$$\frac{dF_V}{d(\ln D)} = \frac{(mD)^4 e^{-mD}}{6} \quad (17)$$

$$\bar{D}_V = \frac{4}{m} \quad (18)$$

Another particle-size distribution function which has been found to prevail in nature is the self-preserving distribution function [DAVIS]:

$$\frac{dN}{dr} = \frac{KV}{20} r^{-4} \quad (19)$$

*Subscripts n, A, and V refer to particle number, area, and volume, respectively.

where $N = N(r)$ = particle number concentration (per cm^3 of aerosol), r is the particle radius, V_T is the volume of the dispersed phase (cm^3 particle phase/ cm^3 of aerosol), $\frac{dN}{dr}$ is the number of particles in the size interval, r to $r + dr$, and K is a constant.

The volume distribution function is given by

$$\frac{dV}{dr} = \frac{4\pi r^3}{3} \cdot \frac{dN}{dr} = \frac{4\pi r^3}{3} \cdot \frac{KV_T}{20r^4} = \frac{\pi KV_T}{15r} \quad (20)$$

or

$$\frac{dV}{d(\ln r)} = \frac{\pi KV_T}{15} \quad (21)$$

Thus, the particle volume (or mass) is the same in every decade range of r . This indicates a greater amount of mass on the small end of the particle size distribution than is indicated by other distributions (e.g., the semilog distribution). The total particle number, N_T , and the total particle volume, V_T (each per cm^3 of aerosol), are found by integrating Eqs. 20 and 21:

$$N_T = \frac{KV_T}{60} \left(\frac{1}{r_{\min}^3} - \frac{1}{r_{\max}^3} \right) \quad (22)$$

$$V_T = \frac{\pi KV_T}{15} \ln \left(\frac{r_{\max}}{r_{\min}} \right) \quad (23)$$

where

$$K = \frac{15}{\pi \ln \frac{r_{\max}}{r_{\min}}}$$

Equations 22 and 23 are the normalization factors for Eqs. 20 and 21, respectively. To use them, maximum and minimum particle sizes must be specified. This is a special feature of this distribution function.

The name, "self-preserving" distribution, is based on the empirical observation that in nature, persistent or stable aerosols approximate this distribution, even when N and V (above) change with time. The main idea here is that the aerosol is in a dynamic equilibrium, subject to agglomeration and sedimentation processes, and that removal of particles according to the stirred-settling concept occurs in a way that reestablishes the self-preserving function [DAVIS].

The results of the analysis by Davis are illustrated in Figs. 12-15. Figure 12 shows five representative self-preserving particle-size distributions normalized for total particle volume. Figure 13 shows the (approximate) self-preserving size distribution achieved experimentally by highly coagulated aerosol soon after nucleate condensation. Figures 14 and 15 show reductions, with time, of mass concentrations of confined aerosol by simultaneous coagulation and settling; comparison of the two figures shows the difference between $r_{\min} = 0.01 \mu\text{m}$ and $r_{\min} = 0.10 \mu\text{m}$. The fraction remaining airborne, ϕ/ϕ_0 , in the two figures can be converted to other particle densities and tank heights since $\ln(\phi/\phi_0)$ is directly proportional to (height)/(density).

Fig. 12. Self-Preserving Particle-Size Distributions (normalized for $r_{\max}$ and $r_{\min}$) [DAVIS]

A major problem in developing analytical models of aerosol behavior has been the inability to make a definite determination of the initial particle-size distribution of aerosols, *i.e.*, at the source of generation by nucleate

Fig. 13.

Size Distribution of an Agglomerated
Stainless Steel Oxide Aerosol [DAVIS]

Fig. 14. Removal of Particles from Aerosol by Coagulation
and Settling ($r_{\min} = 0.01 \mu\text{m}$)

Fig. 15. Removal of Particles from Aerosol by Coagulation and Settling ($r_{\min} = 0.1 \mu\text{m}$). Tank Height = 10^3 cm. Particle Density = 10 g/cm^3 [DAVIS].

condensation of supersaturated vapor. The self-preserving particle-size distribution requires the specification of $r_{\max}$ and $r_{\min}$, which in general are not known. Castleman has described mathematical and experimental studies at Brookhaven in which the log normal and self-preserving distributions have been combined [CASTLEMAN]. A computer code has been developed: Transient Removal of Aerosol Particles (TRAP), which includes all simultaneous effects of agglomeration, settling, etc., including a source term for continued introduction of aerosol. Essentially, the log normal parameters r_g (geometric mean radius) and σ_g (geometric standard deviation) are introduced into the self-preserving distribution function in place of $r_{\min}$ and $r_{\max}$. Parametric calculations for aerosol generated by nucleate condensation of supersaturated vapor indicate that, prior to times when particle removal becomes significant, the number-density distribution remained close to log normal, with σ_g converging to about 1.37 for all cases.

The calculations for aerosol production from nucleate condensation are not of direct interest to us, since in accidents, materials of the greatest concern to us are not vaporized. However, the calculational models do

Fig. 16. Effect of Vessel Height, h , on Aerosol Concentration for an Instantaneous Source Model.

Bases: $C_0 = 10.0 \text{ g/m}^3$, $r_g = 0.134 \text{ } \mu\text{m}$ [CASTLEMAN]

consider simultaneous agglomeration and settling from any starting conditions. As an illustration, see Fig. 16, which shows the effect of the height of the settling chamber on settling with simultaneous agglomeration as determined by the TRAP code. Although agglomeration reduces the settling time for any given height, the rate of removal by settling of the specified aerosol ($C_0 = 10 \text{ g/m}^3$, $r_g = 0.134 \text{ } \mu\text{m}$, $u_g = 1.37$) is only 90% in 3 h for 1-m height. (Of course, such particles are effectively removed by standard fiber filters.)

C. Relation of Surface Energy to the Semilog Particle-Size Distribution Function

In this report section, D is the particle diameter, $D_{\min}$ is the minimum particle diameter of the distribution, and $D_{\max}$ is the maximum particle diameter of the distribution.

From the particle number distribution

$$\frac{dN}{dD} = Ke^{-mD} \quad (24)$$

We note that the surface area, dA , associated with dN is given by:

$$\frac{dA}{dN} = \pi D^2 \quad (25)$$

which is then distributed as

$$\frac{dA}{dD} = \frac{dA}{dN} \cdot \frac{dN}{dD} = \pi K D^2 e^{-mD} \quad (26)$$

The total surface area A_T is given by

$$A_T = \int_{D_{\min}}^{D_{\max}} \pi K D^2 e^{-mD} dD \quad (27)$$

$$= \left[\frac{\pi K}{m^3} e^{-mD} (m^2 D^2 + 2mD + 2) \right]_{D_{\max}}^{D_{\min}} \quad (28)$$

It is appropriate to take the limits as $D_{\min} = 0$ and $D_{\max} = \infty$, in which case

$$A_T = \frac{2\pi K}{m^3} \quad (29)$$

We may now write the area distribution in terms of the fraction of total area, dF_A , in the interval, D to $D + dD$.

$$\begin{aligned} \frac{dF_A}{d(\ln D)} &= \frac{dA}{A_T d(\ln D)} \\ &= \frac{(mD)^3 e^{-mD}}{2} \end{aligned} \quad (30)$$

This distribution has a mode (maximum frequency) at $D_m = D_A = 3/m$. By calculation, less than 1% of the total surface area is possessed by particles larger than $3D_m$ (three times the mode). On the other hand, a comparably small fraction of area is found on the small side of the mode only when the particle size is much smaller, i.e., $D < 10^{-2}D_A$.

We now apply the parameters of the semilog function to the break-up of a brittle solid of volume V_0 by absorption of impact energy ΔE , where the specific energy for creating new surface area by fragmentation is ϵ in units of energy/surface area. From the rupture modulus of a typically brittle solid, $\epsilon = 7 \text{ J/m}^2$.

In this fragmentation process, the total volume of particles resulting, V_T , is equal to the original solid volume, V_0 , and we know that $V_T = \pi K/m^4$ in terms of parameters of the semilog function. Thus,

$$\begin{aligned} V_0 &= V_T \\ &= \pi K/m^4 \end{aligned} \quad (31)$$

$$\begin{aligned} A_T &= \frac{\Delta E}{\epsilon} \\ &= 2\pi K/m^3 \end{aligned} \quad (32)$$

Equations 31 and 32 can be solved for the two unknowns, K and m :

$$m = \frac{\Delta E}{2\epsilon V_0} \quad (33)$$

$$K = \left(\frac{\Delta E}{2\epsilon} \right)^4 \cdot \left(\frac{1}{\pi V_0^3} \right) \quad (34)$$

With K and m determined, and with the mode of the distribution based on surface area known to be $\bar{D}_A = \frac{3}{m}$, we can relate $\bar{D}_A$ to ΔE and ϵ as follows:

$$\bar{D}_A = \frac{6\epsilon V_0}{\Delta E} \quad (35)$$

Similarly, since the mode of the distribution based on the volume is $\bar{D}_V = \frac{4}{m}$

$$\bar{D}_V = \frac{8\epsilon V_0}{\Delta E} \quad (36)$$

From the above, knowledge of the values of ϵ and ΔE allows the particle-size distribution (and the absolute quantities) to be determined. For example, if $\epsilon = 7.0 \text{ J/m}^2$, if $\Delta E = 1 \text{ kg} \cdot \text{m} = 9.8 \text{ N} \cdot \text{m} = 9.8 \text{ J}$, and if $V_0 = 10 \text{ cm}^3 = 10^{-5} \text{ m}^3$, then the maximum surface area of particles would be $A_T = 1.4 \text{ m}^2$ and the modal diameter of the semilog distribution (based on surface area) resulting would be $D_A = 6(7)(10^{-5}) = 4 \times 10^{-5} \text{ m} = 40 \text{ } \mu\text{m}$. The practical problem in using

this equation is that the total input energy in mechanical impact is only partially absorbed as inelastic deformation of the material; usually, the largest fraction of the input energy is dissipated in processes other than fracture of the target material.

Another variable is the entrainment process which renders the particles airborne. The basic features of the processes by which particles in contact with one another and with a solid substrate are rendered airborne by entrainment in moving air were reviewed in the preceding progress report [STEINDLER-1978D].

III. PYROCHEMICAL AND DRY PROCESSING METHODS PROGRAM
(Milton Ader, R. Barletta, J. K. Bates, C. H. Bean,
T. G. Gerding, L. J. Jardine, D. K. Kroeck,
Michael Krumpelt, K. M. Myles, B. B. Saunders,
and Seymour Vogler)

A. Introduction

A Pyrochemical and Dry Processing Methods (PDPM) Program was established at the beginning of FY1978 in the Fuel Cycle Section of the Chemical Engineering Division at Argonne National Laboratory (ANL). This program is an expansion of the National Fuel Cycle Program for reprocessing fuel by processes that will reduce the risk of proliferation of nuclear weapons. Argonne has been designated by the United States Department of Energy (DOE) as the lead laboratory for PDPM, with various reprocessing developments being performed at other DOE laboratories and by industrial contractors.

The program has been administratively divided into individual work packages, four of which are being done at ANL. Purchase orders have been placed for eight work packages, and a subcontract has been placed for an additional work package.

Each work package is being managed for conformance to established statements of work, program objectives, a cost plan, a milestone plan, and a management plan in accordance with Uniform Contractor Reporting Guidelines (UCRG) as required by DOE.

B. Management

(C. H. Bean, K. M. Myles, and Seymour Vogler)

1. Program Evaluation

Chemical Engineering Division management and PDPM management personnel met with the DOE/NPD Technology Branch in Germantown on August 2 and 3, 1978. This meeting provided program guidance and direction, as well as input to proliferation criteria. The long-range potential for applying pyro-reprocessing to fast breeder reactor fuels will affect which fuel types and fuel cycles must be studied in the pyro program. Subjects that require immediate analysis are the refabrication of fuel products derived from pyro reprocessing, and a comprehensive analysis of a "Pyro-CIVEX" process comparable to that which has been made for the aqueous "Purex-CIVEX" process. Studies were initiated at ANL to address both of these subjects.

The ANL PDPM Program management was requested by DOE-HQ to assist ORNL in conducting a study to analyze the potential of PDPM reprocessing vis-a-vis comparable aqueous methods to meet the requirements for an

"exportable technology." Meetings were held at ANL on September 7 and at Germantown on September 18 among DOE, ORNL, and ANL representatives to discuss terms, scope of work, schedules, study plans, and liaison between ANL and ORNL.

At the meeting on September 7, it was agreed that DOE-NPD (Nuclear Power Development) would review process and proliferation criteria prepared by ANL and would resolve any differences that might exist from the preliminary criteria identified by DOE on August 22, 1978. This review was to be completed by September 18. They further agreed to define criteria which determine "exportability" and recognized a need to establish radiation level criteria by September 18.

ANL submitted a preliminary pyrochemical flow sheet for ORNL review. This flow sheet is being developed for a pyro-Civex study effort at ANL as requested by DOE-NPD in August, 1978, with emphasis on nonproliferation and was not based on any specific process currently under investigation for the PDPM Program. It was agreed that ANL would provide ORNL with a more detailed "reference" flow sheet based on this preliminary flow sheet and also an explanation of why this reference flow sheet is representative of nonaqueous chemical reprocessing. In addition, ANL agreed to provide a preliminary process and any mass balance data and/or engineering flow sheets that became available by September 18.

Because of the absence of data for determining the health, safety, and economic aspects of the reference pyrochemical flow sheet, its comparison with the more established Purex process in these areas would be meaningless. It was understood that DOE-NPD would clarify the intent of these provisions in the ORNL study.

ORNL agreed to provide a study plan to DOE-NPD by September 18, and the due date of the draft report of the ORNL study of pyroprocesses was extended to January 15, 1979 by DOE.

At the meeting on September 18, the process and proliferation criteria prepared by ANL were identified by NPD as reference criteria to be applied to the ORNL study. Radiation level criteria were not specifically defined, but it was suggested by NPD that radiation levels comparable to those applied to the Purex-CIVEX analysis be applied to the pyro process.

The reference pyrochemical reprocessing information supplied by ANL on September 18 consisted of (1) a description of the process chemistry; (2) flow sheets for a head-end process, coprocessing of uranium-plutonium oxide fuel by zinc dissolution, and tail-end processes for producing FBR (U-Pu) O_2 fuel; and (3) engineering and plant design information.

The extent to which the health, safety, and economic aspects of the reference pyrochemical flow sheet would be analyzed was not resolved by NPD although it was stated by NPD that the ORNL study would follow very closely what EPRI did for CIVEX on the aqueous process. The EPRI study did not have a cost analysis.

A study plan proposed by ORNL on September 18 included input from consultants identified as Rockwell International at Rocky Flats, GE at San Jose, and Bechtel Corporation. Input from consultants would include black-hat analysis of the reference pyrochemical process for proliferation resistance, a detailed analysis of the process, a conceptual plant design and process operation, and an economic analysis.

On September 25, PDPM management met with the Rockwell International Rocky Flats personnel to review the scope and objectives of the ORNL study effort and to discuss the rationale for the reference pyrochemical flow sheet.

2. Program Management

PDPM management personnel visited all contractors during the month of August to review technical progress, to discuss FY1979 program plans and management plans, and to introduce the CEN Division Project Quality Engineer (PQE) to contractor personnel who are responsible for implementing quality assurance. Preliminary analyses and literature surveys required for flow sheet preparation are completed or near completion by all contractors. Facilities and equipment needed to perform laboratory-scale experiments are in place and operable for all contractors except those that did not receive authorization to start work until the third quarter of FY1978. Programs planned for FY1978 include those experiments needed to resolve identified process limitations, determinations of the technical feasibility of selected processes and preparation of process engineering designs based on work completed in FY1978 and experimental process demonstrations completed in FY1979. Capital equipment needed for work in FY1979 was discussed.

Current statements of work for individual PDPM Work Packages require the contractor to provide and maintain a quality assurance program which identifies the policies, procedures, and standards that will be used to achieve the work package objectives. Mr. Jay D. Geller, CEN Division PQE, reviewed quality assurance policies and procedures and quality assurance plans at each contractor facility. In FY1979, submission of a copy of the quality assurance manual of each contractor to the ANL Quality Assurance Division for review and approval will be required. Also, a quality assurance plan must be prepared for each work package. The CEN/PQE offered to provide assistance in preparing these documents, if requested. Work packages will be audited for conformance to the prepared quality assurance plans in FY1979.

Statements of work were prepared for nine separate work packages at eight separate contractor facilities and multipurpose DOE laboratories, based on negotiated contractual effort for FY1979. This effort was consistent with planned funding for FY1979. Purchase requisitions for research and contract requests were prepared and processed for this effort with advance funding for FY1979. When NPD notified us of a reduction in the available funding for PDPM in FY1979, changes were made in several work packages that resulted in redirection and reduction of effort consistent with the reduced funding. It was decided to terminate Work Package No. 06, Aluminum-Alloy Processing of Thorium- and Uranium-Based Fuels, and Work Package No. 11, Reprocessing of Thoria-Urania Fuel in Molten Salts Containing ThCl_4 . AIROX, CARBOX, and RAHYD Processing in Work Package No. 08 is to be terminated; effort on this work package is to be redirected to provide support to other PDPM processes. The effort on Work Package No. 07, Chloride Volatility Processing of Thorium-Based Fuels, will be phased out early in FY1979, and some exploratory studies and experiments on molten-zinc separations will be initiated in this work package.

A new work package, No. 13, Engineering Support for PDPM Processes, is planned for FY1979. This work package will provide engineering assistance to proliferation analysis, special studies, program management, materials applications, process equipment design, draft conceptual process engineering, and process scale-up for all other work packages within the scope of the PDPM Program.

C. Engineering Analysis and Separations Processes

In the engineering analysis, prior work has been examined and evaluated. From these evaluations, a flow sheet has been devised for each of the reprocessing techniques. Gaps in the data (which must be filled to provide operable flow sheets) will be filled by experimental work carried out under separation process subtasks.

1. Materials Development for PDPM

(R. M. Arons* and J. Y. N. Wang*)

The project involves the anticipation, identification, and scoping of potential materials and fabrication problems associated with the various candidate processes in the PDPM Program. By analytical and experimental methods, means will be devised to resolve these problems. The fuel state after reprocessing and its effect upon refabrication will be considered.

*Materials Science Division, Argonne National Laboratory.

a. Engineering Analysis

A subcontract with R. J. Teitel Associates to assist ANL in the determination of materials requirements for various candidate PDPM processes terminated at the end of FY1978. This contract was let in an effort to identify potential materials problems by study of the literature and PDPM contractor reports on selected nonaqueous reprocessing methods. The information to be provided to ANL by RJT is to include a list of candidate materials for construction of reprocessing hardware, along with a rationale for their selection, a bibliography and summary for each process reviewed, and recommendations on critical experiments which would supplement the literature and provide missing information.

Three interim progress reports have been received to date. The first report delineates the methodology used to assess material requirements. The second report contains a key word subject list used in the literature survey, a list of abstract compilations searched, and a list of candidate metallic materials to be examined. The third report contains a list of the significant entries in the bibliography being prepared and a list of (1) candidate compounds which are being examined and (2) the metals listed in the second report.

The final report for the subcontract is under preparation and is expected by October 20, 1978.

b. Experimental

(1) PDPM Environmental Test Facility (PETF)
(R. M. Arons* and D. J. Dorman*)

The PETF has undergone a number of iterative design improvements, and the design is now finalized. The PETF has the capability of mixing molten metals and salts at $\leq 900^{\circ}\text{C}$ under an argon atmosphere. A schematic of the test cell is shown in Fig. 17. The cell consists basically of an inner crucible to contain molten metals and molten salts, a rotary turbine-type pump for mixing the molten metal through the salt, an outer crucible to contain an argon atmosphere and to provide a secondary container in the event of failure of the primary crucible, an electrically heated furnace, and a temperature controller for the furnace. Specimens will be supported in the melt by a collar with radial hooks (not shown) which affixes to the pump and supports flat specimens with central holes. The entire pump and specimen fixture assembly may be withdrawn from the melt (while still within the argon atmosphere) to allow cooldown of the assembly without freezing specimens into the metals or salts.

*Materials Science Division, Argonne National Laboratory.

Fig. 17

Schematic of PDPM Environmental Test Facility.

The materials of construction are as follows: the pump is all tantalum with graphite bearings, the inner crucible may be alumina, graphite, or tungsten (depending on which metals and salts are tested), and the outer crucible is mullite. The cap of the outer crucible and all other hardware which will be exposed to vapors from the melt will be constructed of Type 304 stainless steel. The temperature will be monitored with a thermocouple, protected by a tantalum, graphite, or alumina sheath and immersed directly in the melt. A series of water-cooled baffles (not shown) will condense and collect any vapors above the melt.

In a preliminary simulation test, a pump has been used successfully to mix molten metal (Wood's metal) through a lighter immiscible liquid (water). This preliminary test is thought to oversimulate any expected process requirements since the difference in specific gravity between the two simulant liquids far exceeds that of any two proposed process liquids. After optimizing the pump design in these preliminary tests, a prototype pump was fabricated of Type 304 stainless steel and was tested in a mixture of molten

zinc and a molten salt consisting of $2\text{MgCl}_2:\text{KCl}:\text{NaCl}$. The pump functioned successfully for approximately 10 min, at which time the lower impeller dissolved in the molten zinc. Based on the successful demonstration of the pump design, we have proceeded with fabrication of tantalum hardware.

(2) Metallic Materials

(J. Y. N. Wang*)

Tungsten-Rhenium Alloys. The fabrication of tungsten is difficult because the material exhibits brittle characteristics at ambient temperatures. It has been reported [KLOPP] that the ductile-brittle transition temperature (DBTT) for a worked tungsten sheet (electron-beam melted quality) is approximately 113°C . However, the transition temperatures of two dilute alloys, containing 1.9 and 9.1 wt % rhenium, were approximately -60 and -70°C , respectively. If there is no sigma-phase precipitation, a further decrease in DBTT is expected in alloys with higher rhenium contents (e.g., W-25 wt% Re).

Samples of the W-25 wt% Re alloy in plate and sheet form (0.7 to 0.3 cm thick) were obtained for corrosion tests in PDPM environments. Because information furnished by the supplier regarding the minor element concentrations and metallurgical history of the material was insufficient, a pretest chemical analysis and a microexamination of the samples were necessary.

Microstructural examination of 10-mil-thick W-25 wt% Re alloy revealed that the material exhibited a rolled structure. Some recrystallization due to hot working was evident. Sigma phase, which is brittle in nature, was not found. Microhardness tests are being performed in conjunction with the scanning-electron microscopic (SEM) analysis. Subsequently, the material will be annealed at 900°C before corrosion testing under PDPM conditions.

Kennametal Alloys. Two alloys (W-2 and W-10) were obtained from Kennametal, Inc., for corrosion tests. The materials contain about 90.0 and 97.4 wt % tungsten, respectively, with small amounts of copper, iron, and nickel. The supplier claims that these materials can be machined to any desirable shape.

Microstructural examination and SEM analysis showed that the matrix of these materials contained copper and silicon precipitates. Copper, iron, and nickel were prevalent at the grain boundaries. Thus, a strong possibility exists that these materials will be susceptible to intergranular penetration in molten zinc (one of the molten metals in PDPM systems).

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Other potentially fabricable materials, such as W-30% Re-18% Mo, Mo-30% W, Mo-0.5% Ti, Ta-10% W, Ta-2.5% W, and Ta-8% W-2% Hf, were obtained from various sources and are being examined metallographically before corrosion testing in PDPM environments.

(3) Ceramic Materials

(R. M. Arons*)

We have elicited interest from eight ceramic fabricators, in providing us with both technical assistance and test samples. The ceramic fabricators are:

- (a) AVCO Corp., Wilmington, MA.
- (b) Ceradyne, Inc., Santa Ana, CA.
- (c) Carborundum Company, Niagara Falls, NY.
- (d) Kawecki Berylco Industries, Inc., Reading, PA.
- (e) Materials Technology Corp., Dallas, TX.
- (f) National Beryllia Corp., Haskell, NJ.
- (g) Norton Company, Worcester, MA.
- (h) Union Carbide Corp., New York, NY.

Materials received from these vendors are shown in

Table 13.

Table 13. Materials Received from Outside Vendors for PDPM Screen Testing

Oxides	Nitrides
Al ₂ O ₃ (two sources)	AlN
BeO	Si ₃ N ₄ (five types, two sources)
MgO	Si ₂ ON ₂
MgAl ₂ O ₄	BN
ThO ₂	
Y ₂ O ₃	
ZrO ₂	
Borides	Carbides
TiB ₂ (three sources)	Graphite (PG)
ZrB ₂	SiC (four types, three sources)
ZrB ₂ -SiC-C composite (three types)	TiC

*Materials Science Division, Argonne National Laboratory

(4) Tungsten Metallization

(R. M. Arons* and J. T. Dusek*)

Enhancement of the density of tungsten coatings on $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ ceramics is being addressed by two techniques: (1) chemically activated sintering with transition metal sintering aids and (2) modifications of the approach developed at LASL for slip-casting of tungsten [HAUTH].

We have successfully fabricated small crucibles of highly dense ceramic having adherent, crack-free tungsten coatings. Cracks were eliminated by appropriately blending alumina powders and selecting tungsten powders as coating materials, utilizing those combinations of tungsten and ceramic which yielded similar shrinkages upon firing. Coatings were also shown to have excellent thermal-shock resistance by cycling from room temperature to $>900^\circ\text{C}$ (and back down to room temperature) a total of six times. No damage was observed.

The persistent problem of poor tungsten density (previously reported) has also been surmounted by two means. Both the use of a NiCl_2 additive and the use of improved application methods resulted in two coated specimens being produced having relatively high tungsten density. Work is continuing to determine the variables which control tungsten density so that reproducible high-density coatings can be prepared. Work also continues on characterizing successful coatings and measuring their density.

A parallel program is under way to investigate the use of consolidated plasma-sprayed tungsten coating on graphite for PDPM hardware. Prior investigations of plasma-sprayed coatings showed them to be permeable to molten salts. It is claimed, however, that infiltration with a nickel-salt sintering aid, followed by appropriate heat treatment will give more complete sintering and will result in a coating of 94% of theoretical density [TAYLOR]. We have received specimens of plasma-sprayed tungsten coatings on graphite substrates from Union Carbide Linde Division and plan to heat-treat them appropriately at ANL. After heat treatment, the densified coatings will be tested in the PETF for corrosion properties.

2. Carbide Fuel Reprocessing(Micheal Krumpelt, B. B. Saunders, Milton Ader,
R. E. Barletta, and D. K. Kroeck)

In this program, potential reprocessing methods for carbide fuels are studied. In principle, carbides can be burned to oxides and then reprocessed like oxide fuel. However, a direct reduction of the carbides into a metal

*Materials Science Division, Argonne National Laboratory.

solvent or an oxidation into a salt phase is more attractive for pyrochemical processes. Two alternatives are presently considered. In the first, carbides are dissolved and partially separated in liquid bismuth. This is an independent new process for carbides. In the second, carbides are oxidized into a salt phase, using zinc chloride or cadmium chloride. The salt phase is then contacted with a liquid metal to partially separate the actinides from the fission products. The second alternative is a head-end step for salt transport processing (being studied in other segments of the PDPM Program).

a. Molten Bismuth Reprocessing
(R. E. Barletta, B. B. Saunders, and D. K. Kroeck)

The conceptual flow sheet for this process was presented in the preceding quarterly report [STEINDLER-1978D]. Fission products are separated from actinides by the reaction or dissolution of some of the carbides to form bismuthides. The unreacted fission product carbides and bismuthides are lighter than bismuth and along with free carbon would float on the bismuth and would be separated. Uranium carbide dissociates to a very limited degree (dependent on the solubility of uranium in bismuth). PuBi_2 and ThBi_2 are denser than bismuth, are of limited solubility in bismuth, and are expected to settle in bismuth along with unreacted uranium carbide. Plutonium is much more soluble in bismuth than is thorium. However, the temperature may be lowered to reduce the solubility of the plutonium whereupon the precipitated PuBi_2 would be collected.

A glove box operating with a once-through argon atmosphere has been completed and bismuth has been melted in a graphite crucible in the furnace tube attached to the glove box. Although modifications of the glove box were completed, for experiments to measure the solubility of carbides in bismuth, it was necessary to dismantle and move the box to permit laboratory renovations.

While laboratory renovations are in progress, effort has been directed to a literature search on the properties of the carbides. A report entitled The Structure and Reactivity of Carbides will be issued during the next quarter.

b. Molten Cadmium/Salt Reprocessing
(Milton Ader)

A diversion-resistant pyrochemical processing scheme for spent monocarbide fuels was presented in the preceding report [STEINDLER-1978D]. The initial steps involve (a) conversion of the actinide and various fission product carbides to chlorides by reaction with CdCl_2 dissolved in $\text{MgCl}_2\text{-NaCl-KCl}$ eutectic (m.p., 396°C) and (b) reduction of the salt phase

with a cadmium-magnesium alloy, thereby partitioning the fissile, fertile, and fission product elements between the salt and metal phases. Cadmium—rather than zinc-based oxidizing and reducing agents were chosen to allow operation at temperatures below 650°C with readily available container materials such as mild steel and Series 400 steels. In essence, this processing concept serves as a head-end step for introducing carbide fuels into various pyroprocesses (e.g., salt transport).

Laboratory experiments testing this concept will be carried out in an inert atmosphere because of the sensitivity of actinide monocarbides and anhydrous chlorides to moisture and oxygen. A two-tiered, three-module CENHAM glove box [MALECHA] equipped with a helium recirculation-purification system has been set up and tested. A furnace well that opens into the glove box has been attached to the underside of the glove box, and various service lines (cooling water, helium, vacuum) have been installed. Other auxiliary equipment has either been fabricated in our shops (crucibles, stirrers, radiation shields, samplers, etc.) or bought (resistance furnace, temperature controller, balance, etc.). All of the equipment is now being assembled and subjected to shakedown runs before the glove box is sealed for helium-atmosphere operation. The initial experiments will investigate the rate of reaction of UC or ThC as a function of temperature and CdCl₂ concentration in 50 mol % MgCl₂-30 mol % NaCl-20 mol % KCl.

3. Thorium-Uranium Salt-Transport Processing
(Michael Krumpelt, L. J. Jardine,
J. K. Bates, and T. J. Gerding)

The objective of this program is to examine concepts for the selective transfer of spent thorium-based fuel constituents between molten alloys and/or molten salts and to develop process flow sheets for the thorium-based oxides and metal fuels. Initial flow sheets will be constructed based upon published data and thermodynamic evaluations. These flow sheets will then be analyzed in more detail. Potential problem areas and missing data will be identified as portions of an engineering analysis subtask. Laboratory-scale experiments will be instituted as a separations-processes subtask in order to generate data required to establish the feasibility of selected flow sheets.

a. Thorium "Salt-Transport"
(J. K. Bates)

Pyrochemical processes involving salt-transport* and metal-precipitation steps are currently being investigated for use in projected thorium-based fuel cycles. The reference flow sheet (Fig. 18, previously published in [STEINDLER-1978D]) has been designed to meet proliferation standards and is applicable to plutonium-thorium transmuted and undenatured thorium-uranium breeder fuels. The necessary criteria are that the fissile

*In the salt transport step, the necessary separations are effected by selective transfer of various fuel constituents from an initial liquid metal donor alloy, to a molten salt transport phase, and to a final acceptor alloy.

Fig. 18. Reference Flow Sheet For Thorium-Based Fuels - ANL.
 FP-1: Xe, Kr, ^3H ; FP-2: I, Br, Cs, Rb, Ba, Sr, Sm, Eu, Se, Te; FP-3: trivalent rare earths, Y; FP-4: Zn, Nb, Mo, Tc, Ru, Rh, Pd, Hg, Cd, In, Sn, Sb.

streams be coprocessed (Th:Pu/U of 4:1) and be diversion-resistant by the inclusion of some fission products. The rough draft of a topical report describing the reduction, solubility, and hydriding aspects of this process has been completed, and a paper describing the process titled "A Nonaqueous Reprocessing Method for Thorium-Based Fuels" (Bates, Jardine, Krumpelt) has been accepted for presentation at the American Chemical Society Meeting, The Actinide Separations Symposium (April 1979).

As support for the process, experiments investigating both the solubility of thorium in cadmium-magnesium alloys and the reduction rate of high-fired thorium by calcium are in progress. Experiments to study the solubility of thorium as a function of temperature and alloy composition have been completed. Detailed discussion of the results has been deferred until

data have been obtained from the analytical laboratory. The apparatus to carry out the reduction studies is being assembled, and it is expected that the experiments will be completed during the next quarter.

b. Formation of Hydrides in Zinc-Magnesium Alloys
(Michael Krumpelt and J. K. Bates)

(1) Introduction

Plutonium and uranium can be separated from noble metal fission products (FP-4) by the salt-transport method. The recovery of both actinides from the zinc-magnesium acceptor alloy is accomplished by distilling off the solvent alloy. Since large quantities of zinc and magnesium need to be distilled, the distillation equipment would be large. An alternative method of actinide recovery based on precipitation of the hydrides was proposed by [BATES]. Hydriding as a means of recovering thorium from liquid magnesium solutions had been investigated by Woerner and Chiotti [WOERNER] and Chilton et al. [CHILTON]. The first authors extended their work later to alloys of magnesium with zinc or aluminum [CHIOTTI-1964] and found a higher solubility and hence more difficult recovery of thorium hydride in the zinc-magnesium solution than in pure magnesium. The present work was undertaken to estimate the plutonium hydride solubility in zinc-magnesium for a range of compositions.

(2) Solubility of Plutonium Hydride

The equilibrium concentration of plutonium in a liquid metal under one atmosphere of hydrogen and with solid PuH_2 as the precipitate is given by

$$\ln x_{\text{Pu}} = -\frac{1}{RT} \Delta G^\circ_{\text{PuH}_2} - \ln \gamma_{\text{Pu}} \quad (1)$$

[CHIOTTI-1964] where x_{Pu} is the mole fraction, γ_{Pu} the activity coefficient of plutonium in solution, and $\Delta G^\circ_{\text{PuH}_2}$ is the standard free energy of formation of PuH_2 .

The activity coefficient of plutonium in the zinc-magnesium system is known from experimental work by others. In pure zinc, the activity coefficient of plutonium is given by

$$\ln \gamma_{\text{Pu}} = -\frac{44700}{RT} + \frac{24.6}{R} \quad (2)$$

[JOHNSON-1964B]. In pure magnesium, the values are

$$\log \gamma_{\text{Pu}} = 1.348 - \frac{277.1}{T} \quad (3)$$

[JOHNSON-1966].

Activity coefficients in the alloy are given in graphical form in [JOHNSON-1966] and [JOHNSON-1969]. The data from all three investigations have been combined in Fig. 19 to give the activity coefficient of plutonium at 500, 600, and 800°C as a function of alloy composition. The activity coefficient has a positive deviation from linearity.

The free energy of formation of plutonium hydride is quoted by [CHIOTTI-1964] as

$$\Delta G^\circ_{\text{PuH}_2} = 2.3 RT(7.13 - \frac{8165}{T}) \quad (4)$$

By use of Eq. 1, the equilibrium concentration of plutonium in pure magnesium can be calculated to be 0.027 at 1073 K. Plutonium hydride would precipitate if initially present at concentrations greater than 2.7 at. %. Similar calculations were made for various alloy compositions at 800°C, 600°C, and 500°C. The results are plotted in Fig. 20.

(3) Process Applications

Typical plutonium concentrations in acceptor alloys are in the range, 1 to 5 at. %. In a practical process, a recovery of 75% or more of the plutonium would be desirable before recycling of the alloy. The data in Fig. 20 show that such recoveries would be possible only with alloys containing at least 75 at. % magnesium.

However, for an alloy to be acceptable for the salt transport process, it must also be a satisfactory acceptor alloy. Since a typical acceptor alloy contains a high percentage of zinc, whether a suitable hydriding alloy would also be effective as an acceptor alloy needs to be demonstrated. The salt transport effectiveness of a donor-acceptor system can be calculated by using a previously established method [KNIGHTON-1969C]. It may be shown, that after S cycles, corresponding to the circulation of a quantity Sn_sX of transport salt where n_s is molten of transport salt and X is the fraction of transport salt contacted by the acceptor alloy, the fraction, ϕ , of the

Fig. 19. Activity Coefficients of Plutonium in Liquid Zinc-Magnesium

solute initially present in the transport salt-donor system which has been transferred to the transport salt-acceptor alloy system is given by

$$\Phi = \left(1 - \frac{F_A}{1 - F}\right) (1 - F^S) \quad (5)$$

where $F = (1 - F_D) (1 - F_A)$ and F_A and F_D are the fractions of solute either transferred or backtransferred in one equilibration [KNIGHTON]. Applying this equation to a donor-acceptor system consisting of a Mg-28 at. % Zn (Mg-50 wt % Zn) acceptor alloy at 600°C and a Mg-91 wt % Cu donor alloy at 800°C, it is possible to predict the number of cycles required for uranium

Fig. 20.

Equilibrium Concentration of
Plutonium Under One Atmosphere
of Hydrogen

and plutonium transfer. As is evident in Fig. 21, after 10 cycles, >99% of the plutonium has been transferred to the acceptor alloy and 57% of the uranium has been transferred. Thus, the number of steps needed for separation using this acceptor alloy is nearly the same as for more conventional acceptor alloys. However, to achieve plutonium recovery of >99.3%, it is necessary to use ten times as much salt as acceptor alloy. If $n_s/n_a = 0.5$ where n_s is moles of transport salt and n_a is the quantity of acceptor alloy, the maximum amount of plutonium that can be transferred is only 97.07%.

The conclusion is that a magnesium-zinc alloy which is suitable for hydriding (Zn-50 wt % Mg) can also be used as an acceptor alloy in the salt transport process if (a) the ratio $n_s/n_a = 0.1$ is tolerable or (b) incomplete removal of plutonium-uranium can be accepted. In the latter scheme the plutonium would not be lost, but would be with the depleted uranium.

Fig. 21. Salt Transfer of Plutonium and Uranium, Using a Mg-50 wt % Zn Acceptor Alloy. Conditions: Mg-50 wt % Zn (or Mg-28 at. % Zn) at 600°C and Mg-91 wt % Cu at 800°C.

c. Waste Stream Analysis, Accumulation of CaO in Molten Salt
(L. J. Jardine, T. J. Gerding, and D. K. Kroeck)

(1) Introduction

Several flow sheets under development in the PDPM Program for reprocessing oxide fuels employ a reduction step utilizing calcium metal, together with a metal alloy of cadmium and either zinc or copper and a cover salt containing CaCl_2 . The current "reference" salt transport flow sheet for thorium oxide fuels (Fig. 18) is an example. The basic reduction reaction is:

where M = uranium, thorium, plutonium, fission products, etc. One of the reaction products, CaO, may be concentrated (≥ 15 mol %) in the CaCl_2 system [WENZ].

Calcium fluoride is typically added to the CaCl_2 to lower the melting point of the cover salt and to increase the wetting of the oxide fuel by the molten alloy. Also, some potassium chloride might be added to the cover salt to collect the radioiodine released during the reduction [KRUMPELT].

In the past, discard of this CaCl_2 cover salt as a solid waste when it becomes loaded with CaO has been proposed. During reduction, the alkali and alkaline earths (*i.e.*, FP-2) and probably iodine fission products also collect in the cover salt so that the salt would be classified as a "high-level" waste. The strategy of discarding this waste attracted a great deal of criticism of all pyro flow sheets developed during 1960 to 1970, primarily because the quantities of radioactive solid waste salts would be much larger than the quantities of radioactive wastes from Purex flow sheets. For example, the volume of salt waste (*i.e.*, CaO-CaCl_2) from the reduction step alone is estimated to be about 850 L/Mg of oxide fuel reduced if a cover salt loading of 30 mol % CaO in CaCl_2 salt is optimistically assumed. The high-level wastes from the Purex process, when converted to a vitrified form occupy a volume of about 70 L/Mg of oxide fuel [JARDINE-1978C]. The objective of this task is to examine concepts that would reduce the volume of wastes generated in pyro flow sheets.

The mass balances for Eq. 1 and the assumed salt loading of CaO stated above are shown in Fig. 22, Case I. There are two basic alternatives in addition to directly discarding the CaO -loaded reduction cover salt as a solid waste. These are illustrated in Fig. 22 as Cases II and III. Further details of both alternatives are next given. These alternatives reduce the volume of solid wastes.

Summarizing, Case II assumes that physical separation (*e.g.*, filtering, settling, etc.) of the CaO reduction product from the salt phase as a discrete solid phase is possible. The solid CaO waste would have a volume of about 130 L, and ideally 99% of the salt could be recycled, reducing the volume of solid wastes. Since the alkalis and alkaline earths remain in the salt phase, probably as chlorides, a small fraction of the total salt volume (*e.g.*, 1/100) must be bled off each cycle in order to accommodate additional fission products from new fuel. Thus, if the steps of Case II were achievable, the solid waste volume would be about 140 L, which is approximately one-sixth that for Case I.

Case III generates a minimal amount of waste and also reduces the raw material input (*e.g.*, calcium). The concept is based on fused salt electrolysis of CaO ; this regenerates calcium metal for recycle from the

Fig. 22. Simplified Illustration of Basic Alternatives (Cases I, II, and III) for Spent Cover Salt From Calcium Reduction of Oxidic Fuels (salt is CaCl_2). All amounts are in kilograms.

CaO , effectively removing the CaO from the salt. The oxygen originally associated with the oxidic fuels is removed as a gas (e.g., CO/CO_2), which is assumed to be scrubbed clean and released through a stack. The latter step may be compared with removing the oxygen as a bulky solid oxide (in the previous cases). A solid waste of about 8L due to salt bleed-off remains. Unproven schemes (e.g., electrolysis) to remove the alkali and alkaline earths, and thereby reduce further the volume of waste associated with the salt bleed-off step are possible and are being sought. Thus, electrolysis (Case III) has the potential of reducing the volume of waste streams from the reduction step by two orders of magnitude in comparison to previous pyrochemical flow sheet practices (Case I).

(2) Literature Review of Previous Work

In earlier laboratory-scale experiments at ANL, a two-step equilibrium phase-separation technique designed to remove CaO from reduction-step salts was examined [WEBSTER-1972A, 1972B]. The sequence of process steps is described below and summarized in Fig. 23.

Fig. 23. Conceptual Separation Scheme to Remove Solid CaO From Reduction Step Salts [WEBSTER-1972A].

The technique was based on phase changes that occur in a mixture of CaO and CaCl₂; these have been described in the phase diagram work of [WENZ]. The first step in removing CaO consists of heating above 835°C the salt containing greater than 19 mol % CaO. This produces a two-phase mixture of (a) a solid phase of CaO and (b) a liquid phase containing 18.5 mol % CaO in solution. The solid CaO phase was found to settle in several hours [WEBSTER-1972A]. Hence, after separation CaO could be discarded as a solid waste, in effect reducing the waste volume [WEBSTER-1972A].

The second step consists of cooling the residual liquid salt phase (now containing less CaO) to about 750°C. After equilibration, another two-phase mixture is produced consisting of (a) a solid phase of CaO₂·CaCl₂ and (b) a liquid salt phase containing 6.5 mol % CaO in CaCl₂. By experimentation, settling was found to be an ineffective means of separating phases, and a porous frit filtration technique was examined. A filtration experiment yielded a liquid phase containing about 8.5 mol % Ca, which is close to the expected liquid phase eutectic composition of 6.5 mol % [WEBSTER-1972B]; the modest discrepancy was attributed to equilibrium not being reached. The filtered liquid (containing about 6.5 mol % CaO) could be recycled to the reduction step where it would pick up more CaO.

The solid phase, $\text{CaO} \cdot 2\text{CaCl}_2$, presents a different problem. It could be added to freshly discharged reduction step salt for another recycle through phase separation but probably could not be discarded as a waste because this would represent a large loss of CaCl_2 . Removal of the $\text{CaO} \cdot 2\text{CaCl}_2$ phase from the filter by raising the temperature enough to liquify it was suggested [WEBSTER-1972A].

Some difficulties are inherent in this type of approach. In general, the separations of liquid from solid phases, the key steps of the process, are likely to be very difficult to carry out and would require innovative development. Reduction of waste salt volumes by factors of 3 to 4 may be achievable [WEBSTER-1972B] which is comparable to our earlier estimate of reducing waste salt volumes by a factor of 6. Further development of the equilibrium phase-separation technique has not been done because an electrochemical scheme (discussed next) appeared to have a much greater potential of reducing the volumes of waste streams.

(3) Fused Salt Electrolysis of CaO

A concept being examined is based on fused salt ($\text{CaCl}_2 \cdot \text{CaF}_2$) electrolysis of CaO . The cathode reaction generates calcium metal for recycle. If a carbon anode is used the anode reaction yields oxygen which reacts in situ with the anode material to generate CO/CO_2^* . The net electrolysis cell reaction is:

This reaction is the basis of the mass balances presented as Case III in Fig. 22. This cell reaction regenerates calcium metal for recycle to the reduction vessel; the oxygen is essentially removed from oxidic fuels not in a large volume of solid waste but as CO/CO_2^* which can be scrubbed/cleaned for release as a common gas. Hence, a large waste volume may be significantly reduced.

An electrochemical cell for operation in a furnace tube of an inert atmosphere dry box has been designed and is being constructed to examine fused salt electrolysis of CaO . The initial cell design calls for a molten metal cathode that is more dense than the fused salt electrolyte (e.g., $\text{CaCl}_2 \cdot \text{CaF}_2 \cdot \text{CaO}$). Collection of the calcium directly in an alloy may be a convenient engineering means of physically collecting the calcium metal

*The relative amounts of CO and CO_2 depend on the specific electrolyzing conditions of a cell. In this discussion, it is assumed that only CO is formed.

for recycle. A graphite anode will be used, and the anode reaction will yield CO/CO₂. Initial cell experiments with a mixture of about 2 wt % CaO in CaCl₂·15 wt % CaF₂ salt are planned.

4. U-Pu Salt Transport Processing

(J. Knighton, C. Baldwin, W. Averill, M. Boyle, J. Reynolds, T. Santa Cruz, S. Sontag, A. Younger, and J. Zoellner)*

a. Introduction

The purpose of this work package is to develop pyrochemical processes and associated hardware to coprocess uranium and plutonium contained in spent LWR and FBR reactor fuels. The primary objective is to develop a process capable of producing a proliferation-resistant product suitable for reactor use. This proliferation resistance can be accomplished by coprocessing and/or by producing fission product-contaminated plutonium. In addition, waste management of products and by-products, for both interim and ultimate disposal, will be explored.

The technical goals of this work package are (1) to develop a viable flow sheet for producing by pyrochemical means a proliferation-resistant product suitable for reactor use--by either coprocessing or producing a partially decontaminated plutonium product, (2) to identify key problems and conduct early proof-of-principle experiments on key problems that challenge the feasibility of the flow sheet, (3) to prepare a process description and design criteria for a conceptual Pyrochemical Processing Facility (PPF), (4) to prepare a conceptual design for a full-scale Pyrochemical Processing Plant, and (5) to evaluate containment of fission products and management of waste products.

b. Engineering Analysis

(1) Process Evaluation

During the last quarter of FY 1978, material balance calculations were performed for one of three pyrochemical process flow sheets under consideration--coprocessing of FBR core and axial blanket fuel by Pyroredox [ANL].

The material balance presented here should not be considered final and complete. This material balance helps (a) to provide the technical base for developing the computer model, (b) to define key problems

*Rockwell International - Rocky Flats.

that challenge the feasibility of the process, and (c) to establish volumes of process materials for determining full-scale crucible development requirements.

Process Evaluation of Coprocessing of Uranium and Plutonium from FBR Core and Axial Blanket Fuel by the Pyroredox Method. Ground rules for processing FBR

core and axial blanket fuel are: (a) uranium and plutonium from FBR core and axial blanket are coprocessed, (b) 75% of the rare earth (FP-3)* fission products are removed, (c) 25% of the FP-3 elements stay with the plutonium to enhance diversion resistance, (d) there is quantitative removal of the other fission products (FP-1, FP-2, and FP-4), (e) 99+% of the plutonium is recovered and (f) there is 95+% uranium recovery.

A preliminary material balance was made for each major process operation. From these preliminary material balance calculations, the composition and quantity of each feed and product stream was determined (Fig. 24), the process volumes were estimated, and the fission product heating associated with each process product was estimated (Table 14).

Feed to Process. One core and axial blanket subassembly for a 1000-MWe fast breeder reactor contains [AI]:

Cladding--103.3 kg Type 316 stainless steel associated with the fuel section.

Active section--mixed oxides (UO_2 , PuO_2 , and oxides of fission products) = 132.5 kg.

UO_2 (U)	115.41 kg	(101.73 kg)
PuO_2 (Pu)	12.73 kg	(11.22 kg)
O (as UO_2 and PuO_2)	15.187 kg	
O (as FPO_2)	0.675 kg	
FP	3.685 kg	

Fission product weight (kg/subassembly)

FP-1	0.498
FP-2	0.847
FP-3	0.929
FP-4	1.411
TOTAL	3.685

*For convenience, the fission product elements are divided into four groups: FP-1, FP-2, FP-3, and FP-4. Elements in each group have a similar behavior in the process. FP-1 fission products are volatile and consist of tritium, Xe, and Kr. FP-2 fission products are I, Br, Cs, Rb, Ba, Sr, Sm, Eu, Se, and Te. FP-3 fission products are the rare earth elements that form +3 chlorides--Y, La, Ce, Pr, Nd, Pm, Gd, and Tb. FP-4 fission products are refractory and noble metal elements--Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, and Sb.

Fig. 24. Conceptual Process for Coprocessing Uranium and Plutonium Oxide in One FBR Core and Axial Blanket Subassembly by Pyroredox

The fuel description is based on the ORIGEN code:
Power = 92.25 MW, Burnup = 50506 MWd, Flux = 4.17×10^{15} N/cm²·s, 30-day cooling.

Discussion during a recent visit to Rocky Flats by ANL Program Management personnel led to changes in the program effort on this program and the program concerned with the fabrication of process-size refractory metal vessels.

Table 14. Fission Product Loading and Power Densities After Coprocessing of One Reference FBR Core Fuel Subassembly by Pyroredox

PROCESS STREAM	Total Wt, kg	FP Stream	FP, kg	Volume at STP, ^a	W/kg FP	Total W	W/L
Volatiles	0.498	FP-1	0.498	87.472	23.022	11.465	0.131
Discard Zn-Cladding	516.5	-	-	70.8	-	-	-
Spent Salt from First Calcium Reduction	332.716	FP-2	0.847	144.80	805.736	682.458	4.713
Discard from FP-3 Acceptor	25.440	FP-3	0.697	4.59	3262.097	2273.682	495.355
Spent Alloy from Oxidation	1996.600	FP-4	1.411	279.432	2987.41	4215.236	15.085
Spent Salt from Second Calcium Reduction	264.933	-	-	147.39	-	-	-
Spent Salt from Third Calcium Reduction	278.449	-	-	154.910	-	-	-

^aDoes not consider recycle of process solvents.

Effort in evaluating the coprocessing of uranium and plutonium and the separation of uranium from plutonium by the Pyroredox method has been set aside in favor of coprocessing of uranium and plutonium by the salt transport method. In addition, work will begin on producing a conceptual design for a full-scale pyrochemical plant for coprocessing FBR fuel by the salt transport method.

A defensive engineering analysis will be conducted to evaluate the diversion resistance and proliferation resistance of the salt transport process. The computer program will be expanded to incorporate the ORIGEN Code being used at Rocky Flats with the HAMMER Code being used by Energy Systems Group, Canoga Park. The combined program will be used to optimize process conditions and to determine the ultimate effect of changes in process conditions on reactor neutronics. The computer program will also be used in the defensive engineering analysis to determine the effects of process changes on diversion resistance and proliferation resistance.

Greater effort will be spent in evaluating the vacuum distillation step and in examining alternatives which might make this operation unnecessary. In conjunction with the waste management engineering analysis, laboratory studies will begin immediately to evaluate methods of recycling reduction salts.

Experimental Plan. An experimental plan for the U-Pu Salt Transport Processing program, which was submitted to ANL in July, 1978, has been revised to reflect the recent program changes. The plan has been reviewed and has received approval from ANL. This plan highlights the experimental work to be done and provides a schedule for timely completion of the proposed tasks. Details will be incorporated in the revised program plan for fiscal year 1979.

(2) Literature Search

During the past quarter, the literature search was completed. Abstracts have been written on each flow sheet step including decladding, oxide reduction, FP-3 removal, salt transport, and vacuum distillation. These have been consolidated and, along with an abstract on corrosion and tables of the free energies of formation of the chlorides, oxides, and fluorides and the vapor pressures of the elements between 800 K and 1400 K, have been combined into a final topical report which has been submitted for typing.

The final topical report is not complete or comprehensive. Changes and additions will be made periodically as new information comes to light. It is hoped that this report will form the foundation of an eventual document which can be used as a handbook of pyrochemistry.

The general outline is as follows:

1. Introduction
2. Reference Spent Fuel
3. Process Operations
 - a. Decladding
 - b. Oxide Reduction
 - c. Fission Product Partitioning
 - i. FP-3 Removal
 - ii. Salt Transport
 - iii. Pyroredox
 - d. Vacuum Distillation
 - e. Fuel Refabrication

4. Summary and Future Goals
5. Supplements
 - a. Effects of Corrosion on Container Materials
 - b. Free Energies of Formation
 - i. Oxides
 - ii. Chlorides
 - iii. Fluorides
 - c. Vapor Pressures of the Elements

(3) Pyrochemical Partitioning of Metals

The ability to partition elements between a liquid alloy and a molten salt is a means of pyrochemically recovering actinides from spent nuclear reactor fuels. Once the constituents of an oxide fuel pellet are transformed to elemental form, the fission products are removed from uranium and plutonium in a liquid-liquid extraction process, using liquid alloy and molten salt as immiscible liquid phases. The chemical basis for the separation of uranium and plutonium from the fission products is the equilibrium partitioning of these elements between immiscible molten salt and metal phases. Reagents chosen for performing the partition operation are either strong oxidizing or reducing agents or are neutral in their reactivity. The large variety of alloys and salts that are liquid at desired operating temperatures (600-900°C) allows considerable latitude in choosing partitioning options.

In the transfer of a specific metal between a liquid alloy and a molten salt, the oxidation number of the metal changes. In the liquid alloy phase, its oxidation number is zero, implying the elemental state; in the molten salt phase, the oxidation number is a positive integer, implying that a salt has formed. Transfer between phases is denoted by the electrochemical reaction:

where M is the specific metal transferred and RY_r is a reagent salt of complementary oxidizing power to that of M. Y is some univalent anion. The conjugate species are the salt of the specific metal, MY_m , of oxidation number m and a metal of complementary reducing power. This equation represents an equilibrium reaction which may favor the transfer either to or from the liquid alloy. The direction of transfer is regulated by thermodynamics. If we let K be the thermodynamic equilibrium constant for Eq. 1, the value may be expressed:

$$K = \frac{A_R^{m/r} A_{MY_m}}{A_M A_{RY_r}^{m/r}} \quad (2)$$

where A_M , A_{RY_r} , A_R , and A_{MY_m} represent the activities of the species of Eq. 1. The equilibrium constant may be expressed in terms of the standard free energy changes of the reaction:

$$\begin{aligned} -RT \ln K &= \Delta G^\circ_{f,MY_m} - \frac{m}{r} \Delta G^\circ_{f,RY_r} \\ &= \Delta G, \end{aligned} \quad (3)$$

where $\Delta G^\circ_{f,MY_m}$ and $\Delta G^\circ_{f,RY_r}$ are the standard free energies of formation of MY_m and RY_r , respectively.

A distribution coefficient, D , is useful in describing the concentration of the species of interest in each phase at equilibrium by the expression:

$$D = \frac{x_{MY_m}}{x_M} \quad (4)$$

where x_{MY_m} and x_M are the mole fractions of the specific metal compound in the molten salt and the specific metal in the liquid alloy. By definition, the activity of a species, A_s , is equal to the product of the mole fraction, x_s , and the activity coefficient, α_s . Therefore, Eq. 2 may be written:

$$K = D \frac{\alpha_{MY_m}}{\alpha_M} \left(\frac{A_R}{A_{RY_r}} \right)^{m/r} \quad (5)$$

By further rearrangement, the distribution coefficient may be expressed in logarithmic form as:

$$\log D = \frac{-\Delta G}{2.3 RT} + \log \alpha_M - \frac{m}{r} \log A_R - \log \alpha_{MY_m} + \frac{m}{r} \log A_{RY_r} \quad (6)$$

This expression describes the distribution coefficient in terms of the standard free energy change, the composition of the liquid alloy, and the composition of the molten salt [JOHNSON-1964].

However, for ease in practical applications of the partitioning extractions, the distribution coefficient may also be expressed in terms of the weight percent of the solute in the phase. Let K_d express the distribution coefficient as:

$$K_d = \frac{\text{wt \% of solute metal in salt}}{\text{wt \% of solute metal in alloy}} \quad (7)$$

The transfer of a solute between immiscible liquid phases in liquid-liquid extraction is quantified by the following extraction factor relationship:

$$\lambda = K_d \frac{s}{m} F \quad (8)$$

where λ is the extraction factor which is expressed as

$$\lambda = \frac{\text{weight of solute metal in salt phase}}{\text{weight of solute metal in alloy phase}} \quad (9)$$

and s/m is the salt-to-metal alloy weight ratio; F is the fraction of equilibrium reached. The extraction factor is a function of its terms and dependent on their variability. The distribution coefficient is dependent on temperature, salt composition, and alloy composition. The salt to metal alloy ratio is dependent on the weights of salt and alloy in the feed. The fraction of equilibrium reached is dependent on the contact time of the immiscible phases and the degree of mixing in the operation.

(a) Modes of Extraction

Three modes of extraction are evaluated below: cross-current, countercurrent, and single stage [KNIGHTON-1976].

Crosscurrent Extraction. In each extraction stage of crosscurrent extraction, a fresh extractant phase contacts the phase which contains the solute to be transferred. This concept is illustrated in Fig. 25.

The expression for the fraction of the solute partitioning to the alloy phase (f_m) for crosscurrent extraction is:

$$f_m = \frac{1}{(1 + \lambda)^n} \quad (10)$$

where n is the number of contact stages in the extraction.

Fig. 25. Crosscurrent Extraction*

Countercurrent Extraction. In countercurrent extraction, the two phases flow through the extraction stages in opposite directions. This concept is illustrated in Fig. 26.

Fig. 26. Countercurrent Extraction*

The expression for the fraction of the solute partitioning to the alloy phase (f_m) in countercurrent extraction is:

$$f_m = \frac{\lambda - 1}{\lambda^{n+1} - 1} \quad (11)$$

Single-Stage Extraction. In single-stage extraction, the immiscible salt and metal phases are equilibrated in a single extraction. This is the simplest case for either the crosscurrent or countercurrent extraction modes. This concept is illustrated in Fig. 27.

The expression for the fraction of the solute partitioning to the alloy phase (f_m) in single-stage extraction is:

$$f_m = \frac{1}{1 + \lambda} \quad (12)$$

*Phase A = phase from which the solute is extracted
Phase B = phase into which the solute is extracted

Fig. 27.

Single Stage Extraction

Phase A = phase from which the solute is extracted

Phase B = phase into which the solute is extracted

Single-stage extraction is the simplest mode of implementing an extraction process.

The crosscurrent extraction mode decreases the overall amount of extractant needed to achieve the same extraction factor as the number of stages increases. However, each stage used increases the number of unit operations per extraction process.

The countercurrent extraction mode also decreases the amount of extractant phase needed to achieve a given extraction factor. This mode of extraction lends itself most readily to a continuous operation rather than a batch operation. However, in order to implement countercurrent extraction, a multistage contactor needs to be constructed of materials that are inert to the phases and solutes [PIERCE].

(b) Salt Transport

Salt transport is the purification technique whereby a metallic solute is selectively transferred from one liquid alloy (donor) to another liquid alloy (acceptor) by circulating a molten salt between the two alloys [JOHNSON-1974; KNIGHTON-1969B].

In the transfers the solute metal is first oxidized by the molten salt at the salt-donor alloy interface; subsequently, the solute metal salts are reduced by the acceptor alloy at its interface with the molten salt.

In the pyrochemical partitioning of metals, the salt transport process is used to separate the FP-3 elements from uranium and plutonium and likewise to separate uranium and plutonium from the FP-4 elements.

FP-3 Removal. A product of the oxide reduction operation is an alloy containing fission products (FP-3, FP-4), uranium, and plutonium. In FP-3 removal, the fission products (which are more easily oxidized

than uranium and plutonium are) are extracted from the liquid alloy phase into a molten salt phase. The fission products removed in this extraction are the lanthanides and yttrium.

Extraction could be by either crosscurrent or counter-current extraction. The related literature suggests the use of magnesium chloride (in the molten salt phase) as an oxidizing agent [CHIOTTI-1961, 1965, DAWSON, DWYER, JOHNSON-1964A, KNIGHTON-1976, STEUNENBERG, VOGEL-1968, 1969]. For convenience, the molten salt is usually made up of magnesium chloride and other halide salts, and the liquid alloy contains magnesium.

Once a satisfactory amount of the FP-3 has been transferred from the metal alloy to the molten salt, the molten salt is removed. The liquid alloy containing the uranium, plutonium, and the remaining fission products is then fed to the next operation. The molten salt can be reused.

FP-4 Removal. The salt transport procedure for separating uranium, plutonium, and residual FP-3 elements from FP-4 elements is illustrated in Fig. 28.

Fig. 28. Salt Transport Process

At the donor alloy uranium, plutonium, and the residual FP-3 elements are oxidized by magnesium chloride in the salt. The chlorides formed are extracted into the salt phase, and the magnesium metal reaction product is extracted into the donor alloy phase. The salt is transferred from the donor alloy to the acceptor alloy, where the chlorides of the FP-3 elements, uranium, and plutonium are reduced by magnesium. The reduced metals are extracted into the acceptor alloy, and the magnesium chloride reaction product is extracted into the salt phase.

The magnesium chloride consumed at the donor alloy is regenerated at the acceptor alloy. For the overall reaction, the salt composition remains constant, and the salt can be reused indefinitely. For each mole of uranium or plutonium transferring between the donor and acceptor alloy, 3/2 mole of magnesium chloride transfers in the reverse direction.

The FP-4 elements remain in the donor alloy because they are not oxidized by magnesium chloride.

The basis for transfer of partitioned elements between the donor alloy and acceptor alloy is the difference in their equilibrium distribution coefficients between the alloys and the salt.

(c) Pyroredox Operation

The Pyroredox process [see Section III.C.4. b(1)] is a two-step purification technique for separating uranium and plutonium from FP-4 elements. Following removal of most of the FP-3 by extraction into a salt phase, uranium, plutonium, and the residual FP-3 elements in the liquid alloy are oxidized by zinc chloride, and the resultant chlorides of uranium, plutonium, and FP-3 elements are taken up by a salt phase. The FP-4 elements remain in the zinc metal reaction product. After separation of the salt and metal phases, the chlorides in the salt phase are reduced by calcium metal. The uranium, plutonium, and FP-3 metal produced may be taken up by a solvent metal phase. The calcium chloride product of this reduction reaction is taken up by the salt phase.

The literature references to the Pyroredox technique include: [ADER, DAWSON, GIBSON, KNIGHTON-1976, LONG, REAVIS-1959, 1961, 1962].

Some notable difficulties involved with the Pyroredox operation are the highly exothermic reactions due to the use of strong oxidizing and reducing reagents and the need for a reagent that can be used to transfer magnesium.

(d) Calcium Reduction and Recycle. A literature search of calcium oxide and calcium chloride reduction methods was begun. One promising method is based on a report in which uranium dioxide was prepared by reacting calcium oxide with uranium tetrafluoride in fluoride melts [GORBUNOV]. Uranium tetrachloride should react in the same manner. This allows the use of depleted uranium tetrachloride, as shown below, to react with calcium oxide which has been separated from the main process stream:

The free energy of this reaction at 1000 K is -92.0 kcal per mole of UCl_4 reacted. The resultant uranium dioxide is insoluble in the calcium chloride

and can be separated by taking advantage of density differences. Electrolysis of calcium chloride salt produces metallic calcium and chlorine gas (a commercial metallic-calcium manufacturing method). Depleted uranium oxide can be "regenerated" to the tetrachloride form by either of the following reactions:

or

The free energies of these reactions at 1000 K are -53.4 and -52.4 kcal/mol of UO_2 reacted, respectively.

Figure 29 gives a flow sheet of several alternative calcium and halide salt recycle methods.

Fig. 29. Calcium Recovery Flow Sheet, Depicting Several Alternative Recycling Methods

The direct calcium oxide electrolysis uses consumable graphite anodes and has been demonstrated on a bench scale [THREADGILL]. During electrolysis of either the calcium oxide or the calcium chloride, strontium and samarium (two elements from the FP-2 group) should electrolyze first, allowing calcium purification and recovery by cooling the melt and removing the cathode. Controlled-potential electrolysis of the halide salts should reduce fission products (iodine, bromine, selenium, and tellurium) to their elemental states and allow separation without reducing the calcium chloride. The remaining fission products will remain in the halide salt and thus necessitate a bleed stream to prevent excessive buildup of these fission products.

(4) Vacuum Distillation

This discussion of vacuum distillation is by no means complete but is rather a cursory look at vacuum distillation.

Metals can be separated from each other and from other materials by vacuum distillation by taking advantage of differences of vapor pressure. There are two basic methods of doing vacuum distillation. The first is the static collection method, in which the volatiles are collected on a cooled surface. The condensed volatiles are removed after distillation is complete. Selection of a compatible collector material is essential to facilitate removal of the solidified material and to prevent leakage of vapor from the system. The second method is the gas sweep collection method whereby the volatiles are drawn off from the system. This technique has been employed to prevent leakage of vapor at the junction of the crucible and the reflux collector [CHILENSKAS].

Targets of high-purity metal, rare earth isotopes [KOBISK], and actinide metals [ADAIR] have been prepared by vacuum distillation. Magnesium separation from plutonium [LAWROSKI-1959, pp. 73-75] and magnesium-zinc separation from plutonium [WINSCH-1965A] as well as other separations by distillation, have been accomplished [BEEDERMAN].

The conditions for the magnesium-zinc separation from plutonium were a temperature of 660 to 700°C at 40 mm Hg. Winsch and coworkers [WINSCH-1965A] felt that the rate of distillation for their apparatus was limited by the heat-dissipating capacity of the condenser since uncondensed vapors would escape from the condenser.

In other work, plant-scale equipment was designed to separate zinc and magnesium from uranium [MILLER]. With the design used, all but 0.09 wt % (av.) of the metal vaporized was collected in the condenser.

In vacuum distillation, metals may splatter when the temperature of the system is raised above the boiling point of the alloy. To avoid excessive splattering, vacuum distillation should be conducted in two steps. During the first step, the temperature should be maintained below the

boiling point of the solution to drive off the more volatile components.' This low-temperature operation would allow the volatile components to be removed with a minimum of splattering. On the basis of experience, large changes in the temperature and pressure of the melt during the first few hours of distillation should be avoided [LENC].

(5) Corrosion Considerations

In the pyrochemical reprocessing of nuclear fuels, containment becomes a major consideration because of the extremely corrosive nature of the materials involved. A failure of the container during reprocessing operations could result in a radioactive spill that would be most difficult and expensive to rectify.

The container materials under consideration at Rockwell International-Atomics International include tungsten, molybdenum-30 wt % tungsten, and tantalum.* Special attention is directed to joining tungsten sheets by brazing to form a container. The joining materials being considered include solder-type brazes: PALCO (palladium-cobalt), PALNIRO (gold-palladium-nickel), gold, silver, PALNISIL (palladium-nickel-silver), NIORO (nickel-gold), and reactive or vanishing type brazes--niobium (once named columbium), zirconium, tantalum, platinum, boron, and iron.

Corrosion appears to occur in the presence of liquid zinc, molten halides, salts, and liquid alloys of uranium and plutonium. Reprocessing conditions include temperatures up to 850°C in an inert atmosphere. The liquid to be contained consists of two phases: a denser liquid metal phase and a supernatant molten salt phase.

Tantalum, molybdenum-30 wt % tungsten, and tungsten are being considered as materials of construction because of their high melting points and relative nobility. Any consideration of molybdenum and tungsten should recognize that the oxides spall easily.

Tantalum oxide is somewhat different. Because tantalum expands much faster during heat-up than does the oxide, the oxide film cracks and provides little protection. In one atmosphere of oxygen, tantalum can be heated to 1250°C before catastrophic oxidation occurs [ARCHER, BYALABZHEZKII, HAMPEL, LI]. Tantalum also becomes embrittled by either hydrogen or nitrogen [BARTO, HAMPEL].

Neither tungsten nor tantalum is a suitable container for pure molten uranium. Extensive dissolution of both tantalum and tungsten containers takes place at 1200°C, and the attack on tungsten at 900°C is rated as severe [VOGEL-1964A].

*The fabrication of process-size refractory metal vessels is discussed in section III.C.5. of this report.

(a) Nobility of Tantalum, Molybdenum-30 wt % Tungsten, and Tungsten with Zinc and Halide Flux

Three container materials (tantalum, molybdenum-30 wt % tungsten, and tungsten) have been tested with molten zinc and with alloy and halide fluxes duplicating reprocessing conditions. Tantalum is moderately corroded in pure molten zinc, but when the zinc is diluted to even zinc-5 wt % magnesium, tantalum shows no corrosion [DE KANY, LAWROSKI-1961A].

The containment of both molten salt flux and liquid zinc in tantalum causes additional problems. The combined system is more corrosive to tantalum than is either component alone. The resultant corrosion is rated as severe.

Drying the halide flux prior to use significantly reduces the degree of corrosion, but when calcium chloride-containing mixtures are used the rate is still approximately 0.0076 cm in 100 h. Replacing calcium chloride with lithium chloride resulted in 0.0025 cm less corrosion per 100 h to tantalum (or molybdenum) [LAWROSKI-1961B].

Molybdenum-30 wt % tungsten is reported to be more resistant to liquid zinc than is tantalum. Shafts, 3/4 in. in diameter, made of molybdenum-30 wt % tungsten have given several years of service in the zinc industry [BURMAN]. Impellers fabricated of arc-cast molybdenum-30 wt % tungsten showed a weight loss of 1% after more than 2000 h at temperatures between 910 and 1110°F, [NAIR, BURMAN].

Molybdenum-30 wt % tungsten underwent 0.05 cm of leaching while withstanding 500 h of noble metal extraction conditions (with agitation at 800 rpm) and 500 h of reduction conditions [LAWROSKI-1962B]. However, 0.01 to 0.02 cm of attack occurred when molybdenum-30 wt % tungsten was exposed to two successive extraction steps (one for 400 h and the other for 500 h) [LAWROSKI-1963A, 1963D]. Evidently, the reduction step is much more corrosive to molybdenum-30 wt % tungsten than is the noble metal extraction step.

Tungsten is more resistant to zinc than either tantalum or molybdenum. It is not attacked by liquid zinc-magnesium alloys and molten salt fluxes containing $MgCl_2$, $CaCl_2$, MgF_2 , and $ZnCl_2$ at temperatures up to 850°C [LAWROSKI-1961B, 1962C, 1963D]. In the noble metal extraction processing step, the depth of attack on tungsten after 500 h at 800°C with 460 rpm agitation was less than 0.002 cm. Results were the same for both pressed and sintered tungsten and sintered and rolled tungsten.

The modulus of rupture of pressed and sintered tungsten is 65,000 psi after 500 h of exposure to the salt-metal system of the skull reclamation process. That of sintered and rolled tungsten is 145,000 psi after the same exposure [LAWROSKI-1963D].

(b) Tantalum Crucibles

Tantalum crucibles have been used successfully to contain zinc alloys and molten salt phases [KNIGHTON-1965, 1969A, LAWROSKI-1961C, 1962A]. In one of these systems, two welded tantalum crucibles 12.7 cm in diameter by 20.3 to 30.5 cm high contained zinc-magnesium alloy and salt flux phases, including 47.5 mol % CaCl_2 , for 24 h. The result was "no apparent corrosion." However, one crucible cracked at the bottom weld during remelting, and the other withstood the remelt [LAWROSKI-1961C]. Zinc chloride was not a constituent of the molten salt in any of these tests. In a later experiment, a tantalum crucible developed cracks and holes after 100 h from attack by ZnCl_2 vapors [LAWROSKI-1962B].

(c) Tungsten Crucibles

Tungsten crucibles have been used to contain liquid zinc and molten halide fluxes [LAWROSKI-1961A, 1962A, 1962C, 1963B, BURRIS, VOGEL-1964A, 1964C, 1965A, 1965B, 1966, KNIGHTON-1969A]. Fabrication was accomplished by several alternative methods: (a) pressing and sintering, (b) shear forming or spinning, (c) plasma-spraying of free-standing shapes, (d) heliarc welding, or (e) plasma spraying on a substrate.

Pressed and Sintered Tungsten Crucibles. Tungsten crucibles have been successfully fabricated by pressing and sintering in sizes up to 35.6 cm in diameter by 60.3 cm high [VOGEL-1964A, 1965B, 1966]. Two pressed and sintered tungsten crucibles have been used in a skull reclamation process pilot plant. They were used twice a week for process operation times ranging from 8h to nearly 48 h. One crucible was used for one year and the other for six months with no visible signs of corrosion. However, the older of the two crucibles cracked during remelting of a full charge of salt and a 50 wt % magnesium-zinc alloy (which filled the crucible to about 60% of its volume). Crucible failure during remelt was explained as being due to the difference in melting points of the salt phase and the metal phase. The denser metal phase melted at 358°C, whereas the upper rigid layer of salt melted between 550 and 600°C. Stress on the crucible when the metal expanded before the salt melted caused the crack [VOGEL-1964B, 1964C].

The physical condition of the tungsten crucible after ten runs in the reduction furnace was acceptable. The inner wall was covered with an adherent, black pebbly mixture of metal and flux weighing about 2 kg. The external surface of the crucible was clean, and no damage to the crucible itself was evident. About 4 kg of condensed zinc, magnesium, and salt was on the heat shield assembly, which rested on the tungsten crucible. This quantity was judged to be slight and did not interfere with the operation of the furnace [VOGEL-1966].

Shear-Formed and Spun Crucibles. A shear-formed tungsten crucible (27.9 cm in diameter by 45.7 cm high) and a spun crucible (10.2 cm in diameter by 15.3 cm high by 0.46 cm thick) have each successfully contained liquid metal and molten salt fluxes [VOGEL-1964C, 1966].

Another spun tungsten crucible (12.7 cm in diameter by 26.7 cm high by 0.63 cm thick) has been used intermittently for three years to contain salts, plutonium, and plutonium alloys at temperatures up to 900°C. During the last three to four months, it has been used daily to contain molten zinc-magnesium alloy and molten chloride salts in an experimental pyrochemical development program. No corrosion has been apparent from this usage [KNIGHTON-1978].

Plasma-Sprayed Free-Standing Crucibles. Flame-sprayed free-standing tungsten crucibles were sintered and then used to contain liquid metal and molten salts. A report stated "no apparent corrosion" but later said the flux and metal phases did penetrate the crucible [LAWROSKI-1962A].

Later, plasma-sprayed free-standing tungsten crucibles that had not been sintered were used and failed. It was found that sintering was necessary to contain the salt-metal system [VOGEL-1964C, 1966]. The most successful plasma-sprayed crucible (10.2 cm in diameter by 15.3 cm high by 0.63 cm wall) failed after containing various zinc alloys for 1000 h. Failure was attributed to physical or thermal shock, acting on residual stresses in the crucible after fabrication [VOGEL-1966]. Plasma-sprayed tungsten crucibles might be ideal disposable containers for pyrochemical reprocessing.

Joined Tungsten Crucibles. A heliarc-welded tungsten crucible, 27 cm in diameter by 53.3 cm high by 0.23 to 0.25 cm thick with integral mixing baffles, was tested in the skull reclamation process pilot plant. It withstood process operations for one run, but in the second run it developed an irregular circumference crack extending around about one-third of the circumference of the crucible. The crack appeared in and above the lower circumferential weld [VOGEL-1964C, 1965B]. Prior investigation had shown that there was excessive grain growth and porosity in the vicinity of the weld. Cold-working did help, but the strength of the weld was still one-third the strength of the parent sintered and rolled tungsten. The resultant breaking stress of 50,000 psi was judged to be sufficient to withstand process operations [LAWROSKI-1962B, VOGEL-1964C].

No brazed tungsten crucibles have been fabricated nor exposed to process conditions. However, all types of tungsten have been successfully brazed, using alloys from the Ta-V-Nb and Ta-V-Ti ternary systems. Other brazes that were tested successfully included pure rhenium, which gave

the braze with the greatest ductility. Niobium and molybdenum failed as brazing materials for tungsten. The niobium and the molybdenum brazes were porous and developed severe cracks. Post-joining thermal treatments were used and did improve the ductility of the joints [GILLILAND]. Nibrobrazo No. 120 was used successfully to braze tungsten to 430 stainless steel [LAWROSKI-1963C]. Although no tests have been reported regarding the corrosion resistance of the alloys from the tantalum-vanadium-niobium and the tantalum-vanadium-titanium ternary systems nor of rhenium to process conditions, these brazes will probably show good corrosion resistance.

No riveted tungsten crucibles have been fabricated or tested under process conditions. Riveted tungsten crucibles would probably fail because of tungsten's notch sensitivity. The tungsten sheets would eventually break around the rivets under conditions of stress.

Tungsten-Coated Crucibles. Initially tested were substrates of molybdenum, tantalum, grade ATJ graphite, mullite, PYROCERAM 9608, and type 446 stainless steel upon which the tungsten was vapor deposited to about 0.013 cm thickness. Each of the substrates was 1.27 cm tubing or pipe except for the graphite, which was a crucible (4.92 cm in diameter by 6.35 cm high). All were coated internally and cycled between 100 and 800°C except that graphite was cycled between 170 and 800°C. Metallographic examination showed that all bonding between base material and tungsten was mechanical. However, the surface of the graphite allowed the tungsten to penetrate into pores and interstices of the graphite, giving a tenacious bond. The graphite crucible was the only sample that came through six thermal cycles with no visible change. The molybdenum substrate was rated next best; it experienced slight cracking of the coating after 3 cycles and cracking and flaking after 36 cycles [LAWROSKI-1962A].

Samples of alundum 7.6 cm square were also tested as substrates for tungsten with good results. No change in the coated samples occurred when they were cycled between 300 and 800°C. The samples had been coated by a variety of plasma-spraying techniques [LAWROSKI-1963C]. In spite of the good initial tests, no report was found of alundum being used to fabricate a test crucible.

Tungsten-Coated Graphite Crucible. The tungsten-vapor-deposited graphite crucible discussed above was partially filled with zinc-5 wt % magnesium at 700°C for 48 h, after which the alloy was allowed to freeze in place. Contraction cracks were then observed through the zinc alloy, through the tungsten coating; and through the graphite, indicating that the mechanical bond between the tungsten and the graphite was at least as strong as the grade ATJ graphite [LAWROSKI-1962A].

A three-inch-square coupon of type CS graphite, coated with 0.025 cm of plasma-sprayed tungsten, showed no corrosion when thermal cycled between 300 and 800°C [LAWROSKI-1963C].

Tungsten-Plasma-Sprayed Stainless Steel Crucible.

A test-size (26.7 cm in diameter, 53.3 cm high and 0.32 cm thick) crucible was fabricated of type 430 stainless steel, sprayed with an intermediate nickel-chromium-boron layer (Nicrobraz No. 120), and then sprayed with 0.076 to 0.089 cm of tungsten. Tungsten particles smaller than 12 μ m in diameter were employed for the plasma spraying. The coated crucible was sintered in hydrogen at 1150°C for 10 h by the vendor. During the sintering, the intermediate layer diffused both into the substrate and into the tungsten. The crucible withstood four thermal cycles between 300 and 900°C and four cycles between room temperature and 900°C; there was slight spotting on the bottom of the stainless steel crucible which was attributed to a small amount of oxygen in the argon atmosphere. Then a charge of 50 wt % magnesium-zinc alloy was thermal-cycled in the crucible, but the tungsten coating cracked and peeled [VOGEL-1964A, VOGEL-1964B]. Stainless steel had been considered a desirable substrate for a process crucible because of stainless steel's resistance to $ZnCl_2$ vapors.

Prior research had shown the method of applying the plasma coating to be important. When tungsten was plasma-sprayed onto a stainless steel coupon and thermal cycled, the coating cracked at the corners of the coupon. When intermediate layers of molybdenum and tantalum, respectively, were applied prior to tungsten coating and then thermal-cycled, the coating separated. Besides the Nicrobraz No. 120 method mentioned above, use of another method of applying tungsten coating to stainless steel resulted in no corrosion to the crucible when it was thermal-cycled. This method involved applying the coating in eight graded layers--the first layer being 100% stainless steel and the final layer being 100% tungsten. The intermediate layers were appropriate proportions of the two [LAWROSKI-1963C].

Tungsten-Plasma-Sprayed Silicon Carbide Crucibles.

A test-size (26.7 cm in diameter, 38.1 cm high, and 1.6 cm thick) crucible fabricated of silicon carbide was sprayed with 0.076 to 0.089 cm of tungsten. The coated silicon carbide crucible was sintered in argon at 1150°C for 10 h.

This crucible, like the stainless steel crucible, withstood four thermal cycles between 300 and 900°C and four cycles between room temperature and 900°C. There was a slight reddish-brown cast to the tungsten coating, attributed to slight surface oxidation of the tungsten by oxygen or water contaminants in the argon atmosphere. The silicon carbide crucible was used to contain several zinc-magnesium liquid alloys and a charge of molten salt flux, and no deleterious effect on the tungsten coating was apparent.

After the silicon carbide crucible had rested on a shelf for one week after use, the tungsten coating cracked horizontally (about half way up the wall of the crucible). The crack was attributed to (1) penetration of salt flux into pores of the crucible (which indicated imperfections

in the tungsten coating) and (2) subsequent expansion of the salt as it absorbed water from the room-temperature air [VOGEL-1964A, 1964B].

The report did not specify which form of silicon carbide was used as the crucible substrate. Prior investigations had shown both the nitride-bonded and the oxide-bonded silicon carbides to be good substrates for tungsten plasma-sprayed in a variety of atmospheres [LAWROSKI-1963C].

(d) Molybdenum-30 wt % Tungsten Crucibles

No molybdenum-30 wt % tungsten crucibles have been fabricated or tested. When this alloy was used in other forms with liquid zinc and molten halide fluxes, there has been considerable molybdenum leaching and a resultant loss of strength. However, this alloy probably is still sufficiently noble to be used as the material for a limited-life crucible.

(e) Metals Tested for Reprocessing Conditions

Pure molybdenum shows gross intergranular corrosion upon contact with liquid zinc for 100 h and completely disintegrates upon contact with zinc for 300 h [LAWROSKI-1961A]. It would not be a suitable material for even a limited-life crucible.

Titanium, Thermenol, Haynes No. 25 alloy, Haynes Multimet alloy, Haynes Stellite alloy No. 6B, nitrided steel, cyanided steel, Colmonoy 6 spray-coated on mild carbon steel, vitallium, and Armour Research Foundation tungsten alloys No. 98, No. 97, No. 95, and No. 90 all disintegrate completely after 100-h contact with liquid zinc at 750°C. Under the same conditions when in contact with zinc-46 wt % magnesium, all of these metals suffered severe corrosion [DE KANY].

Tantalum-7.5% tungsten showed less than 0.001 cm of corrosion after 300 h in contact with zinc at 850°C and under the same conditions with various zinc-magnesium alloys showed no corrosion. Tantalum-7.5% tungsten showed better corrosion resistance to zinc than did tantalum [LAWROSKI-1961A].

(f) Transfer Tubes and Agitator Blades

Transfer tubes must be fabricated of a material that is resistant to molten halide salts and liquid metals. They must be available in lengths suitable for equipment. Tungsten appears to be the material that is most resistant to the molten halide salts and liquid metals. However, tungsten has low impact strength or notch sensitivity. When it is used as a shaft, it will break where it is pinned to another shaft or to the agitator [LAWROSKI-1962A]. In addition, it is difficult to machine.

For these reasons, tungsten was rejected as a material for transfer tubes and agitator blades in favor of the material with the next best resistance to process conditions, molybdenum-30 wt % tungsten. Molybdenum-30 wt % tungsten is more machinable and has greater impact strength [GROSVENOR].

A molybdenum-30 wt % tungsten crucible and agitator was used in two successive noble metal extraction runs (one of 400 h and the other of 500 h), at 460 rpm. The molybdenum-30 wt % tungsten agitator showed a 3.8% weight loss (equivalent to 5% of the molybdenum content), which was attributed to molybdenum leaching. Under the same conditions, a tungsten-iron-nickel agitator section disintegrated. Rolled tungsten and sintered tungsten agitator sections showed negligible corrosion [LAWROSKI-1962C].

An agitator and a shaft of molybdenum-30 wt % tungsten were exposed to oxide-reduction conditions for another 500 h at 525 rpm. (The oxide reduction conditions were previously shown to be the more corrosive conditions for this alloy and were used first.) Abrasion between the alloyed shaft and the tungsten crucible cover evidently caused the shaft to break partway through the following 500-h noble metal extraction run, leaving the agitator immobile for part of the time under the less corrosive conditions. An inspection of the system after oxide reduction showed pitting corrosion on both the shaft and the agitator blade, with more pitting (up to 0.051 cm) on the agitator blade. Inspection after operation at noble metal extraction conditions for 500 h showed no additional corrosion of the shaft or the agitator blade [LAWROSKI-1962C].

(g) Summary

Tungsten appears to be the only one of the three metals researched (tungsten, molybdenum-30 wt % tungsten, and tantalum) having enough corrosion resistance for use as a container. Molybdenum-30 wt % tungsten is subject to pitting and molybdenum leaching by liquid zinc and molten halide flux--especially those specified for oxide reduction operations. With 0.051 cm pitting experienced in 1000 h (equivalent to 100 full-scale runs), molybdenum-30 wt % tungsten appears to be usable as auxiliary equipment (such as agitator blades, shafts, and transfer tubes) or as a limited-life crucible. In view of the low resistance of tantalum to zinc chloride and mixed salts, it does not appear to have enough corrosion resistance to be used for either the container or the auxiliary hardware.

Tungsten possesses excellent corrosion resistance to reprocessing conditions, but it is difficult to machine and has low impact resistance. These problems have discouraged the use of tungsten for auxiliary equipment and have led to the use of a variety of methods of crucible fabrication.

Pressed and sintered tungsten crucibles have the best performance record. These crucibles have been fabricated in the largest sizes and have been the most extensively tested under process conditions. The only

pressed and sintered crucible to fail cracked when a charge of salt and metal was allowed to freeze and then remelted in the crucible. The failure was attributed to a stress in the bottom of the crucible where the denser metal melted first and expanded beneath a rigid salt layer.

Spun and shear-formed tungsten crucibles have a perfect record of absence of corrosion but have not been fabricated in as large a size as pressed and sintered crucibles nor used as extensively under processing conditions. The limitation on the size that can be made is the only drawback to these crucibles.

Much easier crucible fabrication than by pressing or spinning can be achieved by the use of plasma-spraying, vapor-deposition, welding, and brazing techniques. Crucibles tested under process conditions include crucibles prepared by plasma spraying and welding. Also, one very small graphite crucible was prepared by coating it with tungsten by vapor deposition. This crucible was successfully tested, but vapor deposition was new at the time and this crucible was not followed by other crucibles.

Brazed tungsten crucibles have not been fabricated or exposed to process conditions. Initial investigations indicate that Ta-V-Nb and Ta-V-Ti ternary system brazes and rhenium brazes might be successful and that molybdenum brazes and niobium brazes might fail.

A heliarc-welded tungsten crucible has been fabricated by cold working; it was used under process conditions for one run and a portion of another before it cracked in the vicinity of the weld. The weld had one-third the strength of the parent sintered and rolled tungsten and was characterized by grain growth and porosity.

Plasma-sprayed free-standing tungsten crucibles have contained process materials for up to 1000 h before failing. Plasma spraying on a substrate gives better strength to the crucible, but a substrate should be selected having a coefficient of thermal expansion similar to that of tungsten to achieve a good fit over the range of processing temperatures; also, the surface of the substrate should be porous to achieve a good bond between the substrate and the coating. The substrate should have some resistance to process conditions because of the possibility of failure of the tungsten coating. Investigations indicate that silicon carbide, graphite, and aluminum may be usable as substrates, and that Pyrocera 9608, stainless steel, mullite, tantalum, and molybdenum may be unsuitable. A plasma-sprayed coating on a free-standing crucible is 92% of theoretical density, and problems with these crucibles have been related to their porosity.

Investigation of brazing and vapor deposition techniques should yield a more easily fabricated permanent crucible. Plasma-sprayed free-standing crucibles may be used as limited-life crucibles.

Other metals that have been investigated have had inadequate resistance to zinc. These include titanium, Therminol, Haynes No. 25 alloy, Haynes Multimet alloy, Haynes Stellite alloy No. 6B, nitrided steel, cyanided steel, Colmonoy 6 spray-coated on mild carbon steel, vitalium, and Armour Research Foundation tungsten alloys No. 98, No. 97, No. 95, and No. 90. Tantalum-7.5% tungsten withstands pure zinc but has not been tested further.

(6) Computer Modeling of Selected Flow Sheets

A computer program being constructed for use in modeling selected pyrochemical flow sheets is near completion. The program will be used to calculate mass balances around each step in the flow sheet. Ultimately, an upgraded version of the program will be interfaced with the ORIGEN code to produce a tool which will optimize process conditions and minimize process operations.

The overall flow sheet for the codified program is shown in Fig. 30.

The decladding calculations are performed in subroutine "DECLAD." This algorithm (calculational procedure) is based on the manual calculations used to determine zinc requirements for decladding. The calculations determine total cladding of the subassembly from input data on the dimensions of the assembly; from this, the amount of zinc needed is calculated.

The reduction mass balances algorithm is also based upon the manual calculations used to generate the material balances shown in previous monthly reports. This procedure is carried out in a subroutine similar to the decladding calculations. The subroutine used to calculate the reduction material balance is "REDUCT." This subprogram calculates the total amount of calcium, copper, magnesium, and cover salt needed for reduction and to produce the transport donor alloy of proper composition.

The following stages of calculations are performed step by step and in the same order that transport occurs. The calculational procedure for each stage starts by initializing the variables involved in the calculations and calling a subroutine designated "TRANS" which computes the amount of each component transferred to the salt.

"TRANS" accomplishes equilibrium mass balances based on a recursive iterative procedure:

$$\text{Total } A_{i,j} = \sum \bar{E}_k \text{ (to equilibrium)} \quad (16)$$

where $A_{i,j}$ is the variable associated with the number of kilograms of the i^{th} species in the j^{th} phase. Based on the criteria for equilibrium:

$$K_{d_{i,j}} = \frac{\text{wt \% } A_i \text{ (acceptor phase)}}{\text{wt \% } A_i \text{ (donor phase)}} \quad (\text{an equilibrium quantity}) \quad (17)$$

Fig. 30. Outline of Computer Program for Modeling Flow Sheets

(CONTD.)

where the i and j refer to species and phase, respectively. This summation is repeated for each component being transferred until equilibrium is approached, at which time the step size, ϵ_i , is reduced successively until the difference between the calculated temporary K_d and the true K_d is less than 1×10^{-6} . At this point, the entire sequence is repeated until the required number of passes for this particular stage are performed.

This subroutine is self-contained and need only have the acceptor and donor phases specified and the general input data for the distribution and stoichiometry coefficients specified.

The subroutine has been tested and has worked on part of a previously hand-calculated system. The next stage of development involves testing it on a multipass problem.

Once the transport computations have been completed, a printout of mass balances around each step of the operation will be provided.

Work remaining on the program consists of completion of the input-output subroutines for the acquisition, generation of input data for the unit operation in salt transport processing, and for the satisfactory display of the results of the mass balance calculation. The calculations produce data of a complex nature--both with regard to the final mass balance on products and with respect to the stage-wise intermediate mass balances.

Additionally, an optimization routine has been found that will allow employment of the mass balance program in an objective function for an optimum-seeking algorithm. The flow chart for this optimization routine is shown in Fig. 31. Refinement of this program will be necessary, once the two large routines are combined.

(a) ORIGEN Code

The ORIGEN computer code is being used to estimate the fission product content of spent FBR fuel assemblies with 100,000-MWd burn-up. The results will be used in the material balance calculations since it is felt that 100,000 MWd is a more realistic burn-up for a commercial FBR reactor than the 50,600 MWd which was used in preliminary material balance calculations.

(b) Fission Product Partitioning

Discussions were held with on-site analytical lab people about the applicable techniques for assaying fission products in metals and salts from the salt transport process. Many techniques (spark source, atomic absorption, and plasma emission spectrometry, X-ray fluorescence, tracers, neutron activation, and others) were discussed.

Fig. 31. Hooke and Jeeves Algorithm Logic Diagram

The most applicable for the wide element range is spark source spectrometry, although back-up methods to resolve interferences will be necessary. Further discussions with Rocky Flats personnel and other PDPM contractors are planned.

(c) Development of Training Video Tapes for PDPM Personnel

A series of audio-visual tapes are being produced at Rocky Flats. The final product will be a set of tapes dealing with the theoretical background of the PDPM effort. These will serve to teach new personnel, operators, and researchers the fundamentals surrounding pyrochemistry.

The series of video tapes being produced for the PDPM program pertains to four topics: phase diagrams, furnace and process control, separation processes, and pyrometallurgy. The outline of the phase diagram presentation follows:

I. Phase Diagrams

A. Fundamentals

1. Concept of Equilibrium

- a. Physical demonstration
- b. Chemical equilibrium illustration

2. Concept of phase

- a. Physical demonstration
- b. Illustration of a single one-component phase diagram and its use and construction
- c. Illustration and application of the Phase Rule

B. Two-Component Phase Diagram (isomorphous, ideal)

- 1. Discussion of the two-phase region from a physical standpoint
- 2. Illustration of the energy drive for the two-phase region
- 3. Illustration of the physical result of solidification in the two-component, ideal, isomorphous system
- 4. Demonstration and use of the Lever Rule
- 5. Significance of the two-phase region
- 6. Use of the two-phase region in PDPM application
- 7. The miscibility gap

C. Two-Component Systems (non-ideal and invariant reactions)

- 1. Application of the Phase Rule in the two-component system
- 2. Positive and negative deviation from ideality in isomorphous systems
- 3. Formation of the eutectic invariant system by overlap of negative deviation from ideality and a miscibility gap in the solid phases

4. Expansion of the eutectic concept to eutectic-like systems:
 - a. Eutectic
 - b. Monotectic
 - c. Metatectic
5. Evolution of the peritectic invariant system by overlap of ideal two-phase development and miscibility gaps in the solid phases
6. Evolution of a peritectic-like syntectic by the overlap of a positive deviation from ideality development and a miscibility gap in the liquid phases
7. Illustration of the combination of invariant reactions in a realistic phase diagram
 - a. Cooling reactions involving solid-liquid and solid phase transformation reactions
 - i. hypoeutectic, hypoperitectic
 - ii. hypereutectic, hypoperitectic
 - iii. hypereutectic, hyperperitectic
 - b. Use of temperature-time cooling curves to establish the phase boundaries in a complex phase diagram
 - c. PDPM applications
- D. Three-Component (Ternary) System and Direct Applications
 1. Construction of a ternary diagram
 2. Removal of temperature as a two-dimensional variable (phase rule)
 3. Ideal and non-ideal construction and projections into the ternary system
 4. Invariant reaction projections into the ternary system
 5. Composition shifts in ternary systems
 6. Application to salt systems
 7. Discussion of specific binary systems (Cu-Mg, Zn-Mg, $\text{CaCl}_2\text{-KCl}$, $\text{CaCl}_2\text{-CaF}_2$, MgCl-MgF_2)
 8. Discussion of specific ternary systems ($\text{CaCl}_2\text{-KCl-CaF}_2$, $\text{CaCl}_2\text{-KCl-ZnCl}_2$)

The first audio-video training type, titled "Phase Equilibria," has been completed. A preview will be held with Rocky Flats PDPM and pyrochemical personnel prior to final editing. A copy of the final, edited tape will be presented to ANL for distribution.

Taping on the other topics will be delayed until extensive work on the computer program for the salt transport process has been completed.

(7) Cu-Mg-U Ternary Phase Diagram

A contract has been let to the Colorado School of Mines, Metallurgical Engineering Department, to develop a ternary diagram of the uranium-copper-magnesium system for the temperature range between 500 and 900°C. The investigation will be conducted by Dr. David Olson, Professor of Metallurgical Engineering, and Dr. William Averill, Assistant Professor of Metallurgical Engineering, Colorado School of Mines, Golden, Colorado.

During the investigation, a determination will first be made of the solid phases which are in equilibrium with the melt over the temperature range of 500 to 900°C. This will be accomplished by study of the microstructure and by analysis of these solid phases, using both X-ray diffraction and scanning electron microscopy (SEM). Next, the liquidus profile, with respect to temperature over the entire temperature range of the entire ternary system, will be determined. Last, the solidus profile will be determined for this system. Emphasis will be placed on the copper-rich region from about 50 wt % magnesium and from about 5 wt % uranium. The copper-rich region will be determined first in order to provide data of immediate application to flow sheet evaluation in the PDPM program.

Reagents are presently on order. Equipment, including gloveboxes and furnaces, is being prepared to begin the experimental studies.

(8) Reports

During the quarter, J. B. Knighton wrote and submitted a document entitled "Pyrochemical Processing Of LWR and LMFBR Fuels" for publication in Radiochimica Acta.

c. Separations Process

(1) Salt Purification Laboratory

Title II Engineering review for the Salt Purification Laboratory was held July 26, 1978. Input from this review was entered in the final engineering package. The engineering package was turned over to maintenance personnel on August 23, 1978. The expected completion date is now September 30, 1978.

All items on hand have been installed in the Salt Purification Laboratory. Still to be received are a sink top and a vacuum pump.

An experimental plan prepared for the Salt Purification Laboratory describes the establishment and proposed use of the laboratory and the expected time for completion of specific tasks.

Operational safety analyses and procedures will be drafted for the Salt Laboratory in conjunction with the installation of equipment.

At a recent briefing at Rocky Flats in August by the ANL PDPM representatives, an adequate equipment inventory system was requested. In compliance with this request, blank equipment inventory tags have been obtained and will be used to identify all items costing \$300 or more. A typical tag will contain the following information:

ANL-D-3-001

where ANL = Argonne National Laboratory

D = PDPM Activity Number

3 = Salt Purification Laboratory

001 = Item Number

A form (Fig. 32) has been prepared for use in conjunction with the tagged equipment. The form will list both of the property numbers, an equipment description, location, original cost, the user, and the date of procurement.

(2) Proof-of-Principle Experiments

Proof-of-principle experiments will be conducted to investigate the key problems that challenge the feasibility of uranium-plutonium salt transport processing. Modification of equipment for use in this work is under way.

Furnace covers for two stationary furnaces have been modified. The new covers have been provided with ports for taking samples of molten salts and metals and have been fitted with thermocouple wells. The samples will be taken using porous tantalum frits as described in an earlier report [WINSCH-1965B]. The stationary furnace glovebox area must be equipped with both a vacuum line and an argon supply line to provide an inert atmosphere or a vacuum to the sample tube and fixture. A design package has been completed and submitted to Engineering personnel for approval. The package will contain a short description of the modifications, design drawings, location, intended use, and construction notes. Upon approval, maintenance personnel will proceed with the modifications.

RFP # - DPA - 0035 -076047
 PDPM # - ANL - D3 - 002
 Name of Item: Precision Rotator, Pine ASR2-149

 Location of Item: Bldg. 779, Room 131

 Original Cost: \$1,550

 Responsible User: T. D. Santa Cruz

 Date: 15 September 78

Fig. 32. Equipment Inventory Form

Graphite liners are being fabricated to support the small magnesium oxide crucibles to be used for experiments in the stationary furnaces. The liners are expected to be completed very soon.

Drawings of modifications of the well for the dual-axis tilt-pour furnace have been completed. The furnace well will be provided with a flange, allowing it to be easily removed in the event of failure. An engineering package is being prepared for review and approval by Facilities Engineering and Construction personnel.

The lid for a dual-axis tilt-pour furnace has been sent to the R&D machine shop for modification which will provide it with features similar to those of the stationary furnaces.

The design work on the calibration unit (goniometer) for the tilt-pour crucibles is two-thirds complete. The goniometer will be used with the newly designed tilt-pour crucibles to determine the tilt angle needed to effect reasonably clean decantation of the salt phase from the alloy phase.

The OSA (Operational Safety Analysis) has been written for the stationary furnaces and has been submitted for approval. The OSA for the tilt-pour furnace will soon be drafted.

Auxiliary equipment for the semi-works experimental studies/engineering development operations has been ordered. The equipment includes high-frequency induction power systems for high-temperature furnaces, controllers, recorders, and material for crucibles. Other equipment on order for the proof-of-principle work includes thermocouples, tantalum frits and tubing for sampling, tantalum sheet for the construction of crucibles, and ceramic crucibles.

Key personnel are being trained to familiarize them with glovebox operations and with the handling and control of nuclear materials preparatory to beginning the proof-of-principle experimental studies.

5. Fabrication of Process-Size Refractory Metal Vessels

(C. Edstrom,* C. Baldwin,* R. Corle,* L. Johnson,* and A. Phillips)*

a. Introduction

Pyrochemical processing of nuclear fuels requires crucibles, stirrers, and transfer tubing that will withstand both the operating temperatures and the chemical attack from molten salts and metals used in the process. The ability to fabricate the necessary hardware is critical to pyrochemical processing. For economics and safety in the pyrochemical process, a crucible large enough to contain the entire fuel rod is needed. Tungsten, a material known to withstand the temperature and chemical attack, is presently not available in sheet sizes large enough to provide the desired surface area of large crucibles. This indicates that joining, coating, and/or forming processes should be developed to make it possible to achieve the desired shape and size.†

b. Engineering Analysis

The topical report summarizing the literature search on tungsten fabrication is being typed in final form. This report summarizes the literature data on tungsten joining, chemical vapor deposition, and fabrication. Tungsten is the main subject; however, the report also summarizes literature on molybdenum and the work performed at Argonne National Laboratory on other crucible materials for pyrochemical processing of nuclear materials.

Discussions with several tungsten suppliers provided helpful information on the fabrication of PDPM hardware.

The method of producing a crucible, suggested by Fred Bydash of Schwarzkopf Development Corporation (the U.S. representative for Metallwerk

*Rockwell International-Rocky Flats.

†See also section III.C.4.b.(5) of this report.

Plansee), is riveting and then sealing the joints by plasma spraying. Metallwerk Plansee has had greater success with riveted tungsten crucibles than with welded crucibles. Welded crucibles tend to crack at the nonductile weld upon cooling due to concentration of thermal contraction stress at the joint. In a riveted crucible also, the stress concentrates in the joint, but the rivets accept the movement without failure. The riveted crucibles sounded very acceptable until it was found that water seeps through plasma-sprayed joints due to the porosity of the coating.

Several alternatives to riveted crucibles exist. One alternative is electron beam welding of the joints to make the seal. Then rivets are used for joint strength. Another alternative is to coat the riveted crucible with a chemical vapor deposited (CVD) coating. CVD provides coatings with nearly 100% of theoretical density. A final alternative is to improve the density of the plasma spray coating with a nickel nitrate substrate. This leaves 0.1 wt % nickel as an alloy with tungsten after sintering at approximately 1200°C and yields a density of 97% of theoretical [TAYLOR].

For transfer tubing, Metallwerk Plansee can provide 30.5 cm-long tungsten tube by drilling solid rod. However, Mr. Bydash suggests that diffusion-bonding of tungsten foil to molybdenum tubing be tried. The advantage here is that molybdenum is available in 610-cm lengths and is easier to machine than tungsten.

Molybdenum-30% tungsten tubes are available from Thermo-Electron in 2.5-cm-diameter by 305-cm length. These tubes are produced by gun drilling.

In a discussion of molten-metal pumps with Richard Shandler of The Carborundum Co., the following information was obtained:

- (a) The molten metal pumps made by Carborundum consist of a graphite body, a molybdenum-30% tungsten shaft, and a graphite impeller.
- (b) A pump constructed entirely of molybdenum-30% tungsten alloy was once made, but it cost \$15,000. The advantages of the pump did not offset its high cost, and such a pump was never produced for sale.
- (c) The Carborundum Co. coats some graphite pumps with silicon carbide to protect the graphite from oxidation in the presence of molten aluminum. This coating has a high density and may be adequate to prevent the reaction of uranium and plutonium with carbon.

The scope of work has been changed recently to direct more effort into evaluating materials other than tungsten and produce either a "long life" or a "limited life" crucible. This work is being coordinated with similar efforts at ANL (Section III.C.1. of this report).

One alternative material being considered is tungsten or tantalum coated with chromium oxide. The chromium oxide fills pores in the metal and leaves a surface which is not wet by many molten metals and salts. Applications of the technique include improving the density of plasma-sprayed tungsten or coating other materials which are not compatible with the molten metals and salts.

Coating of individual particles of tungsten powder with chromium oxide prior to pressing and sintering should improve the as-sintered density and may improve ductility. A ductility improvement is expected because the coating should isolate the particle and establish a permanent fine grain size.

Other surface densification projects will soon be under way such as an investigation of a ceramic. One shortcoming of ceramic crucibles has been their brittleness. Under-fired ceramic crucibles have improved ductility but greater porosity. To prevent leaks in an under-fired ceramic crucible, we propose coating the inside surface. One coating we plan to evaluate is silico-tungstic acid ($\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 26\text{H}_2\text{O}$). Coating of alumina discs with this acid followed by thermal drying will leave tungsten-silica in the pores at the alumina surface. These discs will then be tested to evaluate the integrity of the coating.

c. Separation Processes

Three tungsten blanks supplied by AMAX and two blanks supplied by GTE Sylvania have been drawn. Three blanks were formed through three drawing operations, making 12.7-cm-ID by 12.7-cm-high cups. Only minor defects were present in the three cups. Another blank (supplied by GTE Sylvania) cracked in the final draw operation due to a stress riser having been left on the inside lip during the second draw. A fifth blank (supplied by AMAX) cracked prior to the second draw during chamfering of the cup edges by rotary grinding. This failure apparently was a result of excess residual stress left in the drawn part.

The best procedure found for drawing tungsten starts with coating the blank with glass (Graphite Products LS1482 plus Dow Corning 9772) and heating it to 1125-1175°C in an argon atmosphere. The draw dies are heated to approximately 800°C and the punches to approximately 700°C. A wafer of fiberglass and asbestos soaked in "Dag" is placed on the top and bottom of each blank. (This wafer helps insulate the hot tungsten blank from the cooler tools and provides some lubrication.) After drawing, each blank is stress-relieved by heating to 1175-1200°C, soaking for 1 h at this temperature, and slow-cooling in the furnace at 50°C per hour.

There are several benefits of this revised drawing procedure. First, the glass lubricant on the blank reduces the amount of oxide formed. Second, the new stress-relieving operation (controlled cooldown in the furnace) appears to be important. When the former cooldown procedure of placing the hot tungsten in brick dust was followed with two blanks, they cracked.

During the visit of Messrs. Myles, Vogler, and Geller to Rocky Flats in August, a spinning pass was made on a drawn tungsten cup. This pass is the first in a series of four to make a 12.7-cm-ID by 26.7-cm-high crucible. The operation went smoothly and everything looked good until recovery of the part from the brick dust, when two longitudinal cracks were found (Fig. 33). We believe that this crack developed during cooldown in the brick dust since no one observed it develop during spinning.

Fig. 33. Drawn Tungsten Cup Spun August 8, 1978.
NOTE: Spinning contact begins at base
of crack.

A molybdenum sheet of 40-mil thickness has been shipped to Electro-Fusion Company, San Francisco, California, for welding to form a crucible. The design of the welded joints on this crucible provides for

maximum flexibility during heat-up and cooldown to help protect the brittle weld. Figure 34 shows the design.

Fig. 34. Design of Crucible to be Fabricated from Molybdenum Sheet.

From this same sheet of molybdenum, a 12.7-cm-ID cup was drawn out of a 14.9-cm-dia blank. The draw temperature was 400°C. This cup serves as the bottom of the crucible and was drawn to test the tooling. This tooling is to be used to make tungsten cups as bottoms of brazed tungsten crucibles to be made at Rocky Flats.

Linde Division of Union Carbide is plasma-spraying two tungsten crucibles. When these crucibles are received in October, they will be coated with nickel nitrate and sintered. The plasma-spray process is capable of producing full-size crucibles. Of concern is whether or not the plasma-sprayed layer will be dense enough to provide a leak-proof vessel. Sintering of the nickel nitrate should increase the density to 97% of theoretical. Hopefully, the low concentration of nickel in the coating will not present a corrosion problem. Whether it does will be learned in service life tests.

Two sintered tungsten crucibles are on order and are due on September 28, 1978. One crucible will be electrochemically machined to reduce the wall thickness from 1.27 cm to 0.64 cm or less. This will lighten the

crucible and make it possible to determine if a "thin-walled" sintered crucible will leak. CVD coating of the "thin-walled" sintered crucible is also being considered.

Two molybdenum crucibles to be coated with chemical vapor deposited (CVD) tungsten are on order. One crucible will be coated with the new, low-temperature, fine-grained tungsten. The other will be coated by the standard method. This will allow the merits of each method to be examined by service life testing. We chose to coat molybdenum because the technology is on hand for making a large molybdenum crucible. It is doubtful that graphite is available having the proper thermal coefficient of expansion for tungsten in the size required for a 0.28 m^3 (10 ft^3) crucible.

Four 1.27-cm-thick molybdenum blanks have been received. These will be drawn and spun into 12.7-cm-ID by 26.7-cm-high crucibles. These four crucibles will be used to examine CVD coating, to evaluate promising ceramic coatings, and to determine the life of molybdenum as a "limited-life" crucible.

Samples of tungsten sheet brazed with NIORO (82% gold-18% nickel) at 1000°C have been coated with plasma-sprayed tungsten. Testing of these samples for compatibility with copper-magnesium and calcium chloride began in late September.

6. Chloride Volatility Processing of Thorium-Based Fuels (R. L. Bennett)*

a. Introduction

The objective of this research and development is to determine the feasibility of a chloride volatility coprocess for recovering irradiated thorium-based fuels. Prior work has been evaluated to obtain data and information about the current status of technology. This data and information is being organized in a block diagram of the chloride volatility process.

A report has been prepared which describes the existing data and information and the conceptual block diagram. The report is organized to permit evaluation of the technical feasibility, safety, and nonproliferation attributes of the chloride volatility process. Tests are being conducted with simulated fuel to establish technical feasibility and to provide bases for cost estimates.

*Babcock and Wilcox.

b. Engineering Analysis

(1) Work Accomplished during this Report Period

All earlier chloride volatility work had the conventional objective of producing decontaminated, separated fertile and fissile materials. It has been difficult to achieve separation of thorium from uranium and decontamination from fission products. Today's objective is almost the opposite and may be easier to achieve. We believe this makes the chloride volatility coprocess an extremely attractive method for reprocessing spent fuels.

Draft copies of the topical report on chloride volatility processing were submitted to ANL during the second week of August. This milestone culminates a review, collation, and evaluation of a surprisingly and gratifyingly abundant literature trove.

In general, the physical, chemical and thermodynamic data determined by various investigators of the chloride volatility process are in agreement. Some inconsistency has been seen, but a lack of data presents a greater problem. Heat of formation data at any temperature other than 298 K are unusual. Data for heat of fusion, heat of vaporization, and boiling point must be determined by experimentation in this work package. Still to be resolved are inconsistencies in vapor pressure data in the ranges of temperature used in the chloride volatility coprocess.

Identifying satisfactory materials of construction presents the greatest challenge to establishing the feasibility of the chloride volatility coprocess. Combination of high temperature with extremely aggressive reagents presents a formidable problem. Materials development and testing must be an integral part of this work.

Decladding is the only step in the process which has been demonstrated at commercial scale. Chlorination and fuel dechlorination have been tested only at a bench scale, and there has been very little experimentation with radioactive compounds. The remaining process steps--refabrication, ash oxidation, ash solidification, and off-gas treatment--have been developed for similar processes, but their feasibility in this application needs to be demonstrated.

Kinetic data are largely missing for hydrochlorination, chlorination, and dechlorination reactions. The behavior of thorium and the fission products is only partially described in the literature. A better understanding of the behavior of these materials is needed to conclusively demonstrate the feasibility of the chloride volatility process.

The Babcock and Wilcox Chloride Volatility Group hosted Mr. Myles and Mr. Geller of ANL on August 3 for a status review and a discussion of several administrative details. Each member of the investigative

team presented a status summary in his area of responsibility. Current opinions as to proliferability of the several process operations were sought by ANL personnel from most of the speakers. Among the administrative details, quality assurance was examined and property management was explained by ANL. Babcock and Wilcox's established quality assurance program was reviewed and was judged to be eminently satisfactory for the feasibility studies now in progress.

(2) Work Plans for the Following Quarter

Revisions of and corrections to the topical report requested by ANL will be performed. Representatives of Babcock and Wilcox will attend the Second Semi-Annual Pyrochemical and Dry Processing Methods Program Review on November 7 and 8.

c. Separation Processes

(1) Work Accomplished during this Quarter

The apparatus for chloride volatility experimentation was assembled and leak-tested. The system is fully operational, and experimentation has been started.

(a) Decladding Experiments

A schematic of the apparatus used for the decladding experiments is shown in Fig. 35. Hydrogen chloride is metered through a rotameter and is diluted with nitrogen prior to being preheated. The nitrogen-HCl gas mixture enters the three-zone quartz reactor and contacts the Zircaloy tubing at reaction temperature. The $ZrCl_4$ formed, nitrogen, hydrogen, and excess HCl are maintained above the sublimation point of $ZrCl_4$ until they enter a cold trap where $ZrCl_4$ is desublimed. The HCl, nitrogen, hydrogen, and a portion of the desublimed $ZrCl_4$ are passed through a packed bed (Al_2O_3 spheres, 6-14 mesh) where the remaining $ZrCl_4$ is filtered from the gas stream. Hydrogen chloride is then scrubbed from the gas in a series of H_2O and KOH scrubbers.

A sample port downstream from the scrubbers then allows the collection of gas samples used to analyze for hydrogen. Hydrogen analysis has proved to be a good method for monitoring the reaction rate.

Six experiments have been performed in the hydro-chlorination decladding portion of the project. Experiments D-1 through D-5 were conducted with Zircaloy-4 tubing, and experiment D-6 was conducted with a thorium oxide pellet. The experimental conditions are shown in Table 15.

The data gathered during experiments D-1 and D-2 have limited value because the experiments were interrupted several times due to plugged lines. Experiment D-4 was terminated early because the reaction was proceeding too slowly. The Zircaloy-4 sample for experiment D-5 was cleaned

Fig. 35. Hydrochlorination Reactor Schematic

with acetone to remove grease and dirt. The highest reaction rates for de-cladding were obtained in this experiment. Reaction rates for experiments D-1, D-2, D-3, and D-5 are shown in Fig. 36. The extent of conversion of Zircaloy to ZrCl_4 is shown in Fig. 37 for the same experiments.

From the results (Fig. 37), it can be seen that the reaction rate is still strongly dependent on gas velocity, indicating that a mass transfer mechanism is controlling.

Kinetic evaluations cannot be made accurately until conditions are found at which mass transfer no longer controls the reaction.

In experiments D-4 and D-5, packed beds of 6-mesh and 14-mesh alumina 5 and 1.5 in. deep, respectively, were used to capture ZrCl_4 . Nevertheless, some ZrCl_4 passed through the beds. The gas-like behavior of ZrCl_4 will need to be eliminated in a pilot-scale process by reacting it with steam to form the oxide. If this is not done, clogging of process lines will be a major problem.

A ThO_2 pellet was exposed to decladding conditions in experiment D-6. A total of 765 μg of thorium was volatilized in 59 min. (At this reaction rate, it would take about seventeen months to volatilize the entire pellet.)

Table 15. Conditions and HCl Utilizations for Hydrochlorination Experiments

	Exp. D-1	Exp. D-2	Exp. D-3	Exp. D-4	Exp. D-5	Exp. D-6
Zircaloy-4 tubing surface area, cm ²	16.64	15.85	16.51	16.84	16.87	--
Zircaloy-4 tubing weight, g	3.66	3.52	3.59	3.60	3.69	--
ThO ₂ pellet diameter, cm	--	--	--	--	--	1.053
ThO ₂ pellet length, cm	--	--	--	--	--	1.397
ThO ₂ pellet weight, g	--	--	--	--	--	10.851
Temperature, °C	450	450	450	450	450	600
HCl Concentration in N ₂ , vol %	60	60	60	62	79	79
Total gas velocity at operating temperature, cm/s	1.8	3.7	5.8	15.0	11.0	6.4
Avg. HCl utilization, %	7.7±0.5	4.1±0.3	4.9±0.3	--	2.2±0.1	--

The proliferation resistance of the decladding process depends on the separability of thorium from uranium in this step. Obviously, thorium will hydrochlorinate at a very low rate, even in extreme conditions. If uranium also reacts very slowly, thorium-uranium separation would be difficult. Work should be performed in this direction to better determine the relative volatilities of these two elements under decladding conditions.

(b) Chlorination Experiments

The basic objective of the current chlorination experiments is to determine the technical feasibility of chlorination as a process for effecting complete volatilization of the thorium and uranium contents of declad fuel. Experimentation is also the source of information on the physical behavior and operational characteristics of the reactants and products--information needed to make the transition from technical feasibility to engineering practicality.

A total of seven chlorination experiments have been conducted. The first two experiments were shakedown runs that served to establish the operability of the system. The products from experiments C-3 and

Fig. 36. Reaction Rates for Zircaloy Decladding. Numbers in parentheses are total gas velocities.

C-4 have been analyzed but the analyses for experiments C-5 and C-6 have not been completed yet. Experiments C-3 and C-4 were also the most successful runs overall--with respect to volatilization, temperature control, and freedom from plugging at the scrubber inlet conditions and results of experiments 3 and 4 are reported in detail in Table 16, and the experimental apparatus is portrayed schematically in Fig. 38.

All experiments except the preliminary operability runs used 80/20 ThO₂/UO₂ sintered pellets. During an early run, it was found to be impractical to chlorinate a whole pellet. The reduced surface area presented an unnecessary handicap to gas--solids contact, retarding the rate of reaction. The pellet for experiment C-3 was crushed manually and the pellet for experiment C-4 was fragmented by heating to 450°C in air.

Reagent grade chlorine (Cl₂) and carbon tetrachloride (CCl₄) were each metered to the reaction tube. A rotameter was used to meter chlorine gas and a motor-driven infusion pump was used to meter

Fig. 37. Extent of Conversion of Zirconium to ZrCl_4 during Experiment

*Mass transfer term; "3.5" is equivalent to 100% reaction. Y, the conversion factor is equal to (quantity reacted)/(quantity originally present).

liquid CCl_4 to the vaporizer. The infusion pump used consists of a precision-bore syringe whose piston is moved by a screw-driven crosshead. A variable-speed (stepwise) motor rotates the screw at a constant rate. The infusion pump was calibrated while metering CCl_4 and was found to give good reproducibility. The float for the rotameter metering chlorine stuck frequently, however, undoubtedly giving less accurate metering than the CCl_4 pump did.

Preheating occurred in three stages. In the vaporizer, chlorine and CCl_4 streams joined and the mixture was heated to about 124°C . The mixed gases passed through a helix of Inconel 600 tubing which was heated to 350°C . The final heating stage was the first section of the three-zone furnace which was set at the reaction temperature of the experiment.

Table 16. Chlorination of Sintered ThO₂/UO₂

	Experiment C-3			Experiment C-4		
Fuel type	ThO ₂ /UO ₂			ThO ₂ /UO ₂		
Heavy metal oxide wt, starting, g	11.250			11.514		
Wt. ratio, ThO ₂ /UO ₂	80/20			80/20		
Fuel preparation method	Crushing of pellet			Fragmented by oxidation		
Chlorinating agents	CCl ₄ -Cl ₂			CCl ₄ -Cl ₂		
Chlorinating agents, vol ratio	30-70			30-70		
Chlorinating agents, total, cm ³ gas/min	520			520		
Chlorinating agents velocity, cm/min	40			40		
Reaction zone temp, °C	800			750		
Duration of chlorination, min	325			250		
Heavy metal oxide wt, ending, g	0			0.272		
Chlorination, %	100			97.6		

Materials Accountability	Uranium	Thorium	Th	Uranium	Thorium	Th
			Th + U			Th + U
1. Weight of solids at the reactor outlet	0.04±0.01 g	2.74±0.01 g	0.99	0.07±0.01 g	3.98±0.01 g	0.98
2. Weight of solids in HCl scrubber	1.06±0.03 g	1.67±0.02 g	0.61	1.03±0.03 g	1.95±0.02 g	0.65
3. Weight of solids in caustic scrubber	0.01±0.001 g	<0.01±0.001 g	0.36	0.01±0.001	<0.01±0.001 g	0.33
4. Weight of solids in boat at end of expt.	0	0		0.05±0.005 g	0.22±0.0005 g	0.81
5. Total recovered	1.11±0.04 g	4.41±0.03 g	0.80	1.16±0.04 g	6.15±0.03 g	0.84
6. Total recoverable	1.98±0.05 g	7.91±0.05 g	0.80	2.03±0.05 g	8.10±0.05 g	0.80
7. Overall recovery	56%	56%		57%	76%

Fig. 38. Chlorination Reactor. TIR, Temperature Indicator Recorder; TIC, Temperature Indicator Controller.

The reaction temperature, a dependent variable, was obtained from the solid-state furnace-zone controllers and was recorded. Before chlorine was allowed to flow, the system was purged and brought to temperature equilibrium with nitrogen flowing. Once chlorination began, the uranium chloride and thorium chloride formed were absorbed in a weak HCl solution. Carbon tetrachloride and water condensed in the reflux condenser and returned to the water-HCl scrubber; chlorine went on the caustic scrubber, which was used for waste gas purification.

The analyses provided the basis for a materials accountability balance of the thorium and uranium (Table 16). For these feasibility tests, however, the basic objective was a determination of the temperature and time required for complete volatilization from the quartz boat.

We were able to completely chlorinate and volatilize the thorium and uranium, and completion was relatively simple to assess because the tubular quartz reactor retained good transparency throughout the runs. When the clamshell furnace was opened briefly, only a momentary drop in temperature occurred.

The accountability data in Table 16 show a pattern of high thorium content at the reactor outlet and high uranium content in the scrubber, which is a result of the lower volatility of ThCl_4 than of the UCl_x compounds.

The volatility difference was also demonstrated in the experiment that used ThCl_4 and UCl_4 as the starting materials. Eight grams of ThCl_4 and two grams of UCl_4 were placed in separate boats in the same reactor tube and were periodically observed as the temperature was increased. No carbon tetrachloride was used; the gas was chlorine. As the temperature increased above 500°C , reddish brown clouds of vapor from the UCl_4 boat filled the reactor. By 650°C , most of the uranium had vaporized away. At slightly above 700°C the ThCl_4 liquefied, but was not vaporizing away at an observable rate. At 800°C , the rate was observable; shortly after the temperature was increased to 825°C , the boat was empty. This demonstration illustrated not the vaporization rates, but the different temperatures at which the two actinides vaporize. The apparent temperature difference could be reduced, of course, by vastly increasing the chlorine gas flow rate and sweeping the vapors away at a higher rate. We chose to use the gas velocity planned to be used in the other runs because we were primarily studying the operability of the overall system.

Experiment C-5 was ostensibly operated at 700°C but was aborted when a failing thermocouple generated only partial voltage. Experiment C-6, meant to repeat experiment 5 at 700°C , was terminated upon failure of the system glassware.

(c) Fuel Dechlorination

The fuel dechlorination step involves the conversion of the actinide chlorides into oxides by reaction with steam-saturated air at temperatures up to 1000°C . Sixteen dechlorination experiments were completed during this quarter. In an experiment anhydrous UCl_4 , anhydrous ThCl_4 , ThO_2 , or $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ were reacted with moist air and dry air at various temperatures.

The sample was placed in an alumina boat in a quartz-tube reactor and was inserted in a muffle furnace when the reaction temperature was reached. A metered air stream was drawn through the tube by a vacuum pump. Upstream from the vacuum pump, the exhaust gas was drawn through a condenser and a series of scrubbers. Effluent samples were collected and were analyzed periodically for chloride. The product was analyzed at the end of the experiment. The total chloride concentration in the product must be below 500 ppm for the material to be suitable for fuel fabrication. The conditions and results are presented in Table 17.

In experiments FDC-1 through FDC-14, the metered air stream was drawn through a boiling-water steam generator upstream from the quartz reactor. The effluent generated in this case was HCl . (When only dry air was fed to the reactor, the effluent was chlorine.) In order to collect and analyze the exhaust gases for chloride, the effluent treatment system was modified by installing a deionized H_2O and a KI scrubber. Only the total effluent (not portions) produced in these experiments could be collected for

analysis. No data are presented for the second experiment since equipment failure prevented the collection of meaningful data. Following FDC-15, the condenser was not rinsed and the excess chloride found in FDC-16 is probably the chloride missing from FDC-15. Addition of the excess chloride in FDC-16 to the chloride detected in FDC-15 would account for the sample weight loss observed in FDC-15.

Two-stage dechlorination was performed in experiments FDC-8 to FDC-14 in an effort to remove the major portion of the chloride at a relatively low temperature ($\leq 500^\circ\text{C}$) to minimize corrosion problems. The temperature can then be increased to effectively remove the remaining chloride without major corrosion. Chloride removal at 500°C and total chloride removal are shown in Table 17.

Table 17. Fuel Dechlorination

Experiment No.	Material Evaluated	Reaction Temperature, $^\circ\text{C}$	Initial Sample Wt, g	Sample Weight Loss, g	Chloride Found ^a Chloride In %	Chloride Removal at 500°C , ^b %	Chloride Concentration in Product, ppm
FDC-1	UCl ₄	500-1000	0.98	0.28	80 $\pm$ 8	98 ⁺² ₋₁₀	c
FDC-3	UCl ₄	600	1.00	0.29	88 $\pm$ 9	--	c
FDC-4	UCl ₄	600	1.77	0.50	77 $\pm$ 8	--	c
FDC-5	ThCl ₄ ·8H ₂ O	500	4.60	2.19	79 $\pm$ 8	--	--
FDC-6	ThCl ₄	500	4.81	1.39	91 $\pm$ 9	--	9100
FDC-7	ThCl ₄	550	9.29	2.99	92 ⁺⁸ ₋₉	--	9400
FDC-8	ThCl ₄	500-1000	11.74	3.64	99 ⁺¹ ₋₁₀	97 ⁺³ ₋₁₀	--
FDC-9	ThCl ₄	500-1000	4.70	1.34	84 $\pm$ 8	95 ⁺⁵ ₋₁₀	480
FDC-10	ThO ₂	1000	2.67	0.02	--	--	633
FDC-11	ThCl ₄	500-1000	8.45	2.42	82 $\pm$ 8	94 ⁺⁶ ₋₁₀	Awaiting analytical results
FDC-12	ThCl ₄	500-1000	10.29	3.45	93 ⁺⁷ ₋₉	96 ⁺⁴ ₋₁₀	
FDC-13	ThCl ₄	500-1000	10.54	3.07	94 ⁺⁶ ₋₉	96 ⁺⁴ ₋₁₀	
FDC-14	ThCl ₄	500-1000	11.57	3.44	94 ⁺⁶ ₋₉	86 $\pm$ 9	Awaiting analytical results
FDC-15 ^d	ThCl ₄	500	4.15	0.86	25 ⁺⁴⁰ ₋₃	--	
FDC-16 ^d	ThCl ₄	500-1000	4.19	1.19	134 ⁺⁰ ₋₄₀	--	

^a Total Chloride Removed = 100 $\frac{\text{total chloride accounted for}}{\text{total theoretical chloride}}$

^b Chloride Removal at 500°C = 100 $\frac{\text{chloride removed at } 500^\circ\text{C}}{\text{total chloride accounted for}}$

^c Only X-ray analysis was performed.

^d Experiments FDC-15 and FDC-16 used air rather than an air/steam mixture as a reactant for the pyrohydrolysis reaction discussed in the following subsection of this report.

(d) Ash Oxidation

Ash oxidation is a process similar to fuel dechlorination and, because steam-saturated air is the reactant, it may also be called a pyrohydrolysis reaction. Twelve ash oxidation experiments were conducted during this report period with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (sometimes with added Al_2O_3 or SiO_2 to accelerate chloride removal). In addition, two CsCl, one Zircaloy, and two $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ samples were pyrohydrolyzed, as described below. Moist air was the reactant gas, and various temperatures were used. The test conditions are shown in Table 18. The same apparatus and procedure were used for the ash oxidation experiments as were used for the fuel dechlorination experiments.

The results are shown in Table 19. Alumina boats were used for experiments AO-1 through AO-6. A different brand of alumina boat was used in experiments AO-7 and AO-8, but the same lots of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and Al_2O_3 were used. In experiments AO-1 and AO-3, conducted at $<800^\circ\text{C}$, chloride removal was negligible, and so these results are not included in the tables. The chloride removal rates experiments AO-2, AO-4, AO-5, and AO-6 (plotted in Fig. 39) are essentially identical. The low initial rates for experiments AO-4 and AO-6 are due to some of the first sampling period representing reaction at low temperature. The chloride removal rates in experiments AO-7 and AO-8, shown in Fig. 40, were much higher than in the preceding runs. In these two runs, it was obvious from discoloration of the boat that the samples had reacted with the boat material. Probably, the much higher reaction rate in AO-7 is due to the sample contacting a greater surface area of the boat compared to the platinum boats and to the higher temperature. It was concluded from these experiments that alumina boats are not satisfactory since the test material reacts with them. It also appears that the second type of boat is more active than the alumina that was added to samples. As a result, platinum boats were used in all later experiments. Also, a more active alumina was added to the samples. The 1000°C temperatures were causing the quartz reactor to devitrify. Also, the pyrohydrolysis product was a solid lump rather than a powder. It was therefore decided to limit the reaction temperature to 900°C .

The chloride evolution rates for the four final $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ experiments are plotted in Fig. 41. The low initial chloride evolution rate in experiment AO-9 is due to a low steam flow at the beginning of that experiment. Chloride evolution rates in the experiments with (1) active alumina in the samples and (2) platinum boats (AO-9, AO-11, and AO-12) are slightly higher than in the earlier runs with the inactive alumina boats, even though the temperature was $100\text{--}200^\circ\text{C}$ lower. This indicates that the addition of active alumina improved the reaction rate.

The very high chloride removal rates obtained with active alumina boats (experiments AO-7 and AO-8) were not duplicated. This was due to two factors. First, a higher temperature was used for AO-7 and AO-8. Second, the alumina boats were larger than the platinum boats. This resulted in the sample being in a thicker pile in the platinum boat and less surface area being exposed.

Table 18. Experimental Conditions for Ash Oxidation

Exp.	Material in Sample	Sample Wt, g	Preheat Temperature, °C	Preheat Time, min	Soak Temperature, ^a °C	Soak Time, min
AO-2	BaCl ₂ ·2H ₂ O	0.90	700	25	900 1,000 1,050	40 15 5
AO-4	68% BaCl ₂ ·2H ₂ O 32% Al ₂ O ₃	0.78	850	5	1,000	60
AO-5	50% BaCl ₂ ·2H ₂ O 50% Al ₂ O ₃	0.26	1,000	5	1,100	140
AO-6	50% BaCl ₂ ·2H ₂ O 50% Al ₂ O ₃	0.31	700	40	1,000	50
AO-7	50% BaCl ₂ ·2H ₂ O 50% Al ₂ O ₃	1.06	--	--	1,100	60
AO-8	BaCl ₂ ·2H ₂ O	0.13	--	--	1,080	60
AO-9	50% BaCl ₂ ·2H ₂ O 50% Al ₂ O ₃	0.26	--	--	900	60
AO-10	BaCl ₂ ·2H ₂ O	0.23	--	--	900	60
AO-11	50% BaCl ₂ ·2H ₂ O 50% Al ₂ O ₃	0.41	--	--	900	75
AO-12	50% BaCl ₂ ·2H ₂ O 50% SiO ₂	0.41	--	--	900	60
AO-13	50% CsCl 50% Al ₂ O ₃	0.39	--	--	900	60
AO-14	50% CsCl 50% SiO ₂	0.39	--	--	900	60
AO-15	LaCl ₃ ·6H ₂ O	0.38	--	--	800	61
AO-16	54% LaCl ₃ ·6H ₂ O 46% SiO ₂	0.67	--	--	800	42
AO-17	ZrCl ₄	0.21	--	--	300	25

^aTemperature of reaction.

Table 19. Results of Ash Oxidation Experiments

Exp.	Measured Weight Loss, mg	Calculated Weight Loss, mg	Initial Chloride Content, mg	Chloride Removed, %	Residual Chloride, %
AO-2	150 ± 5	165 ± 5	0.26	16 ± 2	83 ± 10
AO-4	90 ± 5	101 ± 5	0.15	19 ± 2	81 ± 10
AO-5	50 ± 5	46 ± 5	0.038	91 ⁺⁹ ₋₁₀	a
AO-6	29 ± 5	36 ± 5	0.045	38 ± 4	a
AO-7	190 ± 5	192 ± 5	0.154	95 ⁺⁵ ₋₁₀	a
AO-8	50 ± 5	46 ± 5	0.038	93 ⁺⁷ ₋₁₀	a
AO-9	60 ± 5	47 ± 5	0.038	84 ± 1	16 ± 1
AO-10	39 ± 1	44 ± 5	0.066	20 ± 1	79 ± 1
AO-11	75 ± 1	71 ± 5	0.059	92 ± 1	6 ± 3
AO-12	75 ± 1	71 ± 5	0.059	92 ± 1	4 ± 3
AO-13	98 ± 1	b	0.042	b	b
AO-14	195 ± 1	b	0.042	b	b
AO-15	183 ± 1	175 ± 5	0.114	68 ± 1	27 ± 3
AO-16	a	a	0.108	60 ± 1	a
AO-17	90 ± 5	111 ± 10	0.127	99 ± 1	a

^aNot determined.

^bInvalid. Because of cesium volatility, weight losses could not be used to calculate chloride removals.

Fig. 39.

Chloride-Removal Rate for Ash Oxidation Experiments AO-2, AO-4, AO-5, and AO-6

Fig. 40.

Chloride-Removal Rate during Ash Oxidation Experiments AO-7 and AO-8

Fig. 41.

Chloride Removal Rate during Ash Oxidation Experiments AO-9, AO-10, AO-11, and AO-12.

The form of the curves in Fig. 39 through 41 can be explained in terms of topochemical kinetics. Interaction of oxygen and steam with barium chloride occurs at a gas-solid interface. The reaction rate depends on the rate of H_2O diffusion into the crystal lattice and the rate of crystal-chemical conversion. The thickness of the layer of solid reaction products increases continuously, hindering the diffusion of H_2O into the reaction zone and diffusion of HCl out of that zone.

[TETEREVKOV] studied the oxidation of $FeCl_2$ with dry air and found that an Erofeev equation applies. It has the form

$$x = 1 - e^{-kt^n}$$

where x = weight percent conversion

t = time, min

k and n = constants

Taking logarithms twice gives:

$$\log [-\log(1 - x)] = \log k/2.303 + n \log t$$

If the logarithm of $1 - x$ is plotted as a function of time on log-log paper, a straight line will be obtained unless there is a change in reaction mechanism indicated by a change in slope. The results of experiments AO-10, AO-11, and AO-12 are so plotted (Fig. 42). Due to the reactivity of the boats being in question, only these three final experiments with $BaCl_2$ are plotted. (Experiment AO-9 is not plotted because of a low initial steam flow.)

The plot of experiment AO-11 results is a curved line. This is believed due to the large sample used and the low rate of reaction of $BaCl_2$ with Al_2O_3 . The reaction gases at the bottom sample layer must diffuse through the reaction product and then through the sample. This would delay the reaction in the lower sample layers. Reaction of $BaCl_2$ with SiO_2 (in experiment AO-12) is much more rapid than reaction of $BaCl_2$ with Al_2O_3 in the early stages, but then slows while the last traces of chloride are being removed.

Following the $BaCl_2 \cdot 2H_2O$ runs, two runs were made each with 0.2 g $CsCl$ in the sample. In one case, 0.2 g Al_2O_3 was used as an accelerator, and in the other, 0.2 g SiO_2 was used. In both runs, more than 90% of the cesium volatilized. About 50% of the volatilized material was collected in the condensate during the first 20 min, and 20% was collected in the condensate during the following 40 min. A trace was found in the bubblers. A deposit noted near the furnace outlet was determined to contain cesium, but the exact quantity could not be determined.

To allow cesium volatility from $CsCl$ melts and from Cs_2O melts to be compared, several samples were fired in dry air for 3h at $850^\circ C$. Table 20 gives the compositions of these mixtures and the quantities of cesium volatilized.

Clearly, cesium is more prone to volatilize from CsCl than from Cs₂O:

Table 20. Cesium Volatility Samples

Mixture	Sample Composition				Cs Volatilized, %
	CsCl, %	Cs ₂ O, %	SiO ₂ , %	Al ₂ O ₃ , %	
AO-Cs-1	49	--	--	51	100
AO-Cs-2	49	--	51	--	100
AO-Cs-3	--	50	35	15	100
AO-Cs-4	--	37	34	29	20
AO-Cs-5	--	19	45	35	20

Fig. 42. Erofeev Equation Plot of Percent Conversion

A 0.38-g sample of LaCl₃·6H₂O and a 0.67-g sample containing 54% LaCl₃·6H₂O were pyrohydrolyzed. In both runs, a temperature of 800°C was used. As expected LaOCl formed in both runs.

This compound was identified by X-ray diffraction. Chloride removal was 68% in the first run and 60% in the second run. The solid residue from the first pyrohydrolysis contained 27% of the original chloride, and 95% of the total chloride was accounted for. Reaction was essentially complete in 5 min, making it impossible to plot the rate data as a function of time. The chloride-removal rate during the first 5 min was about 10mg Cl/min. The condensate was not analyzed for lanthanum, but carryover is thought to have been small.

One sample containing 0.21 g ZrCl_4 was pyrohydrolyzed at 310°C. Chloride evolution was very rapid. Chloride removal was 99%. Less than 0.03% of the zirconium volatilized.

To determine the effect of chlorides on glass formation because fission products may be stored in glass, melt tests were performed to observe homogeneity and leach rates. Samples were prepared as 20-g melts by grinding for five minutes in a SPEX shatter box and then heating at 900°C for 3 h in alumina crucibles. The samples were furnace cooled.

The samples were:

- a. pure frit
- b. 61% frit plus 37% BaO
- c. 70% frit, 19% BaO, plus 11% $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
- d. 65% frit plus 35% fission product simulation mix
- e. 65% frit, 20% fission product simulation mix, plus 15% ZrCl_4

Table 21 presents the frit composition. Table 22 shows the composition of the fission product simulation mix.

Table 21. Glass Frit Composition

	wt%
SiO_2	37
B_2O_3	15
ZnO	29
Na_2O	19
	100

Table 22. Composition of Simulated Fission Product Mix

	%
BaO	26.2
ZrO_2	21.7
La_2O_3	18.1
CeO_2	14.9
Nd_2O_3	12.1
Pr_2O_3	5.8
Sm_2O_3	1.2
	100.0

The frit formed a clear, homogeneous light-green glass which fractured upon cooling. When not ground, the frit forms a colorless glass. The color change is due either to impurities from the grinder or color centers exposed by grinding. These hypotheses can be tested by grinding a sample in an alumina grinder.

The frit plus BaO formed a microcrystalline solid; X-ray diffraction showed it to be $\text{Ba}_2\text{ZnSi}_2\text{O}_7$. Samples c, d, and e formed solid opaque glasses, which appeared to be homogeneous when fractured prior to grinding. Samples d and e each contained a large quantity of bubbles. Samples c, d, and e have been ground, and each -45 +60 mesh fraction of the ground samples will be Soxhlet leach tested.

(e) Materials Evaluation

The ability to produce pellets from thorium powder that had been prepared in dechlorination experiments was studied. A sample of the powder was screened to determine its approximate particle size range. Then the sample was ground in a mortar with a pestle and was screened again. The results are shown in Table 23.

Table 23. Screen Analysis Of ThO_2 Powder

	Before Grinding, %	After Grinding, %
-100 mesh	26.6	6.3
-100 +200 mesh	14.2	12.1
-200 +400 mesh	16.8	10.9
-400 mesh	42.4	70.7

Two pellets were pressed from the ground powder. One pellet was made of -400 mesh powder, and the second pellet was made of +400 mesh powder. Good green pellets could be produced when Nopcowax binder and Sterotex lubricant were added. Densities of green and sintered pellets are shown in Table 24. Sintering was performed in air at 1500°C for 1 1/2 h.

Table 24. Densities of ThO_2 Pellets

	Pellet Pressed at 3.45×10^8 Pa from +400 Mesh Powder	Pellet Pressed at 1.1×10^8 Pa from -400 Mesh Powder
Green Density, g/cm^3	5.74	6.55
Sintered Density, g/cm^3	8.05	9.04

Sample pellets were prepared for study of the sintering behavior of ThO_2 that had been prepared in a dechlorination experiment. Three pellets were pressed. Data for the green pellets are shown in Table 25, and data for the pellets after they had been sintered are shown in Table 26.

Table 25. Green Pellets for Dilatometer Study

Pellet	Diameter, cm	Length, cm	Weight, g	Density, g/cm ³	Comments
1	0.6972	0.8565	1.9140	5.85	As received, pressed at 2.76×10^8 Pa (20 ton/sq in.)
2	0.6993	0.8316	2.0375	6.38	Pressed at 8.97×10^8 Pa (65 ton/sq in.)
3	0.6965	0.8621	1.9804	6.03	-400 mesh powder, pressed at 6.21×10^8 Pa (45 ton/sq in.)

Table 26. Sintered^a Pellets for Dilatometer Study

Pellet	Diameter, cm	Length, cm	Weight, g	Final Density, g/cm ³
1	0.6071	0.7605	1.8910	8.59
2	0.6142	0.7369	2.0126	9.23
3	0.6066	0.7668	1.9496	8.80

^aSintering was done in air at a heatup rate of 275°C/h up to 1600°C.

Sample pellet 1 served as a base for comparison of various techniques of improving sintered density. All samples were sintered in the same manner; the heatup rate was a constant 275°C/h up to 1600°C after which samples were allowed to cool. Sintering was done in air. Densification behavior during sintering, as measured with a dilatometer, is shown in Figs. 43 and 44.

No densification occurs in any sample until the temperature exceeds 900°C (1652°F). At temperatures between 2000°F and 2600°F, densification is rapid, but it begins to decrease just as rapidly at temperatures above 2600°F. These experiments show that the higher the green density, the higher is the density after sintering.

Samples of the ThO_2 powder derived from the chloride were examined (Figs. 45 and 46), using a scanning electron microscope. Some interesting observations were made. The ThO_2 powder derived from chloride

Fig. 43. Density of Thoria Pellet Samples 1, 2, and 3 as a Function of Temperature during Sintering.

Fig. 44. Rate of Densification of Thoria Pellet Samples 1, 2, and 3 as a Function of Temperature during Sintering.

Oxalate-Derived ThO_2

Chloride-Derived ThO_2

Fig. 45. Scanning Electron Microscope Micrographs of Oxalate-Derived and Chloride-Derived ThO_2 . 1000X

Oxalate-Derived ThO_2

Chloride-Derived ThO_2

Fig. 46. Scanning Electron Microscope Micrographs of Oxalate-Derived and Chloride-Derived ThO_2 . 5000X

has a much rougher surface than that derived from the oxalate. The oxalate-derived material showed the rectangular structure, which is common to such powders. The smallest chloride-derived ThO_2 particles were about $1\text{ }\mu\text{m}$, and agglomerates formed from a number of these needle-like structures. Initial indications from the limited results obtained are that the chloride-derived powder is fairly easy to sinter. Its pressing characteristics appear to be very good.

(f) Off-Gas Treatment

Bench-scale experimental work needed for conceptual design of the initial condenser system of the off-gas treatment system was completed. As reported below, chemical analyses of the system condensates and gas effluents were performed. These analyses were then used in evaluating the application of a condenser or a series of condensers in the first processing steps of the integrated, untreated gaseous effluent streams from the pyrohydrolysis, ash oxidation, and decladding steps of the main sequence of chloride volatility fuel reprocessing.

Of primary importance in the experimental analyses of the condenser sequence was the pathways of chlorine, hydrogen chloride, carbon tetrachloride, water vapor, and various "model" fission product chlorides through the condenser system as a function of the temperature of the condensers. Of secondary importance in these evaluations, but noted as part of the experimental framework, were the evaluation of the design efficacy of the condenser and other experimental equipment, corrosion and degradation of the materials used in the experimental apparatus, and methods of chemically analyzing the various product streams in the experiments.

The first step in all experiments was provision of a mixed chlorine, hydrogen chloride, water vapor, and carbon tetrachloride gas stream. The chlorine and hydrogen chloride gases were provided from small, type "D" gas bottles and were metered into the experimental system through calibrated rotameters. The carbon tetrachloride and water streams were injected into the system via calibrated infusion pumps and were vaporized in a flask in a heating mantle with small glass beads for providing high surface area. The combined streams were then fed into a tube furnace that heated the gas mixture to the temperature desired as the condenser inlet temperature.

For experiments in which analog fission product chlorides were injected, these materials were injected by placing them as a powder in a small "bomb" type stainless steel reactor. The reactor could be heated to vaporize the material, which would be valved into the main gas stream before its injection into the condenser system.

Although the rotameter system for measuring the inlet chlorine and hydrogen chloride rates was calibrated prior to experimentation, it did not give accurate measurements of the total inputs of these gases in each experiment due to an inability to maintain exact, invariant flow

readings on the float indicators. It is also believed that some corrosion occurred in the chlorine rotameter and compromised its readings.

Of the seven experimental runs reported here, five were performed (of necessity, at the time) with an Inconel 600 reactor tube in the tube furnace. Early in the experimental work, it was discovered that the mixed chlorine/hydrogen chloride/water vapor/carbon tetrachloride gas stream had an extremely corrosive effect on this reactor. As a result, nickel chloride formed and subsequently was deposited in the system, and a large fraction of the injected chlorine was removed from the gas stream. Acquisition and use of a fused quartz reactor tube alleviated this problem in the two final experiments, but corrosion was never entirely eliminated since it was necessary to use, particularly in the gas feed system and at various system joints, stainless steel and tygon tube and fittings in contact with the gas stream. Therefore, degradation products still formed in the system.

The following is a description of the seven experimental runs and their associated mass balances.

Experiment OG-1 consisted of a single condensation step at approximately 5°C condensation temperature, using a mixed $\text{Cl}_2/\text{HCl}/\text{H}_2\text{O}/\text{CCl}_4$ stream of mass ratio 1:2:25:8. The mixed gas stream was heated to approximately 200°C in the tube furnace and was injected into a spiral-type borosilicate glass condenser cooled by water whose temperature was about 5°C.

The condensate from this condenser was collected in a connected flask held in an ice bath for cooling. The gaseous effluent was passed through a series of three scrub flasks. The first flask contained deionized water (for the collection of HCl and other Cl^- species), and the second and third flasks contained a potassium iodide solution (for the retention of chlorine). Table 27 shows the total material balance, as determined by means of inlet gas stream measurement and analytical evaluation of the samples from downstream solutions.

As noted above, major corrosion of the Inconel reactor material resulted in large losses of Cl_2 and HCl from the gas stream.

In experiment OG-2, the condenser and operating conditions were the same as in experiment OG-1, except that the $\text{Cl}_2/\text{HCl}/\text{H}_2\text{O}/\text{CCl}_4$ inlet ratio was altered to approximately 1:2:3:6. Again, extensive corrosion was noted in the furnace reactor. Table 28 shows the material balance observed for this run.

In experiment OG-3, a mixed $\text{Cl}_2/\text{HCl}/\text{H}_2\text{O}/\text{CCl}_4$ stream was condensed at about 5°C, this time at an inlet ratio of 1:6:3:9. The special type of condenser used in experiments OG-1 and OG-2 was replaced with a Friedrich borosilicate glass condenser to improve contact of the inlet gas stream with the heat transfer surface. Table 29 shows the mass balance achieved in this experiment.

Table 27. Material Throughput in Experiment OG-1

Cl ₂ , HCl, CCl ₄ , H ₂ O	Furnace	5°C Condenser	H ₂ O Scrubber	KI Scrubber	KI Scrubber
Comp.	Furnace Inlet	5°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution	
Cl ₂ , g	6.45	0.024	0.021	<0.002	
HCl, g	10.3				
CCl ₄ , g	40.1	40.1			
H ₂ O, g	126	64.2			
Cl ⁻ , g		6.2	0.021		

Table 28. Material Throughput in Experiment OG-2

Cl ₂ , HCl, CCl ₄ , H ₂ O	Furnace	5°C Condenser	H ₂ O Scrubber	KI Scrubber	KI Scrubber	Residue
Comp.	Furnace Inlet	5°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution		Residue
Cl ₂ , g	11.3	0.017	0.036	0.533		
HCl, g	22.5					
CCl ₄ , g	65	22.7				
H ₂ O, g	28.2	10.3				
Cl ⁻ , g		3.2	7.66			2.6

Table 29. Material Throughput in Experiment OG-3

Cl_2 , HCl , CCl_4 , H_2O				
	Furnace	5°C Condenser	H ₂ O Scrubber	KI Scrubber
Comp.	Furnace Inlet	5°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution
Cl_2 , g	6.73	0.018	0.003	0.039
HCl , g	42.9			
CCl_4 , g	23.9	8.4		
H_2O , g	58	19		
Cl^- , g		8.8	12.0	

In experiment OG-4, a mixed $\text{Cl}_2/\text{HCl}/\text{H}_2\text{O}/\text{CCl}_4$ gas stream in an approximately 1:7:7:2 ratio was condensed at approximately -30°C . The condensation temperature was maintained by dry ice-cooled isopropyl alcohol circulated through a Friedrich-type condenser. The condensate was collected in a dry ice-cooled flask connected to the condenser. The off-gases were treated in the same way as in previous experiments. Table 30 presents the mass balance obtained in this experiment.

Table 30. Material Throughput in Experiment OG-4

Cl_2 , HCl , CCl_4 , H_2O				
	Furnace	-30°C Condenser	H ₂ O Scrubber	KI Scrubber
Comp.	Furnace Inlet	-30°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution
Cl_2 , g	8.8	0.0139	0.0014	0.04
HCl , g	55.8			
CCl_4 , g	16	13.6		
H_2O , g	50	38.9		
Cl^- , g		15	19.6	

In experiment OG-5, there were sequential condensations at 30°C and -30°C of a mixed gas stream of $\text{Cl}_2/\text{HCl}/\text{H}_2\text{O}/\text{CCl}_4$ in the mass ratio 1:6:6:2. In addition, a small amount (about 5%) of the total chlorides of barium, nickel, molybdenum, and zirconium was injected. The condensates were collected and the off-gas treated as in previous experiments. However, the chemical analyses of the collected samples now included additional measurements--for zirconium, barium, molybdenum, and nickel. The material balances obtained are shown in Table 31.

Experiment OG-6 was a repeat of experiment OG-5, except that the initial condenser temperature was 50°C rather than 30°C, and the Inconel tube furnace reactor was replaced with a quartz tube. The resulting mass balance is shown in Table 32.

Experiment OG-7 was another repeat of experiments OG-5 and OG-6 except that the first condensation was at approximately 0°C and the second at approximately -50°C. The gas and metal chlorides input were also essentially the same. The mass balance resulting is shown in Table 33.

A number of conclusions can be made based on the data shown above.

- a. Although hydrogen chloride gas will condense to its solubility limit in the condensed water, complete removal of HCl gas would be extremely difficult to obtain where the $\text{HCl}/\text{H}_2\text{O}$ ratio in the gas stream exceeds this limit.
- b. Chlorine tends to pass through the condenser system.
- c. Carbon tetrachloride and water vapor tend to condense at the same place in the apparatus, forming two separate phases in the condensate.
- d. The chlorides of zirconium and molybdenum probably hydrolyze in the mixed gas streams generated in these experiments, depositing as oxides even upstream from the first experimental condenser. Most of these materials (molybdenum, barium, zirconium, nickel) were found to remain inside the volatilizer "bomb." Complete condensation of such materials and other fission product "chlorides" could probably be accomplished in an ambient-temperature desublimator.
- e. All mixtures of chlorine, hydrogen chloride, water vapor, and carbon tetrachloride in the gas stream were extremely corrosive to any Inconel, stainless steel, tygon, and polypropylene surfaces contacted. In particular, their reaction with Inconel produced large amounts of nickel chloride which could not be properly measured and related to the Cl_2 , HCl, and CCl_4 mass balances.

Table 31. Material Throughput in Experiment OG-5

Comp.	Furnace Inlet	30°C Condensate	-30°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution	Leak	Wash
Cl ₂ , g	3.78	0.039	0.003	0.044	0.405		
HCl, g	24.1						
CCl ₄ , g	9.8						
H ₂ O, g	24.6	19.9	1.9				
Ba, g	0.56	<0.0003	<0.0003	<0.002			0.17
Mo, g	0.24	0.005	0.0001				0.004
Ni, g		0.04	0.002	0.0002		<0.001	
Zr, g	0.4			<0.0002		0.06	
Cl ⁻ , g	0.94	9.0	1.61	17.7			0.98

Table 32. Material Throughput in Experiment OG-6

Comp.	Furnace Inlet	50°C Condensate	-30°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution	Residue
Cl ₂ , g	6.45	0.045	0.185	0.443	2.63	
HCl, g	41.1					
CCl ₄ , g	16.8	0	6.8			
H ₂ O, g	41.6	9.0	10.0			
Ba, g	0.34	<0.0003	<0.0004			0.3
Mo, g	0.27	0.00003	0.00003			0.003
Ni, g	0.23	0.0001	0.0004			0.06
Zr, g	0.39	<0.0002	<0.0002	<0.0002		
Cl ⁻ , g	1.44	4.0	0.813	18.71		

Table 33. Material Throughput in Experiment OG-7

Comp.	Furnace Inlet	0°C Condensate	-50°C Condensate	H ₂ O Scrubber Solution	KI Scrubber Solution	Residue
Cl ₂ , g	6.9	0.0147	0.045	0.108	0.715	
HCl, g	44					
CCl ₄ , g	23.9	4.7	3.4			
H ₂ O, g	47	42.7				
Ba, g	0.34	<0.0004	<0.0004	<0.002		0.9
Mo, g	0.27	<0.0001	0.00003	<0.00003		0.003
Ni, g	0.23	0.0003	0.0001	0.0003		0.11
Zr, g	0.39	<0.0002	<0.0002	<0.0002		
Cl ⁻ , g	1.44	11.2	2.16	16.1		

(g) Corrosion Tests

Four corrosion tests (CT-1, CT-2, CT-3, and CT-4) were completed this quarter. In each test, the test system was purged with nitrogen during heatup after which a dry chlorine atmosphere was used at 600 and 700°C simulating the chlorination step. Carbon tetrachloride was not used in these screening tests.

Superalloys of three manufacturers were used in the tests. The three manufacturers are Cabot Stellite Div. (formerly Haynes Stellite), Huntington Alloys Div. of International Nickel Corporation, and Duriron Corporation. The Cabot Stellite product line is typified by Hastelloy and Haynes alloys. Inconel and Incoloy are Huntington alloys, and Chlorimet is a chlorine-resistant alloy of Duriron Corporation. All sample coupons were welded with filler metals obtained from the alloy manufacturers. Welding was with a single bead of filler metal, using the TIG welding process.

Samples were exposed in our 6-in.-dia by 53-in. Inconel 600 furnace. Following experiment CT-1, we installed a 5 1/2-in.-dia alumina sleeve in the Inconel shell. This protection had two purposes--to minimize cross-contamination from the corrosion products of the Inconel wall and to protect the Inconel reactor from the deliberately damaging effects of corrosion testing.

The sample holder is shown in the schematic drawing of the test apparatus (Fig. 47). Test coupons were isolated from the metal support rod by an alumina sleeve and were separated from one another by alumina spacers.

Flowing chlorine (not a sealed-off static atmosphere) was used in all tests (1) to ensure that there would be sufficient chlorine to obtain the desired corrosion and (2) to remove volatile corrosion products from the corrosion zones.

The screening tests have eliminated several alloy compositions from consideration. Preliminary test results are shown in Table 34. Experiments CT-1, CT-2, and CT-3 were performed at 600°C and experiment CT-4 at 700°C. Exposed samples from experiments CT-1, CT-2, and CT-3 were photographed and then cleaned in 15% HCl with a rubber stopper. Also, cleaned samples from CT-1 were photographed.

We plan to avail ourselves of an offer of Cabot Stellite to evaluate the exposed samples in their Kokomo corrosion laboratories.

Fig. 47. Corrosion Tester. Modified pulsed fluidized-bed reactor

In summary, the candidate alloys at this point in the testing are:

Sample 113 - Nickel 201, 33 mil/y.
 Sample 111 - Inconel 600, 210 mil/y.
 Sample 112 - Incoloy 800, 322 mil/y.
 Sample 110 - Inconel 601, 456 mil/y.

Hasteloy C-4 was inadvertently omitted from the 700°C test. This was the best of the Stellite alloys in the three 600°C tests but still significantly poorer than the candidate alloys at 600°C.

Corrosion losses are reported in mils per year because this is the unit used by both the National Association of Corrosion Engineers and the American Society for Testing Materials. The values are calculated from:

$$\text{mil/y} = \frac{\text{mg loss} \times 534}{\text{surface area (mm}^2\text{)} \times 0.00155 \times \text{h of exposure} \times \text{density (g/cm}^3\text{)}}$$

Table 34. Preliminary Results of Corrosion Tests

Alloy	Sample No.	Surface Area, mm ²	Corrosion Loss, mil/y ^a			
			CT-1	CT-2	CT-3	CT-4
			5.5 h 600°C	6.0 h 600°C	8 h 600°C	5.25 h 700°C
C-276 ^b	100	5346	460	619	170	omitted
B-2 ^b	101	11756	318	217	103	23283
C-4 ^b	102	10765	332	210	75	not yet tested
Nb	103	5346	1315	966	276	omitted
X ^b	104	5346	490	233	80	15505
188 ^b	105	5346	621	174	93	omitted
25 ^b	106	5346	691	194	76	destroyed
20 ^b	107	5346	1160	501	103	omitted
400 ^c	108	d	d	—	—	—
C-3 ^e	109	2029	777	+3 ^f	17	1017
601 ^c	110	12925	No test	10	38	456
600 ^c	111	12764	No test	+4.3 ^f	13	210
800 ^c	112	11981	No test	2.2	23	322
201 ^c	113	13232	No test	0.24	32	33

^aEstimated tolerance (see text).^bCabot Stellite Div. alloy.^cHuntington Alloys Div. alloy.^dMonel 400; 60 g was lost from a 141-g sample.^eDuriron Corp. alloy.^fCleaned sample showed a weight gain.

Before exposure, samples were surface-cleaned and finished with No. 150 Aloxite cloth, followed by No. 200 cloth. After a test exposure, the samples were cleaned with 15% HCl and a rubber stopper. Instead of fresh coupons being used for each test, the same sample coupons were repeatedly exposed. This repeated exposure was deliberately adopted to permit the protective effect of passivation (if it occurred) to be revealed by prolonged exposure. Passivation would be missed in a short test. Although passivation apparently did occur - note the high losses in test CT-1 and the large weight gains for the C-3 and 600 alloys - it should also be noted that our proposed process is to utilize a fluidized bed whose mild abrading action would be expected to inhibit a protective layer being retained. Final selection of an alloy cannot be done until all of the unique or controlling conditions can be duplicated. This can not be done in screening tests.

A favorable factor is that it is planned to operate the pulsed fluidized bed batchwise. At the proposed rate of 2.3 five-hour batches per day, the reactor would be empty about half the time. Even though the furnace would be held at operating temperature continuously, a nitrogen purge after each chlorination would eliminate the corrosive action during most of the nonprocessing time and a corrosion rate reported as 33 mils/y would represent something significantly less than 33 mils of corrosion per year.

Since corrosion is a chemical reaction, the rule of thumb that a reaction rate doubles for each 10°C increase in temperature directs us to seek the lowest temperature at which ThCl_4 and UCl_x completely vaporize. Even if the general rule grossly exaggerates the chlorination corrosion rate for our specific conditions, chlorination for 8h at 650°C would be much wiser (as an example) than chlorination for 4h at 750°C . Accordingly, in our chlorination experiments, we seek to determine the lowest temperature at which complete volatilization can be obtained. Even though corrosion per year is reduced if reactor operation is decreased, this has a lower priority because such a reduction of corrosion rate is a linear function, whereas reduction of corrosion rate by lowering the temperature is a power function.

Of course, corrosion could be avoided by specifying a ceramic such as fused silica or high-purity alumina. Another demonstrated material of construction for chlorine and chlorides is graphite. However, there are problems of nonmetallic construction related to fragility, machinability, seals, couplings and adaptors, poor heat transfer, probability of catastrophic failure (relative to metal), and others. These problems would be magnified and compounded by the added complexities of remote operation. A comprehensive search for a usable (though possibly expendable) metal is justified. At present the most promising metal is pure nickel. The first sample to fail completely was Monel 400 (sample 108). The failed Monel swelled to several times its original size and came to look like a cocoa-colored biscuit. That failure showed that all grades of Monel are unacceptable because the other three grades are merely modifications (with sulfur or aluminum) to improve machinability or strength.

The most spectacular failure was that of Haynes Alloy No. 25 (sample 106) which at 600°C ranked midway among the 14 samples tested, but was destroyed at 700°C. This cobalt-chromium-tungsten-nickel alloy is designated a high-temperature alloy. Although a massive failure should have little effect on other measurements, unfortunately it seriously increases the possibility of interference with other tests being run simultaneously. Haynes alloy No. 25 completely vaporized, depositing feathery, gold crystals on all other samples being tested. Whether the effect was to retard or accelerate corrosion of the other seven samples is not known.

The estimated reliability of the corrosion rate listed in Table 34 is $\begin{matrix} +14\% \\ -29\% \end{matrix}$. In arriving at this, the following were considered:

Wt loss

1. Weighing, fresh sample	$\begin{matrix} +0.25\% \\ -3.0\% \end{matrix}$
2. Cleaning, degree of	$\pm 0.5\%$
3. Weighing, cleaned sample	$\pm 0.25\%$

Area

measurement of length, width, thickness and hole diameter.	$\pm 3\%$
--	-----------

Time	$\begin{matrix} +15\% \\ -5\% \end{matrix}$
------	---

Density	$\pm 0.025\%$
---------	---------------

Temperature	$\begin{matrix} +10\% \\ -2.5\% \end{matrix}$
-------------	---

Total	$\begin{matrix} +14.025\% \\ -29.025\% \end{matrix}$
-------	--

The total tolerance is not obtained by direct addition of the individual tolerances. Weight loss is directly related to the calculated corrosion rate, and area, time, and density are inversely related. If the true temperature is higher than the observed temperature, the corrosion rate at the true temperature should be lower than that measured. The signs on area, time, density, and temperature, therefore, must be reversed before summing for a total. Time was rated at +15%, -5% because the recorded time is based on the interim between starting and stopping of the chlorine flow. At shutdown as the nitrogen purge dilutes the chlorine and the furnace cools down, corrosion undoubtedly continues, which means that the actual exposure time is greater than the stopwatch time. Therefore, the actual corrosion rate should be lower than the reported corrosion rate.

(2) Work Planned for next Quarter

The chloride volatility project will be redirected in FY1979. Minimal experimental work will be performed on the volatilization of thorium chloride and uranium chloride. Determining the minimum temperature for complete volatilization of the thorium and uranium is still the fundamental objective. Now that we have a better picture of the volatility of the fuel constituents as a function of temperature, we will modify the experimental design to achieve the desired results.

7. Molten Nitrate Salt Oxidation Processes

(L. L. Burger,* L. G. Morgan,* and
R. D. Scheele*)

The objective of this work is to identify chemically feasible non-aqueous reprocessing methods within the framework of nonproliferation. The study will examine treatment of ceramic fuels by molten salts and will emphasize the use of molten nitrate systems. The incorporation of other nonaqueous steps will be considered, where applicable to the development of a conceptual process.

a. Engineering Analysis

Preparation of the topical report entitled "Review of Physical and Chemical Properties of Molten Nitrates Applicable to Nuclear Fuel Processing" continued during this report period.

The unexpectedly large volume of literature that must be reviewed has created difficulties in completing the topical report within the specified time frame. However, several important aspects of interest have been clarified by supporting laboratory studies conducted and reported under the Separations Processes (subsection b below) portion of this work. Study of the behavior of actinide oxides in molten alkali metal nitrates has made a major contribution to an area where either the existing literature was incomplete or contradictory reports existed. Results of these supporting studies are still to be integrated into the topical report.

b. Separations Processes

Studies conducted during this report period included:

- Development of a procedure for laboratory-scale production of 100% nitric acid.
- Study of the behavior of actinide oxides in molten alkali metal nitrates.

*Pacific Northwest Laboratory

- Preliminary studies of selected individual fission products in equimolar sodium nitrate-potassium nitrate.
- Study of the effects of added anions on the behavior of uranium dioxide in equimolar sodium nitrate-potassium nitrate.
- Development of analytical methods.

(1) Development of Procedure for the Production of Laboratory-scale Quantities of 100% Nitric Acid

After the initial actinide oxide reaction with the molten alkali metal nitrate in our preliminary proposed molten nitrate salt oxidation process, the melt is sparged with an inert gas containing 100% nitric acid vapor to produce a soluble uranium species. Thus, in determining the feasibility of this process step, the ability to produce 100% nitric acid is of importance (100% nitric acid cannot be purchased commercially).

The production of laboratory-scale quantities of 100% nitric acid has been described below. The procedures are straightforward, produce a product of acceptable purity, and should not be difficult to expand to either engineering demonstration or plant scale.

The two procedures used for the generation of 100% nitric acid are each a variation of a standard technique. These standard techniques plus comprehensive physical and chemical properties of nitric acid are given by [LEE]. The two procedures are: (1) distillation of a mixture of concentrated nitric and sulfuric acids under reduced pressure and (2) reaction of sodium nitrate with concentrated sulfuric acid, followed by distillation, under reduced pressure, of the nitric acid produced.

The experimental apparatus for both methods of production was fabricated (entirely of glass). All chemicals were obtained commercially and were of ACS reagent grade purity. A water-cooled condenser was utilized to condense the pure nitric acid distillate, and the receiving flask was maintained at the temperature of ice.

A pale-yellow product was obtained in all trials, indicating that some decomposition of nitric acid had occurred. Product densities at 22°C ranged from 1.502 g/mL to 1.5133 g/mL; the accepted density of pure nitric acid is 1.5129 g/mL at 20°C. Sparging the collected product at room temperature with dry air did not remove the yellow color. The average yield for both methods was approximately 90%.

The reversible equilibrium of

describes the decomposition of nitric acid upon exposure to either heat or light. Nitric acid concentration in our product exceeds 99%, and none of the

decomposition products which may be present are detrimental to our process. Therefore, either of the methods produces an acceptably pure nitric acid product.

(2) Behavior of Plutonium Dioxide in Molten Alkali Metal Nitrates

Analytical results have been obtained for the study of the behavior of plutonium dioxide in equimolar sodium-potassium nitrate, referred to in the preceding quarterly report. Under the conditions cited therein, plutonium dioxide did not react. It did not form a soluble species either with the original melt or upon the addition of 100% nitric acid vapor. The analytical results are based on alpha energy analyses of samples of the molten phase taken throughout the experiment.

The observed behavior of plutonium dioxide noted in this preliminary study must be verified by further experimental studies. The experimental apparatus must be modified so that procedures identical to those utilized in previous uranium dioxide studies can be followed. These additional studies are not scheduled until early in FY1979 since equipment modifications must first be made.

It is apparent, however, that the chemical behavior of plutonium dioxide in the equimolar sodium nitrate-potassium nitrate melt is not identical to the behavior of uranium dioxide.

(3) Determination of Alkali Metal Uranate Composition

During this report period, studies to determine the composition of the alkali metal uranates formed in the various alkali metal nitrate melts were initiated.

Uranium dioxide has been reacted with the following melts: sodium nitrate, equimolar sodium nitrate-potassium nitrate, and lithium nitrate-potassium nitrate eutectic containing 42.2 mol % lithium nitrate. A 20:1 mole ratio of nitrate to uranium dioxide was utilized in each case. Reaction was conducted in a muffle furnace at a temperature of 425°C for 4.5 h.

The solidified and cooled salt cake obtained after reaction was dissolved by adding distilled water. Residual brownish solids were filtered and thoroughly washed with distilled water on a fritted glass filter. The filter and solids were dried in a vacuum oven at 120°C for two days.

Determination of the alkali metal concentrations in the salt solutions was done by atomic absorption; uranium content was determined by X-ray fluorescence, utilizing strontium as an internal standard. X-ray powder diffraction patterns were also obtained and compared with patterns of known compounds. The results of these analyses are given in Table 35.

Table 35. Compositions of Alkali Metal Uranates

Constituent	Alkali Metal Nitrate System		
	NaNO ₃ , wt %	NaNO ₃ -KNO ₃ , wt %	LiNO ₃ -KNO ₃ , wt %
Li	--	--	1.07%
Na	6.68%	6.18%	--
K	--	0.71%	3.17%
U	76.1%	75.2%	75.0%

It was assumed that oxygen is the other constituent of the compounds, whereupon empirical formulas for the products from each salt system were obtained. The elemental ratios obtained are subjected to some variation due to uncertainties in the analytical data. The uranium analyses are estimated to be valid within $\pm 2\%$. Independent analytical determinations have shown that the original uranium dioxide contains approximately 0.5% iron plus a trace of silica. The analytical data were not adjusted for these minor impurity levels.

A product in both the sodium nitrate and the equimolar sodium-potassium nitrate melts was a diuranate species, $U_2O_7^{2-}$. Analysis of the product obtained from equimolar sodium-potassium nitrate indicates that sodium is the favored cation in the compound; less than 10% of the alkali metal is potassium. X-ray powder diffraction data provide the evidence that the diuranate species is formed in both of these melt systems.

The product obtained from the lithium nitrate-potassium nitrate eutectic is not identifiable as the diuranate ($U_2O_7^{2-}$), the uranate (UO_4^{2-}), or a mixture of these species. The X-ray powder diffraction pattern for this product is not that of any compound identified to date. The ratios of the alkali metals found for this system are of interest, however. The product has approximately a 2:1 atomic ratio of lithium to potassium, indicating that lithium is the preferred cation.

Based on the above data, it appears that the stability of the uranate product formed is in the order of: $Na \gg K > Li$. Additional studies and determinations of uranate compositions from various nitrate melts will be conducted in FY1979 as necessary to forecast cation behavior and the effect on subsequent process steps.

(4) Behavior of Individual Fission Product Compounds in Equimolar Sodium-Potassium Nitrate Melts

Analytical results have been obtained for the experiment (reported in the preceding quarterly report) on the behavior of uranium dioxide and a simulated fission product mixture* in equimolar sodium-potassium nitrate. Samples were analyzed for the elements of interest by spark source mass spectrometry. Results are semiquantitative, but the detection level was approximately 1 ppm on an atomic basis.

After dissolution of the solids with nitric acid vapor, samples of the molten phase were taken and analyzed. In addition to uranium, only cesium and cerium were present in the melt in concentrations exceeding the detection limit. It must be noted, however, that after addition of nitric acid vapor was terminated, a very small amount of solids was observed. The possibility exists that insufficient nitric acid was added.

After thermal decomposition of the soluble uranium species, dissolved cesium, cerium, and molybdenum were present in the molten phase at detectable levels.

Analyses of the final solids indicated that they contained all of the fission product elements of concern. These elements were: antimony, cerium, cesium, iodine, molybdenum, niobium, palladium, rhodium, ruthenium, samarium, strontium, yttrium, and zirconium. Both iodine and ruthenium were found in the solids, indicating that even if these formed volatile species they were not completely released in the time period of the experiment.

The rare earths and most other elements, (except the noble metals) were expected to form soluble species during the addition of nitric acid vapor. In addition, it has been claimed [BRAMBILLA] that both iodine and ruthenium are volatilized during reaction of the molten nitrate with the oxide fuel. In contrast to the claim that both iodine and ruthenium are lost to the gas phase, other literature exists [C.E.N.] which claims that both iodine and ruthenium will be found in the molten phase. Still another claim [AVOGADRO-1971] states that most of the fission products other than the noble metals are either volatile or soluble in the nitrate melt--even without the addition of nitric acid vapor. Later, however, Avogadro [AVOGADRO-1972] reported that iodine is stable as iodide in molten nitrates and that part of the ruthenium is in the molten phase, that part of it volatilizes, and that most of it remains with the solids produced. Most other fission products such as the rare earths, barium, strontium, zirconium, etc. were expected to be found in the solids [AVOGADRO-1972].

*Mixture consisted of oxides of antimony, cerium, molybdenum, palladium, rhodium, ruthenium, samarium, strontium, yttrium and zirconium; cesium iodide; and potassium hexaniobate.

Our results are not in accord with the behavior of the rare earths and certain other fission products expected upon the addition of nitric acid vapor to the melt. Because of this, both the experimental method used for the determination of fission product behavior and the analysis technique chosen are matters of concern.

It was recognized that the chemical form of our fission product mixture would not be identical to that found in irradiated fuel, but it was hoped that the behavior of our simulated material would be enough like that of fission products to allow use of the synthetic blend. Based on our analytical results, behavior may not be similar--hence, our concern.

In addition, it was difficult to analyze our samples by spark source mass spectroscopy. Apparently, the large concentrations of alkali metal cations present were responsible for considerable sample disintegration in the arc.

Alternative techniques of determining fission product behavior are being considered and are expected to be incorporated into future experimental studies. Preparation of a coprecipitated uranium-fission product compound followed by calcination, reduction, and sintering in an attempt to more closely approximate irradiated fuel composition and form is one alternative being considered. Fission product concentrations in the final material would be those predicted for fuels irradiated in fast breeder reactors. Addition of fission product tracers is also being evaluated as an alternative analytical technique, provided that the tracer can be incorporated into the same matrix as would the isotope that would be produced by fission.

Additional qualitative experiments have been conducted to aid in determining the behavior of individual fission product elements. Each element of interest was added as a compound to the sodium nitrate-potassium nitrate, which was then melted. Visual observation of the fission product compound behavior was the only test utilized in these qualitative experiments.

Upon the addition of antimony oxide, tin(II) oxide, or samarium oxide, there was no evidence of reaction with the nitrate melt or of dissolution. Addition of zirconyl nitrate resulted in the evolution of nitrogen dioxide from the melt and the formation of a white insoluble precipitate.

Addition of palladium nitrate to the melt system produced a black melt and black insoluble solids. Upon dissolution of the cooled and solidified salt cake with distilled water, it was observed that a palladium mirror had formed at the meniscus of the melt.

Niobium was added as potassium hexaniobate (exact composition unknown). There was no visible evidence of reaction or solubility.

A potassium ruthenium nitrite compound (exact composition unknown) was added to the nitrate melt. The original compound was amber. Black solids formed in the melt and settled to the bottom of the reaction vessel, leaving a green supernate. When the solidified and cooled melt was dissolved in distilled water, nearly all of the ruthenium present appeared to dissolve.

Antimony oxide was dissolved in concentrated hydrochloric acid, and the resulting solution was evaporated to dryness. (The product of this treatment is probably either SbCl_3 or SbOCl .) These solids were added to the nitrate melt; evolution of nitrogen dioxide was observed, after which a white precipitate formed. There was no evidence of dissolution at any time.

Cesium iodide added to the nitrate system appeared to dissolve completely, as did molybdenum trioxide.

The results of these qualitative tests and those obtained by spark source mass spectroscopy in the experiment referred to above indicate that of the elements tested thus far, we may expect to find some of the cerium, cesium, iodine, molybdenum, and possibly ruthenium as soluble species in the equimolar sodium nitrate-potassium nitrate melt. Both qualitative and quantitative studies of fission product behavior are continuing.

(5) Effects of Added Anions on UO_2 Behavior in Equimolar Sodium-Potassium Nitrate Melts

Preliminary experiments were performed to determine the effects of added anions on the behavior of uranium dioxide in molten alkali metal nitrates. Qualitative experiments have been conducted in which chloride (Cl^-), fluoride (F^-), and carbonate (CO_3^{2-}) ions were added. The initial interest was to determine if added anions could produce a soluble uranium species without the addition of 100% nitric acid vapor to the nitrate melt.

In these preliminary experiments, the halide ions were added as uranyl halides to a mixed halide-nitrate melt system. Upon the addition of uranyl chloride (UO_2Cl_2) to a 6 mol % potassium chloride - 94 mol % potassium nitrate melt system, there was no visible evidence of either reaction or solubility of the uranyl chloride. Identical results were obtained utilizing a 5 mol % sodium chloride - 95 mol % sodium nitrate melt.

Uranyl fluoride, UO_2F_2 , was added to a 9 mol % potassium fluoride - 91 mol % potassium nitrate system. A slight yellow tinge was observed in the molten phase. There was no evidence of color in the molten phase for a similar melt composed of 3.5 mol % sodium fluoride - 96.5 mol % sodium nitrate.

The addition of carbonate ion to equimolar sodium nitrate-potassium nitrate melts did not produce a soluble uranium species when the melt was reacted with uranium dioxide. However, when reaction does occur,

the effect of added carbonate ion is considerable. Additions of carbonate ion, not exceeding the solubility limit, have the effect of lowering the temperature required for reaction and also decreasing the time required for reaction. For example, equimolar sodium nitrate-potassium nitrate with added carbonate ion reacts with uranium dioxide (20:1 mole ratio of nitrate to uranium dioxide) at 300°C within 1 h. Without the addition of carbonate ion, the reaction requires a temperature of approximately 420°C and a time period of 2 to 3 h.

A concise summary of the stability and behavior of carbonate ion in molten nitrates is given in the excellent review by Plambeck [PLAMBECK]. Carbonate ion is known to be stable in fused nitrates over a period of at least several hours at temperatures less than or equal to 350°C. The solubility of sodium carbonate at 250°C in equimolar sodium nitrate-potassium nitrate has been interpreted from thermodynamic data to be 2.3×10^{-2} mol/kg of nitrate or 2.1×10^{-3} mol CO_3^{2-} /mol NO_3 .

The equilibrium represented by

is not supported by experimental evidence in the molten nitrate systems. Carbonate ion can, however, be regarded as a Lux-Flood base (oxide ion donor) toward acids (oxide ion acceptors) in the nitrate system, although direct reaction of the carbonate ion is the preferred interpretation--not reaction with equilibrium oxide ion.

Based on visual observation, we have determined the solubility of sodium carbonate to be approximately 1.7×10^{-2} mol CO_3^{2-} /mol NO_3 at 300°C. We have developed a method (discussed briefly in a following section) for quantitative determination of carbonate ion in this system. Quantitative determinations of the solubility of sodium carbonate in equimolar sodium nitrate-potassium nitrate will be made in FY1979.

Preliminary experiments have been conducted to determine the quantitative relationship between added sodium carbonate and the reaction of uranium dioxide in the melt system. Sodium carbonate was added to equimolar sodium nitrate-potassium nitrate in the ratio of 1.39×10^{-2} mol CO_3^{2-} /mol NO_3 . This amount of carbonate does not exceed the solubility limit. A molar excess of carbonate with respect to uranium dioxide was maintained in these experiments (1.39 to 2.09 mol CO_3^{2-} /mol UO_2).

The reaction of uranium dioxide with the above solution was allowed to go to completion at temperatures of 300 to 350°C. The cooled and solidified salt cake was then dissolved in distilled water, and a total carbonate analysis was performed on the aqueous solution. The results of four preliminary trials conducted thus far indicate an average loss of 2.1×10^{-3} mol of carbonate as a result of reaction.

Consider the Lux-Flood acid-base reaction given by

as a possible reaction path once the diuranate species is formed. Based on the amount of uranium dioxide present in each case, this reaction would require 2.7×10^{-3} mol of carbonate to go to completion. This value compares very favorably with our figure of 2.1×10^{-3} mol of carbonate lost, especially since the uncertainty in the analyses of total carbonate has averaged $\pm 5\%$.

Further tests to quantify the effects of added carbonate ion on the reaction of uranium dioxide, including analyses of the uranate produced, will be conducted in FY 1979.

One other aspect of the effect of added anions to be considered is the possibility of utilizing selected additives to precipitate otherwise soluble species in the nitrate melt. We have shown in this work that adding sodium carbonate to a nitrate melt containing soluble strontium nitrate produces an insoluble precipitate--presumably, strontium carbonate. Similar results have been obtained when sodium sulfate was added to a nitrate melt that contains soluble strontium nitrate.

To investigate the effect of adding sulfate ion to the nitrate melt, the solubility of sodium sulfate in equimolar sodium nitrate-potassium nitrate has been determined. A portion of a sodium sulfate-saturated melt at 300°C was obtained and dissolved in distilled water. On the basis of precipitation of barium sulfate from this aqueous sample and gravimetric analysis, a solubility of approximately 5.96% for sodium sulfate in the nitrate melt was indicated.

Addition of molybdenum trioxide (MoO_3) to the nitrate melt produced visible evolution of nitrogen dioxide. This observation cannot be explained on the basis of Mo(VI) and is due (presumably) to the presence of some molybdenum in a lower oxidation state. The material formed is, however, soluble in the nitrate melt (the solubility limit has not yet been determined).

Addition of soluble strontium nitrate to an equimolar sodium nitrate-potassium nitrate melt containing the soluble molybdenum species produced an insoluble precipitate that is also insoluble in water. The existence of an aqueous-insoluble strontium molybdate is known, and it is believed that we have formed such a species in the melt.

Possible fission product interactions, as demonstrated by the behavior given for strontium and molybdenum, must be carefully considered and determined for this nitrate melt system and for each step of the proposed process.

These preliminary studies of the effects of added anions in nitrate melts have shown:

- Uranyl chloride and uranyl fluoride have negligible solubility in halide-nitrate melt systems.

- Addition of carbonate ion does not produce a soluble uranium species in equimolar sodium nitrate-potassium nitrate, but does lower the temperature and decrease the time required for reaction of uranium dioxide.
- The quantity of carbonate ion lost during the melt reaction of carbonate with uranium dioxide is consistent with the reaction given by

- Soluble fission product species can be precipitated by the addition of specific reagents to the melt.
- Interactions of fission products must be considered and their behavior determined.

(6) Development of Analytical Methods

The quantitative results necessary for analysis of each proposed process step require accurate analytical data. Standard analytical methods are utilized to the maximum extent possible, but occasional development of specific analytical techniques is required. The details of the specific techniques developed in support of our project goals are not reported herein, but are documented and are available.

Thus far, the specific techniques developed have included (1) quantitative determination of iron in uranium dioxide (or uranate compound), and (2) the determination of total carbonate in equimolar sodium-potassium nitrate.

It is anticipated that additional development will be required to determine which actinide and fission product species are present, either in the melt or as insoluble precipitates, as anionic or cationic species. It is expected that the techniques of ion exchange and ion chromatography will be utilized in this area. It is also expected that the feasibility of utilizing ion chromatography for quantitative alkali metal analyses will be determined.

Accurate analyses of the partitioning of fission products in each proposed process step are still to be verified. The utilization of specific radioactive tracers will be tested.

(7) Proposed Conceptual Process Flowsheet

Figure 48 represents a proposed conceptual process flowsheet based on the studies conducted in FY1978. In FY1979, each proposed process step will be examined in detail so that accurate feasibility determinations can be made.

Fig. 48. Conceptual Process Flow Sheet

8. Molten Salt Processes Applied to Nuclear Fuels

(H. F. McDuffie,* Duane H. Smith,* and G. W. McDonald,*)

The purpose of this program is to establish chemical bases for proliferation-resistant methods that utilize molten salts and/or metals for reprocessing nuclear reactor fuels.

a. Progress

(1) Engineering Analysis

In one step of the molten salt process under consideration, fissile and fertile materials are transferred from molten lithium chloride into molten bismuth-lithium alloy, after which the two phases are separated. Detailed analyses are needed of the temperature dependencies of the redox distribution coefficients of various solutes in the LiCl/Bi-Li solvent pair so

*Oak Ridge National Laboratory.

that the optimum temperature for the critical separations step can be determined. The choice of operating temperature will impact on three important areas: (1) separation factors, (2) solubilities of the actinides in bismuth, and (3) materials problems. In general, raising the temperature will have a favorable effect on (2), an unfavorable effect on (3), and effects on (1) which may be either favorable or unfavorable.

It is convenient to write the redox distribution coefficient, D_M , as

$$\log D_M = n \log N_{Li} + \log K_M \quad (1)$$

where n = oxidation of the metal (M^{n+}) in the salt phase, N_{Li} = mol fraction of lithium in bismuth, and K_M = constant. All published experimental values of $\log K_M$ which we have found are summarized in Table 36. Ferris et al. [FERRIS-1972A] measured the redox distribution coefficients of La(3), Nd(3), Sm(2), Eu(2), and Ba(2) over the temperature range 625-750°C more extensively and showed that the data for each element are accurately fit by the equation, $\log K_M = A + B/T$, where A and B are constants characteristic of each element, M . Published values of A and B for these elements are listed in Table 37. It is striking that for all known divalent sixth-row elements $B = (2070 \pm 120)K$. Likewise La(3) and Nd(3) exhibit the same temperature dependence-- $B = (10,300 \pm 700)K$, within $\pm 6\%$. These values of A and B are based on measurements at four to eight different temperatures for each element.

For the actinides (except uranium), values of K_M were apparently measured at only two temperatures, 640°C and 700°C (Table 36); nevertheless, it is useful to calculate values of A and B for these elements also. We have done so, and these values are listed in Table 38.

Despite the uncertainties in A and B being larger for the actinides than for the rare earths, certain trends seem clear:

(1) B 's for the divalent seventh-row elements are small and probably are close to the values of B for sixth-row elements.

(2) Absolute values of B for the trivalent actinides (except uranium) are also small (-1000 to -5000). Since the sign of B is positive for the lanthanides, the lanthanide-actinide separation factors will improve with increasing temperature for neptunium, plutonium, americium, and curium.

(3) For uranium, B is positive and apparently quite large. Although this behavior seems anomalous compared to that of the other trivalent actinides, it appears less so when compared to either the behavior of Nd(3) (immediately above uranium in the periodic chart) or to the behavior of Th(4) and Pa(4) (immediately to the left of uranium in the periodic table). The value of B for uranium would be considerably smaller if we ignored the two values reported for $\log K_U$ at 640°C, but there is no known reason to do so. As the temperature is raised, less uranium is transferred from LiCl into

Table 36. Values of $\log K_M$ Reported for the Solvent Pair, LiCl/Bi(Li)^a

M^b	$\log K_M$	Reference
<u>T = 750°C</u>		
La(3)	6.820 ± 0.1	[FERRIS-1972C]
<u>T = 700°C</u>		
La(3)	7.185 ± 0.2	[FERRIS-1972A]
Nd(3)	7.831 ± 0.2	[FERRIS-1972A]
Pm(3)	7.45 ± 0.4 (est.)	[FERRIS-1971]
Sm(2)	2.756 ± 0.1	[FERRIS-1972A]
Eu(2)	2.133 ± 0.1	[FERRIS-1972A]
Th(4)	13.772 ± 0.2	[FERRIS-1972A]
Pa(4)	15.8 ± 0.4	[FERRIS-1972A]
U(3)	10.192 ± 0.2	[FERRIS-1972A]
Np(3)	10.369 ± 0.3	[FERRIS-1972A]
Pu(3)	10.223 ± 0.3	[FERRIS-1972A]
Am(2) ^c	7.155 ± 0.1	[FERRIS-1972A]
Am(3) ^c	10.377 ± 0.2	[FERRIS-1972A]
Cm(3)	9.589 ± 0.2	[FERRIS-1972A]
Cf(2) ^c	5.37 ± 0.1	[FERRIS-1972A]
<u>T = 675°C</u>		
U(3)	10.11 ± 0.3	[FERRIS-1972A]
<u>T = 650°C</u>		
La(3)	7.847 ± 0.1	[FERRIS-1972C]
Ce(3)	8.312 ± 0.384	[MOULTON]
Eu(2)	2.279	[FERRIS-1972B]
Eu(2)	2.284 ± 0.025	[MOULTON]
Na(1)	0.164	[RICHARDSON-1970B]
K(1)	1.099	[RICHARDSON-1970B]
Cs(1)	1.503	[RICHARDSON-1970A]
Sr(2)	1.024 ± 0.141	[MOULTON]
Ra(2)	1.757	[YOUNGBLOOD]

(contd)

Table 36. (cont.)

M ^b	log K _M	Reference
<u>T = 640°C</u>		
La(3)	7.796	[FERRIS-1972B]
La(3)	7.973 ± 0.2	[FERRIS-1972A]
Ce(3)	8.633 ± 0.2	[FERRIS-1972A]
Nd(3)	8.633 ± 0.2, 8.374	[FERRIS-1972A, B]
Nd(3)	8.582 ± 0.1	[FERRIS-1972C]
Pm(3)	7.71 (est.)	[FERRIS-1972B]
Sm(2)	2.886 ± 0.1	[FERRIS-1972A]
Th(4)	15.358 ± 0.2	[FERRIS-1972A]
Pa(4)	17.84 ± 0.4	[FERRIS-1972A]
U(3)	11.278 ± 0.2	[FERRIS-1972A]
U(3)	11.197	[FERRIS-1972B]
Np(3)	10.330 ± 0.2	[FERRIS-1972A]
Pu(3)	10.126 ± 0.2	[FERRIS-1972A]
Am(2) ^c	7.658 ± 0.3	[FERRIS-1972A]
Am(3) ^c	9.955 ± 0.1	[FERRIS-1972A]
Cm(3)	9.406 ± 0.2	[FERRIS-1972A]
Cf(2) ^c	5.419 ± 0.1	[FERRIS-1972A]
Cf(3) ^c	8.966 ± 0.1	[FERRIS-1972A]
Ba(2)	1.702 ± 0.05	[FERRIS-1972A]
<u>T = 630°C</u>		
Eu(2)	2.301 ± 0.05	[FERRIS-1972A]

^aFor measurements of log K_M for La, Nd, Sm, Eu, and Ba at other temperatures, see [FERRIS-1972A]; see also Table 37.

^bOxidation number in the salt phase in parentheses.

^cSee [FERRIS-1972A] for the relative importance of the two oxidation states.

bismuth. This has two effects: (a) the separation factor for uranium from the rare earths becomes smaller, and (b) above about 700°C, the distribution coefficient of plutonium and neptunium become larger than the distribution coefficient of uranium.

(4) The temperature dependencies of log K_M are even larger for protactinium and thorium than for uranium; hence, the effects discussed above for uranium are accentuated for these elements. However, since protactinium and thorium form tetrachlorides, their separation factors from trivalent elements depend on the reductant metal (Li) concentration, as well as on the temperature.

Table 37. Temperature Dependence of $\log K_{Ln}$
Reported for the Solvent Pair
LiCl/Bi(Li): $\log K_M = A + B/T^a$

Lanthanide(Ln) ^b	A	B	Std. deviation of $\log K_{Ln}$
La(3)	-2.6585	9697	0.1
Nd(3)	-3.3568	10900	0.08
Sm(2)	0.7518	1950	0.05
Eu(2)	-0.1584	2250	0.05
Ba(2)	-0.6907	2189	0.02

^a[FERRIS-1972A]; T = 898-1023K (625-750°C)

^bOxidation number in the salt phase in parentheses.

Table 38. Approximate Values of A and B in the
equation, $\log K_{An} = A + B/T^a$

Actinide (An) ^b	A	B	No. of Data
Th(4)	-10.339	23,462	2
Pa(4)	-15.21 (est)	30,180 (est)	2
U(3)	-8.021	17,519	4
Np(3)	+10.962	-577	2
Pu(3)	+11.698	-1,435	2
Am(2)	-0.492	+7,441	2
Am(3)	+16.793	-6,243	2
Cm(3)	+12.371	-2,707	2
Cf(2)	+4.625	725	2

^aCalculated from data in Table 36.

^bOxidation number in the salt phase is in parentheses.

The draft report of the literature review for work package 10 (event 110.1) has been written during this quarter [SMITH-1978]. Its scope includes dissolution of oxide fuels in molten salts; the redox distribution coefficients of lanthanides, actinides, and alkali metals between bismuth and molten alkali chloride solvents; and thermodynamic data for the prediction of distribution coefficients between bismuth and alkali chloride or fluoride solvents (standard free energies of formation, activity coefficients, and data for calculating these). Also reviewed are the oxidative extraction of the actinides from bismuth into ammonium chloroaluminate (NH_4AlCl_4) and recovery of product from the latter salt. More than three hundred citations are given.

(2) Separations Processes

Actinides that have been isolated in bismuth are next transferred into ammonium chloroaluminate (NH_4AlCl_4). Scouting experiments were begun to test the postulated oxidative extraction of fissile, fertile, and actinide species from bismuth as illustrated by the following equation:

In one experiment, about 10 g bismuth containing a small amount of uranium was placed in a quartz tube along with 3.47 g of zone-refined NH_4AlCl_4 . The tube was evacuated, the salt was melted to compact it, and the tube was then sealed under vacuum. The tube was heated to 330°C for 5 h with periodic mixing by tilting and was then cooled. Subsequent analyses showed that the original bismuth had contained 45 ppm U; after contact with the salt, the bismuth contained only 2.62 ppm uranium. The salt sample from this experiment contained 144 ppm uranium. Clearly, the uranium had moved to the salt phase.

A second experiment repeated the first except that there was only 15 min of exposure of bismuth to salt at 330°C . The final bismuth contained only 1.99 ppm uranium, and the final salt phase contained 713 ppm uranium. This confirmed essentially complete extraction of uranium in a minimum of contact time.

An experiment was done to test the extraction of thorium from bismuth by NH_4AlCl_4 . Exactly 10.0 g bismuth, containing 1.45 wt % thorium was placed in a quartz tube along with 1.56 g NH_4AlCl_4 . The sealed tube was heated for 17 h at 335°C . After cooling and separation of the phases, the bismuth contained 185 ppm thorium, some of which might have been present as surface inclusions of salt. The final salt phase contained 4.83% thorium. (A small amount of brown solid, which formed immediately upon initial melting of the tube contents and did not thereafter dissolve, contained 11.1% thorium.)

These systems probably contained UBi_2 (or ThBi_2) in addition to dissolved uranium (or thorium) before reaction with HCl took place. Hence, these scouting experiments probably demonstrate the extractability of ThBi_2 and UBi_2 , as well as that of the metals dissolved in the bismuth.

Since scouting studies indicate that uranium and thorium can be extracted from bismuth into ammonium chloroaluminate, the solubilities of UCl_4 and ThCl_4 in the salt are also of considerable importance. A value of 23.8% (units unclear) had previously been reported for the solubility of UCl_4 in NH_4AlCl_4 [ORNL]. In one pair of our experiments, 1 wt % amounts of ThCl_4 or UCl_4 dissolved completely in NH_4AlCl_4 at 375°C . Subsequent measurements yielded solubilities of 1.84 wt % ThCl_4 at 350°C , 1.1 wt % ThCl_4 at 375°C , and 7.0 wt % UCl_4 at 375°C . It appears that the previously reported value for UCl_4 solubility may have been too high.

The next step in the molten salt process is the recovery of actinide chlorides from ammonium chloroaluminate by "distillation" of the solvent at about 400°C. In a duplicate pair of distillation experiments, the starting material contained 15 g of NH_4AlCl_4 and 1 wt % amounts (0.15 g each) of ThCl_4 and UCl_4 . The first distillation was stopped with 47 wt % of the NH_4AlCl_4 left in the bottoms, the second with only 14 wt % undistilled (based on N, Th, and U analyses). After the distillations were stopped, the distillates contained 0.005 and to 0.01 wt % uranium and 0.002 to 0.006 wt % thorium. Obviously, very little of the uranium or thorium carried over. The aluminum/nitrogen ratios in the bottoms indicated the presence of a nonvolatile compound which contained aluminum but not nitrogen. This compound may have been aluminum oxychloride.

A draft report of these scouting experiments conducted during June through August, 1978, was written this quarter [MCDONALD]. This document reports on the synthesis and purification of ammonium chloroaluminate, its successful use for the oxidative extraction of uranium and thorium from liquid bismuth at 335°C; the recovery of uranium chloride and thorium chloride from ammonium chloroaluminate by "distillation" of the latter salt at 400°C, and the approximate solubilities of uranium chloride and thorium chloride in the chloroaluminate salt.

b. Plans for Next Quarter

We plan to continue experiments with ammonium chloroaluminate. The literature review will be submitted, and our work will be presented at the PDPM review meeting in November. An annual report will be written.

9. Reprocessing of Thoria-Urania Fuel
(P. Chiotti* and L. E. Burkhart*)

These studies pertain to the separation of fission product elements from simulated spent $(\text{Th,U})\text{O}_2$ fuel. The reaction media are to be molten chloride salts and molten metals such as zinc, tin, lead, bismuth, or mixtures of these. However, the principal effort will be with KCl-LiCl , KCl-MgCl_2 , and KCl-NaCl-MgCl_2 eutectics and liquid zinc. Two processing techniques were investigated: (a) conversion of $(\text{Th,U})\text{O}_2$ to carbide with volatile fission products vaporized, after which the carbide might or might not be reconverted to the oxide and (b) extraction of uranium and noble fission product elements from $(\text{Th,U})\text{O}_2$ solid solution into a molten salt.

a. Conversion of $(\text{Th,U})\text{O}_2$ to $(\text{Th,U})\text{C}_x$
(O. N. Carlson* and L. Shiers)*

Because of the inertness of high-density $(\text{Th,U})\text{O}_2$, its conversion to $(\text{Th,U})\text{C}_x$ is considered an advantageous first step in fuel reprocessing. Available thermochemical data indicate that volatilization of many of the

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fission product elements can be achieved during the conversion step by heating in vacuo. The less volatile elements (such as zirconium, niobium, molybdenum, technetium, ruthenium, and possibly yttrium) are expected to be in the carbide at the end of the conversion step. It also appears to be technically feasible, during reconversion of the carbide to the oxide, to remove molybdenum and ruthenium as the volatile oxides, MoO_3 and RuO_4 .

(1) Experimental

Work was continued on study of the feasibility of converting $(\text{Th}, \text{U})\text{P}_2$ fuel to a carbide as a front-end step in fuel reprocessing. The experimental approach is to determine the optimum conditions for converting to the corresponding carbides a mixed oxide containing representative fission product oxides. The carbide product is then evaluated for completeness of the reaction and for removal of volatile fission products.

A series of runs was carried out in which compacted mixtures of oxide and graphite powder were converted (1) to the corresponding monocarbide $(\text{Th}, \text{U})\text{C}_{0.8}$ by heating at 2025, 2240, and 2325°C for 1 h and also (2) to the dicarbide at 2425 and 2525°C. The results of the oxygen and nitrogen analyses of the carbides and of the diffraction studies are given in the first five rows of Table 39. The percent conversion to the carbide shown in the table was determined from the residual oxygen content, it being assumed that all of the oxygen was present as the oxycarbide. The major phase present (shown in the rightmost column of the table) was identified by X-ray diffraction. Preliminary indications are that at pressures of 0.05 to 0.1 Torr, temperatures above 2400°C are required for conversions of greater than 95%.

Runs 94 and 96 were carried out at lower pressures (about 2×10^{-4} Torr) to determine the effect of ambient pressure on the conversion reaction, as well as on the removal of fission product elements. Vacuum fusion analyses of these two runs are unavailable at this time.

Of particular note is Run 85 in which sol-gel ThO_2 pellets were packed in graphite powder and heated to 2435°C (i.e., just below the ThC_2 -C eutectic temperature). One pellet disintegrated completely and the other underwent extensive reaction and disintegration during conversion to the carbide. Thus, it would appear that chemically inert sol-gel ThO_2 pellets can be readily converted to the more reactive carbide by high-temperature treatment.

A series of experiments was carried out to determine the feasibility of removing appreciable amounts of fission product elements, either during the carbide conversion step or during subsequent electron beam melting. In the conversion step, the main variables investigated were temperature and pressure; residence time was the major variable in the electron beam

Table 39. Carbide Conversion of ThO₂ and (Th,U)O₂ Containing Fission Product Oxides

Run No.	Charge ^a	Wt, g	Heating Temp, °C	Heating Time, min	Pressure, ^b 10 ⁻³ Torr	Carbide Analysis		Conversion to Carbide, %	Major Phase (X-ray)
						Oxygen, %	Nitrogen, ppm		
47	ThO ₂ , C	55	2200	50	400+190	0.76	360	90	ThC
51	ThO ₂ , C	57	2420	50	170+135	0.32	83	95	ThC ₂
55	(Th,U)O ₂ , F.P., C	42	2425	50	220+170	0.17	83	97	(Th,U)C ₂
60	(Th,U)O ₂ , F.P., C	43	2240	50	300+350	0.34	53	95	(Th,U)C
63	(Th,U)O ₂ , F.P., C	48	2025	50	400+175	2.40	86	63	(Th,U)C
80	(Th,U)O ₂ , F.P., C	57	2530	50	83+36				(Th,U)C ₂
85	Sol-Gel ThO ₂ , C	2	2435	50	78+33				ThC ₂
86	(Th,U)O ₂ , F.P., C	55	2325	60	140+36				(Th,U)C
94	(Th,U)O ₂ , F.P., C	49	2300	80	60+0.22				(Th,U)C
96	(Th,U)O ₂ , F.P., C	57	2385	80	20+0.14				(Th,U)C ₂

^a(Th,U)O₂ contains 9.3 wt % UO₂.^bPressure range from the beginning of reaction to the end of heating time.

melting experiments. Emission spectroscopic analyses standards were developed and used to determine the degree of fission product removal. As is seen for Runs 23a and 80a of Table 40, the only elements removed in any significant amounts during conversion to the dicarbide at 2400°C and 2530°C, respectively, are barium and strontium. Similar results are obtained for conversion to the monocarbide, (Th,U)C_{0.8}, either at 2150°C or 2325°C (runs 29a and 86a respectively). All of these runs were carried out at the minimum pressures of 3.5×10^{-2} Torr obtainable by evacuation with a mechanical pump. As is seen in Table 40, for runs 94a and 96a the analytical data show no evidence of increased volatilization of any of the rare earth elements during carbide conversion at the lower pressures listed in Table 39.

The data show, however, significant decreases in lanthanum, neodymium, praseodymium, and yttrium after electron beam melting (Runs 23b, 29b, 80b, and 86b), showing the effects of the higher melting temperature and/or lower pressures obtainable in the electron beam furnace. No removals of molybdenum, ruthenium, or zirconium were observed, however. In electron beam melt runs 23b and 29b, weight losses of 15 to 20% were encountered along with a significant decrease in the U:Th line intensity ratio indicative of considerable vaporization of the uranium. In runs 80b and 86b, in which more controlled melting conditions were used, the weight losses were reduced to 10.5% and 6.6%, respectively, and the U:Th ratio remained constant (Table 40).

(2) Reconversion of (Th,U)C to (Th,U)O₂

The possibility of removing molybdenum and ruthenium as volatile oxides by oxidizing the carbide after the conversion step was investigated. First, (Th,U)O₂ containing fission product additions was converted to the carbide; then it was reoxidized by heating in air at 800°C for 2 h (run 55, Table 39). The experiment was repeated starting with monocarbide (run 94a) and dicarbide (run 96a). These were each oxidized in a stream of pure oxygen at 840°C for 12 h and then submitted for analysis by emission spectroscopy. The results (Table 41) for the three different carbide series indicate that some loss of molybdenum occurred and that in the longer runs in pure oxygen (runs 94 and 96), some ruthenium may also have been removed. The unexpected loss of cerium in runs 55 and 94 is not observed in run 96.

Because of the critical importance of temperature control in this work, attempts were made to determine the melting point of the mixed carbides used in this study. Of particular concern was the effect of uranium on the melting points of ThC and of ThC₂-C eutectic. A melting point of $2350 \pm 25^\circ\text{C}$ was obtained for (Th, 9%U)C, which is at least 150°C lower than the melting point of ThC reported in [SMITH-1975A]. This difference from the reported melting point is attributed to experimental error in our measurements, rather than 2350°C being the true melting point.

In a review of the uranium and plutonium carbide literature, [HOLLECK-1969] reports that the addition of 9% U to ThC₂ has very little effect on the melting point of thorium dicarbide, lowering it from 2650°C to about 2625°C. The possible lowering of the melting points of the

Table 40. Summary of Fission Product Removal during Conversion Step and Subsequent Electron-Beam Melting

Run	Carbide Charge	Temp °C	Condition	Fraction of F. P. Element Present										U:Th ^a
				Ba	Ce	La	Mo	Nd	Pr	Ru	Sr	Y	Zr	
23	ThC ₂ + F.P.	2400	Oxide Charge	—	0.85	0.36	0.90	1.12	0.35	0.43	0.40	0.20	1.26	
23a	ThC ₂ + F.P.		Converted Carbides	—	.79	0.28	0.72	0.79	0.44	0.73	<<0.1	0.27	1.10	
23b	ThC ₂ + F.P.		Electron Beam	—	<<0.2	<<0.09	0.74	<<0.25	<<0.08	0.53	<<0.1	<<0.05	0.69	
29	(Th,U)C + F.P.	2150	Oxide Charge	—	0.85	0.37	0.90	1.12	0.35	0.41	0.40	0.20	1.25	
29a	(Th,U)C + F.P.		Converted Carbides	—	0.81	0.20	~1.05	0.42	0.23	~0.83	<<0.10	0.21	~2.20	0.57
29b	(Th,U)C + F.P.		Electron Beam	—	<0.20	<0.09	0.70	<0.28	<0.09	~0.66	<<0.10	<0.05	0.88	0.22
80	(Th,U)C ₂ + F.P.	2530	Oxide Charge	0.40	0.55	0.31	0.62	0.87	0.45	0.29	0.16	0.20	0.80	1.10
80a	(Th,U)C ₂ + F.P.		Converted Carbides	<<0.1	0.78	0.26	0.72	0.82	0.45	0.64	<0.1	>0.3	1.5	1.12
80b	(Th,U)C ₂ + F.P.		Electron Beam	<<0.1	<0.2	0.12	0.85	<0.2	<0.08	0.70	<0.1	0.09	1.05	1.24
86	(Th,U)C + F.P.	2325	Oxide Charge	0.21	0.53	0.26	0.64	0.66	0.33	0.26	0.22	0.19	0.92	1.10
86a	(Th,U)C + F.P.		Converted Carbide	<<0.1	0.34	0.25	0.64	0.24	<0.08	0.45	<<0.1	0.16	1.25	1.10
86b	(Th,U)C + F.P.		Electron Beam	<<0.1	<0.2	<0.1	0.84	<0.2	<0.08	0.80	<0.1	<0.05	1.25	1.09
94	(Th,U)C + F.P.		Oxide Charge	0.33	0.81	0.27	0.62	0.68	0.11	0.24	0.40	0.11	1.03	1.14
94a	(Th,U)C + F.P.		Converted Carbide	<<0.1	0.84	0.18	0.78	0.31	0.11	0.51	<0.1	0.16	1.07	1.24
96	(Th,U)C ₂ + F.P.	2385	Oxide Charge	0.31	0.74	0.34	0.67	0.84	0.55	0.28	0.28	0.12	0.98	1.09
96a	(Th,U)C ₂ + F.P.		Converted Carbide	<0.1	0.80	0.40	0.72	0.97	0.56	0.55	<0.1	0.3	1.10	1.12

^aIntensity ratio of U:Th lines.

Table 41. Reoxidation of (Th,U)C₂ to Remove Nonvolatile Fission Products

Run No.	Condition	Fraction of F.P. Element								U:Th Ratio
		Ce	La	Mo	Ru	Y	Zr	Pr	Nd	
55	oxide fuel	0.85	--	0.92	0.38	0.20	1.26			
	dicarbide	0.85	--	--	--	0.26	--	--	--	--
	reoxidized	0.46	--	0.61	0.43	0.17	1.10	--	--	--
94a	monocarbide	0.84	0.18	0.78	0.51	0.16	1.07	0.11	0.31	1.24
94aR	reoxidized	0.42	0.15	0.42	0.27	0.21	0.86	0.11	0.32	1.13
96a	dicarbide	0.80	0.40	0.72	0.55	0.30	1.1	0.56	0.97	1.12
96aR	reoxidized	0.82	0.42	0.65	0.46	0.29	1.1	0.60	0.90	1.12

binary carbides by the presence of fission product carbides could cause difficulty--particularly in controlling the monocarbide composition if melting should occur during the conversion step. The melting point of the (Th,U)C₂-C eutectic containing the fission product additions was determined as 2420°C ± 25°C, which is about 75°C lower than the melting point of the (Th,10%U)C₂-C eutectic as reported by [PETERSON].

(3) Reaction of ThC_x with ZnCl₂ in Fused KCl-LiCl
(P. Chiotti* and D. Johnson*)

The conversion of (Th,U)C_x to ThCl₄ and UCl₃ by reaction with ZnCl₂ in fused KCl-LiCl eutectic salt has been proposed as one step in the reprocessing of (Th,U)O₂ fuel. Considerable time has been spent on evaluating the kinetics of the reaction

As reported in the preceding quarterly report, the kinetics of the reaction appear very favorable. In experiments in which a typical charge of 900 g of KCl-LiCl eutectic salt, 14 g of ThC_x powder, and 22 g ZnCl₂ was equilibrated at 500°C, reaction was complete in two to three hours. However, only 87 to 90% of the thorium added as carbide had been transferred to the salt. Analyses of the carbide showed an appreciable oxygen content which could in part account for the low thorium recovery in the salt because ZnCl₂ does not convert either ThO₂ or ThOCl₂ to ThCl₄. It was not known whether the unconverted thorium concentrated at the salt-zinc interface or was dispersed in the zinc as either oxide particles or unreacted carbide). Visual examination of the zinc-salt interface after the reduction step (in which magnesium was added, to reduce the ThCl₄) revealed that there was not a continuous

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zinc-rich layer on the bottom of the tantalum container. The zinc-magnesium alloy containing $\text{ThZn}_{8.5}$ was present as separate globules, some of which were surrounded by dark-colored salt indicating that a metal fog might have existed.

It was also noted that earlier work [IVERSON] showed much slower kinetics. In an attempt to resolve this discrepancy, Iverson's laboratory notebook was reviewed for experimental details and the difference in results was assumed to be due to his experimental arrangement. However, results obtained this quarter have revealed a more probable explanation and the experimental arrangement described in the preceding quarterly report was for a related but different experiment.

During this report period, an experiment was conducted with the monocarbide, ThC , at 450°C . As in previous experiments the initial reaction of the carbide was rapid and transfer of thorium to the salt apparently ceased after 3 h. However, calculations from analyses showed that only 50% of the thorium had transferred to the salt. This was due in part to oxygen contamination of the carbide and in part possible inadvertent introduction of air into the reaction chamber during sampling of the salt phase.

A second similar experiment was conducted in which the initial charge consisted of 880 g KCl-LiCl eutectic, 843 g zinc, and 17.31 g of pulverized fused ThC_{2+x} . After the charge reached 450°C , stirring was started and an excess of anhydrous ZnCl_2 was added as in previous experiments. The purpose of adding zinc to the initial charge was to form a continuous layer of zinc on the bottom of the tantalum reaction vessel and hopefully to help agglomerate the zinc produced in the reaction and to eliminate the formation of metallic zinc fog at the metal-salt interface. Unfortunately, the experiment was a failure since practically no thorium was transferred to the salt phase during a 24-h period. Examination of the charge after the experiment showed that most of the carbide had settled under the zinc and had formed a pocket containing mostly carbide.

On the supposition that more vigorous stirring of the zinc to bring the denser carbide to the salt-zinc interface would solve this problem, an additional experiment was conducted with $(\text{Th,U})\text{C}_2$ containing 9.0 wt % uranium. The general procedure and the mass of constituents were the same except that the charge was stirred at 275 rpm and periodically at 600 rpm during four hours of operation. Then the stirrer was operated at 600 rpm continuously for two hours. The uranium and thorium concentrations in salt increased from 416 to 440 ppm and from 0.42 to 0.43 wt %, respectively. Most of the transfer occurred during the first hour. After 16.5 h, the concentrations in the salt were 497 ppm uranium and 0.535 wt % thorium. These percentages represent 28 and 31% of the available uranium and thorium added as carbide.

These results have presented an entirely new perspective on the feasibility of this procedure for converting the carbide to chloride via reaction with zinc chloride. However, the reaction can be carried out

electrochemically, avoiding the use of ZnCl_2 . Other alternatives will be discussed in the summary report.

b. Extraction of Uranium and Fission Product Elements from $(\text{Th,U})\text{O}_2$

The purpose of the current work is to elucidate the chemistry and kinetics involved in producing uranium metal and decontaminated ThO_2 by the reaction of $(\text{Th,U})\text{O}_2$ solid solution in molten salts containing ThCl_4 and thorium metal chips. The noble fission product elements will concentrate in the uranium and the chemically reactive fission product elements will concentrate in the salt. Separation of the fission product elements from the uranium or the salt can be achieved by previously developed methods. The principal advantage of this procedure is that the bulk of the fuel remains as ThO_2 . The limiting factor is the kinetics of the reaction of $(\text{Th,U})\text{O}_2$ in the fused salt, particularly in the case of high-density sol-gel $(\text{Th,U})\text{O}_2$.

(1) Reaction of ThO_2 with Sodium

(J. T. Mason*)

It has been shown by [LARSEN] that a ThO_2 -10 wt % U_3O_8 fuel mixture treated with molten sodium at 400°C for 1 h reacts rapidly with nitric acid, in sharp contrast to untreated fuel. This method was examined to see if similar results could be achieved by treatment of the high-fired sol-gel ThO_2 pellets used previously in this work. These pellets had been fired at 2800°C for 4-5 h.

Four high-fired sol-gel pellets with a total weight of 3.6411 g were held for 1 h at 515°C in pure sodium in a high-purity-helium atmosphere. Two of the pellets were removed and washed with 95% ethyl alcohol to remove adherent sodium. One pellet was put in water with no discernible reaction. The other was treated for 1 h with hot concentrated nitric acid containing 5% sodium fluosilicate. The latter treatment gave no noticeable reaction.

The two remaining pellets were reheated to 615°C in sodium for 2 h with no evidence of reaction. All four pellets were then treated with the hot acid solution for 2.5 h with no indication of reaction visible. The final weight of the four pellets was 3.5974 g, representing a 1.2% net weight loss. The dimensional characteristics of these pellets after the various treatments are compared with the dimensions of typical untreated pellets in Table 42.

It is concluded from these tests that treatment of high-fired sol-gel ThO_2 with molten sodium does not appear to affect the reactivity of this material.

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Table 42. Physical Dimensions of High-Fired Sol-Gel ThO₂ Pellets Before and After Treatment with Sodium and then with Acid

Treatment	Height, in.	Diameter, in.	Weight, g
Untreated	0.135	0.234	0.9102
515°C for 1 h in Na; 1 h in hot conc. HNO ₃	0.135	0.232	0.9100
515°C for 1 h in Na; water-treated	0.134	0.231	0.8984
515°C for 1 h in Na and then 615°C for 2h in Na; acid-treated	0.134 0.134	0.232 0.232	0.9105 0.9110

(2) (Th,U)O₂ - Fused Salt Reaction
(J. T. Mason* and D. Rehbein*)

Previous work [CHIOTTI-1975] has shown that the rate-controlling step in the reaction of (Th,U)O₂ with ThCl₄ and thorium metal in a fused salt is the reaction

whereas the reaction

is relatively rapid. Once the particle surface is depleted of uranium, reaction 1 controls the kinetics of the process.

A number of runs were made in which one or more experimental parameters were varied to determine their effects on reaction rates. The nature and results of these experiments are summarized in Table 43.

Solid solution mixtures of (Th,U)O₂ of four different uranium concentrations were used in these kinetics studies. Three of these (containing 7.8, 4.1, and about 10 wt % uranium) were high-fired sol-gel material obtained from ORNL. The fourth, an 8.2 wt % uranium mixture, was prepared by heating pressed thoria and urania powders to 1800°C in an induction furnace for 3 h. The purpose of this series was to evaluate to what degree the extraction of uranium from the solid solution is a function of the initial uranium concentration, as reported by [CHIOTTI-1975]. The effects on the

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Table 43. Initial Conditions and Final Results of Runs with (Th,U)O₂, Th, ThCl₄, and Salt Reactants

Run	(Th,U)O ₂		Salt (Eutectic)	Th in Salt, wt %	Temp, °C	Ni Balls Added	Total Duration,	Concentration in Final Salt		Remarks
	U wt % conc.,	Mesh						U, ppm	Th, wt %	
61	7.8	<150	KCl-MgCl ₂ - NaCl	6.4	600	NO	90.1	510	5.98	Temp changed to 700°C at 42.7 h.
66	7.8	<150	KCl-MgCl ₂ - NaCl	6.1	700	NO	100.2	780	5.86	
92	8.2	Fine Powder	KCl-LiCl	6.4	600	NO	47.8	864	4.75	Nonsol-gel (Th,U)O ₂ , stirrer failed after 7 h.
97	4.1	<150	KCl-LiCl	5.0	500	NO	90.2	97	4.76	No stirring.
99	4.1	<150	KCl-LiCl	5.2	500	NO	120	344	4.63	Heated in rocking furnace
100	4.1	<150	KCl-LiCl	4.9	500	NO	94.5	56	4.82	Intermittent stirring.
102	8.2	Fine Powder	KCl-LiCl	6.0	600	YES	47.1	3200	6.10	Nonsol-gel (Th,U)O ₂
105	4.1	<150	KCl-LiCl	6.4	700	NO	66.1	1650	6.50	Ni balls added at 54.3 h.
108	4.1	<150	KCl-LiCl	4.0	600	YES	48.3	792	4.08	ZnCl ₂ added at 48.3 h.
111	4.1	<325	KCl-MgCl ₂ - NaCl	5.0	700	YES	51.0			
112	4.1	<325	KCl-MgCl ₂ -	6.3	800	NO	52			Heating in rocking furnace.
117	10	<270	KCl-LiCl	6.6	700	NO	48.4			
119	10	<270	KCl-LiCl	7.4	800	NO	51			Heating in rocking furnace.

reaction rate of uranium concentration, temperature of firing of the fuel, and particle size were studied. The particle size was varied by grinding and selective screening of the oxide materials.

Two eutectic salt mixtures, KCl-LiCl and NaCl-KCl-MgCl_2 , were used in these experiments to evaluate the effect of the salt on the overall kinetics. It was observed by [JHA] that ThOCl_2 is more soluble in KCl-MgCl_2 eutectic, which should expedite the extraction of uranium from the solid solution.

Experiments were run at temperatures of 500 to 800°C to determine the effect of temperature on the reaction rate.

If a surface layer depleted of UO_2 does form on particles during reaction of $(\text{Th,U})\text{O}_2$, it may be possible to abrade away the ThO_2 -rich layer in some way. Three different experimental setups (all using tantalum containers) were employed in an attempt to do this. In the first, a charge of approximately 150 g salt, 10 g oxide, 1 g Th, and 15 g of ThCl_4 in an open crucible was heated in an inert atmosphere containing less than 1 ppm oxygen. In the second, a charge five times the weight of the first charge was heated in a 4-in.-dia steel tube which was closed at one end and flanged at the top. Provisions were made to pull a vacuum, introduce a purified inert gas, stir the sample, measure the sample temperature, and sample the salt during a run. Nickel balls were added to the charge to abrade away the ThO_2 from particle surfaces and expose more UO_2 to the salt mixture.

The third type of vessel was a 1-in.-dia tantalum crucible, into which a 60-g charge was sealed by heliarc welding. The tantalum crucible was sealed in a stainless steel jacket and was heated in a rocking furnace.

The fused salt was sampled periodically during the experiments with open containers and was analyzed for thorium and uranium. These results are shown graphically in Figs. 49 and 50, and the final compositions of the salts is given in Table 43. Even though final uranium and thorium concentrations for runs 111, 112, 117, and 119 (Table 43) are not available, preliminary conclusions can be reached. As is seen in Table 43, runs 97, 99, and 100 were carried out at 500°C using $(\text{Th,U})\text{O}_2$ containing 7.8 wt % uranium. In runs 97 and 100, only about 100 ppm uranium was transferred to the salt which is less than was transferred into the rocking furnace sample from run 99. The lack of adequate stirring may have been a small factor, but it is concluded that a temperature of 500°C is too low to give a reasonable transfer rate. The results for runs 97 and 100 are plotted in Fig. 49, along with the analytical results for experiments at 600 and 700°C (runs 61 and 66, respectively) with $(\text{Th,U})\text{O}_2$ containing 7.8 wt % uranium. Run 61 shows a steady increase in uranium concentration at 600°C with time, followed by a marked increase in uranium transfer to the salt after the temperature was increased to 700°C. Run 66, at 700°C throughout the run, shows a correspondingly higher uranium transfer.

Fig. 49. Uranium in Salt vs. Duration of Reaction of ThCl_4 and Th with $(\text{Th},\text{U})\text{O}_2$. Effects of temperature.

Fig. 50. Uranium in Salt vs. Duration of Reaction of ThCl_4 and Th with $(\text{Th},\text{U})\text{O}_2$. Effects of stirring, abrasion, and temperature.

Runs 92 and 102 (Fig. 50), with oxide having a somewhat higher uranium content, were duplicate runs at 600°C for a period of 47 h. As stated above, the oxide was prepared by heating a mixture of ThO₂ and UO₂ powders at 1800°C with the purpose of obtaining a much more reactive oxide than the sol-gel material. As expected, this material is much more reactive, particularly the material used in Run 102. There was much less uranium transfer in Run 92, due primarily to a failure of the stirrer mechanism after approximately 7 h. The difference in these two runs shows the combined effects of stirring and the abrading action of nickel balls.

In Runs 97 through 108 (excepting Run 102), 4.1 % sol-gel material was used and the combined effects of abrasion and temperature were determined. Run 105 was carried out for 54.3 h at a temperature of 700°C before nickel balls were added. The results are plotted in Fig. 50. Comparison of the uranium content of the final salt with that for similar runs at 500°C (Runs 97 and 100) shows the favorable effect of the higher temperature. Nickel balls were added to the charge after 54 h of Run 105, stirring was continued for an additional 12 h. This resulted in a noticeable increase in the uranium concentration, as seen in Fig. 50. In Run 108, the temperature was held at 600°C and nickel balls were used throughout the experiment. Uranium transfer was intermediate between those for the 500°C and 700°C runs. These results indicate that abrasion of sol-gel by nickel balls increases the transfer rate of uranium into the salt somewhat, but that increasing the reaction temperature has a much greater effect.

In all runs except the rocking furnace experiments, there was no evidence of any metallic uranium in the final product or of any thorium remaining in the metallic state, even though an excess of three to four times the theoretical amount of thorium was added. As discussed in detail earlier in this series of reports, the postulated mechanism for the transfer of uranium into the salt and then its reduction to the metallic state involves a number of possible reactions. The overall reaction, however, is believed to be

To ascertain whether uranium is being produced but not in amounts detectable by X-ray diffraction analysis of the residue powders, some ZnCl₂ was added to the Run 108 product at the conclusion of the experiment. ZnCl₂ is known to react rapidly with any free uranium to form UCl₃. This would be evidenced by an increase in the uranium content of the salt. However, no such increase was detected.

In Runs 111 through 119, the effect of decreasing the powder size of the sol-gel material and of using a different salt was tested. Two of the runs were with 10 wt % uranium in the starting material (sol-gel material recently received from Oak Ridge National Laboratory). Analyses of the final salt from these runs have not yet been completed.

(3) Kinetics of Reaction
(P. Chiotti*)

The experimental data presented in Figs. 49 and 50 show an initial rapid transfer of uranium to the salt followed by a linear increase with time, indicating a zero order reaction. If the initial rapid transfer is presumed to be due to uranium exposed on the surface of (Th,U)O₂ solid solution particles, the subsequent linear transfer could represent layer-by-layer dissolution of the particle surface. Nucleation of either depleted ThO₂ or uranium metal at the particle surface is not believed to be rate-determining, however. With both thorium and uranium present, the concentration of UCl₃ in the salt should also remain constant if:

1. reaction 1 is rate controlling
2. the ThCl₄ concentration in the salt remains constant
3. the concentration of UO₂ in (Th,U)O₂ is constant
4. the total surface area for reaction decreases linearly with time.

One obtains

$$\frac{dx(\text{UCl}_3)}{dt} = \text{constant} = k[x(\text{ThCl}_4)x(\text{UO}_2)] \quad (1)$$

where x is the mole fraction. This represents a zero order reaction. The surface area, A , will decrease with time and so Eq. 1 can be rewritten as

$$\frac{dx(\text{UCl}_3)}{dt} = \frac{cd\Delta m}{dt} = k[x(\text{ThCl}_4)x(\text{UO}_2)]A$$

$$\frac{d\Delta m}{dt} = k'A \text{ and } \Delta m = (m_0 - m)$$

If it is assumed that particles are spherical, we have

$$A = 4\pi r^2 \text{ and } m = \left(\frac{4}{3}\pi r^3\right)\rho \quad (2)$$

where m , r and ρ are mass, radius, and density respectively of a (Th,U)O₂ particle, and m_0 is the initial mass or mass at time $t = t_0$. Taking the derivative of mass with respect to time gives

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$$\begin{aligned}\frac{dm}{dt} &= 4\pi\rho r^2 \frac{dr}{dt} \\ &= -k'(4\pi r^2)\end{aligned}$$

and

$$\begin{aligned}\frac{dr}{dt} &= \frac{-k'}{\rho} \\ &= -k''\end{aligned}\tag{3}$$

Integration gives

$$(r - r_0) = -k''t \text{ and } (r_0 - r) = k''t$$

where r_0 is the initial radius. Solving for r in Eq. 2 and substituting in Eq. 3 yields

$$m_u^{1/3} - m^{1/3} = \left(\frac{4}{3}\pi\rho\right)^{1/3} k''t$$

The moles or mass of uranium transferred to the salt is proportional to the decrease in mass of the particle. Dividing by $m_0^{1/3}$ and rearranging terms gives

$$\left(\frac{m}{m_0}\right)^{1/3} = 1 - \left(\frac{4\pi\rho}{3m_0}\right)^{1/3} k''t.\tag{4}$$

This shows that the mass fraction reacted (to the one-third power) is a linear function of time. However, when the fraction reacted is small, we can write

$$\begin{aligned}\left(\frac{m_0 - \Delta m}{m_0}\right)^{1/3} &= \left(1 - \frac{\Delta m}{m_0}\right)^{1/3} \\ &\approx 1 - \frac{1}{3} \frac{\Delta m}{m_0}\end{aligned}$$

and the change in the mass of the particle or the increase of UCl_3 in the salt is approximately a linear function of time, as has been observed experimentally. Once metallic uranium begins to form, the UCl_3 concentration in the salt should remain constant, but the decrease in particle size should continue to follow Eq. 4.

The sol-gel solid solution $(Th,U)O_2$ obtained recently from Oak Ridge is in the form of extremely uniform microspheres. They are ideally suited for experimental determination of the rate constants presented here. Monitoring of the change in sphere size as a function of time, temperature, $ThCl_4$ concentration, and salt composition would quickly show the relative influence of these factors on the kinetics in a quantitative manner. Lack of funds prohibits this study.

(4) Electrolytic Decomposition of (Th,U)O₂

(F. Chu*)

Study of the anodic decomposition of (Th,U)O₂-carbon mixtures in a fused chloride salt has continued.

Various secondary cells were employed during this report period. To determine the nature of the gas or gases evolved at the cell anode, a cell of the type

was employed. The gases evolved were collected, and qualitative tests were performed. At 600°C with an applied voltage of 0.8 V, no significant gas evolution was observed; at 1.7 V, slow evolution and at 4.0 V rapid evolution of gas at the anode was observed. Analysis of this gas showed primarily CO₂ and some chlorine. No positive test for CO was obtained and it may be assumed that the relative amount of this gas was very small. [MEYER] has studied a similar cell in which the salt employed was a NaCl-KCl-ThCl₄ mixture but at temperatures in the range of 900 to 1000°C. The gas evolved at these temperatures contained appreciable concentrations of CO, as would be expected in the presence of excess carbon at the higher temperatures employed.

One experiment was carried out with each of the cells

and

The percentages for the (Th,U)O₂ solid solution are mole percentages; the salt compositions are given in weight percent. Both cells were operated at 600°C. The change in solute levels of the cell represented by Eq. 2 (samples taken near the center of the cell between the anode and cathode) as a function of time at various applied voltages is shown in Fig. 51. It is evident that no significant reaction had taken place at 0.80 and 1.3 V but there was significant reaction at 4.0 V. The second cell Eq. 3 was operated at 0.8, 1.6, and 4.0 V. At 1.6 V, the uranium content of the salt did not increase significantly; there was only a small decrease in zinc content and a small increase in thorium content of the salt over a 17-h period. Stirring of the salt was started at the end of this period and over a 6.5-h period a significant increase in the uranium and thorium content and a decrease in the zinc content of the salt was noted. At 4.0 V, the change in composition with time was accelerated and the change with time was similar to the rates observed at this voltage in Fig. 51.

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Fig. 51. Salt Composition as a Function of Time and Applied Voltage for the Cell $(\text{Th}, 4\% \text{U})\text{O}_2, \text{C}/\text{KCl}-\text{LiCl}-3\% \text{ZnCl}_2-2.2\% \text{ThCl}_4/\text{Zn}$.

A new constant-voltage power supply designed for operation in the voltage range 0 to 10 V was acquired, making it possible to monitor and record current versus voltage for these cells and to determine the decomposition potential for the cells. Results of measurements with the cell

are shown in Fig. 52. The lower curve was obtained in the first application of voltage to the cell. This curve indicates that reaction begins at an applied potential of 1.2 V and that the main cell reaction is

which has a standard free energy change at 600°C of 119.9 kcal, corresponding to an emf of -1.3 V. The calculated value is in good agreement with the observed value of -1.2 V. As seen in Fig. 4, there was small increase in current at a constant voltage. This change occurred over a period of approximately 15 min. When the applied voltage was slowly reduced, the current did not follow the initial curve and the potential across the cell did not drop to zero. The cause of this effect is uncertain, but is probably concentration polarization and a change in the composition of the anode. The voltage across the cell slowly decayed to zero. On reapplication of voltage, curve 3 was

Fig. 52. Current versus Voltage Plot for the Cell
 (Th, 9% U)O₂, C/NaCl-KCl-MgCl₂- 1.3% ThCl₄/Zn.
 (1) First application of voltage; (2) Indicates
 effect of reduction of voltage; (3) Reapplication
 of voltage; (4) Voltage again reduced to zero.

observed. The applied voltage was again reduced to zero, and the cell voltage slowly decayed to zero. Reapplication of voltage led to curve 4. The initial anode reaction is apparently

As the ThCl₄ concentration builds up in the anode compartment, the following reactions may become significant

The applied potential required to transport pure UO₂ from the anode to the cathode is theoretically zero. Curves 3 and 4 indicate that reaction is initiated at much lower applied voltages and could be due to the transport of UO₂ to the cathode. If this is the correct explanation of the observed cell behavior, a cell in which the anode is pure ThO₂ mixed with carbon should not require a lower voltage to initiate the reaction upon reapplication of a voltage to the cell. Concentration polarization effects will still occur,

with reactions 6 and 7 taking place at the anode. However the decomposition potential for ThOCl_2 or the cell reaction

has an E° value of 1.39 V at 600°C . This E° value compares with 1.3 V for reaction 5. Consequently, the applied voltage required to produce a significant increase in current should remain in the range of 1.3 V.

Termination of funds prevented further investigation of this postulate.

X-ray analyses of the anode oxide did not reveal the presence of free UO_2 . However, because the transport of UO_2 to the cathode via UO_2^{2+} ion should take place much more readily than the transport of thorium under an applied potential, UO_2 is not expected to be present as free UO_2 at the anode.

X-ray patterns of the material deposited at the graphite cathode in cell Eq. (3) showed the presence of a $(\text{Th}, 3.0\% \text{ U})\text{O}_2$ solid solution and zinc. This observation is somewhat surprising. An enrichment of uranium in the oxide was anticipated. In any case, reaction 7 is thought to also take place at the cathode.

In general, these data show that the electrolytic decomposition of a $(\text{Th}, \text{U})\text{O}_2$ solid solution in a fused salt cell is rather complex. A cell design that permits stirring of the electrolyte will greatly improve the kinetics of the overall reaction. However, there must be a compromise between ionic mobility in the salt and physical containment of the charged material. The use of a graphite wool diaphragm between the anode and cathode compartments appears to be promising.

Experiments on the reaction of ThC_x with ZnCl_2 in a fused salt show that once the ThC_x particles are wetted by liquid zinc, reaction stops or becomes very slow. Thermodynamic data indicate that the reaction of ThC_2 with zinc to form $\text{ThZn}_{8.5}$ is favored at temperatures below 800°C . If this reaction occurs at a reasonable rate, wetting of the carbide particles with zinc or submersion of the carbide in liquid zinc should not stop the overall reaction or conversion of the carbide to ThCl_4 . The fact that little or no reaction occurs in the ThC-ZnC_2 salt indicates that either the reaction is kinetically inhibited or the thorium carbides are much more stable than present thermodynamic data indicate. However, electrolytic decomposition of ThC_x in a cell of the type

has been shown to be feasible. To better understand these reactions, an attempt was made to measure the reversible emf of the cell

In the temperature range 400-700°C, the observed emf increased with temperature whereas current thermodynamic data indicate that it should decrease sharply with temperature. However, these data were obtained with the cell in a small furnace in which the temperature gradient was rather large and this observation may or may not be significant. A cell in which a uniform temperature can be established has been set up, and the free energy change for reaction 11 will be determined for the temperature range 400-750°C if funds become available.

c. Engineering Analysis

(L. E. Burkhart* and
D. Rehbein*)

A preliminary flowsheet (Fig. 53, which is a revision of a flowsheet presented in the preceding quarterly report) is presented for a reprocessing cycle to convert irradiated sol-gel oxide fuel to a thorium-uranium metallic fuel by conversion to carbide followed by reoxidation. Next, the "reactive" oxide would be reduced with zinc-5% magnesium alloy, chlorinated, and again reduced with zinc-magnesium alloy. Then, removal of the zinc and magnesium by distillation would be expected to leave the thorium and uranium as a metallic sponge free of fission products.

A major problem in any scheme for reprocessing of nuclear fuels is the containment and storage of the radioactive wastes. On the basis of current thinking, storage times of up to 1000 y may be ecologically safe with proper containment vessels and an optimum storage site. Safety for longer storage times is a more serious problem.

For the processes under consideration at this laboratory, we have considered fractionation of the fission products elements vaporized during the conversion to carbide. In principle, it should be possible to separate these fission products on the basis of their different condensation temperatures. If short-lived and long-lived fractions could thereby be separated, the volume of material that would have to be placed in long-term storage could be reduced.

Spedding and Daane [SPEDDING] have shown that it is possible to perform a rough separation of a mixture of rare earth oxides by utilizing the differences in vapor pressure of the constituents. Their apparatus included a reaction vessel into which a mixture of ten rare earth oxides and lanthanum metal were placed. A fractionating column containing 16 condenser plates, spaced 1 in. apart, was placed atop the vessel. The entire assembly was then heated so that the vessel and the bottom of the tower were at 600°C. After 30 min at temperature, it was found that several of the condenser plates had large deposits while others had very little. Analysis of the deposits showed that a single rare earth was predominant in each deposit; the major constituent differed from plate to plate.

If a fractionating tower of this sort were used (in the step for conversion to carbide, for example), it could at least serve as a basis for the separation of the more volatile fission products.

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Fig. 53. Preliminary Flow Sheet for Reprocessing $(\text{Th,U})\text{O}_2$ by Conversion to Carbide, Oxidation-Reduction, Chlorination, and Reduction. VFP = volatile fission products. NFP = noble fission products. Circled numbers correspond to line numbers in tabulation. Tabulation is on the following pages.

(contd.)

	Line Number										
	1	2	3	4	5	6	7	8	9	10	11
Process Material	Feed	Offgas		Offgas	Feed			Feed		Feed	Offgas
Mass, g	11298	2783	8516	1664	2228	9079	106447	1646	109176	6698	2980
ThO ₂ , g	8394					8394					
UO ₂ , g	557					557					
VFP, g	663	663									
NFP, g	241		241			128					
O, g	127										
C, g	1316										
CO, g		2120									
ThC, g			7759								
UC, g			516								
CO ₂ , g				1490							2980
MoO ₃ , g				118							
RuO ₄ , g				56							
O ₂ , g					2228						
NaCl-KCl-MgCl ₂ , g							106447		106447		
Mg, g								1646			
MgO, g									2729		
COCl ₂ , g									6698		

(contd)

Fig. 53 (contd)

	Line Number										
	12	13	14	15	16	17	18	19	20	21	22
Process Material	Feed					Waste					Product
Mass, g	39270	31274	5087	35761	106349	118944	4487	263605	271472	1621	7868
NFP, g	128			128			128				
Mg, g								11640	11640	1621	
Th ₂ Zn ₁₇ , g	25041								25041		
UZn ₁₂ , g	2109								2108		
Zn, g	11992	31274		35633			4359	251965	232683		
ZnCl ₂ , g			5087								
LiCl-KCl, g					100000	100000					
MgCl ₂ , g					6349	6349					
ThCl ₄ , g						11885					
UCl ₃ , g						710					
Th, g											7377
U, g											491

10. Molten Tin Process for Reactor Fuels

(O. Krikorian,* R. Borg,* J. Grens,*
M. Coops,* and W. Parrish*)

a. Introduction

Our objective in this work is to conduct research and development which will identify chemically feasible pyrochemical and dry processing methods for nuclear fuel within the general frame of nonproliferation. The initial phase of our effort is to evaluate a process known as the molten tin (MTN) process and its application to uranium-plutonium and thorium-uranium (plutonium) fuels in oxide, carbide, and metallic form. We are applying available thermochemical data to the development of flow diagrams for the process and are conducting experiments to establish the key process parameters.

(1) Description of the Molten Tin Process

Molten tin is used as the solvent and reaction medium in the MTN process to separate actinide fuel materials from fission products and other materials. In this process, the actinide nitrides, which are insoluble in molten tin, are precipitated out. The process, described earlier by Anderson, Parlee, and Gallagher [ANDERSON-1972], is viewed here in a broader scope that considers alternative approaches to some steps. A schematic flow diagram of the process as currently envisioned is given in Fig. 54, and a description follows.

Fig. 54. Schematic Flow Diagram of the Molten Tin Process.

*Lawrence Livermore Laboratory.

Initially, the spent nuclear fuel is declad, then dissolved in molten tin contained in a graphite crucible at about 1900 K. Decladding can be accomplished by dissolving the clad in tin at a temperature above about 1200 K, but other decladding methods can also be used and may present advantages. Therefore, it is not considered essential to specify the decladding procedure at this time.

The process used to dissolve the fuel after decladding will depend on the type of fuel being processed. For an oxide fuel, we would use a carbothermic reduction process in which the fuel would be introduced directly into the molten tin at about 1900 K in the presence of excess carbon. Carbon will dissolve in the molten tin and will react with the actinide and fission product oxides under these conditions, converting them to a metallic solution in tin and releasing CO gas. Thus, for example, for a uranium-plutonium fuel,* the principal reaction is

Volatile fission products released during this reaction are swept out by the gaseous CO product; the more refractory fission products follow the actinides into solution. Actinide carbides do not form under these conditions because of the greater stability of the actinide-tin solution. For a metallic fuel, the carbothermic reduction is bypassed since this type of fuel dissolves directly in the molten tin. For carbide fuels, the situation is not so obvious. If the fuels are coated with pyrocarbon, the coating may have to be removed by oxidation; alternatively, modification of the molten tin solvent by the use of additives that enhance carbon solubility may be needed since the solubility of carbon in pure tin is not very high. Either CO or an inert gas can then be used to sweep out the volatile fission products from above the metallic or carbide fuel solutions. After fuel dissolution, fuel reprocessing chemistry becomes identical for the various types of fuels.

After dissolution of the fuel, the actinides are separated from the molten tin by a nitriding reaction that forms an actinide nitride precipitate to accomplish this nitriding step, a nitrogen pressure of about 100 kPa (1 atm) is required at about 1900 K. For a uranium-plutonium fuel, the reaction is

At this stage, significant partitioning of the remaining fission products between the solid (U,Pu)N phase and the liquid tin phase is expected. In particular, Y, Zr, and the lanthanides have the proper size and structural relations to form mixed crystal nitrides with the (U,Pu)N phase. On the other hand, these elements also form extremely stable solutions in molten tin. At present, we are able to make only semiquantitative estimates of the activities of the various elements in molten tin from calculations.

*Although we use uranium-plutonium fuel in the examples that follow thorium-uranium-plutonium fuels are expected to undergo identical reactions.

Experiments need to be conducted to establish the actual partitioning behavior. Retention of a certain amount of highly radioactive fission products in the actinide fuel is consistent with the nonproliferation goal, since a highly radioactive fuel material is a deterrent to theft.

In addition to the (U,Pu)N precipitate, it is possible that a floating nitride (or carbonitride) phase containing the Y, Zr, and lanthanide fission products may form above the molten tin. This floating phase would compete for the fission product elements. If desired, a host material could be added to the melt intentionally to promote a floating phase. The existence or desirability of such a floating phase will depend on experimental results for the nitriding step described above. We are assuming for the present that no floating nitride phase forms in the nitriding process.

Following the nitriding step, the molten tin phase is separated from the fuel nitride by filtration, and the fuel nitride is processed to convert it to the appropriate chemical form required for the new fuel. For an oxide fuel, the nitride would be ignited in air to form (U,Pu)O₂. The oxide could be converted to metal or carbide by further processing if those fuel forms were required. Alternatively, more direct process schemes could be developed to convert the nitride directly to metal or carbide forms. Finally, the fuels in their proper chemical forms would be fabricated into fuel elements by use of conventional techniques.

The tin recovered from the nitriding step, as well as tin recovered from other steps, will have to be further processed in order (1) to concentrate the fission product wastes, and (2) to recycle the tin (a moderately costly solvent) to the process. Details have yet to be worked out for these steps.

(2) Program Summary for This Quarter

The initial "year" of effort for this work actually consisted of the five-month period from May through September, 1978. During the final three months, work was done on both engineering analysis and separations process aspects of the study. The engineering analysis effort consisted of the following tasks:

- Conduct initial literature survey of thermodynamic data
- Conduct initial literature survey of kinetic data
- Develop a conceptual process flow diagram

Separations processes involved the tasks:

- Construct vacuum and furnace equipment
- Begin experimentation on the carbothermic and nitriding reactions in molten tin

All of these tasks were carried out except that the nitriding experiments have not yet begun. Equipment for the nitriding studies is ready, and the experiments should be under way shortly.

Summarizing briefly, the initial effort revealed no basic thermodynamic or kinetic factors that limit development of the MTN process. On the other hand, it is clear that calculated data will not suffice to define the quantitative behavior of the process steps and that experimentation is an essential part of the process evaluation. A flow diagram has been developed for the process, and was revised once.

For experimental work, equipment has been purchased for two induction-heated vacuum furnaces and gas-handling systems; one furnace unit has been put into operation. Arrangements also have been made to utilize the vacuum furnace units in the plutonium facility. Several carbothermic reductions of UO_2 have been conducted to date in the induction furnace; they have confirmed the chemical feasibility of this reaction step.

b. Detailed Results and Discussion

Detailed results and discussion of our program are given in this section in terms of the project tasks defined in the Program Summary above.

(1) Literature Survey of Thermodynamic Data

Sources of information for this literature survey were (1) a selected bibliography compiled by H. F. McDuffie and coworkers at the Oak Ridge National Laboratory [McDUFFIE], (2) computerized and manual searches provided by H. Leonard Fisher and W. Edward Madden of the Research Information Group at the Lawrence Livermore Laboratory, and (3) information sources known by the authors. The searches by Fisher and Madden were particularly useful in identifying some key references on liquid tin systems, and their help in this program is gratefully acknowledged.

The literature survey of thermodynamic data has been organized in terms of six groupings: I. Carbothermic Reduction, II. Carbides, III. Oxides, IV. Ternary Systems, V. Nitrides, and VI. Fission Products in Tin. These are covered in turn.

(a) Carbothermic Reduction

The basic equation for the carbothermic reduction reaction (not in the presence of tin) is represented by

and the temperature dependence of the standard free energy, ΔG° (in cal/mol), for the reaction as written contains all the pertinent information. From this, one can also calculate the equilibrium pressure of CO at any temperature.

One can calculate ΔG° as did Maruya [MARUYA] as follows:

which yields for Eq. 1

$$\begin{aligned} \Delta G_{1823}^\circ &= 178,200 - 80.1T \\ &= -2RT \ln P_{CO} \end{aligned} \quad (5)$$

$$\log P_{CO} = \frac{19,471}{T} + 8.752 \quad (6)$$

The equilibrium pressure of CO in contact with UO_2 and C was directly measured by Bazin and Accary [BAZIN] over a somewhat compressed temperature range, viz., 1468 to 1608 K, from which data they derived the following,

$$\log P_{CO} = - \frac{39,600}{T} + 21.42 \quad (7)$$

which is in rather poor agreement with Eq. 6 that is deemed more reliable. [MARUYA] examined the solubility of oxygen in UC as did Bazin. The amount of retained oxygen generally exceeds that predicted by thermodynamic data, but the excess is assumed to be mechanically occluded or adsorbed. Pialoux and Dode [PIALOUX] studied by X-ray diffraction the ternary phase diagram of U-C-O under fixed pressures of CO.

In the presence of liquid tin, the situation changes. Anderson and Parlee [ANDERSON-1976] experimentally determined the activity of uranium in tin at various concentrations and calculated the corresponding equilibrium pressures of CO listed in Table 44. The very low thermodynamic activity of uranium in liquid tin, relative to its concentration, provides additional driving force to the carbothermic reduction. In summary, therefore, the dependence of the carbothermic reduction of UO_2 upon the CO pressure can be directly calculated from existing data.

The same calculations may be made for the carbothermic reduction of PuO_2 . The free energy of formation of PuO_2 as a function of temperature is well known [ACKERMAN, CLEVELAND] and is given in Eq. 8.

$$\Delta G_f^\circ = -253,480 - 3.45T \log T + 52.48T \quad (8)$$

Table 44. Experimentally Determined Activities of Uranium in Various U-Sn alloys, and Calculated Equilibrium CO Pressure during Carbothermic Reduction.

Temperature, K	U Concentration, wt % (mole fraction)		
	2% (0.0101)	9% (0.0471)	18% (0.0985)
1800 a_U^a	1.96×10^{-4}	5.40×10^{-4}	5.87×10^{-4}
P_{CO} atm	0.037	0.019	0.018
1900 a_U	3.12×10^{-4}	8.55×10^{-4}	9.30×10^{-4}
P_{CO} atm	0.105	0.063	0.060
2000 a_U	4.68×10^{-4}	12.9×10^{-4}	14.0×10^{-4}
P_{CO} atm	0.302	0.182	0.175

^aBased on an activity coefficient of 1 corresponding to a mole fraction of 1.

(for an excellent critical review of the physical chemistry, crystallography, and thermodynamics of plutonium oxides, carbides, and nitrides, see [CLEVELAND]).

For the reduction of plutonium oxide, the following equation applies.

Combining the free energy equations (Eqs. 8 and 4) permits the equilibrium pressure of CO to be readily calculated for the carbothermic reduction of plutonium oxide, Eq. 10.

$$\begin{aligned} \Delta G^\circ &= 197,280 + 3.45T \log T - 92.88T \\ &= -2RT \ln P_{CO} \end{aligned} \quad (10)$$

The ternary system Pu-C-O has been studied (POTTER-1968A) with the aim of establishing the phase diagram. Nevertheless, there are no data concerning the activity of plutonium in liquid tin or for PuO_2 dissolved in solid UO_2 .

The same exercise may also be carried out with thorium oxide. No reports were found dealing with research on the direct carbothermic reduction of ThO_2 . As before, one can easily formulate an expression for the temperature dependence of the equilibrium pressure of CO, by combining the equations for the free energies of formation of ThO_2 and CO.

$$\Delta G^\circ = -296,000 + 46.38T \text{ for } \text{ThO}_2(s), \text{ and} \quad (11)$$

$$-2RT \ln P_{\text{CO}} = 354,200 - 86.78T$$

As was the case for plutonium, no data were found dealing with the carbothermic reduction of ThO_2 in molten tin.

(b) Carbides

It is not certain that carbide compounds will be generated in substantial or even influential quantities by the MTN process. In any case, thermodynamic data describing the simple binary systems, U-C, Th-C, Pu-C, and Zr-C, as well as all other refractory carbides, are reasonably complete and accurate. A good primary reference is the book, "The Refractory Carbides" by [STORMS].

The equilibrium phase diagram for the binary U-C system appears to be reliably established, and Accary [ACCARY] provides a good primary reference. There have been substantial changes in the phase diagram proposed by Hansen and Anderko [HANSEN-1958A], and the 1969 supplement edited by [SHUNK] cites four references later than 1962. An essentially complete tabulation of entropies and enthalpies of formation is given by [HULTGREN], although the phase diagram is somewhat out of date. From the foregoing, we conclude that little if any further research into the U-C system is needed for the molten tin process.

There is an interesting variety of Th-C phase diagrams from which to choose [STORMS, POTTER-1968B, ELLIOTT, FLAHAUT]. The major area of disagreement concerns the presence or absence of intermediate phases on the carbon-rich side of the 50-50 composition. Nevertheless, there is sufficient information to satisfy the MTN process, particularly since one does not expect the C/Th ratio to exceed unity in a carbothermic reduction taking place under a dynamic vacuum. It is stated by [HULTGREN, p. 510] that "All existing free energy of formation values for the solid alloys are uncertain," although values of ΔG are given.

The phase diagram for the Pu-C system also seems to be reasonably well established [HANSEN-1958B] as is the chemistry and crystallography [HANSEN-1958C, CLEVELAND]. Flahaut [FLAHAUT] also gives considerable thermodynamic data.

Table 45 compares the free energy of formation of an actinide carbide with the nitride of the same actinide; in all cases, the nitride is the more stable. Hence, there is no doubt that the actinide oxides can be converted to nitrides, but the solubility of PuN and ThN in molten tin remains in question.

Table 45. Comparison of the Free Energies of Formation of Actinide Carbides and Nitrides at the Same Temperatures

T, K	Compound	ΔG° , cal/mol	Compound	ΔG° , cal/mol
1900	UC ^a	-12,884	UN ^b	-29,800
298	ThC ^c	~-27,000	ThN ^d	-83,600
1000	PuC ^e	-14,900	PuN ^f	-60,000

^a[HULTGRÉN, p. 527]; U(1) and graphite are the standard states.

^b[VOZELLA].

^c[STORMS, p. 168].

^d[WICKS]

^e[CLEVELAND, p. 382].

^f[CLEVELAND, p. 286].

(c) Oxides

The thermodynamic properties of the oxides of U, Th, and Pu are well known [ACKERMAN, CLEVELAND]. There is very little information on the ternary mixed oxides--e.g., (U, Pu)O. However, one would expect the mixed oxide to behave in a nearly ideal manner since the lattice spacings are almost the same for the corresponding uranium and plutonium oxides (see Table 46).

Table 46. Structures and Lattice Constants for Some Actinide Oxides

Compound	Structure	a_0 (KX)
PuO	f.c.c. - B1	4.95
UO	f.c.c. - B1	4.92
PuO ₂	f.c.c. - C1	5.40
UO ₂	f.c.c. - C1	5.45
ThO ₂	f.c.c. - C1	5.59

In any case, a substantial difference in the thermodynamics of carbothermic reduction of the actinide oxides would not be expected.

(d) Ternary Systems

Few data deal with phase equilibria in ternary systems [POTTER-1973]. [HOLLECK-1974] presents a series of phase diagrams at selected

temperatures for Th-C-N, U-C-N, Pu-C-M, Th-N-M, U-N-M, and Pu-N-M, where M is a metallic element. These results, according to the author, are based upon "--new experimental work, thermodynamic data, and theoretical estimations--;" he does not explain his methods in greater detail. Nevertheless, he gives diagrams for all three actinide elements individually combined with N, Zr and C, Zr at temperatures in the vicinity of 1873 K. The phase diagram for Th-C-N also seems well established.

A limited amount of data exists dealing with ternary molten tin systems; unfortunately systems with constituents common to nuclear fuel are not among them. [MOSER-1974, 1977] and various colleagues have used an e.m.f. method to measure thermodynamic activities in liquid Zn-Sn-In, Cd-Bi-Sn, and Zn-Sn-Cd systems. Other studies which involved tin as a minority constituent were not deemed applicable.

(e) Nitrides

Since the MTN process uses selective precipitation of fission product and actinide nitrides as the basis for their separation, the thermodynamics of nitrogen-nitride equilibria in liquid tin for all pertinent elements must be known. A search of the literature has shown some data on thermodynamics of solid metal nitrides, but data on nitride equilibria in liquid alloy systems is sparse. Most important is the behavior of the nitrides of U, Pu, and Th; if Zircaloy cladding is involved, the behavior of zirconium is important also. However, the rare earths and several of the transition elements which form very refractory nitrides may dissolve to some measure in the mixed-nitride precipitate rather than remaining in the molten metal phase. As previously noted, most metal solutes in liquid tin have extremely low activities; countering this is the strength of the metal nitride bond which enhances the stability of the solid phase. Table 47 lists some important physical properties. Among the most noteworthy are the nearly equal values of the lattice spacings. The fact that values of the ionic radii are so similar would favor mutual solubility in the solid state.

Table 47. Lattice Constants, Melting Points, Decomposition Pressure at the Melting point, and Enthalpies of Formation for Selected Nitrides

Compound	a_0 (f.c.c.) (in KX)	$T_{m.p.}$, K	$P_{m.p.}$, atm	$\Delta H_f^{\circ}, 298$ (kcal/mol)
UN	4.880	2800	14.32	-70.4
PuN	4.905 ₅	2563-3043	14.23	-70.2
ZrN	4.536-4.562	3253	7.35	-87.3
ThN	5.144	2903	11.50	-90.6
Mo ₂ N	$a_0 = 5.725$ (hex) $c_0 = 5.608$	873	9.16	-16.6
YN	4.79	>2950	5.89	-71.5
GdN	5.00	-	-	-73.4
SmN	5.05	-	-	-77.2
LaN	5.30	-	6.90	-71.5
CeN	5.01	-	8.09	-78.0
NdN	5.15	-	7.70	-71.6

Thermodynamic data for a number of nitrides and their reference sources are given by Wicks and Block [WICKS]. The enthalpies of formation and vaporization for all the rare earth nitrides were recently reviewed by Kordis and Gingerich [KORDIS]. A technique for predicting the free energy of formation of nitrides where experimental data are not available has also been described [ANDERSON-1970]. This technique relies upon the similarity of oxides and nitrides to establish a correlation with known oxide/nitride thermodynamics so that missing nitride data may be predicted if the oxide thermodynamics are known. Enthalpies of formation are listed in Table 47 for some of the nitrides.

The principal difference between elemental and liquid alloy thermodynamic values is that the free energies of formation differ by the free energy of solution of the metal. However, further complications arise in that multiple nitride-forming elements interact in a solution; these interactions must be taken into account in determining the nitride equilibria. Data on this effect are extremely limited. There is only one reference on the interaction coefficients of U-Gd-N in liquid tin [FUWA].

(f) Fission Products in Tin

We have begun to evaluate some of the literature data on the thermodynamics of solution of fission product and fuel materials in liquid tin. The parameter of most interest is the activity coefficient of fission product and fuel material elements in tin. The activity coefficient is important in determining both (1) the volatilities of the various elements from hot molten tin, and (2) the distribution coefficients of the elements between the hot molten tin phase and the fuel nitride (e.g., UN) phase in the molten tin process. Thus far, we have evaluated data on binary solutions of the fission product elements Ag, Rb, Cs, Sr, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd in liquid tin. Activity coefficients are found to be in the range of 10^{-1} to 10^{-3} for dilute solutions of these elements in tin.

Direct information on activity coefficients is available only for the Ag and La binaries with liquid tin. However, enthalpy of solution data exist for all systems looked at except the binaries of Rb, Cs, and Pm with liquid tin. Furthermore, the enthalpy of solution usually provides the major portion of the numerical value that determines the activity coefficient. Hence, it should be possible to estimate activity coefficients by estimating the balance of the thermodynamic data required. The basic expression relating activity coefficient to the other thermodynamic parameters is:

$$\begin{aligned} RT \ln \gamma_2 &= \overline{\Delta H_2} - T \overline{\Delta S_2}^E \\ &= \overline{\Delta G_2}^E, \end{aligned}$$

where γ_2 is the activity coefficient of the solute referred to the pure liquid solute element with unit activity, $\overline{\Delta H}_2$ is the enthalpy of solution of the solute, and $\overline{\Delta S}_2^E$ is the excess entropy of solution of the solute, and $\overline{\Delta G}_2^E$ is the excess free energy of solution. Once $\overline{\Delta H}_2$ of solution is known, the only thermodynamic parameters that need to be estimated are the $\overline{\Delta S}_2^E$ above, and ΔC_p for formation of the solution. Values of ΔC_p are needed to determine the temperature dependence of $\overline{\Delta H}_2$ and $\overline{\Delta S}_2^E$.

We should emphasize that although these estimation techniques should be of value to our understanding of the molten tin process, they are not a substitute for the actual experiments needed to measure such effects as volatilities and partitioning behavior.

Specific comments on the systems looked at are presented in the following subsections.

Ag, Rb, and Cs Binaries with Sn. Hultgren et al. [HULTGREN] give the following data for the Ag-Sn system:

$$900 \text{ K: } \overline{\Delta G}_{\text{Ag}}^E = 0.542 \text{ kcal/mol, } \overline{\Delta H}_{\text{Ag}} = 1.046 \text{ kcal/mol,}$$

$$\text{and } \overline{\Delta S}_{\text{Ag}}^E = 0.560 \text{ cal/mol-K}$$

$$1250 \text{ K: } \overline{\Delta G}_{\text{Ag}}^E = -4.160 \text{ kcal/mol}$$

The $\overline{\Delta G}_{\text{Ag}}^E$ value at 1250 K corresponds to an activity coefficient of 0.187 for silver in dilute solutions in tin. The trend in $\overline{\Delta G}_{\text{Ag}}^E$ at temperatures between 900 and 1250 K is actually quite large and indicates that γ_{Ag} at our working temperature of 1900 K may be about 0.1.

We have not been able to find any thermodynamic data on the Rb-Sn and Cs-Sn systems. Compounds such as RbSn and CsSn have been reported [HEWAIDY] from which we can infer that attractive bonding forces exist in solutions of Rb-Sn and Cs-Sn. Further, drawing on the analogy of known thermodynamic data in the Na-Sn, Na-Pb, and K-Pb systems; we estimate γ_{Rb} and γ_{Cs} in liquid tin to be about 10^{-2} at 1900 K.

Sr and Ba Binaries with Sn. King and Kleppa [KING]

and Guadagno et al. [GUADAGNO] have measured the $\overline{\Delta H}_2$ of solution of Sr and Ba in liquid tin at temperatures of about 700 K. The data of infinitely dilute solutions are as follows:

	[KING]	[GUADAGNO]	Ave.
$\overline{\Delta H}_{Sr}$	-38.57 ± 0.3 kcal/mol	-37.00 ± 0.4 kcal/mol	-37.8 kcal/mol
$\overline{\Delta H}_{Ba}$	-43.78 ± 0.6 kcal/mol	-43.26 ± 0.4 kcal/mol	-43.5 kcal/mol

No data is available on $\overline{\Delta G}_2^E$ or $\overline{\Delta S}_2^E$ for these systems. However, we would expect $\overline{\Delta S}_2^E$ to be of the order of -10 cal/mol-K by analogy with Hultgren's data on calcium [HULTGREN] with the additional assumption that ΔC_p is close to zero for the Ca-Sn system. The activity coefficients, γ_{Sr} and γ_{Ba} , would be expected to be in the vicinity of 10^2 - 10^3 at 1900 K.

La and Rare Earth Binaries with Sn. Bayanov [BAYANOV]

has summarized the $\overline{\Delta H}_2$ of solution data for lanthanum and rare earths. We obtain the following best values as our initial assessment for $\overline{\Delta H}_2$ at infinite dilution at 800 K:

	$\overline{\Delta H}_2$, kcal/mol
La	-66.7 ± 0.6
Ce	-70.4 ± 0.6
Pr	-63.7 ± 0.4
Nd	-60.0 ± 1.5
Pm	est. -58.6
Sm	-57.3 ± 2.5
Eu	-42.6 ± 2.0
Gd	-54.7 ± 2.6

In the case of La-Sn, data are also available on $\overline{\Delta G}_{La}^E$ from 673 to 973 K [MATIGOROVA]. The $\overline{\Delta G}_{La}^E$ data can be shown to be consistent with the $\overline{\Delta H}_{La}$ data by taking ΔC_p to be 15 cal/mol-K. This then leads to the following temperature-dependent expression for γ_{La} :

$$\overline{\Delta G}_{La}^E = RT \ln \gamma_{La} = -68,500 + 28.00T - 15(T-673) - 15T \ln(T/673).$$

From this, we calculate $\gamma_{La} = 9 \times 10^{-4}$ at 1900 K.

The combined $\overline{\Delta H}_{La}^E$ and $\overline{\Delta G}_{La}^E$ data is also very useful in indicating the magnitude of the $\overline{\Delta S}^E$ to be expected for the rare earths in general. $\overline{\Delta S}_{La}^E$ is about -25 cal/mol-K at 800 K, and thus similar values can be anticipated for the other rare earths. Therefore, based on the $\overline{\Delta H}_2$ data above, the activity coefficients of the rare earths can be expected to be of the order of 10^{-3} at 1900 K.

(g) Volatilities of Fission Products from Tin Solutions

As we mentioned earlier, it is of value from a process standpoint to know the volatilities of fission products from molten tin since the more volatile ones can be removed as part of the process. We can estimate a volatility of comparing the partial pressure of the fission product with the vapor pressure of the tin solvent. Tin has a vapor pressure of 10^{-3} atm at 1873 K. A fission product with a comparable or greater vapor pressure would be expected to have a very high volatility, and it should be possible to remove the fission products almost completely by distilling off a small portion of the tin. An initial estimate of fission product volatilities from tin at 1873 K is given in Table 48. Partial pressures of the fission products were each estimated by multiplying mole fraction times activity coefficient times vapor pressure of the pure element.

(2) Literature Survey of Kinetic Data

The information for the literature survey of kinetic data had the same sources as the thermodynamic data. Data on kinetics for the MTN process were found to be limited to work by [ANDERSON-1970, 1972, 1976] and their coworkers.

The physical and chemical form of the fuel to be reprocessed can dominate the rate of throughput. Such features as the presence of absence of cladding, type of cladding (if present), and the chemical form of the fuel (viz., oxide, carbide, or metal) could each prove to be a controlling factor in the overall kinetics. Nevertheless, we can identify and list with some specificity the potential rate-controlling steps, depending on or within the solid phase. If the carbothermic reduction, for example, occurs within the solid phase, the rate should be governed by the permeation rates of the reactants in the solid phase. If reduction occurs in the liquid phase, the rate would be controlled by the rate of solution of the constituents, as well as their steady state concentration.

Table 48. Estimated Volatilities of Fission Products from Molten Tin Solutions at 1873 K.

A.	Very high (10^{-3} to 1 atm)
	I, Br, Cd, Cs, Rb, and Se
B.	Moderate (10^{-6} to 10^{-4} atm)
	Sb and Te
C.	Low (10^{-8} to 10^{-6} atm)
	Ba, Eu, Sm, and Sr
D.	Very low (less than 10^{-9} atm)
	Ce, Gd, La, Mo, Nd, Pd, Pm, Pr, Rh, Ru, Tc, Y, and Zr

Schicks [SCHICKS-1973] and Schicks, Anderson, and Parlee [SCHICKS-1974] reported on their studies of the kinetics of formation of UN in liquid U-Sn alloys. They derived a kinetic rate equation based upon a model which takes into account the rate of diffusion of nitrogen in the liquid alloy and the reversible formation of UN. The back-calculated function for percent completion of the nitriding reaction as a function of time, using the derived equation, is in good agreement with measurement.

Greenhalgh [GREENHALGH] made measurements of the rate of carbothermic synthesis of UN and PuN from UO_2-C and PuO_2-C mixtures treated in flowing N_2 . He derived a rate equation based upon a diffusion-controlled mechanism and concluded (without backup discussion) that "the reaction rates are rapid enough for an economical nitride process." In any case, at about 230 min, the reaction was 82% complete at a temperature of 1758 K.

(3) Process Flow Diagram

A process flow diagram for the molten tin process along the general lines described in the introduction of this report is given in Fig. 55. The purposes of the diagram are to identify the quantities of mass flow through the process and to give insight on the types and (very approximate) sizing of process equipment required. We find that if we assume a batch type process with an input of 965 kg of UO_2 feed, it would be necessary to handle approximately 4000 kg of charge in the major high-temperature process steps--i.e., the carbothermic reduction and nitriding steps. The amount of tin or the batch size might be decreased if smaller quantities are preferred, but in any event batch processing is reasonable and may present considerable advantages from the standpoints of safety and inventory control.

Fig. 55. Molten Tin Process Flow Sheet Illustrating Mass Flow through the Major Process Steps. All values are kilograms except where noted otherwise.

(4) Laboratory Experimentation

The experimental effort consisted primarily of purchase of equipment and installation of facilities. Originally, the plans called for installation of two induction heating furnaces and a glove box facility for experimentation with materials of low-level radioactivity, adaption of an existing induction furnace in the plutonium facility for use with plutonium-containing experiments, and the installation of induction heating and metallographic equipment in the LLL Hot Cell Facility for experiments with actual fuels. Subsequently, the Hot Cell effort was deferred in view of expected lower budget levels.

By the end of the fiscal year, all orders for equipment had been placed and nearly all had been received. One induction heater for low-level activity was in use, and the glove box facility was nearly operational.

Two induction heating runs were carried out on carbothermic reduction of UO_2 in molten tin. In the first run, 10 g of plasma-formed UO_2 microspheres (150–210 μm in dia.) were added to 50 g of tin in a tall graphite crucible; heating was in vacuum to about 1900 K for about 20 min. A graphite diaphragm containing an aperture was placed halfway up the crucible; the induction coil was positioned on only the lower half of the crucible in an attempt to provide a cooler refluxing chamber in the upper half of the crucible and thereby prevent excessive vaporization losses of tin in the vacuum. Insulation (stabilized zirconia fiber) was used to insulate the crucible all the way to the top. Finally, a graphite lid was placed on top of the crucible. An orifice was provided in the lid for optical pyrometry and escape of evolved gases. Complete retention of the tin was not attained in this first run. Both molten globules and tin vapor were ejected out of the sight hole and a total of 10 g of tin was lost. Metallographic and microprobe analysis indicated less than 10% of the UO_2 had been reduced to form U-Sn intermetallics.

In the second run, the heating assembly was designed to provide better refluxing. The zirconia insulation covered only the bottom half of the crucible. A closed pyrometer viewing well was installed, and vents were provided on sides of the crucible (near the top) for the escape of evolved gases (see Fig. 56 for an illustration of the new assembly).

Fig. 56. Schematic Illustration of the Refluxing Crucible for Containment of Liquid Tin, and of the Induction Furnace.

The run was carried out again at about 1900 K for about 3 h, using fresh materials. Containment of the tin was successful in this run--the total loss was about 2 g. Metallographic and microprobe analyses indicated that about 10% of the UO_2 had reacted.

It appears at this point that carbothermic reduction of pure UO_2 in a pure tin system is quite slow, i.e., 10% reaction in 3 h at 1900 K. However, the work is just getting under way and the effect of some of the system parameters (temperature, impurity effects, use of catalysts) need to be explored before we can draw any definitive conclusions. Containment of molten tin in vacuum under refluxing conditions at 1900 K is a significant finding.

IV. ENCAPSULATION OF RADIOACTIVE WASTE IN METAL (L. J. Jardine, K. F. Flynn, W. J. Meham, and R. E. Barletta)

The major objective of this program is to identify the advantages and disadvantages of encapsulating solidified radioactive waste forms in a metal matrix. The net attributes of metal encapsulation are to be identified by comparing the waste form properties and fabrication methods of this method with those of other well-developed solidification alternatives (i.e., calcination and vitrification in the special case of high-level radioactive wastes).

Laboratory-scale investigations are in progress, specifically aimed at generating data for further assessment of probable or unresolved problem areas. Experimental studies during this report period have focused on the leach rates of simulated waste forms. A study has been initiated to assess the resistance to mechanical impacts of metal-encapsulated waste forms in comparison to that of glass waste forms.

A. Leach Rate Determinations

1. Introduction

Leach rate determinations of a series of proposed radioactive waste forms, using a variety of leaching media, are being performed. These measurements are part of a continuing program directed toward establishing the integrity of radioactive waste material against dispersal from terminal repositories by hydraulic means. Neutron activation analysis (NAA) techniques [STEINDLER-1968A, FLYNN] have been used exclusively in these measurements. In NAA, leaching of radioactive isotopes is determined by measuring their concentrations in the simulated waste* before leaching and in the leachant after leaching. Additional information on these studies can be found in previous reports in this series [STEINDLER-1977, 1978A, 1978B, 1978C, 1978D].

2. Experimental Results

Leach rate measurements for a sintered PW-7a waste form (SWF)[†] in several configurations have been completed. These studies included leach tests of (1) SWF granules in 25°C quiescent distilled water (pH 5.8) and 100°C boiling distilled water (pH 7.3), (2) pulverized material (SWF) tested in a conventional Soxhlet apparatus (refluxed distilled water, pH 7.3), and (3) a small cylindrical ingot (3 cm in diameter by 5 cm high) consisting of 54 g of granules (about 4-mm close-packed) cast in 230 g of lead leached by 25°C quiescent distilled water (pH 5.8). Prior experiments with this waste indicated that although it may have some undesirable characteristics for terminal storage, it

* Gamma ray analyses were made by E. A. Huff.

[†] This sintered waste form (SWF) material was obtained from Battelle Pacific Northwest Laboratories (PNL) in the form of granules. A particulate mixture of 85 wt % PW-7a [BONNER] spray calcine and 15 wt % glass frit was agglomerated with a disk pelletizer, followed by sintering for 1 h at 1000°C. This form was not optimized for leach resistance but was provided for developing the neutron activation leach rate technique.

has certain attributes that make it attractive for studying leach rates in various physical configurations [STEINDLER-1978A]. Paramount among these attributes is the wide range of leach rates (*i.e.*, differing by a factor of 10^6) for the various elements contained in the waste forms.

a. Leach Rates of PW-7a Granules

The results of the incremental leach rates for the SWF granules (about 4 mm spheroids) using both 25°C quiescent distilled water (pH 5.8) and 100°C (boiling) distilled water (pH 7.3), are given in Table 49. Leach rates for fourteen elements could be readily determined. Because of interferences in the gamma-ray spectra, not all elements in all samples were determined. The data in this table have been reported as fraction (of the specific element) leached per day. Conversion of the data to the more conventional grams (equivalent) per square centimeter per day ($\text{g}/\text{cm}^2\text{d}$) was not done here because of ambiguity in the surface area measurements--*i.e.*; $0.9 \text{ m}^2/\text{g}$ by Brunauer, Emmet, and Teller (BET) measurement, compared with $6 \times 10^{-4} \text{ m}^2/\text{g}$ calculated assuming impervious spheres. Meaningful surface area determination is a recurring problem in the evaluation of leach rate data.

The results presented in Table 49 indicate a definite decrease in leach rate with time for all isotopes studied. The rates at 100°C are significantly higher than those at 25°C; however, this difference tends to diminish with time. The elements studied have a very wide range of leach rates--varying from about 10^{-2} for elements such as chromium, selenium, iodine, and cesium to about 10^{-5} for elements such as cerium and europium. The leach rates for alkaline earth elements (*i.e.*, barium and strontium) fall between these extremes. This order of leaching (*i.e.*, alkali metals > alkaline earths > rare earths) is commonly observed in heterogeneous mixtures. The very high initial leach rates (*i.e.*, about 10^{-2}) for elements such as cesium make the the decreasing leach rate with time of only academic concern.

b. Leach Rates of Pulverized PW-7a Granules

Incremental leach rates for pulverized material using the Soxhlet extractor are presented in Table 50. These data too are reported as fraction of the specific element leached per day and can be compared with the data in Table 49. The BET-measured surface area ($2 \text{ m}^2/\text{g}$) for this material is a factor of two greater than the BET-measured surface area for the granules ($0.9 \text{ m}^2/\text{g}$). The surface area for the pulverized material ($2 \times 10^{-2} \text{ m}^2/\text{g}$) calculated from sieving and by assuming particles to be impervious spheres is thirty fold the calculated surface area for intact granules ($6 \times 10^{-4} \text{ m}^2/\text{g}$). These calculations are based on assuming a spherical shape for particles whose size distribution had been determined by sieving. The details of these surface area calculations have been reported previously [STEINDLER-1978D]. The BET-measured surface areas for both materials were significantly greater than the calculated surface area. Since accurate determination of the surface area exposed to the leaching medium remains a major uncertainty, the use of calculated surface areas rather than gas-sorption surface areas (BET) for conversion of experimentally measured fractions leached to area-normalized leach rates is recommended. Leach rates based on calculated surface areas (assuming simple geometric shapes) are conservative, *i.e.*, are upper-limit estimates of the true leach rate.

Table 49. Incremental Leach Rate, fraction leached/day, for PW-7a SWF Granules^a (about 4-mm spheroids)

Isotope Analyzed	25°C Distilled Water (pH 5.8)		100°C (boiling) Distilled Water (pH 7.3)					
	1st (5.1 d) ^b	2nd (5.8 d) ^b	1st (1.1 d) ^b	2nd (1.0 d) ^b	3rd (6.8 d) ^b	4th (9.0 d) ^b	5th (7.0 d) ^b	6th (47.3 d) ^b
⁵¹ Cr	8.0 E-2 ^c	1.2 E-3	6.1 E-1	3.7 E-2	2.6 E-3	7.5 E-4	9.9 E-4	7.2 E-4
⁶⁰ Co	5.0 E-5	2.6 E-5	5.5 E-4	1.2 E-4	2.2 E-5	2.1 E-6	3.7 E-6	3.3 E-6
⁶⁵ Zn	4.0 E-5	1.2 E-5	2.3 E-3	5.4 E-4	6.3 E-5	1.3 E-5	1.7 E-5	2.5 E-5
⁷⁵ Se	d	d	6.8 E-1	5.0 E-2	7.6 E-3	3.4 E-3	4.4 E-3	1.5 E-3
⁸⁵ Sr	2.0 E-4	1.6 E-5	7.7 E-4	d	2.4 E-4	2.9 E-4	6.5 E-4	4.1 E-4
⁹⁵ Zr	1.0 E-4	d	6.8 E-3	9.6 E-4	9.1 E-5	8.4 E-5	5.6 E-5	6.5 E-6
¹⁰³ Ru	d	d	d	d	1.0 E-3	2.6 E-3	d	8.0 E-4
¹¹⁰ Ag	6.0 E-5	d	3.9 E-3	1.8 E-3	2.7 E-3	1.5 E-3	2.0 E-3	1.1 E-3
¹²⁴ Sb	1.7 E-4	d	2.8 E-3	3.9 E-4	9.3 E-5	2.5 E-5	3.8 E-5	6.3 E-6
¹³¹ I	2.2 E-2	4.8 E-2	1.7 E-1	3.1 E-2	9.0 E-3	2.5 E-3	d	1.5 E-3
¹³¹ Ba	2.0 E-4	2.8 E-4	d	d	2.2 E-3	3.0 E-3	d	5.5 E-3
¹³⁴ Cs	3.0 E-2	1.1 E-3	4.9 E-1	9.7 E-2	6.5 E-3	7.2 E-4	8.7 E-4	2.5 E-4
¹⁴¹ Ce	6.0 E-5	1.1 E-5	d	9.7 E-5	2.0 E-5	4.0 E-6	3.3 E-6	7.6 E-7
¹⁵² Eu	2.3 E-5	d	5.3 E-4	1.4 E-4	3.0 E-5	4.6 E-6	4.4 E-6	2.0 E-6

^aSurface area of granules was measured to be 0.9 m²/g by Brunauer, Emmet, and Teller (BET) method and was calculated to be 6 x 10⁻⁴ m²/g assuming impervious spheres.

^bLength of time in days for each sequential leach test.

^c8.0 E-2 corresponds to 8.0 x 10⁻².

^dThese data were not resolved from the gamma spectra.

Table 50. Incremental Leach Rates for Pulverized PW-7a SWF Granules^a in Condensing Distilled Water (pH 7.3) in Soxhlet Apparatus

Isotope Analyzed	Incremental Leach Rate, fraction leached/day			
	1st (1.1 d) ^b	2nd (1.0 d) ^b	3rd (6.8 d) ^b	5th (7.0 d) ^{b,c}
⁵¹ Cr	2.4 E-1	2.0 E-3	3.1 E-4	6.7 E-5
⁵⁹ Fe	d	4.7 E-5	2.9 E-6	5.7 E-6
⁶⁰ Co	2.4 E-5	6.1 E-5	1.8 E-5	6.2 E-6
⁶⁵ Zn	1.7 E-4	1.3 E-4	3.7 E-5	7.8 E-6
⁸⁵ Sr	d	2.0 E-4	7.8 E-5	9.0 E-5
⁹⁵ Zr	1.8 E-3	8.7 E-5	3.7 E-5	6.0 E-6
¹⁰³ Ru	5.5 E-4	2.9 E-4	4.5 E-4	6.1 E-5
¹¹⁰ Ag	2.7 E-4	2.4 E-4	7.0 E-5	9.0 E-6
¹²⁴ Sb	8.1 E-4	1.1 E-4	2.7 E-5	1.0 E-5
¹³¹ I	5.9 E-2	2.4 E-3	1.3 E-3	2.6 E-4
¹³¹ Ba	d	1.9 E-4	1.4 E-4	1.1 E-4
¹³⁴ Cs	4.2 E-1	2.3 E-3	4.1 E-4	8.5 E-6
¹⁴¹ Ce	1.9 E-5	6.1 E-5	1.4 E-6	6.6 E-6
¹⁵² Eu	6.4 E-5	4.6 E-5	1.4 E-6	4.5 E-6

^aSurface area was measured to be 2 m²/g (BET) and was calculated to be 1.5 x 10⁻² m²/g, assuming impervious spheres and a sieving analysis.

^bLength of time in days for each sequential leach test.

^cSamples for the fourth period (test length of 9 days) were lost while being prepared for counting, and the data are not available.

^dThese data were not resolved from the gamma spectra.

c. Comparison of Leach Rates of Granular and Pulverized PW-7a

The leach rates for the granules (Table 49) are compared with those of the pulverized material (Table 50) in Table 51. For simplicity, five characteristic elements (cobalt, strontium, cesium, cerium, and europium) were chosen for the comparison. These elements represent the spectrum of element types associated with nuclear waste material. The data are for the third leaching period for both material forms in order to avoid any anomalies associated with initial effects; the data selected to represent granule data are the 100°C (boiling) distilled water data because of the close similarity (e.g., in pH) of this leaching medium and the leaching medium for pulverized material in the Soxhlet extractor. For comparison purposes, the fraction-per-day leach rates were converted to the more conventional g/cm²d, using both the BET-measured and the calculated surface areas.

Table 51. Incremental Leach Rates for Pulverized PW-7a Granules Compared with Leach Rates of PW-7a Granules^a

Isotope Analyzed	Granules			Pulverized Material		
	Leach Rate, fraction/d	Area-normalized Leach Rate, g/cm ² d		Leach Rate, fraction/d	Area-normalized Leach Rate, g/cm ² d	
		BET	Calculated		BET	Calculated
⁶⁰ Co	2.2 E-5	2.4 E-9	3.6 E-6	1.8 E-5	9.0 E-10	1.2 E-7
⁸⁵ Sr	2.4 E-4	2.6 E-8	3.9 E-5	7.8 E-5	3.9 E-9	5.2 E-7
¹³⁴ Cs	6.5 E-3	7.1 E-7	1.1 E-3	4.1 E-4	2.1 E-8	2.7 E-6
¹⁴¹ Ce	2.0 E-5	2.2 E-9	3.3 E-6	1.4 E-6	7.0 E-11	9.3 E-9
¹⁵² Eu	3.0 E-5	3.3 E-9	4.9 E-6	1.4 E-6	7.0 E-11	9.3 E-9

^aData from the third leach period (Table 49 and 50) for both material forms.

As can be seen from Table 51, when data are reported in this way there are vast differences between the leach rates of the granules and those of the pulverized waste forms. These differences are even larger (one to two orders of magnitude) when corrections for surface area are applied. The fraction leached per day rates for the pulverized material (uncorrected for the greater surface area) are lower than for the granules. One would expect the reverse since at least some increase in surface area would be expected from pulverizing (BET comparative measurements indicate a factor of two increase). These results support two previously stated opinions: (1) Pulverizing the waste form might change its leaching characteristics. (2) Conversion of leach rate data to a specific surface area basis can result in major uncertainties.

d. Leach Rates of Sintered PW-7a Granules and Pyrex Beads Encapsulated in Lead

Results from a relatively long-term leach test in 25°C quiescent distilled water of a small cylindrical (3-cm dia by 5-cm) metal matrix composite consisting of 54 g of 4-mm granules close packed and cast in 230 g of lead (identified as "284 g ingot") are given in Table 52. As before, these data are reported as fraction of the specific element leached per day. For this waste form, it is difficult to estimate the surface area exposed to the leaching medium. Previous studies [STEINDLER-1978D] have shown that these granules are rather porous. Hence, when incorporated into a metal matrix composite using no protective envelope by the method used and of the very small scale selected, there is significant penetration of the leaching medium throughout the composite.

The results given in Table 52 indicate a significant decrease in leach rate with time. However, the rate of decrease is somewhat less than that observed for unencapsulated granules (see Table 49). The leach rate for

Table 52. Incremental Leach Tests for SWF-Granules Waste Encapsulated in Lead in a Very Small(284-g) Composite Using No Protective Envelope in 25°C Quiescent Distilled Water

Isotope Analyzed	Incremental Leach Rate, fraction leached/day								
	1st (2.9 d) ^a	2nd (10.2 d) ^a	3rd (6.8 d) ^a	4th (13.8 d) ^a	5th (17.0 d) ^a	6th (21.0 d) ^a	7th (32.0 d) ^a	8th (37.2 d) ^a	9th (48.9 d) ^a
⁵¹ Cr	3.7 E-2	1.5 E-2	7.1 E-3	5.4 E-3	7.1 E-4	4.4 E-3	3.0 E-3	2.0 E-3	1.3 E-3
⁶⁰ Co	6.1 E-7	1.5 E-6	7.4 E-7	6.5 E-8	2.9 E-8	2.1 E-7	4.3 E-8	1.7 E-7	6.5 E-8
⁶⁵ Zn	6.6 E-6	5.9 E-6	4.2 E-6	2.3 E-7	7.8 E-8	9.7 E-7	1.7 E-7	7.8 E-7	1.4 E-7
⁷⁵ Se	6.2 E-3	2.0 E-3	1.2 E-3	7.3 E-4	4.8 E-4	3.8 E-4	2.5 E-4	1.4 E-4	7.5 E-5
⁸⁵ Sr	b	b	b	b	b	b	b	7.7 E-7	1.3 E-6
¹¹⁰ Ag	b	b	b	b	b	b	b	1.8 E-7	b
¹²⁴ Sb	1.6 E-5	5.5 E-6	4.2 E-6	3.0 E-6	8.9 E-7	1.4 E-6	9.0 E-7	3.4 E-7	6.1 E-7
¹³⁴ Cs	1.0 E-2	3.4 E-3	1.8 E-3	1.2 E-3	1.4 E-3	6.1 E-4	4.0 E-4	2.5 E-4	1.4 E-4
¹⁴¹ Ce	4.5 E-7	2.7 E-6	1.2 E-6	5.4 E-7	1.1 E-7	2.3 E-7	5.7 E-8	2.0 E-7	b
¹⁵² Eu	1.1 E-7	3.3 E-7	5.2 E-7	2.3 E-7	1.6 E-7	1.6 E-7	8.5 E-8	6.5 E-8	8.6 E-8

^aLength of time in days for sequential leach test.

^bThese data were not resolved from the gamma spectra.

the ingot seems to have leveled off to a constant value after about 100 days. Qualitatively, it can be said that the fraction of each radioisotope leached from this ingot is the same as the fraction leached from the granules. The data in Table 52 show that during the course of this experiment (190 d), greater than 10% of some elements (e.g., cesium) was leached from the ingot while only parts per million quantities of other elements (e.g., rare earths) were leached from the same ingot. Hence, leach rates for all elements of concern must be determined in order to establish the integrity of any proposed waste form. Furthermore, comparison with data for unencapsulated granules shows that incorporating this particulate porous waste form into a small-scale metal matrix with no protective envelope did not reduce the surface area exposed to the leaching medium.

A small cylindrical ingot (3-cm dia by 5 cm) containing about 68 g of neutron-irradiated Pyrex (borosilicate) glass beads (4-mm), close packed in a matrix of lead, was fabricated by casting. This ingot had the same size and shape as the ingot used for the SWF studies (i.e., the ingot identified above as "284 g ingot"). The initial radioactivity of specific isotopes in the ingot was determined by gamma-ray analysis [lithium drifted germanium (GeLi) detector] of a 1.3-g unleached sample of the glass beads and by multiplying these results by the weight ratio of the total beads (68 g) to the sample beads (1.3 g). Sequential leach tests using 300 mL of ambient (25°C), quiescent distilled water for each test were performed. Simultaneously, a 69-g sample of unencapsulated beads was leached under the same conditions as were used for the ingot. Comparison of the leach rates of the encapsulated and unencapsulated nonporous beads should identify any effect on the leach rate of the lead matrix.

Preliminary results from these tests indicate that the radioactivity level in the borosilicate glass beads might be too low for meaningful conclusions to be drawn at the low leach rates being observed for this waste form. However, final conclusions cannot be made until more detailed analyses of the data are performed.

e. Discussion of Leaching Conditions

Additional leaching media for the leach rate studies are saturated brine* (at both 25 and 110°C), carbonate-saturated distilled water (25°C), and Argonne National Laboratory tap water (25°C). The pH of each leachant is given in Table 53. Groundwaters characteristically have a pH range of about 5 to 9. As can be seen from Table 53, the leaching media under consideration adequately cover this pH range.

Preliminary measurements have been made of the effect of the solid waste form on the pH of the leachant after extended contact. In the presence of large quantities of Pyrex beads, the pH of 25°C distilled water shifted from an initial value of 6 to a pH of 8. Large quantities of lead

*The brine used in these studies consisted of a saturated solution of salt from the proposed Waste Isolation Pilot Plant (WIPP).

Table 53. pH of Leachants^a

Leach Medium	pH
Distilled Water (25°C)	6.0
Distilled Water (100°C)	7.3
Saturated Brine (25°C)	7.6
Saturated Brine (110°C)	7.6
Distilled Water, Carbonate-Saturated (25°C)	3.9
ANL Tap Water (25°C)	9.7

^aEach pH was measured with a calibrated Sargent-Welch Model NX pH meter at the indicated temperature.

in 25°C distilled water shifted the pH from 6 to about 9.5. In each case, the leaching media was rendered significantly more basic. This effect will be investigated in more detail, and its significance with respect to terminal storage conditions will be evaluated.

The temperature of the leaching medium in a waste repository will depend, in part, primarily on the decay heat generated by the waste. Although the temperature will be relatively low (i.e., below 100°C) for existing (i.e., defense) wastes, the temperature of future reprocessing wastes might be significantly higher. The two temperatures chosen for the current studies (i.e., 25°C and 100°C) are adequate to span the range of temperatures for existing wastes. Further experiments are in progress in which an autoclave is being used to extend these leach studies to higher temperatures (up to about 300°C) and to commensurate pressures.

f. Leaching of Simulated High-Level Glass Waste Containing Uranium

Leach rate studies are continuing on simulated high-level waste (HLW) glass that contains uranium. This waste was obtained from Battelle Pacific Northwest Laboratories (PNL) and has been described previously [STEINDLER-1978D, MCELROY-1977B]. Preliminary results of leaching testing of this glass with 25°C quiescent distilled water have been reported [STEINDLER-1978D]. Leach rates for twelve different elements over a sixty-day period were established.

In other work, leach tests of this material have been instituted using the alternative leaching media listed in Table 53. The results of these tests will help identify the effects of temperature, salinity, and pH on the leach rate of a relatively leach-resistant waste form.

3. Conclusions

The results elucidated in this report support previous assessments that meaningful surface area determinations are a recurring problem in the evaluation of leach rate data. For the present, it is recommended that geometrically calculated surface areas be used, not the gas sorption (BET) measured surface areas, when converting experimentally measured fractions leached to area-normalized leach rates.

There are discrepancies between leach rates as measured with NAA techniques using Soxhlet extractor techniques and those measured using non-pulverizing NAA techniques as described in [STEINDLER-1978A], indicating that pulverizing the waste form can significantly change its leaching characteristics.

The results of relatively long-term (190-d) leach tests of a very small scale metal matrix composites indicate that (at least for this relatively porous waste form) the leach rates for the radioactive waste elements in the composite are only slightly different from the leach rates for these elements in unencapsulated pellets. Incorporating this particular waste form into a metal matrix composite with no protective envelope did not reduce the surface area exposed to the leaching medium. Further tests using metal matrix composites of less porous waste forms (e.g., borosilicate glass beads) and of larger scale are required in order to arrive at definitive conclusions regarding the effects of the metal matrix on leach rates.

Work is in progress on leach rate studies that use other leaching media. Ambient-temperature quiescent distilled water is certainly not representative of any aqueous medium likely to be in a waste repository. Tests wherein the temperature, pH, and salinity of the leaching medium are varied will help establish the effect of these variables on the leaching characteristics of proposed waste forms.

B. Evaluation of Impact Resistance of Metal-Matrix Waste Forms

1. Introduction

Resistance of solid radioactive waste forms to dispersion by mechanical impacts during in-plant storage and transportation is likely to be one of the properties of most concern. A study has been initiated to analyze and evaluate the effects of mechanical impacts on reference metal-matrix waste forms. The effects of primary concern are those bearing on release and dispersion of waste to the environment, including the degree of resistance to groundwater leaching. The objective of this effort is to develop sufficient information on impact resistance so that decisions can be made (by others)

regarding either the need or the effort required for mechanical impact resistance demonstrations of metal-encapsulated solid high-level waste (HLW) forms and for comparison with two well-developed solid HLW alternatives--calcines and glass monoliths. Existing data are to be used wherever possible. Reviews of the current status of metal-matrix technology have been published [STEINDLER-1978D, JARDINE-1978A, 1978B].

The first quarter of work on impact resistance is reported here. Major emphasis was on a literature review of impact methodology and test data relevant to glass and metal-matrix wastes. The literature search was organized around major programs on impact analysis at four laboratories:

1. tests of lead-shielded shipping casks and models at Oak Ridge National Laboratory (ORNL),
2. analysis of models as well as tests of full-scale casks containing ceramic fuel elements at Sandia Laboratories (SL),
3. tests of glass and concrete forms at Savannah River Laboratory (SRL), and
4. tests of glass and metal-matrix composites at the Battelle Pacific Northwest Laboratory (PNL).

Major reports relevant to the objectives of the present program were examined and summarized. Although the cited reports vary in focus, depth, and breadth of treatment, all are believed to contribute useful information on the properties of materials and on methods of analyzing and demonstrating impact resistance of waste forms. A preliminary summary of the state of the art of impact analysis obtained in the literature is given below in approximate chronological order for programs at each of the four laboratories. Included in the discussions of the four programs are reports from other laboratories.

2. Analysis and Tests of Impact Resistance of Shipping Casks Made of Massive Lead Contained in a Steel Shell (ORNL)

This program was oriented to the practical design and demonstration of the impact resistance of shipping casks of a commercial type, particularly as related to 30-ft drop tests on unyielding flat surfaces and penetrators. The properties of lead and steel under dynamic conditions are compared with those for static conditions. For strain rates obtained in 30-ft drops, the dynamic yield point of steel is only slightly greater than the static yield point. Accordingly, it is recommended that the static yield point of steel be used to determine elastic deformations of the steel components of casks [SHAPPERT].

Static properties [PERRY] of cast lead (i.e., commercially pure "chemical lead") are given as follows:

Modulus of elasticity	2.0×10^6
Poisson ratio	0.40 to 0.45

Tensile yield strength	2300-2800 psi
Ultimate elongation	about 33%
Brinnell hardness	4.0 to 6.0

Quantitative models based on rigorous theory have not been developed to the extent of practicality in engineering design. A less rigorous analysis using a pseudo-material property--dynamic flow stress--has been found to be quite accurate for homogeneous materials and generally acceptable for engineering design; this was confirmed in the limited tests made [SHAPPERT]. Dynamic flow stress, σ_D , is defined as the energy absorbed per unit volume of material displaced in plastic deformation: the units are energy/volume = pressure--for example, in.-lb/in.³ = psi. The overall effect of conversion of kinetic energy into energy of deformation can thus be described as

$$W \cdot H = \sigma_D V_D \quad (1)$$

where W is the weight of the cask, H is the height of free fall, σ_D is the dynamic flow stress, and V_D is the volume of material displaced in the impact deformation. Equation 1 assumes that there are no energy absorbers external to the cask. Design of such absorbers to protect the cask proper from impact is also discussed [SHAPPERT].

The dynamic flow stress of common plumber's lead has been measured to be between 3700 psi and 19,000 psi; this rather large range is attributed to variations of crystal size and orientation and possibly to impurities. Compressive yield calculated from static indentation hardness (Brinnell number 4.0) is 5900 psi. Correlation of the impact deformation of small lead spheres indicates a dynamic flow stress of 8500 psi. Impact deformations from cylindrical punches indicated a dynamic flow stress of 10,300 psi. Since for a given energy absorbed, smaller values of the yield stress give greater deformation, it is recommended that to provide a margin of engineering safety, a value of 5,000 psi be used in estimating the deformation of lead-steel composites. The higher value, 10,000 psi, is more realistic for measuring maximum load force in impact decelerations [SHAPPERT].

The above recommendations are supported by independent experimental work, which also concludes that for moderate total strains and velocities (such as are involved in cask drop tests), the strain-rate effects in lead do not preclude the use of small-scale models when standard scaling laws are used [CLARKE-1963, 1965]. Scaling laws are discussed below.

Crushing impacts (where the energy for cask deformation comes from another moving object) can be modeled acceptably, but results in penetration-type impact tests are apparently too dependent on the configurations used to be scaled with confidence [CLARKE-1965].

The applicability of Eq. 1 can be illustrated by specific examples for a cylindrical body. Reported examples are summarized below.

a. Example 1 [SHAPPERT]

In a side drop of a cylindrical cask, the deformation may be described as a flattening of the circular cross section (as in 1, Fig. 57). The volume of lead displaced is given by the product of the area of the segment (Fig. 57) and the cylinder length L , or $LR^2 \left(\theta - \frac{\sin 2\theta}{2} \right)$ where R is the cylinder radius. The energy for this deformation of the lead, w , is the product of this volume and the dynamic flow stress of lead, σ_L :

$$w = \sigma_L LR^2 \left(\theta - \frac{\sin 2\theta}{2} \right) \quad (2)$$

The total volume of the steel end plates displaced is twice the product of the segment area times the plate thickness, t_e , or $2t_e R^2 \left(\theta - \frac{\sin 2\theta}{2} \right)$. The energy, w_e , for this deformation of the end plates is the product of this volume and the dynamic flow stress of steel, σ_s :

$$w_e = 2\sigma_s t_e R^2 \left(\theta - \frac{\sin 2\theta}{2} \right) \quad (3)$$

The total volume of circumferential steel shell displaced is calculated on the basis of the incremental increase of the circumference (ΔC) of the cylinder (at the same length, L) to accommodate an increase in contained volume, ΔV , equal to the above volume of lead displaced in the side-flattened cask; that is, for a cylinder of radius R and length L , $C = 2\pi R$ and $V = \pi R^2 L$, or

$$\Delta C \doteq \Delta V / RL, \text{ or} \quad (4)$$

$$\Delta C = R \left(\theta - \frac{\sin 2\theta}{2} \right) \quad (5)$$

The volume of the shell displaced is the product of the increase in the circumference, ΔC , the thickness of the shell t_s , and the length L . The energy w_s of this deformation of the shell is the product of this volume and the dynamic flow stress of steel σ_s , or

$$w_s = \sigma_s t_s LR \left(\theta - \frac{\sin 2\theta}{2} \right) \quad (6)$$

The partitioning of the total absorbed energy of free fall, WH , into lead and steel can be found for the energy balance:

$$WH = w_L + w_e + w_s \quad (7)$$

where the variables determining the partition are those in Eqs. 2, 3, and 6 above. Note that the calculation assumes uniformity of deformation. This is unrealistic in detail, but is meaningful for the "average" effects of a given absorbed energy.

1. General Type of Deformation

Cylindrical cask of radius R and length L with flattened side.

2. Area of Circular Segment for Displacement of Lead and End Plates

Original cross sectional area of circle = πR^2

Original circumference = $2\pi R$

Area of sector $\left(\frac{2\theta}{2} \right) = R^2 \theta$

Area of segment $\left(\text{chord } B \right) = R^2 \left(\theta - \frac{\sin 2\theta}{2} \right)$

3. Increase of Circumference of Shell

Increment of circumference, ΔC , as a function of increment of volume, ΔV , of cylinder of length, L :

$$\Delta C = \frac{dC}{dR} \frac{dR}{dV} \Delta V$$

$$= (2\pi) \left(\frac{1}{2\pi R L} \right) \Delta V$$

$$= \Delta V / RL$$

4. Width of Flat

Flat width = chord C

$$= 2R \sin \theta$$

5. Note on Angle Relationships

$$\cos 2\theta = 2 \cos^2 \theta$$

$$\sin^2 \theta + \cos^2 \theta = 1$$

$$\sin 2\theta = 2 \sin \theta \cos \theta$$

Fig. 57. Geometric Modeling of Deformation of a Cylindrical Lead-Filled Cask in a Side Drop

An empirical test was made of a cask with a 15-ft fall. This calculation, for the cask dimensions and for $\sigma_L = 5000$ psi and $\sigma_s = 50,000$ psi, predicted an angle θ of 18° . In the actual drop, a measurement of the width of the flattened side showed variation by a factor of two along the length: for the average width, the test angle θ was 11.3° and for the maximum width, the test angle θ was 17° . The calculated distribution of absorbed energies was as follows: the lead absorbed 76% of the energy, the shell absorbed 13%, and the end plates 11%. The predicted deformations were in good agreement with detailed measurements including strain measurements made with strain gages [SHAPPERT, GOODPASTURE].

b. Example 2 [KLIMA]

In an end drop of a cask, the dense and soft lead is expected to slump from the top, expanding at the bottom, and causing the steel shell to expand circumferentially. The downward movement of the lead creates a void space near the top of the cask (if the lead is not bonded to the steel shell). The analysis aims to calculate this void space from the axial and radial strains. The cask is cylindrical and has a central cavity of radius r which is assumed to remain constant.

The volume of the lead and steel remains constant, with uniform axial strain $\epsilon_L = \frac{\Delta L}{L}$ and uniform radial strain $\epsilon_R = \frac{\Delta R}{R}$. The original outer radius is R , and the expanded radius is $R(1 + \epsilon_R)$. For a differential change in length, dL , at constant volume:

$$\pi(R^2 - r^2)dL = \pi[R^2(1 + \epsilon_R)^2 - r^2](1 - \epsilon_L)dL \quad (8)$$

From Eq. 8, neglecting higher order terms in ϵ_R and ϵ_L , the functional relation of ϵ_L to ϵ_R is:

$$\epsilon_L = 2\epsilon_R \left(\frac{R^2}{R^2 - r^2} \right) \quad (9)$$

The strain energy, w_L for lead is given for the dynamic flow stress, σ_L and the deformation ϵ_L as in Eq. 8:

$$w_L = \int_0^L \sigma_L \pi[R^2(1 + \epsilon_R)^2 - r^2] \epsilon_L dL \quad (10)$$

Equation 10 may be simplified as was Eq. 8 by neglecting higher-order products of ϵ_L and ϵ_R :

$$w_L = 2\pi \sigma_L R^2 \int_0^L \epsilon_R dL \quad (11)$$

The deformation energy, w_s , for the steel shell is given similarly in terms of: the dynamic flow stress, σ_s , the shell thickness, t_s , and the circumferential strain, ϵ_c , at radius R :

$$w_s = \int_0^L \sigma_s t_s (2\pi R) \epsilon_c dL \quad (12)$$

Equation 12 can be rearranged, substituting radial strain, ϵ_R for circumferential strain, ϵ_C , to which it is equal:

$$w_s = 2\pi R t_s \sigma_s \int_0^L \epsilon_R dL \quad (13)$$

The sum of the above deformation energies, $w_L + w_s$, equals the impact energy. If actual deformation must be calculated, the form of the deflection curve for the outer shell must be known in order to evaluate the integrals in Eqs. 11 and 13.

The change in volume of the central cavity, ΔV_C , can be calculated directly from the volume displacement of lead for the radial expansion at the original L:

$$\Delta V_C = \int_0^L \pi [R^2 (1 + \epsilon_R)^2 - R^2] dL \quad (14)$$

The change in the central cavity volume at constant inner radius r reflects the change in L.

Eliminating higher order differentials from Eq. 14:

$$\Delta V_C = 2\pi R^2 \int_0^L \epsilon_R dL \quad (15)$$

The deformation energies above in Eqs. 11 and 13 are related to the impact energy by:

$$\begin{aligned} WH &= w_L + w_s \\ &= (2\pi \sigma_L R^2 + 2\pi R t_s \sigma_s) \int_0^L \epsilon_R dL \end{aligned} \quad (16)$$

From Eqs. 15 and 16:

$$\begin{aligned} \int_0^L \epsilon_R dL &= \frac{WH}{2\pi(\sigma_L R^2 + R t_s \sigma_s)} \\ &= \frac{\Delta V_C}{2\pi R^2} \end{aligned} \quad (17)$$

From Eq. 17:

$$\Delta V_C = \frac{R^2 WH}{R t_s \sigma_s + R^2 \sigma_L} \quad (18)$$

The change in the height of the lead, Δh , is given by

$$\Delta h = \frac{\Delta V_C}{\pi(R^2 - r^2)} \quad (19)$$

From Eqs. 18 and 19:

$$\Delta h = \frac{R^2}{\pi(R^2 - r^2)} \frac{WH}{Rt_s \sigma_s + R^2 \sigma_L} \quad (20)$$

This change in height of lead was the deformation to be defined. The calculation is based on independent (nonbonded) axial movement of lead and steel.

For an end drop of 30 ft, the change in lead height of a specific cask was calculated to be $\Delta h = 0.59$ in. for $\sigma_s = 45,000$ psi and $\sigma_L = 5500$ psi. In the actual drop of a 1/12-scale model, the Δh was 0.7 in. The calculated Δh was 20% smaller than the actual deformation [KLIMA]. This is considered an acceptable agreement.

3. Full-Scale Demonstration of Impact-Resistant Spent-Nuclear-Fuel Shipping Systems [SANDIA]

Full-scale crash tests with spent fuel casks mounted on truck trailers or on special railway cars were conducted at up to 130 km/h (80 mph). The impacts were of two types: (1) a cask hit an immovable concrete wall and (2) an immobile cask was struck by a moving railroad locomotive weighing 109 Mg. One cask weighed 20 to 22 Mg and the concrete target was 626 Mg backed by 1580 Mg of earth. The energy of impact was essentially absorbed by crushing of the cask-support-vehicle structure and the cask tie-downs and impact-limiter shields, so that damage to the cask was slight and the cask proper was subject to acceleration of only about 20 gravities. Deformation of the cask was too slight to interfere with normal removal of its head, and only a slight leak was noted (under pressure test) in the most severe test. Some bowing of fuel pins was noted but no clad failures.

Mathematical modeling and one-eighth-scale model tests were made prior to full-scale tests in order to design the full-scale tests most economically and to fulfill the program objective of demonstrating analytical and modeling techniques for predicting damage. Such calculations and tests indicated that inadequate tie-downs would allow the cask to strike the concrete barrier at such a speed that cask damage would be so extensive as to be unacceptable.

In full-scale tests, the speed at which the cask encountered the barrier was about one-half the normal speeds of 60 to 80 mph. Agreement of the calculations and model tests with actual results was considered good.

The model-prototype relations used in scaling the models for deformation tests are summarized in Table 54 [HUERTA]. As shown in the table, for the same density and velocity, the stresses and strains are the same. Total mass and energy are proportional to volume for the same velocity; this applies to kinetic energy as well as elastic energy absorbed. However, acceleration and time effects are not the same in model and prototype, and therefore equivalence depends on the absence of sensitivity of the material to strain rates of the materials. Fundamental considerations underlying these scaling laws have been discussed in relation to experimental tests of fuel capsules in aerospace projects [DUFFEY] and in impact tests of shipping casks [CLARKE-1965].

Table 54. Summary of Model-Prototype Relations [HUERTA]

Property	Prototype	Model ^a
L, Reference Dimension or Length	L_p	$L_m = L_p/n$
y, Deflection, Length	y_p	$y_m = y_p/n$
ϵ , Strain, Length/Length	ϵ_p	$\epsilon_m = \epsilon_p$
σ , Stress or Pressure, $\frac{\text{force}}{\text{area}}$	σ_p	$\sigma_m = \sigma_p$
k, Modulus of Elasticity, $\frac{\text{force}}{\text{area}}$	K_p	$K_m = K_p$
f, Force, force	f_p	$f_m = f_p/n^2$
e, Energy, (force) (length)	e_p	$e_m = e_p/n^3$
m, Mass, mass	m_p	$m_m = m_p/n^3$
t, Time, time	t_p	$t_m = t_p/n$
A, Acceleration, $\frac{\text{length}}{(\text{time})^2}$	A_p	$A_m = nA_p$
V, Volume (length) ³	V_p	$V_m = V_p/n^3$
D, Density, (mass)/(volume)	D_p	$D_m = D_p$
U, Velocity, length/time	U_p	$U_m = U_p$

^aThe numerical relations of the properties of the model to those of the prototype are expressed in terms of the linear scale factor, n.

A fundamental basis of the scaling laws is provided by the similitude relations of dimensional analysis [LANGHAAR]. In static or equilibrium stress-strain relations, there are only two fundamental dimensions, force and length. When impacts are modeled, time is added and mass-length-time (MLT) units may be substituted for force-length-time (FLT) units. By the widely accepted theory of plasticity, the two elastic constants, Young's modulus, E, and Poisson's ratio, μ , are sufficient to characterize the material even for deformations beyond the elastic range (when the material yields in tension or shear), provided that loading is monotonically increased and there are no strain-rate effects. In the absence of time-rate effects, self-deformation of a moving body of a defined volumetric configuration striking a barrier is determined completely by total mass, M, velocity, u, density, ρ , the characteristic length, L, and the constants, E and μ . This is expressed by equating the impact stress, σ , to dimensionally consistent groups of these variables:

$$\sigma = \frac{\mu u^2}{L^3} f \left(\frac{EL^3}{\mu u^2}, \mu, \frac{M}{\rho L^3} \right) \quad (21)$$

For a given material, ρ , E , and μ are the same; furthermore, the variables, M and L occur only in the form $\frac{M}{L^3}$, which equals density ρ , which remains constant for a given material. Thus Eq. 21 becomes

$$\sigma = u^2 \cdot (\text{constant}), \quad (22)$$

and for the same velocity, u , the stress, σ , is the same in model and prototype [LANGHAAR].

This analysis clearly applies only to a continuous material medium and not to the fractured state of brittle failure. The extension to brittle materials is discussed below.

4. Impact Tests of Brittle Materials (SRL)

The impact analysis reviewed in the preceding sections was applied to ductile materials and composites. For brittle materials, deformation beyond the elastic limit results in fragmentation rather than plastic flow, and different methods of characterizing the result of direct impacts are required.

A method of characterizing the result of direct impacts on specimens of glass and concrete was developed at SRL. The compositions of the glass and concrete were described [WALLACE]. Details on the preparation and characterization of the glass also have been reported [KELLEY]. Borosilicate glass was selected in preference to phosphate glass because although both types are susceptible to devitrification, phosphate glass had a 1000-fold increase in leach rate upon devitrification while borosilicate glass had only a factor of two increase.

Static compressive strengths of small glass cylindrical specimens of the type used in the SRL impact tests were measured; they were found to be in the range, 65,000 to 100,000 psi [KELLEY].

Particle-size distribution after impact also was measured, and the total geometric surface area of the particles was calculated. For a given material, the surface area generated per joule of impact energy absorbed was approximately constant. Small cylindrical specimens (1.3-cm diameter, 2.5-cm height) held in a mortar were impacted by a pestle of hardened tool steel (a 2-kg weight falling in a guide tube from a maximum height of 80 cm and providing a single-drop impact energy of 15.7J). Particle sizes were determined with a shaker sieve having five screens with openings in the range, 2.0 to 0.125 mm. For some samples, the material that passed the smallest sieve was also analyzed with a Coulter counter to determine particle size. Repeated impacts were used to obtain cumulative impact energies up to 94J.

Samples of borosilicate glass and of neat concrete showed about the same surface area generation from impacts, approximately $10 \text{ cm}^2/\text{J}$. Concretes containing 40% waste sludge averaged about 2.5 times the surface area per joule. Single impacts on glass produced slightly less surface area than did multiple impacts--i.e., about $8.5 \text{ cm}^2/\text{J}$ [WALLACE].

In these tests, glass produced fewer fine particles of a size likely to become airborne than did concrete. No glass particles were detected smaller than $8 \mu\text{m}$. Comparable tests of concrete with 40% sludge showed 0.2 to 0.4 wt % of the material consisted of particles smaller than $4 \mu\text{m}$.

5. Impact Testing of Waste Glass in Canisters (PNL)

This work was performed in support of risk analyses for the management of high-level waste glass. The test program was undertaken because no data could be found for impact breakup characteristics of encapsulated waste glass. The objectives were, in order of priority, to estimate (1) the quantity of respirable fines produced, (2) the increase in glass surface area, and (3) the impact resistance of the filled canister (i.e., breaching of canister as a failure mode).

Impact tests were conducted using nonradioactive waste glass (type 72-62, composition PW-4b-2) cast as a massive solid in cylindrical 304L stainless steel canisters. Tests were made with glass in the normal state and with material deliberately devitrified. The reference canister was a cylinder of 1-ft diameter and 10 ft long. Models of one-half scale and one-sixth scale were used in tests [SMITH-1975B]. Reduced-scale models were used following the scaling laws formulated by Sandia [DUFFEY] to take advantage of lower cost and available facilities.

A review of the literature was used as a basis of the test design. However, there were conflicting theories of brittle fracture and an absence of data on impact breakup of glass monoliths. Work related to aerospace applications provided a review of the state-of-theory [BARSELL-1971] and method of analysis for spherical capsules containing ceramics [BARSELL-1972].

Review of particle-size distributions in various impact tests showed them to be in disagreement, and the lognormal distribution was adopted for convenience [PELTO]. No special distribution was established by the impact fragmenting process, insofar as could be determined from available reports.

The impact tests [SMITH-1975B] were conducted as follows. The half-scale models were impacted at room temperature and velocities up to 44 ft/s. The one-sixth scale models were tested at room temperature and 425°C and at velocities up to 117 ft/s (80 mph). Normal and devitrified glass were used in both sizes. Canister failures (breaches) consisted of very small cracks, through which little, if any, glass escaped. These failures occurred only at the two high velocities tested; about one-half of the one-sixth scale

models were breached at 66 ft/s and nearly all at 117 ft/s. Unfortunately, no tests were made at these high velocities with the larger models (half-scale) to allow comparison. No effect on breaching of temperature or state of vitrification was found. The edge-on impact of the canister was the most severe, as expected [SMITH-1975B].

The "fraction broken" was measured--i.e., the fraction of glass able to separate freely when the canister metal was carefully removed. The particles removed were sieved to determine the particle-size distribution. The respirable fraction (of size smaller than $10\text{ }\mu\text{m}$) typically ranged from 10^{-8} for control specimens to 10^{-4} for 80-mph impact. Measurements were made of the new surface area created. For control specimens, there was a few percent greater surface area than in a monolith; after 80 mph impact, surface areas were of the order of forty times the original surfaces areas.

When canisters having the same fraction of glass broken were compared, no consistent difference was found between glassy and devitrified specimens nor between small and large canisters. In tests at elevated temperature there was a greater fraction of large particles, but not of particles smaller than about $30\text{ }\mu\text{m}$. This effect of temperature is believed due to lowering of the compressive stress in the glass when it is reheated to 425°C ; the glass is under compression at room temperature because of the different coefficients of thermal expansion of glass and stainless steel. The lower compressive stress, in effect, reduces the impact resistance of glass at elevated temperature as tested on the one-sixth scale model. No other effect of temperature is believed to have been significant [SMITH-1975B].

Particle size distributions were obtained from the sieving measurements. In some cases, the $5\text{ }\mu\text{m}$ fraction for the test specimens appears to be small--i.e., about the same as for the controls. The chief uncertainty is in the size distribution of the material unaccounted for. If the unaccounted-for material were all smaller than $10\text{ }\mu\text{m}$, the effect on this size fraction would be large though this is unlikely. There is considerable difficulty in obtaining accurate screen analyses [SMITH-1975B].

For the deformation behavior of metals (here, metal cylinders), it is well established that the velocities at which edge-on and end-on failures occur are only weakly related to the length/diameter ratio of the cylinder, provided that this ratio is greater than 2. The limited tests of velocity, size, and L/D ratio did not allow verification of prototype behavior from the model tests. However, data obtained on glass fragmenting shows that impact velocity appeared to correlate better with the fraction of glass broken rather than the absolute amount of glass broken, when cylinders of different length are compared (see especially pp. 20, 68, and 69 in [SMITH-1975B]).

In another more basic study [TSAI] of the fractures produced in glass blocks by impact of steel balls, it was shown that fractures start at the surface in the region of maximum tensile stress. This maximum stress occurs at the boundary of the circle of contact of the 1.3-cm ball on the glass surface. Velocities of up to 6.9 m/s were obtained in free fall and in the

range, 9-34 m/s, with an air gun. Shock waves of impact were measured: Rayleigh surface waves showed a velocity of about 3000 m/s and dilational waves of about 5800 m/s. The duration of impact was of the order of 30 μ s. When only small fractures occurred, the coefficient of restitution of elastic energy (as measured by rebound height) was high. At higher impact energies, more energy was absorbed in breakage and the rebound weights varied widely [TSAI].

The short time constant and the high velocity of shock propagation are consistent with the extensive fragmentation of glass throughout the volume (*i.e.*, the effects of impact are not confined to material in the vicinity of the contact point, as is the case for ductile metals undergoing plastic flow).

6. Small-Scale Studies at PNL

Test procedures to evaluate waste forms for impact strength and leach rate are being outlined [MCELROY-1977A]. Risk values are defined in terms of (1) the fraction of particles of size smaller than 0.5 mm and (2) weight loss in a Soxhlet extraction test. Total surface area, leach rate of specific fission products, and thermal stress cracking are also being considered as risk factors.

Data has been collected on the impact fracture of soda-lime-silica glass plate [MCELROY-1977B]. Brunauer-Emmett-Teller (BET) surface area measurements indicate a roughly linear correlation between impact energy and final surface area. In the BET measurement of surface area, impact energy produced an average of $2.9 \times 10^{-3} \text{ m}^2/\text{J}$. From the reported value of surface energy of the soda-lime-silica glass, $2.5 \times 10^{-1} \text{ m}^2/\text{J}$, it appears that only about 1% of the available energy is used in forming new surface area. This is not considered a surprising result [MCELROY-1977B].

Glass marbles (beads) of 3, 6, and 10-mm diameter have been manufactured and encapsulated in lead-10% tin matrix and have been impacted at 158 ft-lb. The specimens were 1.25 in. in diameter and were not retained during impact; *i.e.*, the beads were ejected from the matrix by the impact, which resulted in 20% compression of the specimen. Size analysis of the glass showed that less than 0.5% were smaller than 37 μ m [MCELROY-1977B].

Measurement of particle sizes resulting from the impact tests of various glasses has continued [MCELROY-1977C]. A single stroke of the impact ram actually gives multiple impacts, since it crushes the specimen in stages. A special measurement of the fines of soda-lime-silica glass at 158 ft-lb shows about 1.9 wt % of the fines smaller than 10 μ m. Essentially no particles were found that were smaller than 1.5 μ m.

Impact tests [MCELROY-1977B] were made with glass spheres and uncoated supercalcine cores of simulated wastes and other materials. Particle

size data obtained from screen analyses show considerable scatter, probably because the ram both pulverizes and compacts. The BET method is an alternative sizing method that does not depend (as does screening) on separated and free-flowing particles. The BET measurements of surface areas of impacted cores (with no metal present) indicate that the effect of impact is to increase the surface area of supercalcine by four times and to increase the surface area of glass specimens by more than 500 times. However, the surface area of uncoated supercalcine as measured by BET is much higher than that of glass both before and after impact.

7. Comments on the Literature Reviewed

It is apparent that the impact resistance of metals (particularly steel-lead composites) is high and that of glass and oxide ceramics is low. Chiefly, the high ductility of metals acts to prevent buildup of local stresses and also consumes the impact energy in local plastic flow, whereas in ceramics, the lack of ductility allows shock waves to be transmitted throughout the volume of material so that the absorbed impact energy causes high local stresses and extensive fragmentation. Since fragmentation produces particles of small size and large surface-to-mass ratios, solid wastes of the monolithic glass type that have undergone impacts are more susceptible to dispersion.

It is also apparent that impact deformation is a dynamic and nonuniform process that is too complex to be calculated in realistic detail from rigorous quantitative theory. Semi-empirical theories, dimensional analysis, and simplified reference cases provide systematic guidance for engineering design and experimental verification. Impact-absorbing structures are in many cases the most practical means of providing impact resistance to a portion of a composite material.

Apparently, no studies of the impact resistance of metal-ceramic composites have been done in a systematic manner comparable to studies of lead-steel composites and the demonstration of impact-resistance of shipping casks. Now being compiled are (1) criteria of impact resistance for waste forms, (2) reference designs and design variants of metal-matrix waste forms, and (3) methods of analysis and measurement of impacted specimens, together with (4) properties of materials and (5) calculations of expected deformations for reference cases.

It is expected that the effort under way will result in a systematic (preliminary) evaluation of impact resistance of waste forms and a preliminary outline of an experimental program appropriate to the objectives stated in the introduction.

V. ESTABLISHMENT OF TENTATIVE CRITERIA FOR HULLS TREATMENT
(L. Trevorrow and B. Kullen)

The draft document, Development of Criteria for the Handling of Waste Cladding Hulls and Associated Metal Waste, was assembled and forwarded to cognizant individuals for their review and comments. The reviewers (a total of twenty) were solicited on the basis of their experience in (1) nuclear waste management, (2) fuel reprocessing, (3) the safety aspects of the nuclear fuel cycle, or (4) the development of criteria, standards, and regulations. The solicited individuals affiliations are representative of the research and development field, private commercial enterprise, and various Federal bureaus responsible for regulating the nuclear industry.

Reviewers of the draft have submitted comments during the period. In general, the most common criticism of the draft was that the criteria were presented in a section containing too many details (variables and parameters) to allow the reader to assimilate the criteria, per se. In the same subject area, many reviewers suggested that variables and parameters [see ANL-78-76] could (1) be set off in a separate section and (2) be collected into functional groups in order to reduce redundancy and repetition. Also, some reviewers seem to feel that basic concepts used in the draft need definition and description. "Criterion," for example, should be defined in the terms used in the write-up. Other comments tended to be specific in nature and, understandably, based on the individual reader's expertise and field of interest. These comments are currently being evaluated as guidelines for revising the criteria and the final report.

VI. TRANSPORT PROPERTIES OF NUCLEAR WASTE IN GEOLOGIC MEDIA

(M. G. Seitz, P. G. Rickert,* S. M. Fried,*
A. M. Friedman,* Jacqueline Williams,† and
M. J. Steindler)

A. Introduction

Wastes generated in nuclear reactor fuel during power production include fission products and some actinide elements. Because the wastes are radioactive and are hazardous to health, a requirement is that they remain isolated from the biosphere until they decay to inactive forms. The wastes may be placed within repositories in geologic formations for their permanent disposal.

During a period of thousands of years, a geologic body may become unstable and disrupt a waste repository whereupon groundwater may infiltrate the repository. Groundwater infiltration is considered the most credible mechanism for mobilizing wastes from a disrupted repository in a well-chosen geologic site. To evaluate the concept of nuclear waste disposal in geologic formations, we are examining the behavior of waste elements mobilized by flowing groundwater.

A conceptual drawing of a breached geologic repository is shown in Fig. 58.

Fig. 58. Hypothetically Breached Repository. The reactions of the leached nuclides with the surrounding bedrock will determine the extent to which the nuclides are immobilized. ANL Neg. No. 308-78-733.

*Members of the Chemistry Division.

†Members of the Analytical Group of the Chemical Engineering Division.

Groundwater passing through the repository can leach trace amounts of radionuclides from the solidified wastes. The water can then carry the radionuclides into surrounding geologic formations, where the dissolved radionuclides can react with rock. If radionuclides are leached from the wastes, it is the reactions of the radionuclides with the rock that control the migration or immobilization of radionuclides.

In the past, a variety of experimental approaches designed to obtain quantitative data describing the interactions of nuclides with solutions and rocks were used here. In this report, a new approach termed leach-migration is described in which a solid waste form is used as the source of radionuclides for migration studies. The report also describes a technique that complements techniques described in the preceding quarterly report [STEINDLER-1978D] and that can reduce oxygen concentrations in aqueous solutions to levels at the stability limit of water, *i.e.*, oxygen levels expected in waters in deep geologic formations.

B. Leach-Migration Studies

In previous work, a solution* representative of the groundwaters in contact with each rock studied was formulated by allowing water to react with that rock material [SEITZ]. Then, migration was studied by infiltrating porous rock or rock fissures with such simulated groundwater solutions (referred to below as infiltration experiments).

Still uncertain is the chemical relationship of the speciation of a trace element in an experimental solution to the speciation of the same trace element leached from a solidified nuclear waste. Presumably, any leached element in solution could hydrate, change valence state, or form complex alumino-silicate species. Such species would be difficult to characterize and to synthesize in free-standing solutions. In this work we have chosen to generate leached species experimentally by leaching irradiated glass (simulated high level waste) and to determine their migration characteristics rather than to try to formulate each species.

1. Leach-Migration Apparatus

The apparatus (Fig. 59) used for leaching of solidified simulated waste has the same components as the formerly used high-pressure infiltration apparatus (ANL-78-37) except that a solidified-waste form inside high-pressure tubing replaces the sample-injection valve formerly used. Radionuclides are leached from the solidified-waste form at 80°C. (An elevated temperature promotes leaching and also simulates the temperatures that will exist initially around a waste form if cesium and strontium are not removed from the waste before it is deposited.) Radionuclides leached from the waste form are carried in the fluid stream to the rock column, where their migration characteristics are observed. Coincidentally, the leachability of waste forms by groundwater solution at temperatures and under oxygen and carbon dioxide partial pressures that may exist in geologic repositories may be determined with this apparatus.

*Formerly identified as rock equilibrated water (REW).

Fig. 59. Apparatus for Leach-Migration Experiments in which Nuclides Leached from a Solidified Simulated Waste at High Temperature Migrate through Rock Columns.

2. Leach-Migration Experiments

A sample of simulated high-level-waste glass containing uranium was used as the source of radionuclides in leach-migration experiments. The glass was fused from Pw-8a-3 calcine and 76-68 glass [MCELROY] and had been previously characterized by the Battelle group. A slice of this glass was irradiated in the ANL CP-5 research reactor to activate nuclides (Section IV of this report). Strontium, zirconium, iodine, cesium, uranium, and neptunium are elements of interest for geologic storage and have short-lived isotopes in the glass. Other elements such as a light alkali (sodium) and rare earths are also present as short-lived radionuclides in the glass. The glass had an activity before leaching of 1700 cps/mg as measured in a NaI-well gamma spectrometer.

Two experiments were performed. In Expt. 128-89, 4.87 mg of glass was the source of radionuclides. First, the glass was leached at 80°C in a stream of water that had been reacted with oolitic limestone and which moved at a nominal rate of 0.1 mL/min. The water, containing dissolved nuclides, was then forced through a column of oolitic limestone (1-cm dia, 3.4-cm

height) and the eluate was collected in about 250-mL fractions. The fractions were dried, and the residues were examined for the presence of radionuclides. After eight days, the experiment was terminated and the limestone column was examined for radionuclides.

No gamma activity was observed in the residues or in the limestone column, indicating that the leach rate of the glass was too low to produce detectable levels of radioactivity. This indicates that the etch rate of the glass was less than about 2×10^{-4} g/cm²·d at 80°C since if 5% of the activity of the glass had been leached, it would easily have been measured. In comparison, a leach rate of 10^{-7} g/cm²·d was measured for glass in distilled water at 25°C at Argonne.

A second experiment (Expt 128-95) was performed using 0.35 g of irradiated glass as the waste form. The glass was again heated to 80°C and was leached with a stream of REW solution flowing at about 0.08 mL/min. After passing over the glass, the solution stream was forced through a limestone column. The solution leaving the column was collected in five fractions and each fraction was analyzed for radionuclide concentration. After 1560 mL of solution had been collected, the experiment was terminated and the limestone column was cut into four pieces for analysis.

3. Experimental Results

The solution fractions from Expt. 128-95 were dried, and the residues were analyzed for activity with a NaI-well gamma spectrometer. Radioactivities of the four sections of the limestone column were also determined with the NaI-well spectrometer. The preliminary results discussed here are from these analyses.

Samples obtained as described below are being analyzed. The solution residues were dissolved in small quantities of acid solution. The sections of the limestone core were removed from the stainless steel tubing and epoxy by dissolving them in acid. These samples of solution and rock are being counted again, using a GeLi detection system, to resolve more of the gamma peaks and to eliminate possible interferences.

Information on the eluate fractions and net count rates for Expt. 128-95 is given in Table 55. Count rates at different gamma energies corresponding to 27 different nuclides were determined. Table 55 shows that each fraction of the solution contained radionuclides. With continued elution, there was no systematic increase or decrease in activity. Of importance, the activity of the first sample is comparable to that of the other samples; if it is assumed that activity was delivered continuously to the column, there appears to have been no significant retardation of activity movement by the column. The eluate in the first fraction contained the nuclides, ¹¹⁰Ag, ¹³⁴Cs, ¹⁵⁴Eu, and others.

The activities for three elements vs depth in the four sections of the limestone column are plotted in Fig. 60. These and other elements are present in high concentrations at the top (inlet end) of the column.

Table 55. Sizes, Flow Rates, and Activities of Eluate Fractions from Expt. 128-95

Solution Fraction	Quantity of Fraction, mL	Measured Average Flow Rate, mL/min	Net Count Rate ^a counts/mL
1	250	0.087	74
2	216	0.075	89
3	296	0.068	155
4	200	0.069	81
5	600	0.083	78

^aCounting time was 400 s.

Fig. 60.

Activity of Three Leached Elements along a Column of Oolitic Limestone. Expt. 128-95. The ordinate scale in parentheses pertains to cesium and zinc, the other ordinate scale to silver. ANL Neg. No. 308-78-728.

Generally, each element has a unique distribution, indicating that the radio-nuclides partitioned with the rock column individually, rather than collectively in colloids or tiny glass particles.

4. Discussion

The leach-migration experiments were initiated because it was suspected that radionuclides leached from solidified waste may migrate differently from radionuclides added as soluble compounds to solutions in infiltration experiments.

Of the many elements monitored in these experiments, only the migration of cesium through limestone has been studied in both infiltration and leach-migration experiments. In the earlier infiltration experiment (Expt. 128-56, not reported previously), no cesium activity was detected in any of the eluate fractions. This suggests, qualitatively, that cesium leached from the irradiated glass did behave differently from cesium in solutions formulated from soluble compounds.

Cesium behavior is illustrated by the partition coefficients listed in Table 56.

Table 56. Cesium Migration in Oolitic Limestone

Partition Coefficient, mL/g	Infiltration Expt. 128-156	Batch Experiment	Leach/Migration Expt. 128-95
K_D , at cesium peak	120 ^a	80 ± 70	>120 ^a
K, column end	>15 ^b	--	1.4 ^b

^aThe partition coefficient, K_D , was determined from the movement of the cesium peak (relative to the flowing solution stream) by the formula

$$K_D = \left(\frac{v_w}{v_{Cs}} - 1 \right) \frac{\epsilon}{\delta}$$

where v_w is the velocity of the water stream; v_{Cs} is the velocity of the cesium peak; ϵ , equal to 0.19, is the porosity of the limestone (subject to fluid flow); and δ , equal to 2.35 g/cm³, is the density of limestone. K_D is measured directly in batch experiments.

^bThe partition coefficient, K, was determined by dividing the activity of the column material at the exit end by the activity of the eluate.

The coefficients are from results of the infiltration experiments with a formulated solution, from batch experiments measuring cesium adsorption on limestone in aqueous solutions, and from the leach-migration experiments with irradiated glass. The partition coefficients measured for the cesium peak in migration experiments and the coefficient measured in the batch experiment do not disagree. The partition coefficient, K, measured at the exit column

differs considerably for the infiltration and the leach migration experiments, suggesting that cesium in the leached solution reacts less differently from the cesium in the formulated solutions.

C. Dissolved-Gas Control

In the preceding quarterly report [STEINDLER-1978D], two approaches to the control of dissolved gases in solution were described. In one approach, oxygen and carbon dioxide are removed from nitrogen gas, which is then purged through solutions to remove dissolved O_2 and CO_2 from the solutions. An indicator is used to verify that the oxygen level is below 0.1 ppm in the nitrogen. The purified nitrogen is capable of producing dissolved-oxygen levels in the solutions of about $10^{-10}M$, a level that is below the concentration of trace elements used in some of our experiments.

In the second approach to the control of dissolved gases, dissolved oxygen in a solution is reacted with iron or hydrogen to remove it from the solution. Apparatus used here to accomplish this is depicted in Fig. 61. In the apparatus, aqueous solution is passed through iron filings which react with dissolved oxygen. The iron also reacts with the water itself to form hydrogen gas. With a palladium catalyst present, the hydrogen gas reacts with residual dissolved oxygen. Thus, with excess hydrogen, this device produces solutions having oxygen partial pressures at the stability limit for water ($P_{O_2} = 10^{-78}$ Pa). The iron filings are heated to promote their reaction with water. Excess hydrogen is periodically bled from the vessel. Iron hydroxide, formed by the oxidation of iron, is relatively insoluble and does not affect the composition of the water. Analyses of gas samples from the vessel (Table 57) indicate that the gas is predominantly hydrogen along with a little nitrogen (presumably from air trapped in the iron filings) and with a minor amount of oxygen that may have been introduced during sampling.

Table 57. Analyses of Gas Collected from the Reaction Vessel in which Aqueous Solution Reacted with Iron Filings

Gas	Sample 1, ^a %	Sample 2, ^b %
H ₂	84.5	94.5
H ₂ O	2.6	3.0
N ₂	12.7	2.0
O ₂	0.04	0.01
Ar	0.02	0.01
CO ₂	<0.01	0.5

^aSample 1 was collected from gas generated in the reaction vessel in the absence of the palladium catalyst.

^bSample 2 was collected from gas generated in the presence of the palladium catalyst.

Fig. 61. Reaction Vessel for Lowering the Dissolved-Oxygen Levels in a Solution to the Stability Limit ($P_{O_2} = 10^{-78}$ Pa) of Water. ANL Neg. No. 308-78-430 Rev. 1.

During continued recirculation of the water through the apparatus, a precipitate forms in the reservoir flask when it is exposed to air. This presumably is the result of ferrous iron being oxidized to the more insoluble ferric state. To eliminate iron and thus the reducing potential of the ferrous species, aluminum chips amalgamated with mercury could be substituted to provide a reacting surface in the reaction vessel. Aluminum hydroxide is less soluble in water than are the iron hydroxides.

D. Future Directions

In the future, leach-migration experiments using a solid waste form as a source of radionuclides will be continued. In these experiments, leaching temperature may be used as a controlled variable. Experiments will be done to study migration through rock fissures--fissures between fractured rock surfaces (laboratory-produced fractures or natural rock fractures); in addition to fissures between polished rock surfaces.

VII. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL
BY FLUID FLOW AT HIGH TEMPERATURES
(M. G. Seitz and R. A. Couture)

A. Introduction

To study migration of trace elements in natural geologic formations, we have assembled equipment for pumping solutions through packed mineral columns at elevated temperatures and at pressures high enough to prevent boiling. Fluid-flow experiments have been performed that make it possible to study nonequilibrium phenomena which are difficult to take into account in model calculations in the absence of direct experimental data.

The initial work has focussed on (1) cesium-sodium ion-exchange on kaolinite from room temperature to 225°C and (2) sorption of iodine species by kaolinite at room temperature and at 130°C.

The three previous quarterly reports [STEINDLER-1978B, 1978C, 1978D] give many of the data and discuss the geological interest in this work, some of the capabilities of the technique, and experimental details and problems. In this report, we discuss the theory relating migration rates to ion-exchange constants and summarize our findings.

B. Experimental Procedures

In these experiments, we injected radioactive solutions in trace quantities onto a mineral column, eluted the column with an aqueous solution, and analyzed the effluent to determine the migration velocity of the radioactive material. Temperature, pressure, and flow rate were controlled; the pressures were high enough to prevent boiling of the aqueous solutions.

The mineral kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] has been used in all of the experiments. This mineral was selected for the initial work because it does not swell and is stable at high temperatures, it is mineralogically simple, it is common, and relatively few data on ion exchange with kaolinite have been obtained. Furthermore, fewer ion-exchange mechanisms operate on kaolinite than on swelling clays since no interlayer exchange sites (sites located between the oxygen sheets) are involved.

The columns were prepared by pumping a slurry into an empty tube having a frit at the bottom. Initial porosity after column preparation was about 45%, and compaction by a few percent during the experiments was not serious.

Most of the experimental problems have been solved, at least for temperatures up to 225°C. Plugging of the high-pressure, small-bore (0.025-cm diameter) tubing leading from the columns can be controlled by using tubing having a larger bore (0.05-cm diameter). A filter has been installed to protect the back pressure regulator valve from fine particulate from the column. Because of occasional slight galling of the ferrules which seal the ends of the tube, a column cannot reliably be opened and successfully resealed after it has been used at high temperature.

C. Theory of Migration Rate

Migration rate of a substance through an ion-exchange column is easily understood if the system is at equilibrium and the isotherm is linear, i.e., if the concentration of the substance in the exchanger is proportional to the concentration in the liquid as in our experiments.

Laitenen [LAITENEN] has reviewed the many treatments of flow through chromatographic columns in the literature. With an allowance for the different variables used, the results are identical: the ratio of the migration velocity of a substance to solvent velocity (R_F) is equal to the fraction, f , of the substance in the liquid phase.

One can easily derive this result. If the system is at equilibrium, each solute atom spends a fraction of its time in solution equal to the fraction of atoms in solution. The solute bound to the exchanger is assumed to be immobile, while the dissolved solute is assumed to move with the solvent. Thus, the solute velocity relative to the velocity of the solvent is equal to the fraction in solution: $R_F = f$.

Sophisticated analyses [LAITENEN] predict a spread in velocities. Peak width increases with migration distance and decreases with migration velocity. For two or more substances which are in equilibrium with the mineral in the column, the peak widths, or dispersion in elution volumes for the two solutes, should be proportional to their elution volumes (discussed below). The reason for this behavior is relatively simple. For example, if one of the substances is inert and moves with the water front, a spread or "dispersion" is always observed in the elution peak of that substance because of variations in path lengths and in solution velocities in the column. The elution volume of a second substance is proportional to the elution volume of the inert substance, the proportionality constant being the retardation factor for the second substance. The dispersion in the elution peak of the second substance can be estimated by considering solution flow in the column to consist of many tiny streams having a spectrum of flow velocities by the elution curve of the inert substance.

The stream responsible for the leading edge at 50% maximum on the elution curve (i.e., at an elution volume of $V_I + \frac{1}{2}\Delta V_I$, with V_I the elution volume of the inert substance and ΔV_I the peak half width at half maximum) would generate an elution volume, $V_2 + \frac{1}{2}\Delta V_2$, of the second substance given by

$$V_2 + \frac{1}{2}\Delta V_2 = R \left(V_I + \frac{1}{2}\Delta V_I \right) \quad (1)$$

where V_2 is the elution volume of the second substance and ΔV_2 is the peak half width at half maximum. Similarly, for the trailing edge of the peak

$$V_2 + \frac{1}{2}\Delta V_2 = R \left(V_I + \frac{1}{2}\Delta V_I \right) \quad (2)$$

so that, by difference

$$\Delta V_2 = R(\Delta V_I) \quad (3)$$

Therefore, the dispersion (as measured by the peak width at half maximum, for example) in the elution curve of the second substance is proportional to its retardation factor. Of course, the peak width of the second substance, ΔV_2 , would increase further than predicted by Eq. 3 if the substance were not equilibrated between solid and solution while moving through the column.

If the porosity of the column and the density of the exchanger are known, f is easily transformed into K_d , the ratio of the concentration in the solid to the concentration in the liquid:

$$K_d = \left(\frac{1}{f} - 1 \right) \frac{\epsilon}{\delta(1 - \epsilon)} \quad (4)$$

where ϵ = porosity of the column and δ = density of the solid. No correction need be made for thermal expansion of the solvent, and the density δ of the solid is nearly constant. (K_d could be expressed strictly in mass units,

$$K_d' = \left(\frac{1}{f} - 1 \right) \frac{\epsilon}{(1 - \epsilon)} \frac{\delta_{\text{liquid}}}{\delta_{\text{solid}}}, \quad (5)$$

in which case the density of the liquid would be important.)

K_d is not a fundamental property of the exchanger, but depends on its ion-exchange capacity, which for a substance such as kaolinite depends on its surface area. The exchange constant K is determined by the change in standard free energy for the reaction and is therefore a more fundamental property of the reactants. For an exchanger, R , exchanging two similarly charged ions, A and B , K is related to K_d as follows. The standard states are the pure end members, AR and BR .

γ_A, γ_B are activity coefficients in the liquid
 γ_{AR}, γ_{BR} are activity coefficients in the exchanger
 x_{AR}, x_{BR} are mole fractions in the exchanger
 m_A, m_B are concentrations in the liquid
 q_{AR}, q_{BR} are concentrations of A and B in the exchanger
 Q is ion exchange capacity

$$K \text{ is defined as } K = \frac{\gamma_A m_A \gamma_{BR} x_{BR}}{\gamma_B m_B \gamma_{AR} x_{AR}}$$

$$\text{and } K_d = \frac{q_{AR}}{m_A}$$

$$\text{Since } q_{AR} = X_{AR}Q,$$

$$\begin{aligned} K_d &= \frac{X_{AR}Q}{m_A} \\ &= \frac{\gamma_A}{\gamma_B} \frac{\gamma_{BR}}{\gamma_{AR}} \frac{X_{BR}Q}{K_{mB}} \end{aligned} \quad (6)$$

Thus, under all conditions, $K_d \propto Q$. At trace loadings, as in our experiments,

$$\gamma_{BR} X_{BR} \approx 1 \quad (7)$$

At low solution compositions,

$$\gamma_A/\gamma_B \approx 1 \quad (8)$$

and so

$$K_d \approx \frac{Q}{K_{\gamma AR} m_B} \quad (9)$$

By determining K_d at all values of X_{AR} , it is possible to determine K and the values of γ_{AR} and γ_{BR} by using the Gibbs-Duhem equation. If determination of the activity coefficients is not required, an alternative approach is to define a selectivity coefficient K' , where

$$\begin{aligned} K' &= \frac{m_A X_{BR}}{m_B X_{AR}} \\ &= K \frac{\gamma_B \gamma_{AR}}{\gamma_A \gamma_{BR}} \end{aligned} \quad (10)$$

K' is easily determined from

$$K' = \frac{1}{K_d} \frac{X_{BR}}{m_B} Q. \quad (11)$$

There are also electrostatic interactions which further modify the velocity of an ion through a mineral column. Because of the charge on the mineral surface, the interstitial solution may not be electrically neutral. For a

typical negatively charged surface, anions are partly excluded from the fluid, and cations are concentrated. The charge-imbalanced layer is thin in solution of high ionic strength but thicker in solutions of low ionic strength. When an ionic solution is forced from a column, there is at first a charge imbalance, which causes a potential called the streaming potential. The streaming potential maintains the electrical neutrality of the effluent solution by accelerating the flow of anions and retarding the flow of cations (in the usual case of negative surface charge).

D. Cesium-Sodium Ion Exchange on Kaolinite

Clay minerals have been proposed as an artificial second barrier in geological repositories for radioactive waste. Because of radioactive heating, the temperature in the immediate vicinity of the waste may rise to 200°C or higher. The ion-exchange behavior of clays at high temperatures is of great interest and so migration of cesium in kaolinite by fluid flow has been studied:

The ion-exchange affinity of silicates for slightly hydrated ions such as Cs^+ is reported to diminish somewhat at temperatures approaching 100°C. Determinations above 100°C have been rare, however; therefore, we wanted to learn whether observed trends continue at high temperatures.

Commercially prepared kaolinite, Hydrite R (Georgia Kaolin Co.) was used. The clay had been treated to remove manganese oxides and iron oxides, and consequently was pure white. The mean equivalent spherical diameter was 0.8 μm . X-ray diffraction analysis shown that the clay was very well crystallized, with no impurities detectable. The ion-exchange capacity of the column was found by saturating it with Na^+ in NaHCO_3 and then eluting with NH_4^+ as NH_4Cl . The amount of Na^+ removed from the column was determined by atomic absorption. A correction was made for Na^+ in solution by titrating the eluate for HCO_3^- and subtracting the amount from the total Na^+ . The exchange capacity of the column was 0.52 meq, or 9.1 meq/100 g.

A few measurements were made with samples of other kaolinite from Georgia. Although the latter materials were lithified and had to be ground for use, data with these materials do not contradict our findings with Hydrite R. Therefore, only the Hydrite R data are presented.

Spikes of dissolved cesium-134 in trace quantities were injected onto kaolinite columns, and solutions containing various concentrations of NaHCO_3 were pumped through the columns at constant rates. The columns were each 1 cm in diameter and 5 to 6 cm long. The effluent solutions were analyzed continuously for activity; in two cases, the columns were opened at the end of a run, and the clay was analyzed for activity. The values of f were corrected for the volume of the experimental apparatus and for interactions with the stainless steel. This correction was determined by replacing the mineral column with a union and repeating the injection of the spike. It is probable that there was a small interaction of the cesium with the sintered stainless steel filters in the column, thereby increasing the retention volume slightly.

This interaction could not be measured directly, but a filter of similar thickness and pore size installed in the line was found to retard the flow of Cs^+ by 0.3 mL relative to I^- . The correction for the filters in the column is probably nearly the same as that measured for the filter--about a 0.5% correction to f . The thermocouple used for temperature measurements was checked against a mercury thermometer and found to agree within $1.6 \pm 0.5^\circ\text{C}$. The average temperature is known to within $\pm 0.3^\circ\text{C}$ in most of the experiments.

In three previous experiments, the effective free column was determined by pumping tritiated water through the columns. In two of these the free column volume was also measured gravimetrically and was found to be equal to that measured with tritium. The fraction of cesium in solution was determined by dividing the peak velocity of cesium by the velocity of the solvent. For the data presented here, the free column volume was measured gravimetrically.

The porosity was typically 46% before the experiments and 39% after the experiments. Fortunately, since free column volume also decreases with compaction, the measurement of K_d is only slightly affected by compaction. The effect of compaction is much smaller than the effect of random errors.

The results are shown in Table 58 and Fig. 62. A typical elution curve is shown in Fig. 63. The elution curves are nearly symmetrical, which implies that the isotherm is approximately linear over the range of the experiments.

Table 58. Summary of Cesium-Partitioning Experiments on Kaolinite

Column Number	Temperature, $^\circ\text{C}$	Flow Rate, mL/min	$[\text{NaHCO}_3]$, M	K_d	K'
2	25	0.023	0.50	140	0.0013
7	75.0	0.053	0.100	68	0.0135
7	108.5	0.053	0.100	20.4	0.045
6	156-162		0.100	8.6	0.106
7	160.1	0.053	0.050	20	0.091
	160.1	0.023	0.100	9.7	0.094
6	160.5	0.053	0.100	7.3	0.124
6	160.5	0.023	0.100	8.4	0.109
7	161.7	0.053	0.100	9.0	0.102
7	161.7	0.053	0.100	8.7	0.105
6	210	0.023	0.100	5.0	0.182
7	211.5	0.023	0.100	4.0	0.231

The temperature effect is immediately apparent: kaolinite is about two orders of magnitude less selective for Cs^+ over Na^+ at 170°C than at 25°C . Reproducibility is quite good for column No. 7 at about 162°C (Fig. 62).

Fig. 62. $\text{Na}^+\text{-Cs}^+$ Selectivity of Kaolinite at Low Cs^+ Concentrations as a Function of Temperature. (High values of K' indicate low selectivity for Cs^+ .) The curve represents a model in which the entropy change is assumed to be the difference in entropies of the ions.

Fig. 63. Elution of Cesium-134 from Kaolinite Column by 0.1M NaHCO_3 at 160°C

Duplicate experiments at 161.7°C agreed within 3%. However, all data points taken together show more scatter than we can account for. Possibly, pressure affects the selectivity of kaolinite for cesium, but we have not found a systematic trend of selectivity with pressure. The flow rate was calibrated frequently and was not found to vary appreciably during a run. However, flow

rate has a measurable effect: in two experiments at 160°C (Column 6), increasing the flow rate by 2.3 times decreased the apparent distribution coefficient (apparent value of K_d) by 13%. This suggests that even at 160°C, solution and mineral are not locally in equilibrium with respect to sodium and cesium.

One-tenth normal NaHCO_3 was chosen for most of the experiments in order to minimize the effect of the streaming potential. No effect of the streaming potential has been found. Within an analytical error of about 0.5%, the effluent has the same alkalinity as the influent. Furthermore, iodide is eluted approximately with the water front and is not accelerated appreciably.

For illustration, the observed temperature effect has been compared in Fig. 62 with a model in which the entropy change ΔS° is assumed to be the difference in entropies of the ions, $S^\circ_{\text{Cs}^+} - S^\circ_{\text{Na}^+}$. Agreement appears to be satisfactory in this case.

E. Absorption of Iodine Species on Kaolinite

Iodine-129 is produced in nuclear reactors and has a 17-million-year half-life. Iodine forms anions which are thought to migrate rapidly in groundwater without substantial interaction with common rocks and minerals. Some of our previous experiments [STEINDLER-1978C, 1978D] demonstrated that iodine species can interact strongly with kaolinite columns. Different species of iodine present in a single sample are capable of moving through kaolinite columns at different rates.

Earlier column experiments were performed with samples of ^{131}I (reportedly present as I^- in 0.1M NaOH) obtained from New England Nuclear Company. In the column experiments, diluted spikes were injected into streams of NaHCO_3 solutions and were pumped through kaolinite columns.

In earlier experiments at 130°C, all of the iodine moved through columns of kaolinite at the same rate as the aqueous solution of 0.001M NaHCO_3 .

At room temperature, the iodine moved through columns of kaolinite in as many as three peaks (i.e., with three different velocities). In other experiments, from about 5 to 20% of the iodine moved at the same rate as the solvent, while the remainder of the iodine was greatly retarded. The results were time-dependent: one peak was prominent in one experiment but entirely absent in the next experiment.

In two other experiments, about 5% of the iodine was eluted with the solvent front, while the remainder of the iodine was firmly bound. In one of these experiments, dissection of the column showed that after 99 free column volumes of 0.001M NaHCO_3 and 347 free column volumes of 0.5 M NaHCO_3 had been pumped through the column, the main peak had migrated through only 10% of the column.

We think it is of interest to know what species were bound to the column and why. The ^{131}I samples used were supplied as I^- , but the results strongly suggested that as many as three or possibly more iodine species were present in the experiments. Paper chromatographic results suggest that IO_4^- was present in all of the samples. If IO_4^- was present, then other species, such as HOI and IO_3^- , may have been in the solutions as well. However, only IO_4^- and I^- have been unequivocally detected in the solutions.

In the presence of air, only IO_3^- is thermodynamically stable in these solutions. I_2 is unstable in these very dilute solutions and was not detected in amounts greater than 2% by solvent extraction. HOI is believed to be oxidized; I^- is also unstable, but its oxidation is very slow in basic solutions. Therefore, we prepared samples of radioactive I^- and IO_3^- and determined their absorption by kaolinite.

Iodide was prepared by adding I^- carrier to the radioactive iodide solution from New England Nuclear, oxidizing with $\text{HNO}_3 + \text{NaNO}_2$, extracting I_2 into CCl_4 , and extracting the iodine back into 0.1M NaHSO_3 as I^- . The solution then contained undetectable amounts of IO_3^- (<1.4%), IO_4^- (<1.4%), and I_2 (<7%).

Radioactive IO_3^- was prepared by adding I^- carrier and oxidizing it at pH about 4 in chloride solution with excess Br_2 . The solution was allowed to evaporate to dryness and was then redissolved in water. The resulting solution contained about 90% IO_3^- , 10% I^- , and possibly a trace of IO_4^- , <5%.

The above solutions were then added to 0.001M NaHCO_3 solutions and mixed with various amounts of kaolinite (Hydrite R) which had been washed with NaHCO_3 , with H_2O , and then dried. The pH was adjusted with HCl . The containers were agitated overnight.

Iodide was not adsorbed significantly by kaolinite at pH 7-8, but was adsorbed slightly by test tubes at pH 4. The final I^- concentration was 1.6 μM . HCO_3^- and HSO_3^- concentrations were about 1mM. Paper chromatography showed that the iodine remained as I^- during the experiment. IO_3^- was not absorbed significantly by kaolinite at pH 5.9-7.8. The IO_3^- concentration was $1.5 \times 10^{-8}\text{M}$; the HCO_3^- concentration was 0.001M. Absorption of IO_3^- was slightly at lower pH: K_d <1.2 mL/g at pH 5.3 and <1.6 mL/g at pH $\approx$ 2. However, because of an equipment malfunction, it was not possible to determine speciation at the end of the experiment.

Two possible reasons remain for strong adsorption of iodine species on kaolinite in columns. First, IO_4^- or even HOI may be the strongly adsorbed species. Second, metal oxides, especially FeOOH , might be the adsorbing substance. Iron oxide is observed at the tops of kaolinite columns after high-temperature use. However, the observed oxide does not appear to extend far enough into the columns to account for the results. Saturation of the ion-exchange capacity of the clay does not seem likely, since the solid/solution ratios in the columns were as high as practical and the iodine concentrations, as noted above, were very low.

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