BNL-477

Progress Report
Nuclear Engineering Department

May 1 - September 30, 1957

CLARKE WILLIAMS, Chairman

F.T. MILES, Assistant to Chairman for LMFR

Edited by F. MASLAN

BROOKHAVEN NATIONAL LABORATORY

Associated Universities, Inc.

Upton, New York

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

PRICE $2.25

Available from the
Office of Technical Services,
Department of Commerce,
Washington 25, D.C.

January 1958 900 copies

Summary

Liquid Metal Fuel Reactor Program

REACTOR PHYSICS

The thermal diffusion length of bismuth was measured by a static method involving neutrons from a thermal column which diffuse out through a 4-ft cube of the metal. The result was $L = 40.7 \pm 0.21$ cm at 20°C. Diffusion length measurements are also being performed with graphite-bismuth arrays.

CHEMISTRY AND CHEMICAL ENGINEERING

LMFR Chemical Technology

Salt-metal equilibration experiments continued during the report period on both gram and pound scales. In one series of gram-scale experiments, uranium distributions were measured in the system Bi-U-Mg/NaCl-KCl-$MgCl_2$-UCl_3, no U being present in the metal phase initially. The purpose of the work was to see how partition coefficients for U obtained in this way compared with those obtained when the U was initially all in the metal phase. The former were found to be 4 to 5 times the latter. It was also found that Mg concentration in the metal had little effect on the coefficients for Mg concentrations above 30 ppm. The first of these results is not particularly serious from an engineering standpoint; but the second, if true in practice, would call for some modification of the fuel handling process. The important thing, however, is the extent to which uranium which has been oxidized into the salt from the fuel can be recovered by bringing it back into a more reductive metal phase. This more difficult experiment will now be done.

Some months ago, a research program was started to study the rates of approach to equilibrium in the salt-Ce-Bi system. This information is pertinent to the design of the extraction columns for Loop N. Early results from simple equilibration experiments showed that reaction rates are rapid, in fact too rapid for accurate information to be obtained by that method. At contact times of about ½ min – a lower limit with the apparatus – practically all the Ce was found in the salt phase. A new method utilizing the falling-drop technique will be tried to get more precise transfer rates at shorter and more measurable contact times.

Progress is being made in the development of instrumental analytical methods for determining solute concentrations in fused chloride mixtures and Bi solutions. The following cell was used quite successfully to measure Mg concentration in a bench-scale salt-Bi contactor:

$$Zn/ZnCl_2(1\%\ \text{soln in KCl-NaCl-}MgCl_2\ \text{eut})//$$
$$\text{KCl-NaCl-}MgCl_2\ \text{eut/Mg (Bi)}$$

where // represents the glass envelope.

Absorption spectroscopy shows promise as a method for determining the concentration of uranium in fused chloride mixtures in the neighborhood of 10 ppm; such a method is very desirable for process control purposes in the LMFRE. Both absorption spectroscopy and polarography are being used as tools in studying the fundamental chemistry of fused salt mixtures; and galvanic cells are being used to determine the extents to which fused salt mixtures depart from ideality. This information is necessary in predicting salt-Bi partition coefficients from thermodynamic data.

Expulsion of Iodine and Xenon from LMFR Fuel

For good neutron economy in a typical LMFR breeder, at least 75% of the generated 9.13-hr Xe^{135}, the high cross section isotope, should be continuously removed from the reactor. Both theoretical analysis and the results of an in-pile experiment have indicated that the problem of the controlled removal of Xe from the fuel may be aggravated by the low solubility in the fuel of Xe and also of its iodine precursor. To obtain further data, an experimental program is now under way which involves the irradiation of solid U-Bi-Mg-Zr fuel in both steel and graphite containers.

After removal from the pile, the Bi is melted for various lengths of time and then refrozen. Analysis of these fuel slugs shows that, for the most part,

both the iodine and Xe concentrate almost 100% at the interfaces between the fuel and the container. In these early tests, natural uranium was used and the Xe concentrations were about a factor of 1000 below that anticipated in a full-scale LMFR breeder. In future work, enriched uranium will be used in order to get higher fission product concentrations; and the fuel will be irradiated while in the molten state. It may turn out that one of the biggest problems in Xe removal will be to minimize its deposition on the graphite moderator from the circulating fuel.

LMFR Pilot Plant Studies

The salt mixture to be used in the LMFRE for fuel control and processing purposes is the ternary $NaCl$-KCl-$MgCl_2$, with and without small amounts of $BiCl_3$. To determine satisfactory construction materials for the processing equipment; an extensive corrosion test program has recently been started which includes static, rocking, and loop experiments. Among the materials being tested are low-chrome steels, high-chrome stainless steels, 300 series stainless steels, tantalum, and molybdenum. Preliminary results indicate that type 347 stainless steel will be satisfactory for the straight ternary and molybdenum for $BiCl^3$ mixtures if none of the commoner materials prove to be usable.

Several loops were operated during the report period to obtain corrosion-erosion information and also to test pumps and other components for bismuth service. Other loops are under construction, some at BNL and others in vendors' shops.

METALLURGY

Measurements on the effect of tellurium on the solubility of thorium in bismuth indicate that 1% additions lower the Th solubility at 1000°C from 6.78 to 0.25%. Ten wt % thorium bismuthide slurries produced by quenching from elevated temperature can be made fluid by heat treatment at 800°C for 20 min or 900°C for 5 min. The addition of 0.05 wt % Te to a 5% thorium bismuthide slurry results in no growth of the particles after 16 hr at 800°C, whereas in the absence of Te the particles grow from the 60-μ size to 120 μ. Sectioning of the Th-Bi slurry loop showed that the center of the finned cooler had been plugged with Th-Bi particles. No corrosion or erosion of the impeller was noted after the 14-hr run.

A 1¼ Cr – ½ Mo electromagnetically pumped loop was started; bulk temperatures are 520°C hot leg and 445°C cold leg (525° to 428°C film temperatures). The 2¼ Cr loop has been run for approximately 3900 hr with no corrosion noted in the hot leg and very slight deposition in the cold leg. The first 2500 hr was at 75°C film temperature (500° to 425°C). The remainder of the run has been at 75°C bulk temperature (T_{max}=520°C). The thermal convection loop of low manganese carbon steel containing Ti shows no corrosion after 4300 hr at a 135°C ΔT (T_{max}=520°C). A 2¼ Cr loop operating at 600°C T_{max} which now has a ΔT of 100°C does not show corrosion in the hot leg or excessive deposition in the cold leg.

In a study of the surface reactions of low chrome steels, it has been shown that Bi containing 2.3% Mg gives excellent wetting of the steels. When low chrome steels are contacted with Bi containing Th, films are formed whose thicknesses are proportional to the N to Al ratio in the steel.

Presence of Zr in the thorium bismuthide alloy results in the formation of films which are free of Th. When 1¼ Cr is contacted with Zr-Bi solution, a zirconium carbide layer is formed.

Redetermination of the solubility of U in Bi indicates that solubility at 400°C is 1850 ppm instead of 2050 ppm as formerly determined. In Bi saturated with Zr, the solubility of U is reduced at 400°C from 1850 to approximately 1200 ppm. Present work suggests that anything in excess of 80 ppm Zr in Bi will reduce the solubility of U in Bi.

The diffusion of U into the Bi impregnated pores of a treated graphite sample has been measured at 550°C. The apparent coefficient is roughly 3×10^{-7} cm^2/sec.

MECHANICAL ENGINEERING

Work on the 4-in. utility component test loop was resumed during the past quarter. Arrangements for inspection and operation by Babcock and Wilcox personnel were completed, and changes desired by them are under consideration. Satisfactory tests of pressure transmitters for Bi service were completed. High slip motors for speed control were tested, and a facility for testing flanges is under construction. High Velocity Loops

3 and 4, and Radiation Loop 1, all for metallurgical testing, are under design and construction. The design, procurement, manufacture, and erection of parts for the U-Bi exponential experiments are well under way. Loop N (U-Bi and salt), Loop H-2 (pump test), and magnetic drives (for pumps in sealed systems) are all progressing satisfactorily.

General Activities

REACTOR THEORY

The results of Monte Carlo calculations of resonance capture in U^{238} showed agreement with theory in those resonances where the statistical uncertainty in the calculations is small. The leakage from a slab of hydrogen was calculated for a plane source and $1/v$ cross sections.

Work on the High Flux reactor was concentrated chiefly on improving the cross sections of the Eyewash code.

REACTOR PHYSICS

Water lattice exponential experiments with 0.387-in.-diameter slightly enriched uranium rods are finished except for one intracell flux plot. The measurements on lattices of 1.0%, 0.250-in.-diameter rods have been completed also.

FLUORIDE VOLATILITY PROJECT

The Fluoride Volatility Project suffered a severe setback in May, when the operation of the continuous dissolver pilot plant was suddenly halted by an explosion. The plant had been in operation for about 4 mo and the ninth dissolution run was nearly completed when the accident occurred. In all these runs the fuel charge was added in one batch, and the interhalogen solution was pumped continuously through the dissolver and cooled in an external heat exchanger. Good dissolving rates were obtained. The dissolution rate was found to be a sensitive function of the UF_6 content of the BrF_3 solution in the concentration range of 0 to 2 M%. Above 2 M%, UF_6 exhibited only a slight catalytic effect. At 120°C and 2 M%, the dissolution time for a BNL slug (1.10 in. in diameter by 4.0 in. long) was about 8 hr, and the average overall penetration rate was about 1.5 mm/hr.

The cause of the accident could not be definitely established; but it appears probable that it was initiated by uranium being somehow exposed to interhalogen vapor rather than kept wholly immersed in liquid. Under the former conditions, heat transfer rates can be inadequate to prevent overheating of the uranium. It is now proposed to repair the pilot plant and resume the work, for a great deal still remains to be found out about the kinetics and operational characteristics of continuous dissolvers.

RADIOCHEMICAL TECHNOLOGY

Gamma Irradiation Service

Seven Co^{60} sources were shipped to industrial concerns, totaling 10,626 curies. Gamma irradiation services were provided to 15 industrial concerns and to various on-site users.

Radiation Research

Work on the Food Irradiation Reactor included 20 runs in slab and drum irradiators, in which the distribution of gamma flux in various types of food packages was measured. Considerable data have been accumulated on the corrosion of construction materials by proposed FIR aqueous solutions.

An insight into the mechanism of graft polymerization is being developed by comparing irradiation of the polymer in air to irradiation *in vacuo*.

No significant difference in the rate of dehydrogenation of cyclohexane was detected between unirradiated catalysts and both neutron and gamma irradiated catalysts.

A birefringence study on polymers produced by solid state irradiation of monomers indicated that no preferred orientation was produced.

Process Development Section

A flow sheet has been developed for an aqueous (H_2SO_4-HF) process for recovering uranium from irradiated Zr-U alloys.

Considerable solubility data have been determined for Xe and Kr in organic solvents. Some rate data have been obtained.

ULTIMATE WASTE DISPOSAL

A 500-hr corrosion experiment on possible construction materials for the double kiln calciner was completed, and metallographic examination of the

specimens is in progress. Equipment is being assembled for a test run of a single drum calciner. A long clay column experiment is being set up. Leaching studies are in progress on calcined oxides with a variety of leaching media, and clay column tests are being made on simulated leach solutions. Fuel element dissolution studies are being carried out on a variety of fuel types, with particular emphasis on dissolution of Zr-U alloys in H_2SO_4-HF.

Contents

Summary iii

Reactor Physics Division (4520, 4107.1)* 1
- Reactor Theory 1
- Reactor Physics Experiments 2

Chemistry and Chemical Engineering Division (4107.1, 4620, 5310) 5
- LMFR Research and Development 5
- Volatile Fluoride Project 22
- Fission Product Utilization 27
- Ultimate Waste Disposal 31

Mechanical Engineering Division 35
- 4-in. Utility Test Loop 35
- High Velocity Loops 3 and 4 36
- Radiation Loop 1 36
- Loop N 36

Hot Laboratory Division (5330-7, 5111, 5112) 38
- Special Radioisotope Development 39
- Radiochemical Analyses 41
- Hot Laboratory Operations 41

Metallurgy Division (4107.1, 4540, 5420, 5430) 44
- LMFR Research and Development 44
- Radiation Effects 68
- BNL Pile Studies 75

*AEC budget activity numbers.

Reactor Physics Division

Reactor Theory

JACK CHERNICK

URANIUM-WATER LATTICES

Resonance Capture

The results of Monte Carlo calculations of resonance capture in various resonances of U^{238} have been compared with the prediction of a theory of resonance capture developed at Brookhaven. The comparison was made for lattices having 1:1 and 4:1 volume ratios and fuel rods of 0.6-in. and 0.25-in. diameter; the theoretical model was the slab lattice of U^{238} and hydrogen discussed by N. Corngold in BNL 433. Calculation showed agreement between theory and Monte Carlo calculation to within a few percent in those resonances where the statistical uncertainty in the Monte Carlo calculation is small. The comparisons are being continued. A. HASNAIN

Study of the Resonance Integral in Heterogeneous Systems

The resonance integral in the (narrow resonance) form,

$$\int \left[\frac{S_0}{4N_0V_0} \frac{\sigma_a+\sigma_s}{\sigma_t} G+\sigma_0 \right] \frac{\sigma_a}{\sigma_t} \frac{dE}{E},$$

with cross sections having the Breit-Wigner shape has been analyzed for the case of a spherical lump. Criteria for the validity of the assertion that the integral factors into a geometrical and a nuclear part are derived and discussed. The effect of interference between potential and compound-nucleus scattering upon the resonance capture is also discussed. Finally, a number of equivalence theorems relating to heterogeneous and homogeneous systems are established. P. BAKSHI AND J. CHERNICK

Leakage and Monte Carlo Calculations

The leakage from a slab of hydrogen was calculated for a plane source and $1/v$ cross sections. The method used was an expansion in half-range Legendre polynomials, keeping only the first term. The spatial dependence was obtained by direct integration and the lethargy dependence by Laplace transformation and inversion. The calculation was then extended to regenerative systems containing hydrogen and a heavy moderator. Instead of inverting the Laplace transform, the method of polynomial expansion in lethargy was used. Work on this is continuing.

Monte Carlo calculations of the resonance escape probability in uranium-water lattices with 0.250-in. rods, volume ratios 1:1 and 4:1, and infinite mass for uranium have been completed. Work on 0.600-in. rods, volume ratio 4:1 is now in progress.

Following a suggestion by P. Bakshi, the Monte Carlo code is used to calculate p as a function of rod radius for the 36.9-ev resonance. The radii range from 0.3 cm to about 3.0 cm, and the lattice spacing is adjusted to minimize interference while still retaining good accuracy. At present p has been calculated for $r=0.3$ cm and $r=0.8$ cm.

T. AUERBACH

GENERAL REACTOR PHYSICS

Elastic and Inelastic Scattering

A time-of-flight technique has been employed to study the elastic and inelastic scattering of neutrons from spherical targets of Fe and Pb^{206}.

S. OLEKSA (WITH G.N. GLASOE, H.H. LANDON, AND A. J. ELWYN)

The Variational Formulation of Resonance Capture

A paper, "Slowing Down of Neutrons in Infinite Homogeneous Systems," by N. Corngold has been accepted for publication in *Proc. Phys. Soc. (London)*. The variational principle described has been used to obtain corrections to the narrow resonance formula for simple resonance shapes and is being used to estimate the effect of the perturbations in the neutron spectrum produced by one resonance upon the capture by a resonance at lower energy. This work is being continued. R. SCHERMER AND N. CORNGOLD

Thermalization of Neutrons in a Gaseous Moderator

A solution to the Boltzmann equation describing the system has been obtained without use of the heavy moderator approximation. The solution appears in the form of a series in kT/E and reduces to the heavy moderator solution of Wilkins, Cohen, et al. as the ratio of neutron to moderator atom mass approaches zero. N. CORNGOLD

THE HIGH FLUX INTERMEDIATE REACTOR

Work on the Hi-Fi reactor during the summer was concentrated chiefly on improving the cross sections of the Eyewash code. A new set of thermal cross sections was calculated by averaging the absorption and fission cross sections over Brown's spectrum (DP-194), taking into account the shift in the Maxwellian distribution due to absorption. The Eyewash code was modified to handle the new cross sections. The new code has been applied to the six reactor experiments performed by R.N. Olcott [*Nuclear Sci. and Eng.* **1**, 327 (1956)] and shows considerable improvement over the old code. T. AUERBACH, G. LELLOUCHE, AND J. WEISENBLOOM

Reactor Physics Experiments

WATER LATTICE MEASUREMENTS

Exponential experiments with 0.387-in.-diameter slightly enriched uranium rods are finished except for one intracell flux plot. This measurement will be completed shortly, and combined analysis of all the results from this phase of the studies will begin. Meanwhile the final results of such analysis applied to earlier experiments have been written up for publication as a journal article and as a BNL document.

The measurements on lattices of 1.0%, 0.250-in.-diameter rods have been completed, except that intracell flux traverses have suffered from a large impurity of holmium in some of the dysprosium foils. More dysprosium has been ordered, and correction of the experiments should be quite routine. Clean moderator measurements of the buckling of 1.15% enriched rod lattices are complete, and poisoned lattice buckling experiments are about to begin. These should require most of the next quarter.

Personnel of Westinghouse Commercial Atomic Power have completed the analysis of Brookhaven measurements of buckling of plutonium enriched uranium rod lattices. The rods used in these experiments had 0.387-in. diameters and contained 1% Pu, 0.3% U^{235}, and 98.7% U^{238}. The results are tabulated below.

$\frac{\text{Volume Water}}{\text{Volume Fuel}}$	$B^2(\text{cm}^{-2}\times 10^4)$
2	76.8
3	92.6
4	93.1

The probable errors are unknown but are large.

The delivery of uranium plates for lattice studies has ben delayed by contract negotiations. The total delay will probably be about three months, and plates may not be available before December.

LMFR

During the last quarter considerable effort was devoted to a determination of the chlorine content of the Bi stringers to be used in exponential studies. A system of activation analysis based on gamma-ray counting with the 100-channel analyzer was developed and applied to six samples of bismuth, with the following results:

one sample: 1.5 ppm Cl by weight
five samples: 0.5 ppm Cl by weight

The accuracy at these low contents was about ±75%. The amounts of chlorine observed cannot noticeably influence diffusion lengths or critical sizes in experimental assemblies.

The thermal diffusion length of Bi was measured by a static method involving neutrons from a thermal column which diffuse out through a 4-ft cube of the metal. The result was $L=40.07\pm 0.21$ cm$=9.788$ g/cm^3 at $T=20°$C. This value is in excellent agreement with the diffusion length derived from cross sections given in BNL 325, but the latter contain substantial probable errors; therefore, no definite conclusions can be reached yet concerning the separation of absorption and scattering in the diffusion process in Bi.

Diffusion length measurements are also being performed with graphite-bismuth arrays. Two of these have been constructed. The first contained two parts of graphite to one of Bi, and consisted of 1-in.-square stringers on a 1-in. module (Figure

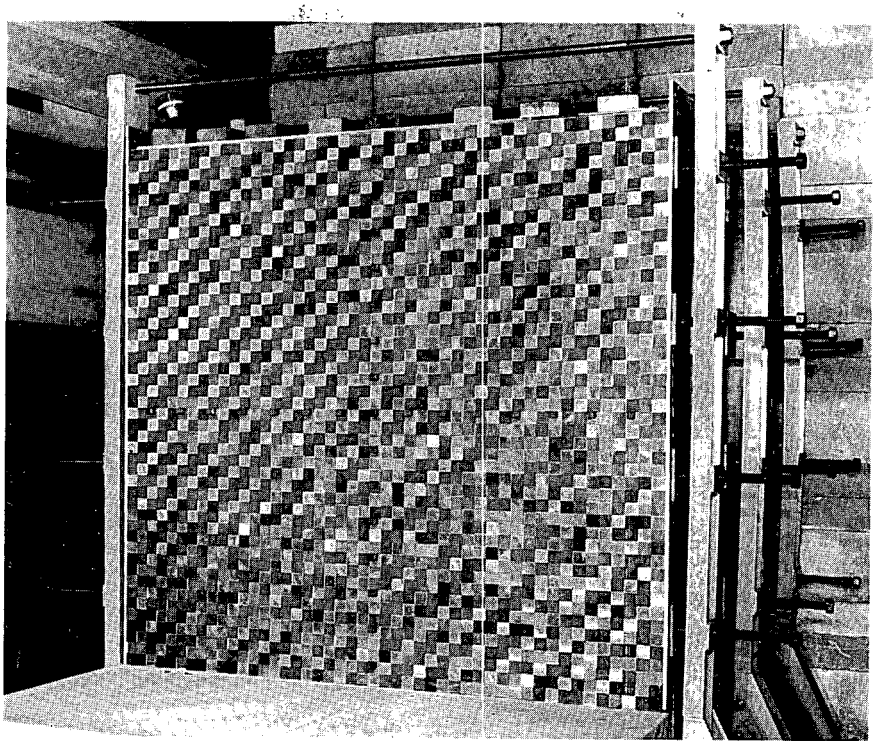

Figure 1. Graphite-Bi array, 1-in. module.

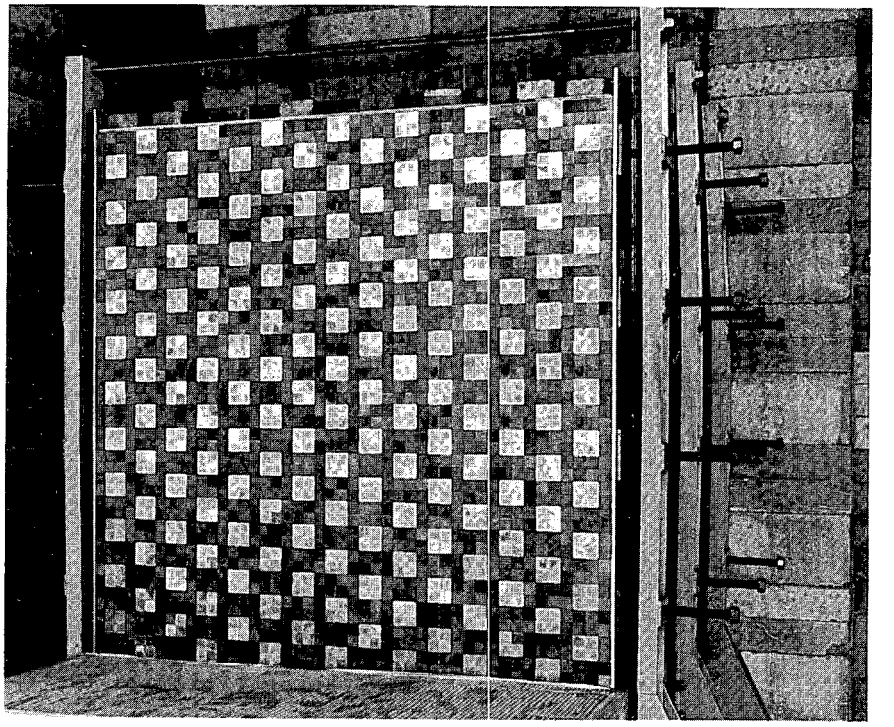

Figure 2. Graphite-Bi array, 2-in. module.

1). The second contained the same graphite and Bi pieces, but the module was increased to 2 in. (Figure 2). The analysis of data for the diffusion length of the 1-in. module stack is still under way. The second set of measurements has not yet been finished.

Design and construction of the neutron source reactor has continued. This reactor is expected to be critical in November or December.

A simplified calculation of the transfer function of liquid metal reactor systems has been coded for the local Remington Rand digital computer. The results show a tendency to resonances at periods equal to the Bi circulation time. This feature is caused by the feeding back for a new pass of delayed neutrons whose precursors were formed in the previous pass. Large Bi inventories and long out-of-pile times such as would be required for high power should eliminate any trend to resonances of this character.

Heat transfer between fuel and graphite of the LMFRE is being explored on the small analogue computer at the Cosmotron. The calculation applies sinusoidal heat source variations, and thus derives a heating transfer function. The computer accuracy is such as to lead to credible results only for sine wave periods greater than 10 sec (reactor pass times).

Chemistry and Chemical Engineering Division

LMFR Research and Development

FUNDAMENTAL STUDIES

Salt-Metal Equilibrium Studies

CORE PROCESSING. When LMFR fuel is treated with fused salt, a little uranium transfers to the salt phase, along with the bulk of the FPS fission products. It is proposed that this U be recovered from the salt by scrubbing it with Bi containing more Mg than the fuel. To test the feasibility of this step, the reduction of UCl_3 by Mg has been investigated in the two-phase system composed of the ternary salt eutectic $MgCl_2$-KCl-NaCl and the alloy Mg-Bi. Mg concentrations in the Bi varied from 9 to 1000 ppm and U concentrations in the salt from 115 to 2650 ppm.

Results indicate that, at comparable Mg concentrations, the value of k_U is 4 to 5 times higher for the reduction of UCl_3 by Mg than for the oxidation of U by $MgCl_2$, where

$$k_U = \frac{\text{mole fraction U in salt}}{\text{mole fraction U in Bi}}.$$

Furthermore, in contrast to the well characterized linear relationships of log k_{RE} versus X_{Mg} (see BNL 472), a plot of log k_U versus log X_{Mg} (Figure 3) exhibits a break at about 30 to 40 ppm Mg and then levels off, so that k_U does not decrease but remains essentially constant with increasing mole fraction Mg. This effect is observed in both the oxidation of U and the reduction of UCl_3. The reasons for this behavior and for the existence of the factor of 4 to 5 are not yet known; however, the existence of more than one oxidation state for the U is suspected. Several different lines of attack on this important problem are being employed.

BLANKET PROCESSING. Exploratory work has been continuing on the fused salt extraction of tracer Pa from Th-Bi alloys containing 1000 ppm Th. The extraction salt consists of the binary eutectic LiCl-KCl containing additives such as $AlCl_3$, $ZrCl_4$, $ThCl_4$, and UCl_3, each of which should be capable of oxidizing Pa.

Experiments in which the alloy was contacted with eutectic containing 1, 3, and 5% by weight of $AlCl_3$ together with 3% $ThCl_4$ (added to repress the Th oxidation) showed that up to 86% of the Pa was extracted by the salt; however, virtually all the Th was oxidized as well. Ideally, the oxidant should oxidize Pa without affecting the Th. $AlCl_3$ is apparently too strong an oxidant and not sufficiently selective.

A series of recently completed experiments with a binary salt solution containing a small amount of $ThCl_4$ showed that 35% of the Pa was oxidized and extracted by the salt. The addition of $ZrCl_4$ and $ThCl_4$ to the salt resulted in the transfer of over 80% of the Pa to the salt phase, whereas UCl_3 + $ThCl_4$ oxidized only about 20 to 30% of the Pa. Qualitatively, these results are in general agreement with the known stabilities of the respective chlorides. Chemical analyses of the salt and metal phases for Th, U, Al, and Zr are at present incomplete.

Other halides systems are being investigated in connection with blanket processing. An attempt is being made to find a low melting halide com-

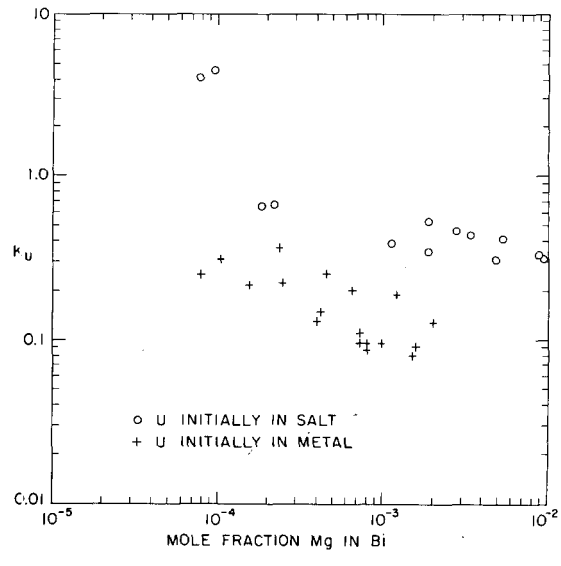

Figure 3. Distribution of U between salt and metal.

plex which will magnify the differences in the chemical properties of Th and Pa to the extent that selective oxidation will result in an efficient separation. One possible system involves the compound $NaAlI_4$, which has been prepared and purified. Equilibrations between molten $NaAlI_4$ and Bi in the range 300° to 500°C are in progress. If the mutual solubility of the two phases is sufficiently low, irradiated Th will be added and the Pa distribution determined.

Kinetics of Salt-Metal Reactions

In designing equipment for contacting LMFR fuel with salt, it is essential to know the rates at which solutes are extracted from one phase into another. Experimental apparatus has therefore been built that will permit rapid sampling of salt and metal phases which have been contacted under controlled conditions. The procedure used and the preliminary results obtained are presented below.

Bismuth metal and Bi-Ce alloys were prepared by hydrogen reduction, filtration, mixing with vigorous agitation, refiltration, and casting into small-diameter storage tubes, either stainless or Vycor. The component salts were treated with HCl at temperatures below their melting points and then degassed under high vacuum, and in the case of $MgCl_2$ the product was sublimed in apparatus conveniently handling $\approx$80g/charge. The ternary eutectic mixture of $MgCl_2$, NaCl, and KCl, 60-20-20 by wt, was prepared under argon in a dry glove box, and subsequently melted under vacuum, filtered, and cast in Vycor storage tubes. Despite this careful purification treatment, some impurity carries through to the mixture, presumably an active metal in the $MgCl_2$, which causes deposition of a black residue during filtration of the mixture. The residue is suspected to be Si metal, as it appears resistant to chemical attack except by HF solutions, and there is some superficial attack on the Vycor casting assembly by the salt mixture that is not attributable to any wetting-freezing-chipping type of mechanism.

The experimental contacting procedure consists of melting salt and metal, bringing them into contact for a known length of time, and then isolating samples of the equilibrated salt and metal phases by filtration. To accomplish this, a cleaned contacting crucible is sealed into a glass assembly and degassed at 500° to 525°C. The stainless crucible is constructed in such a way that samples of the salt and metal phases may be trapped in ¼-in. metal tubes, located under fine and coarse stainless frits respectively, when helium pressure is applied to the system. To date, work has been done only on Bi-Ce alloy as the metal phase.

The desired alloy is prepared in the glove box by dispensing the appropriate lengths of Bi and Bi-Ce master alloy from storage tubes into one side of the glass contacting assembly. The desired quantity of salt mixture, somewhat larger in volume than the metal, is placed in the other side of the glass contacting assembly. After the subsequent degassing and melting steps, the metal mixture falls directly into the contacting crucible, but the molten salt mixture is retained by a medium porosity Pyrex frit. At the start of the contacting period, helium pressure applied to the salt side of the assembly forces salt through the Pyrex frit into the evacuated contacting crucible. Provided the pressure above the crucible is not permitted to rise, filtration of the metal and salt samples does not occur until pressure is applied after the desired contact time has elapsed.

The following tentative conclusions may be drawn from contact experiments with Bi-Ce alloys containing 100 ppm Ce, the volumes of the phases being about 2.7 cc each and the area of contact 8.5 cm^2.

1) Experiments of long time duration (60 min) gave values of about 60 for k_{Ce}. As the contact time was reduced to 2 min, the ratio appeared to remain unchanged. Below 2 min, exchange still appeared to be quite appreciable, with ratios of 20 or more obtainable at contact times of the order of ½ min.

2) Final conclusions cannot justifiably be made at this time; but the following points may be helpful in judging the value of the results. The high rates of exchange obtained would indicate that any third phase material (e.g., oxides) did not physically interfere with Ce transfer. There is no guarantee, however, that the exchange was not a result of the fact that Ce was already present at the interface as the oxide. It is planned to check this factor experimentally. Contact time was difficult to measure for the shorter time intervals when the relative filtration time became quite appreciable. At the shorter times, the salt in the system is probably agitated quite well by the falling salt drops; at

longer times the system is agitated only by convection.

3) The results show that the rapidity of the Ce exchange is so great that an improved experimental procedure will be necessary to obtain more precise data. In this connection it is planned to investigate experimentally a falling-drop method.

Electrolytic Methods

The use of electrolysis at various points in the LMFR fuel processing cycle has often been suggested, and a few experiments, reported earlier, showed the method to have promise as a means of introducing reagents into salt or metal phases, or both. A more complete investigation of electrolytic processes is now being carried out by Horizons, Inc. under a research subcontract, and kilogram-scale apparatus has been set up for this purpose. Preliminary results have shown that it is possible to prepare solutions containing up to 5.3%, and possibly more, $BiCl_3$ in the ternary eutectic mixture by electrolysis in the presence of a molten Bi anode.

Instrumental Analysis of LMFR Process Streams

Development of a Reference Electrode. In the salt contact process proposed for the purification of the LMFR fuel, an electric potential exists at the interface between metal and salt, its value depending on the relative amounts of oxidized and reduced material in that system. A continuous measurement of this potential would be a valuable index of performance. For this, a reference electrode is needed which, when dipped into the salt phase, will give a reproducible emf reading relative to the metal process stream. It should be rugged and easily made and have a half-cell potential which is not itself affected by small changes in the composition of the ambient salt. A half-cell which appears to meet these requirements has been developed. It consists of:

$$Zn/ZnCl_2\,(1\%\text{ soln in KCl-NaCl-}MgCl_2\text{ eut})\,//$$

$$KCl\text{-}NaCl\text{-}MgCl_2\text{ eut}/Mg\,(Bi).$$

The Pyrex serves both as an intermediate electrolyte, permeable to sodium ions, and as a mechanical envelope. The assembly is a test-tube-shaped object which can be lowered into the process salt (Figure 4). The salt will consist of the nearly pure ternary eutectic, and it has been

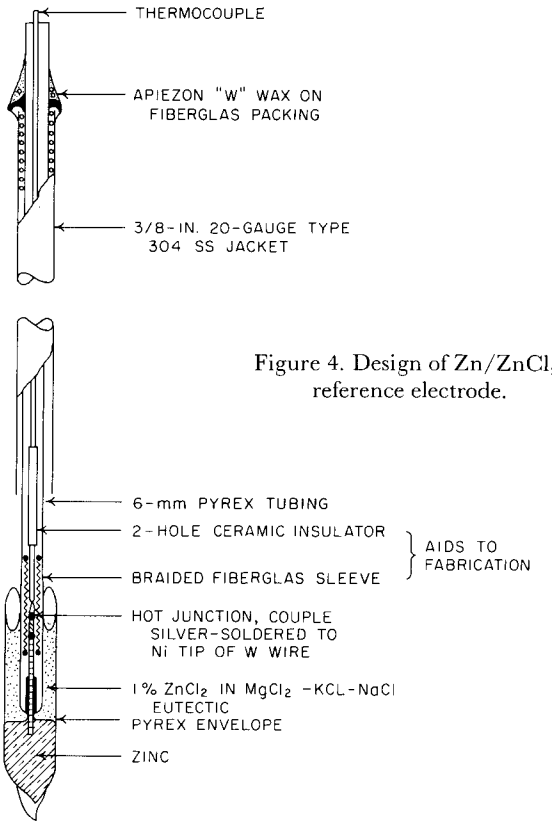

Figure 4. Design of $Zn/ZnCl_2$ reference electrode.

shown experimentally that under such circumstances the diffusion potential introduced by the glass membrane is negligible. Even if it were not, the electrode would have a practical use in revealing any malfunction of the processing system which showed up in a deviation from the usual emf.

The potential at the interface between reactor fuel and process salt is set, for practical purposes, by the ratio of oxidized to reduced Mg, since this is the only element present in both phases in significant amounts. Consequently, if the $MgCl_2$ concentration in the salt is known, the concentration in the Bi phase may be deduced from emf measurements, provided the appropriate activity coefficients are known. This use of the electrode has been demonstrated in a bench contactor. This apparatus consists of a closed stainless steel vessel with a removable tantalum liner. There are provisions for controlled heating, blanketing under purified helium, stirring, and sampling.

The contactor was prepared, and some 4000 g Bi were vacuum melted in it. Small amounts of Mg, Zr, natural U, and activated Ce were added, in that order, during June and July. Analyses of

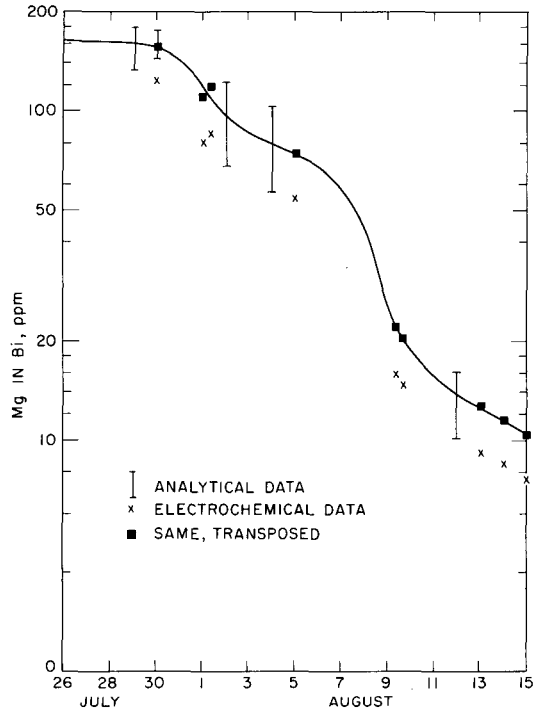

Figure 5. Electrode readings and Mg concentrations in a bench contactor.

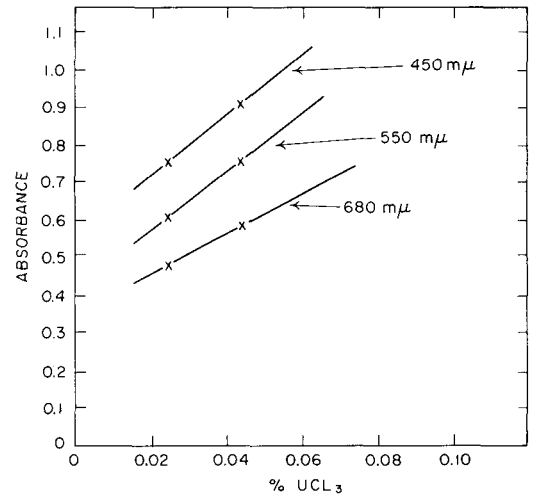

Figure 6. Absorbance of UCl_3 in fused salt.

samples showed no significant loss of Mg in that period. On July 26, about 1000 g pretreated salt (ternary eutectic $MgCl_2$-NaCl-KCl) were added, both phases were sampled, and the first three reference electrodes were lowered into the salt through a gas-tight seal. An unexplained loss of Mg from the metal, beginning with the addition of salt, continued to the end of the reporting period.

Figure 5 presents data from the chemical analysis of samples and concentrations calculated from potentials measured between the reference electrode and the Bi. The former are of low precision, although some improvement is hoped for. Data from the three electrodes show internal consistency and, if all such estimates are multiplied by 1.4, can be brought into line with the analytical data. The thermodynamic data are not so accurate that such a disparity is unexpected.

Spectrophotometry of Fused Salts. Absorption spectroscopy promises to be a useful method both for investigating the fundamental chemistry of fused salt mixtures and for routine measurements of concentrations. A research program of the first type has been inaugurated here at Brookhaven, and exploration of analytical possibilities is being carried on at the University of New Hampshire under a subcontract.

The BNL work employs a modified Beckman Model DU instrument (described briefly in the previous progress report) in connection with the properties of BiI_3. During the present report period, an electronic power supply, a photomultiplier, and an ultraviolet source were received, installed, and tested. Some changes were made in the high temperature furnace and temperature regulating system to provide a more uniform temperature distribution throughout the heating block. As yet the apparatus has been used only for gaseous BiI_3 in the range 300°C to 500°C. At the lower temperatures its spectrum consists of a double peaked curve, the maxima occurring at 336 mμ and 419 mμ. As the temperature is increased, a new, very sharp peak appears at 428 mμ whose intensity increases with temperature, while that of the 419 peak decreases. At present the determinations are being extended to shorter wavelengths and to mixtures of Bi and BiI_3.

At New Hampshire, H. Haendler has set up apparatus using a Perkin-Elmer Model 12-c spectrometer and has developed techniques for obtaining the spectra of fused salt mixtures in which the chief material, or "solvent," is the ternary eutectic $MgCl_2$-NaCl-KCl. To this, varying amounts of colored chlorides such as $CuCl_2$, $CoCl_2$, and UCl_3 have been added, and the absorbance of the resulting mixtures obtained as a function of concentration at various wavelengths. Figure 6, which

gives some preliminary results on UCl_3, illustrates the sensitivity of the measurements and their potential usefulness for analysis. Measurements will soon be made in the ultraviolet, where the uranium absorption is believed to be much stronger than in the visible, with a consequent gain in analytical sensitivity.

CHROMOPOTENTIOMETRY IN FUSED SALTS. A cell has been designed and constructed which will be used in a study of chromopotentiometry in fused salt systems. This technique involves the measurement of the potential of a polarizable electrode during the constant current elecrolysis of a depolarizer dissolved in a supporting electrolyte. The time required to consume the depolarizer in the vicinity of the electrode is measured and is a function of the depolarizer concentration and its diffusion coefficient. This technique offers some promise as an analytical tool for the continuous determination of reducible substances such as U in the salt phase and, under suitable conditions, of oxidizable substances in the Bi phase.

The all-quartz cell contains two platinum working electrodes and a Pt-$PtCl_2$ reference electrode. The ternary salt eutectic $MgCl_2$-KCl-NaCl is the supporting electrolyte. Measurements will be carried out at 500°C.

Thermodynamics of Salt Mixtures

RESULTS OF GALVANIC CELL MEASUREMENTS. Knowledge of the thermodynamic properties of salt mixtures is necessary for the prediction of distribution coefficients of elements between salt and metal phases. Experimental determinations of certain of these properties are therefore under way, and some results have been obtained.

The partial molar free energy of $MgCl_2$ in a number of $MgCl_2$-KCl melts of different compositions has been measured by a galvanic cell method. The cells employed have been of the form:

(a) $Mg(s \text{ or } l)/MgCl_2(x), KCl(1-x)/Cl_2$

or

(b) $Mg(X^1 \text{ in Bi}, l)/MgCl_2(x), KCl\ (1-x)/Cl_2$.

In cells of type (a) the emf is a function of the free energy of formation of $MgCl_2$ and of its activity in the mixture; with type (b) an additional quantity is involved, the activity of Mg in the Mg-Bi alloy. Since good data on this quantity are available from earlier work on electrode concentration cells, described in previous progress reports, emf values obtained from type (b) cells are as useful as those from type (a) for getting the desired information.

Table 1

Quantities Derived from Cell Measurements at 800°C

X_{MgCl_2}	$-\Delta F$, kcal	γ_{MgCl_2}
0.550	117.1*	0.32
0.469	118.1**	0.23
0.470	118.6*	0.19
0.400	119.2*	0.163
0.325	123.1*	3.1×10^{-2}
0.090	131.5*	2.2×10^{-3}

*Obtained with type (b) cell.
**Obtained with type (a) cell.

In practice, type (b) cells have the advantage that equilibrium values of the emf are reached sooner than in the others and appear to be more reproducible. In the high temperature region Mg is somewhat soluble in the salt. This may lead to erroneous results, both because the electrode reaction may be different if there is metal dissolved in the salt and because the salt which contains dissolved Mg attacks its Vycor container. By replacing the pure Mg electrode with liquid Bi containing 0.1 mole fraction Mg, the Mg metal activity is reduced from unity to about 10^{-4} and its equilibrium concentration in the salt becomes negligible as does its vapor pressure, which can otherwise be troublesome. Both types of cells have been used in the present series of experiments, and satisfactory agreement was usually found, as may be seen from the results shown in Table 1.

A photograph of the experimental arrangement is shown in Figure 7. The left-hand electrode is a molybdenum cup which hangs, by a threaded connection, from a graphite rod which also serves as an electrical lead. The cup contains the liquid Bi-Mg alloy. It is almost entirely enclosed, communicating with the surrounding salt only through a hole 0.078 in. in diameter. The salt, which does not appear in the photograph, is contained in the inner Vycor cup. The chlorine-graphite electrode, on the right, is contained in a Vycor sheath which forms an anode compartment. This communicates to the bulk of the salt through a frit at its lower end. The restrictions at the two electrodes are of course designed to prevent depolarization of the cell.

Measurements have been made on six different salt mixtures, each over a temperature range. Some typical results are presented in Table 1. The first column gives the mole fraction of $MgCl_2$ in the salt mixture; the second, the free energy of the reaction

$$Mg(l)+Cl_2 \rightarrow MgCl_2\,[\text{in } MgCl_2(x),\ KCl(1-x)];$$

and the third, the activity coefficient of $MgCl_2$ in the mixture.

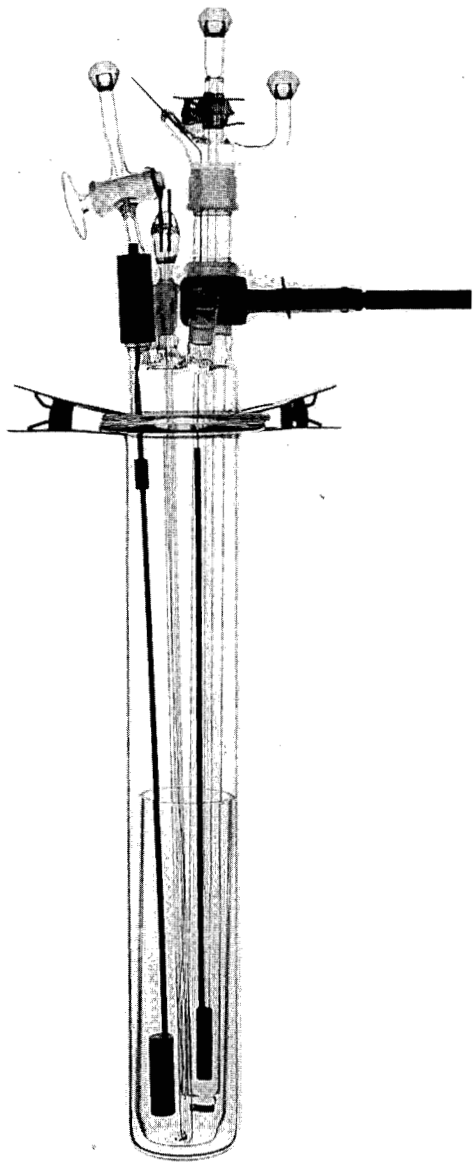

Figure 7. Cell used for emf measurements of salt mixtures.

The values of the activity coefficients of $MgCl_2$ in the mixtures were calculated from the observed emf's and published values of the standard free energy of formation of $MgCl_2$. We expect soon to obtain a value of our own for this quantity by a measurement on a cell in which $X_{MgCl_2}=1$.

VALUES CALCULATED FROM PHASE DIAGRAMS. Good freezing point – composition diagrams have been published for the systems LiCl-KCl, KCl-$MgCl_2$, KCl-$CaCl_2$, KCl-$FeCl_2$, $CaCl_2$-RbCl, and $CaCl_2$-CsCl. By the use of equations developed by Carl Wagner (*Thermodynamics of Alloys*, Addison-

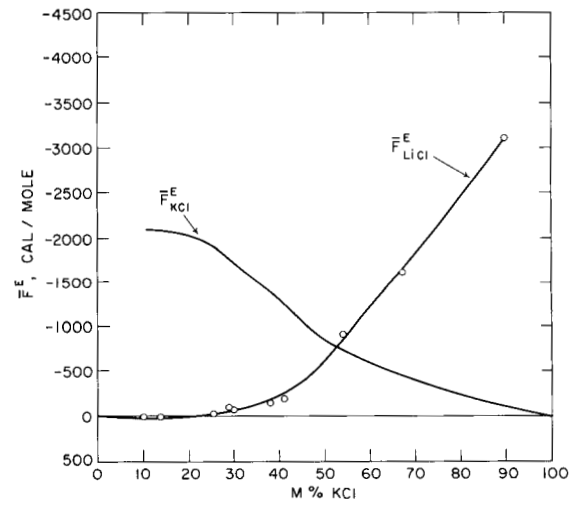

Figure 8. Partial molar excess free energy of mixing in the system LiCl-KCl.

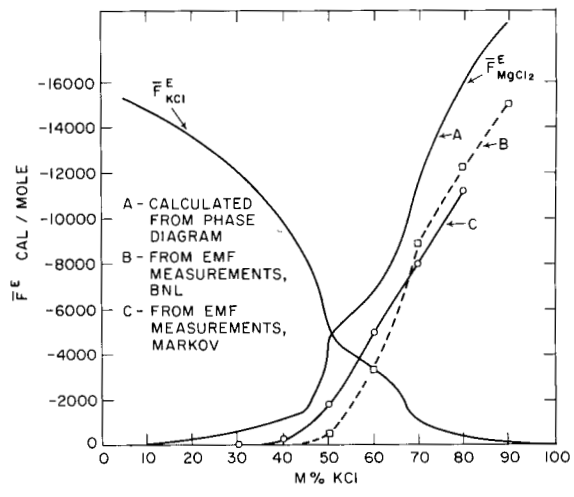

Figure 9. Partial molar excess free energy of mixing in the system $MgCl_2$-KCl.

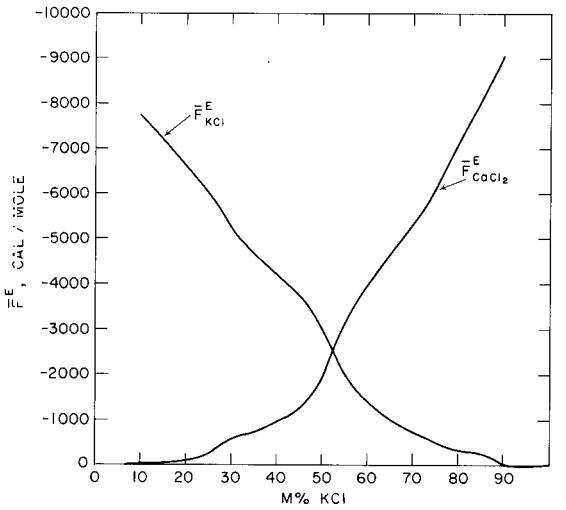

Figure 10. Partial molar excess free energy of mixing in the system $CaCl_2$-KCl.

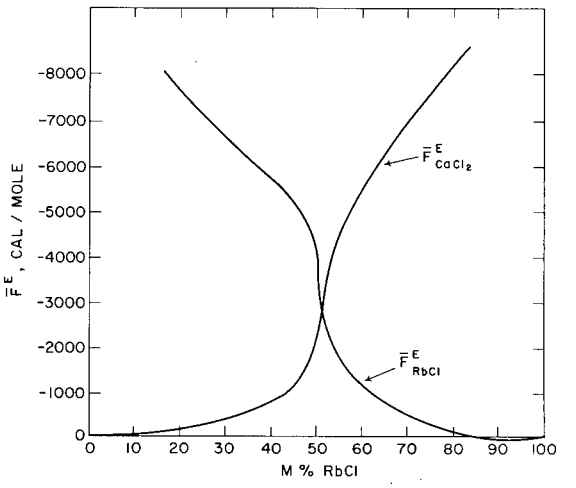

Figure 11. Partial molar excess free energy of mixing in the system $CaCl_2$-RbCl.

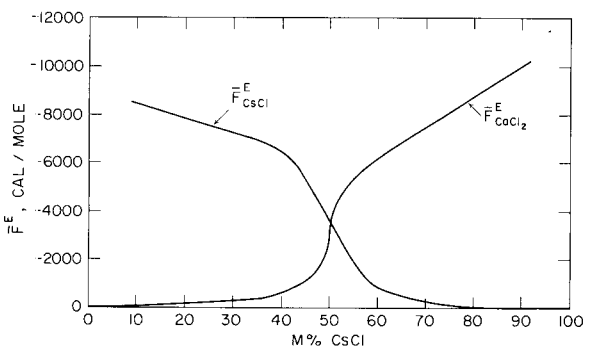

Figure 12. Partial molar excess free energy of mixing in the system $CaCl_2$-CsCl.

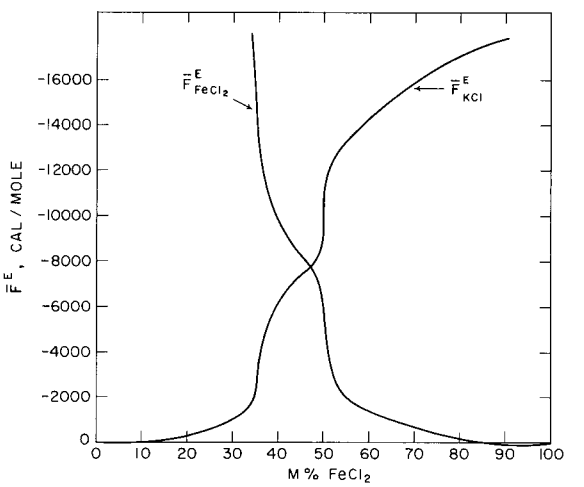

Figure 13. Partial molar excess free energy of mixing in the system KCl-$FeCl_2$.

Wesley, 1952) and others for determining thermodynamic properties of mixtures from the phase diagrams, the partial molar excess free energies of mixing for these systems have been determined. The results are shown in Figures 8 to 13. No temperature is specified for these curves, the assumption of "regular" solution having been made in the calculation. For regular solutions, the partial molar excess free energy is independent of temperature.

Figure 9 includes, in addition to the calculated curve, points derived from the results of the galvanic cell measurements presented in the preceding section, and a third set of points derived from the published results of Markov et al. [*Zhur. Fiz. Khim.* **29**, 51 (1951)]. It is to be remembered that the calculated curves are based on certain assumptions, and the figures are to be used only when no direct experimental data are available, as a first approximation. A detailed account of the method of calculation will be submitted for journal publication shortly.

BENCH CONTACTOR STUDIES

Equilibrium distribution coefficients for U, Zr, and fission products between Bi and salt are determined in bench-scale contactors. These are 4 to 6-in.-diameter vessels which have provisions for temperature control, agitation, and sampling of each phase. During the report period, construc-

tion of the improved contactors, which were described in the last report, continued. One is nearing completion and three others are well along.

In preparation for experiments with $BiCl_3$, an existing tantalum-lined contactor was charged with Bi-U-Mg-Zr-Ce and salt. However, $BiCl_3$ was not immediately added to the salt because of instability of the solute concentrations in the Bi. Prior to salt addition, the solute concentrations in Bi were steady at 1000 ppm U, 220 ppm Mg, 320 ppm Zr, and 19 ppm Ce. Within the precision of the measurement, these concentrations corresponded to complete recovery of the solutes added.

Upon addition of salt, scum which had formed on the surface of the Bi following the addition of Mg and Zr almost disappeared; and in the ensuing 3-week period the concentration of Mg in Bi decreased to less than 20 ppm. The concentrations of other solutes fell to 780 ppm U, 260 ppm Zr, and 1 ppm Ce, and transfer to the salt phase was observed. At the end of the 3-week period, approximately 25% of the U and Zr originally present could not be accounted for. Immediately following a further addition of Mg to the Bi, the concentration was 260 ppm, and in two weeks it fell to 40 ppm. Complete analyses for other solutes are not yet available.

The reason for the instability of the Mg concentration has not been established. Inadequate removal of oxidizing impurities in the salt during pretreatment with Mg-Bi solution may be responsible. A further addition of Mg is to be made in an attempt to stabilize the concentration.

This slow loss of Mg from the Bi, which has been observed before in bench contactor work, although an annoyance in experimental work, would present no problem in an LMFR fuel processing plant.

A batch of 150 lb ternary eutectic is being prepared for use in the bench contactors and Loop M; it should be available before the end of October. Construction of a 10-in. pretreatment tank is nearing completion.

CHEMICAL TECHNOLOGY

Concentration of Xenon and Iodine at Bismuth-Graphite and Bismuth-Steel Interfaces

The fate of Xe and its precursor iodine after their generation in the Bi-U fuel is of considerable importance in the over-all neutron economy of the LMFR. A theoretical analysis by McMillan (BNL 353) showed that Xe has a tremendous tendency to concentrate on liquid Bi surfaces. For a spherical volume, the number of Xe atoms on the surface was estimated to be about 10^8 times the number dissolved in the Bi at 300°C. At 500°C, this ratio came close to 10^5.

To test the above theoretical conclusions and to verify certain observations on the accumulation of iodine and Xe on solid surfaces during operation of Loop B, an experimental program has been under way during the last 5 months.

The experiments involve the irradiation of graphite and 2¼ Cr – 1 Mo steel capsules filled with Bi containing 500 to 1000 ppm natural U, 350 ppm Mg, and 350 ppm Zr. After removal from the pile, the Bi was melted in the capsules and kept at 500°C for periods ranging from 10 min to 117 hr. After cooling, the concentrations of I^{131} and Xe^{133} in the center of the capsule were compared with those of the same isotopes at, and close to, the interface. A typical capsule was 10 cm long, 1.6 cm o.d., and 1.27 cm i.d. Prior to filling, the capsule was cleaned and degassed at 800°C for 3 hr. On the average, 20 samples were taken from each capsule and analyzed for I^{131}, Xe^{133}, and U. Results obtained in a preliminary series of six capsules (two made of steel and four of graphitite "G") are shown in Table 2. In these experiments no attempt was made to study systematically the effect of any single variable. The purposes of this preliminary series were simply to determine roughly the extent to which iodine and Xe concentrated on interfaces and to establish a framework for future, more precise experiments. However, in spite of the limitations of the experiments, the following conclusions are warranted.

1) When the concentration of iodine generated by fission reaches a level of about 10^{11} to 10^{12} atoms/g Bi (capsules S-010, S-020, G-010, G-020), the iodine concentrates at the interface between the Bi and the container wall. The concentration at the interface is about 1000 times higher than that in the bulk of the Bi for the steel capsules (S-010 and S-020), and about 100 times higher for the graphite capsules (G-010 and G-020).

2) When the concentration of Xe reaches a level of about 10^{11} to 10^{12} atoms/g Bi (capsules S-010, S-020, G-010, G-020), its concentration near the Bi-steel interface is about 10,000 times

that in the Bi (capsules S-010 and S-020). This ratio for graphitite "G" is only 10 (G-020). The difference between the steel and graphitite capsules is believed to be due to the fact that Xe diffuses through the latter, and either escapes from the capsule or is held so firmly in the interior of the graphite that the analytical method used was incapable of detecting it. This penetration by fission-product gases has been found in other experiments and confirmed by autoradiographs and material balances. Improved techniques now being developed should provide more information on this point in the near future.

3) When the concentrations of iodine and Xe are lower, i.e., about 10^9 atoms/g, the differences between interface and core concentrations are much smaller though still statistically significant at the 95% level (Xe in G-040, iodine in G-030 and G-040). For iodine the concentration ratios vary from slightly less than 10 for G-030 to 100 for G-040. For Xe the ratio is only about 3 for G-040, and no significant separation was observed in G-030. These lower Xe ratios are attributed again to the loss of Xe from the interface to the graphite.

As a sort of blank run, an experiment was conducted in which the Bi was not melted at all. The results (Table 3) show that the concentration of Xe near the interface was somewhat lower than in the center of the slug; i.e., the concentration difference is in the opposite direction to that observed previously. A comparison between the Xe present and that calculated indicates that this is probably due to depletion of Xe from the Bi immediately adjacent to the graphite walls. In the case of iodine, no significant difference between the interface and internal concentrations was measured. The same applies to the concentration of U. The results of this experiment show that the concentration differences measured in capsules S-010, S-020, G-010, G-020, G-030, and G-040 can only be explained by removal of the Xe and iodine from the bulk of the Bi while in the liquid state.

To rule out the possibility that the method of cooling the Bi had an effect on the observed differences between concentrations at the interface and in the interior of the Bi, two experiments were performed. The first was identical to the first six described above, except that the Bi was kept in the molten state only momentarily. The analytical re-

Table 2

Results of In-pile Experiments on Behavior of Iodine and Xenon in LMFR Fuel

	Capsule					
	S-010 (2¼ Cr – 1 Mo steel)	S-020 (2¼ Cr – 1 Mo steel)	G-010 (Graphitite "G")	G-020 (Graphitite "G")	G-040 (Graphitite "G")	G-030 (Graphitite "G")
Log Xe^{133} conc. in core	7.826±0.610	7.306±0.746		9.244±0.178	10.069±0.200	9.155±0.111
Log Xe^{133} conc. at interface	11.747±1.160	11.825±0.658		10.269±0.191	10.560±0.050	9.247±0.175
Log I^{131} conc. in core	8.696±0.840	8.871±1.042	10.295±0.200	9.175±0.484	9.413±0.660	8.553±0.212
Log I^{131} conc. at interface	11.668±0.430	11.381±0.773	11.800±1.000	11.157±0.320	11.418±0.124	9.235±0.280
U conc. in core, ppm	1027	—	(a) 1140; (b) 1202	1194	570	549
U conc. at interface, ppm	850	1037	(a) 1080; (b) 1174	1121	568	430
Time of irradiation, hr	336	226	336	39	312	3
Approximate flux	2.12×10^{12}	2.12×10^{12}	2.0×10^{12}	1.33×10^{12}	2×10^{12}	2×10^{12}
Time at 500°C, hr	117	117	75	75	72	75

All concentrations expressed as atoms per g Bi.
Limits correspond to 95% confidence level.
Figures are averages of at least three separate analyses.
Concentrations refer to time of withdrawal from 500°C furnace.

Table 3

Results from Experiment in Which Bismuth Was Not Melted

Isotope	Log conc. at interface	Log conc. in bulk of Bi		
Xe^{133}	11.4669	12.0453	Av log Xe conc. at interface	11.3933
Xe^{133}	11.6506	12.2908	Av log Xe conc. in bulk	12.1242
Xe^{133}	11.0623	12.0365	Av difference of log conc. at interface and log conc. in bulk	$-1.258 < -0.731 < -0.204$
I^{131}	11.55922	11.67142	Av log I conc. at interface	10.9890
I^{131}	10.94972	10.91202	Av log I conc. in bulk	11.0528
I^{131}	10.45822	10.57492	Av difference of log conc. at interface and log conc. in bulk	$-0.154 < 0.064 < 0.280$
			U conc. at interface	921 ppm
			U conc. in bulk	996 ppm
			Time of irradiation	69 hr

Table 4

Results of Experiment Involving Immediate Quenching of Melted Bismuth

Isotope	Log conc. at interface	Log conc. in bulk of Bi		
Xe^{133}	12.3936	12.3420	Av log Xe conc. at interface	11.9683
Xe^{133}	11.8227	12.1135	Av log Xe conc. in bulk	12.0984
Xe^{133}	11.6887	11.8398	Av difference of log conc. at interface and log conc. in bulk	$-0.556 < -0.1301 < 0.296$
I^{131}	11.3196	11.1209	Av log I conc. at interface	11.1715
I^{131}	11.0234	11.1552	Av log I conc. in bulk	11.1705
I^{131}	11.1716	11.2355	Av difference of log conc. at interface and log conc. in bulk	$-0.438 < -0.002 < -0.434$
			U conc. at interface	972 ppm
			U conc. in bulk	1033 ppm
			Time of irradiation	39 hr

sults showed no significant differences in concentrations at the interface and in the interior for either iodine or Xe. A slight depletion of Xe from the interface region was again noticed, as in the case of G-050, and presumably for the same reasons. The results of this experiment (Table 4) showed that the results obtained earlier were not significantly affected by the quenching process. The second experiment to verify the same point consisted of inserting a 3.6-mm-diameter graphitite rod in the center of a standard graphitite capsule (G-070) and following the usual procedure. The results are given in Table 5.

It is estimated that the concentrations of both Xe and iodine at the inner interface were roughly twice those at the outer interface on an area basis. This indicates that the quenching process concentrates the solutes in the liquid ahead of the solidification front. If this is so then the high concentrations at the outer interfaces in the first six experi-

Table 5

Results of Experiment with Graphite Rod Present In Capsule

Isotope	Log conc. at outer interface	Log conc. at inner interface		
Xe^{133}	10.3218	10.0828	Av log Xe conc. at outer interface	10.2362
Xe^{133}	10.2412	10.0867	Av log Xe conc. at inner interface	10.0547
Xe^{133}	10.1457	9.9977	Av difference of log conc. at outer and log conc. at inner interface	$0.0575 < 0.1815 < 0.3055$
I^{131}	11.4296	11.1280	Av log I conc. at outer interface	11.3286
I^{131}	11.3594	11.1236	Av log I conc. at inner interface	11.0406
I^{131}	11.1968	10.8701	Av difference of log conc. at outer and log conc. at inner interface	$0.1715 < 0.2880 < 0.4046$
			U conc. at outer interface	1069 ppm
			U conc. at inner interface	1012 ppm
			Time of irradiation	41 hr

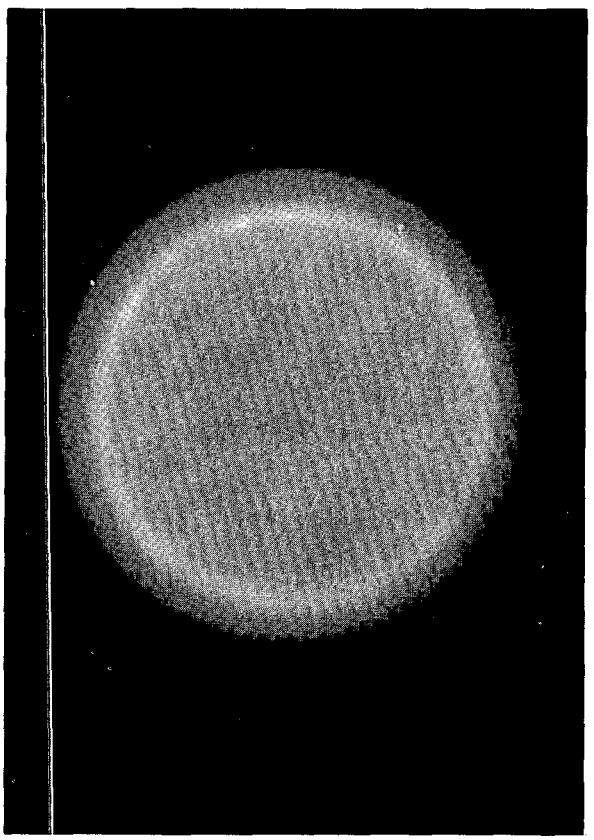

Figure 14. Autoradiograph (4×) of sample (from experiment S-020) showing accumulation of fission products at Bi-steel interface.

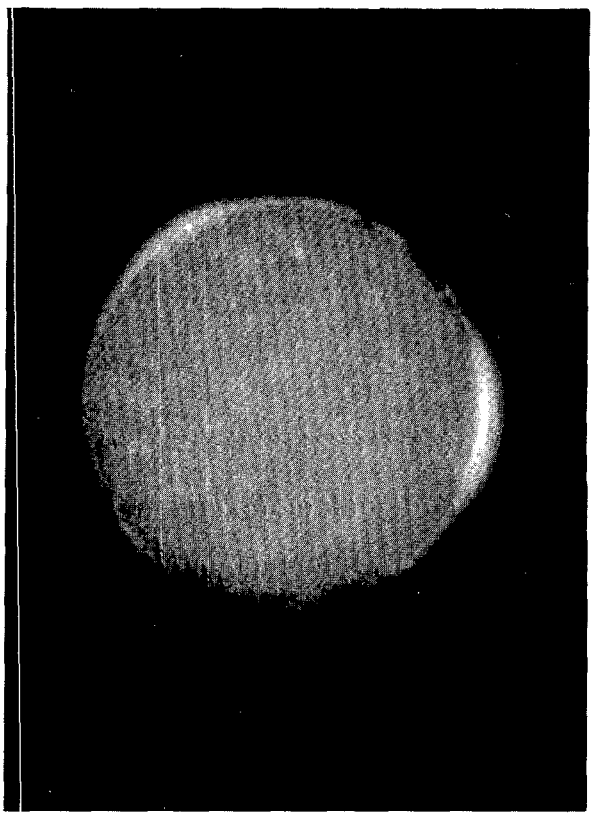

Figure 15. Autoradiograph of sample (from experiment G-010) showing accumulation of fission products at Bi-graphite interface and penetration of graphite by radioactive gases.

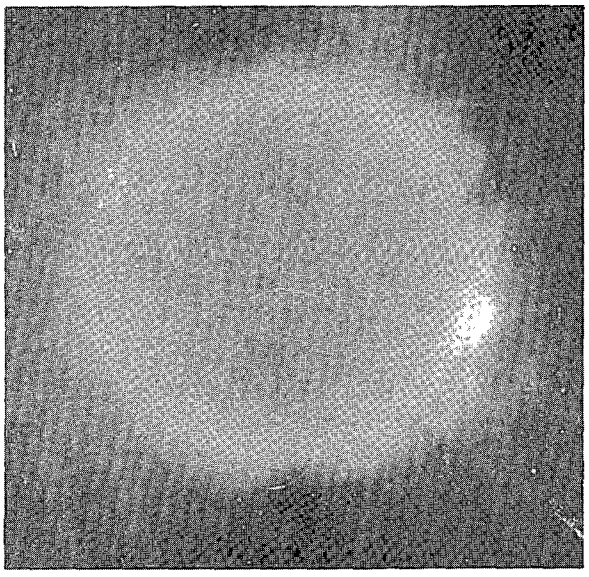

Figure 16. Autoradiograph of sample (from experiment G-040) showing the graphite wall permeated by radioactive fission gases.

ments are in no way due to the quenching process but are due to a natural tendency for the iodine and Xe to concentrate at interfaces. This point should not be considered as definitely proved, however, until further experiments at higher concentration levels are completed.

In all the experiments described here, extensive use has been made of autoradiography for better understanding and qualitative confirmation of the analytical results. Figure 14 shows a typical autoradiograph of a sample from experiment S-020. The central circular area shows the moderate residual activity of the U-Bi fuel. This central area is surrounded by a line of very high activity which coincides with the Bi-steel interface. The high intensity of this line suggests that a substantial accumulation of fission products has occurred at the interface. The line of high activity is followed outwards by a ring which represents the steel wall. The activity shown by this ring is due to activation of some of the constituents of the steel.

A similar autoradiograph obtained from a graphite experiment (G-010) is shown in Figure 15. In this case, again, the fuel region is surrounded by a region of high activity at the Bi-graphite interfaces. This zone is not as sharply defined and regular as the high-intensity line of Figure 14. It appears that the sources of the activity have penetrated in the graphite ring, and two distinct pockets of activity can be seen at 11 and 3 o'clock. The graphite walls are not visible.

Penetration of the graphite by active fission products is shown more clearly in Figure 16, which is an autoradiograph of a graphite ring after all the U-Bi had been removed. The irregularities are in accordance with the observed heterogeneity of graphite.

It should be noted that fission products other than iodine and Xe may be and possibly are involved in the formation of the high-intensity regions. The penetrations in the graphite appear to be due to radioactive gases exclusively.

The results of all these experiments show that iodine and Xe concentrate very heavily on surfaces in contact with the U-Bi fuel. There is evidence that Xe and radioactive gases penetrate the graphite and are immobilized therein. This may present a very serious problem in keeping down the LMFR fission-product poisoning to the low levels required for economic breeding. The reported experiments, however, have been limited by the available neutron flux of the BNL pile to concentration levels about 1/1000 those anticipated in an LMFR breeder. Extrapolation of the present results to the LMFR levels is not justifiable because it is conceivable that, because of saturation effects, the concentrations at the interfaces may not increase proportionately. The penetration of Xe in the graphite, as contrasted to its accumulation at interfaces, is, however, a potentially serious problem because of the large surfaces available inside the graphite.

With the preliminary series reported here completed, experiments are under way and planned for the near future to determine the following:

1) Relationship of concentrations of Xe and iodine at interfaces to those in the bulk of the Bi when the generated concentrations of these isotopes are of the order of 10^{13} to 10^{14} atoms/g Bi.
2) Behavior of iodine and Xe in a system in which there is relative motion of the liquid metal past the graphite walls as contrasted with the static systems hitherto investigated.
3) Rate of establishing the measured separations in both static and dynamic systems.
4) Quantities of Xe which penetrate a given volume of graphite under a given set of conditions.

5) Rates of permeation of Xe into graphite.
6) Comparison of several types of graphite which may be used in an LMFR core.
7) Effect of temperature on the observed phenomena.

The results of this program are deemed necessary for determining the feasibility of using an unclad graphite core in the LMFR.

Fused Salt Corrosion Experiments

Screening tests for possible container materials for fused salt are being performed in static capsules and in rocking-furnace capsules. Static tests in a gamma radiation field have been planned.

The salt, KCl-NaCl-$MgCl_2$ eutectic, containing 0 to 5% $BiCl_3$, is present alone or with fuel (1000 ppm U, 350 ppm Mg, 250 ppm Zr in Bi). Materials to be tested include Ta, Mo, 2¼ Cr – 1 Mo steel, Inconel, Hastelloy C, and the following stainless steels: 304 ELC, 310, 316, 347, 410, and 446. Capsules made of these materials are made from fully annealed seamless tubing, usually ½-in. size. Standard surface preparation is by sandblasting. Polished tabs which are inserted into the capsules are also made from the same tubing. All tests are run under a positive pressure of purified helium at a nominal temperature level of 500°C for 1000 hr. Temperature differences of 50°C between hot and cold ends of the capsules are used in the rocking-furnace tests. This difference, while arbitrary, is thought to be a reasonable one to be expected in a processing plant. This temperature difference will be used with hot end temperatures at 500° and 550°C. Later a difference of 100°C with a hot end temperature of 550°C will be used. At the completion of the tests, the solutions are analyzed for fuel constituents and corrosion products, and the capsules and tabs are examined metallographically.

Static tests with salt alone are carried out at 500°C for 1000 hr in glass capsules with polished tabs. In tests with both salt and Bi present, the liquids and tabs are contained in capsules which are open at one end and made of the same material as the tabs. The capsules are contained in glass envelopes.

To date only salt mixtures containing 1% $BiCl_3$ have been used in the static tests. Ta and Mo were tested during the report period. After exposure the Ta tabs were found to be covered with a loosely-adhering black layer which is suspected of being metallic Bi. Also, the tabs were quite brittle. Although etching of the tabs for metallographic inspection was not completely successful, both intergranular and transgranular attack were found. No attack of Mo could be detected metallographically, although weight losses of 2 to 3 mg/cm^2 were measured.

In the rocking-furnace experiments, the capsules are 12½ in. long over-all (10 in. uncrimped) and are closed at both ends. The closures are made by crimping in a hydraulic ram with subsequent inert arc welding. In filling and sealing a capsule, a sandblasted tube is first closed at one end, and a polished tab made of the same material as the capsule is inserted and restrained in the closed end by partial crimping. The closure is then leak-tested with a mass spectrometer leak detector, and the capsule is degassed at 900°C for 4 hr in a quartz tube. It is then transferred to glass apparatus in which equal volumes (about 3.5 cc) of salt and of fuel are charged to it under an argon cover. Upon cooling, the glass envelope is removed, and the open end of the capsule is quickly connected to a purified helium and vacuum system. After purging several times, the capsule is filled with helium to a pressure of 3 psig. The open end of the capsule is then crimped without disconnecting the capsule from the inert gas system. The capsules are then leak-tested at 500°C in glass tubes which are directly connected to a mass spectrometer leak detector.

The rocking-furnace apparatus has provisions for six furnaces. The furnaces are made of Mullite tubes (18 in. long; 1¾ in. bore) which are uniformly wound with resistance heating wire over ⅔ of their length, starting from one end. The tubes are mounted in insulating firebrick contained in a metal can. Capsules placed in a furnace become hotter at one end than at the other, and the temperature difference may be varied by moving the capsule along the axis of the furnace. The tab is contained in the hot end of the capsule.

Each furnace accommodates four capsules held together with steel strapping. A thermocouple is placed in the center of the nest at each end. Measurement of temperature in this fashion has been compared with measurement by couples inserted in wells running into a capsule. No error resulted at the hot end, but cold end skin couples read 20°C low.

The furnaces are mounted on a frame which is automatically tilted alternately in one direction and then in the other. The total cycle time and the delay at each extreme position (50° from horizontal) may be varied. The fluid flow caused by the tilting action is through a temperature difference, and mass transfer corrosion is promoted. In current tests the cycle time is 120 sec with a 30-sec delay at each extreme position, and the temperature difference is 50°C, the hot end being at 500°C.

The first tests with this equipment have been for the purpose of finding construction materials for the extraction columns in Loop N. Duplicate capsules of each material are being tested. Four materials have been tested to date: types 347, 410, and 446 stainless steel, and Inconel. Radiographs of the capsules showed plug material in the cold ends of the Inconel and type 446 stainless steel capsules, but nothing in the others. The metallographic results are not yet available. In preparation for tests on other materials, leak testing of crimps made in tubes of 2¼ Cr – 1 Mo steel, tantalum, Hastelloy C, and type 304 ELC stainless steel is under way.

In an LMFR processing plant, gamma activity from dissolved fission products in the salt may be expected to reach 200 C/cc. Decomposition of the salt at the operating temperature is not anticipated; but corrosion tests in a radiation field have been planned. Polished specimens will be suspended in salt contained in a vessel heated to 500°C and located in a Co^{60} field providing 300,000 r/hr. Vessel fabrication is in progress. Initial tests will involve types 347 and 410 stainless steel and tantalum.

PILOT PLANT OPERATIONS

Loop G

This is a figure-eight loop, constructed primarily of 2¼ Cr – 1 Mo steel, for circulating molten U-Bi solution for corrosion test work. Circulation is maintained by a modified Ruthman canned-rotor centrifugal pump. Resistance heaters are used to supply heat to the loop, and a forced-air finned-tube cooler is used for heat rejection.

During the present report period, the work was concerned mainly with the second run of the loop (3000 hr) with a new set of test specimens. In preparing for the present run, several changes were made in the pump and piping, and the loop was rinsed several times with clean Bi to remove U. The changes made and the procedures followed up to the time of the conditioning runs were as follows:

1) A spare liquid metal valve was removed.
2) A temporary pipe spacer was inserted in place of the hot leg test section.
3) The cold test section (at the exit of the finned cooler) was removed and replaced by pipe containing a thermocouple well.
4) Radiographs of the right-angle test section were made; these showed no attack.
5) The pump was modified to include the most recent baffle arrangements as developed in water test work.
6) The loop was charged and flushed with Bi twice to lower the U concentration to 2 ppm, in order to permit conditioning runs to be made in the absence of U.
7) Following flushing runs, the new furnace test section was installed and heat-treated.

The start of loop conditioning runs was delayed twice by dump valve failures which forced the dumping of the loop. Both valves had been in service and at operating temperature for one year prior to failure. Metallographic examination showed failure to be due primarily to intergranular corrosion of the bellows material (430 SS).

On July 9, a successful start-up was made and test run No. 2 was begun. The sequence of events from then to the present time was as follows:

1) Conditioning run – isothermal operation at 525°C (977°F).
   a) On July 9, Bi containing 330 ppm Mg and 300 ppm Zr was charged into the loop and circulated at 4.8 gpm for 24 hr. The flow rate was then reduced to about 2¾ gpm and maintained for 5 days.
   b) After 6 days' operation the loop was dumped, and radiographs of the furnace test section were made. No corrosive attack was observed.
   c) A 4.8-gpm flow rate was established and maintained for 5 days during which time U was added to the Bi stream. The U concentration stabilized at 1040 ppm after a loss of 8%.
2) ΔT operation.
   a) A 75°C temperature differential was established on July 29. The hot leg temperature was controlled at 525°C (977°F). A 4.8-gpm flow rate was maintained.

b) After 120 hr of operation, radiographs of the test section were made, which showed no attack, and an electromagnetic flowmeter was installed for testing. The flowmeter test is described elsewhere.
c) The loop was charged again on August 17, and after a short isothermal run the 75°C (164°F) temperature differential was re-established.
d) After 170 hr of operation a furnace heater failure forced the shutdown of the loop. Repairs were made and the temperature differential and flow were established on August 30. The loop has been in continuous operation since that time.

The loop was shut down on September 27 because the standby power generator was out of order and it was considered unwise to operate without it. At shutdown run No. 2 had clocked 962 hr under ΔT conditions.

Loop H-1

This unit is an isothermal liquid-metal-pump test loop constructed of 2¼ Cr – 1 Mo steel. A 5-hp, 3450-rpm canned-motor centrifugal pump circulates the Bi through the 1-in. I.P.S. loop.

Run No. 1. The run in progress at the end of the last reporting period was continued for a total of 308 hr of operation under the following conditions:

Flow: 17 gpm
Head: 17.6 ft Bi
Temperature: 540°C (1004°F)
Concentration: Zr 335 ppm, Mg 300 ppm, balance Bi
Impeller diameter: 2.875 in.
Impeller width: 0.8125 in.

The loop was shut down because of the failure of the bellows seal in the throttle valve.

The loop was rebuilt to include the following units: a Taylor Instrument Company diaphragm-sealed NaK-filled Bourdon pressure transmitter; a Manning, Maxwell and Moore diaphragm-sealed NaK-filled Bourdon pressure transmitter; a multiprobe liquid level indicator for ultimate use in Radiation Loop 1. In addition to these items, three impeller sizes were tested.

Run No. 2. This run was made under the following conditions:

Flow: 24.8 gpm
Head: 23.4 ft Bi
Temperature: 550°C (1022°F)
Concentration: Zr 400 ppm, Mg 350 ppm, balance Bi
Impeller diameter: 3.33 in.
Impeller width: 0.5 in.

During the first few hours of operation at 550°C (1022°F) the impeller information shown in Table 6 was obtained. The loop was operated for 283 hr at 550°C (1022°F). A leak at a pipe weld necessitated a shutdown for repair. The loop was restarted and run for an additional 217 hr. Periodic radiographic examination of a metallurgical test piece during the 500 hr of operation revealed no evidence of corrosion. During this run the Taylor pressure transmitter failed and was removed after 500 hr. This unit had been subjected to severe pressure cycling in the pressure transmitter test rig. This test is described elsewhere in this report. The loop was restarted and run for an additional 90 hr. At this time the loop was shut down and dismantled to make room for testing the pump for Radiation Loop 1.

Radiation Loop 1 Pump Test

It is desirable to check the performance characteristics and mechanical reliability of the pump for this in-pile loop before installation. Construction of both the pump and Loop H-1 is under way at this time.

The loop will now include the following items:

1) A 10-hp, 3450-rpm canned-motor centrifugal pump and sump assembly. As this unit will be used for radioactive service, materials and

Table 6

Impeller diameter, in.	Shut-off head, ft Bi	Full flow, gpm	Full flow head, ft Bi	Efficiency at full flow, %
1) 3.875	37.1	26.4	27.8	11.6
2) 3.60	32.8	25.1	25.1	16.7
3) 3.33	27.2	24.8	23.4	20.6

Impeller width = ½ in.

construction are being completely controlled. Some pump details are as follows:

Flow: 6 gpm
Head: 31 ft Bi
Temperature: 400°C (752°F)
Impeller diameter: 3.6 in.
Impeller width: 0.5 in.
A 6-probe side-arm liquid level indicator.

2) A thermal flowmeter consisting of a heat source, upstream and downstream thermocouples, and a microvolt recorder. At a constant heat input the temperature rise in the Bi is proportional to the flow.
3) An electromagnetic flowmeter utilizing a ½-in. stainless steel pipe cell with a 10-mil 2¼ Cr – 1 Mo liner.
4) An orifice plate with two bellows-sealed pressure transmitters of the differential transformer type manufactured by the M.S.A. Research Co.
5) A Manning, Maxwell and Moore NaK-filled pressure transmitter.
6) A throttle valve, two dump valves, surge sample tanks, dump tank, and appropriate piping.

This loop should be in operation by the middle of October.

Loop H-2

This new loop, the design of which is complete, is to be constructed of 2¼ Cr – 1 Mo steel and will be used for testing pumps for molten Bi service. The pumps to be tested include a Findlay electrodynamic pump, a Byron-Jackson centrifugal pump, and a C.H. Wheeler centrifugal pump. All these pumps have a nominal capacity of 10 to 15 gpm at a 30-ft head. The loop will accommodate one pump at a time, but pump replacement will be made with a minimum of piping revision. Besides the pump, the principal components of the loop are a surge tank with a liquid level side arm, an air cooler, an orifice, and a dump tank. The loop is constructed of 1-in. and ½-in. piping. Because of the large inefficiency of the pump, it was considered necessary to install the air cooler to maintain uniform temperature conditions in the loop.

The process design for the loop and revision No. 1 to this design were completed during this period. The mechanical design was initiated in June and completed during August. Drawings were reviewed, approved, and released for construction.

Loops L-5 and L-6

These are small thermal convection loops for testing construction materials for fused salt service. L-5 is made of type 347 stainless steel and L-6 of type 410. They will both circulate the eutectic mixture $NaCl$-KCl-$MgCl_2$ and will have cold and hot leg temperatures of 450° and 500°C, respectively. Construction work on these loops is nearing completion.

Loop M

This stainless steel forced-circulation salt loop has been described in previous reports. It should be in operation by the end of October.

Loop N

This is to be an out-of-pile loop used to test the design of continuous countercurrent extraction columns and their capacity to separate fission products and U from LMFR fuel by fused salt extraction. It will consist of two interconnecting loops, a 2¼ Cr – 1 Mo steel loop containing Bi and a type 347 SS loop containing salt, supplying one of two extraction columns with fuel and molten salt. The loop will be operated at temperatures between 450° and 550°C and with flow rates (0.5 gpm Bi, 0.05 gpm salt) to the columns corresponding to those required to process the fuel from a 500-Mw LMFR.

Two types of experiments will be performed in Loop N. In one (mass transfer batch experiments) molten salt and U-Bi containing one or more rare earth fission products will be pumped at constant flow rates from their respective supply tanks, countercurrently through an extraction column, and into their respective receiver tanks. From a knowledge of the steady-state influent and effluent concentrations of rare earth fission products in both, the separative capacity of the extraction column can be determined. In the other type of experiment (mechanical test) Bi and salt will be circulated continuously and countercurrently through an extraction column, around their respective loops, and back into the column. In this type of experiment, the long-time mechanical operating characteristics of the column will be studied, including carry-over tests.

A contract to design and build this loop was awarded to the Catalytic Construction Company and approved by the AEC on July 2. The fabricator will be O.G. Kelley of Boston, Mass. Several meetings have been held between BNL and Catalytic personnel to discuss various aspects of the loop design. To date the engineering flow diagram and 11 vessel drawings have been approved for construction by BNL. It is expected that an acceptable vessel arrangement drawing will be approved by BNL before September 30. All Catalytic drawings should be completed and approved by BNL before October 31, 1957. Delivery of the completed loop at BNL is expected in May 1958. Catalytic is investigating the feasibility of shipping the entire loop in one piece from Boston to Upton.

Specifications are being prepared for the loop instrument panel, and formal quotations will be requested from outside vendors preparatory to placing an order for its fabrication.

Orders have been placed with the Ruthman Machinery Co. for 3-hp, 1750-rpm Bi pumps (material, 2¼ Cr – 1 Mo steel) and salt pumps (material, type 347 SS), and delivery is expected in November. Mechanical drawings are being prepared for canned magnetic coupling drives for these pumps. These will permit simplified speed control of the pumps, since the motors will not be canned. This will also minimize the number of auxiliary connections (electric, thermocouple, etc.), and the motors will not need to be cooled. As soon as the pumps are received, they will be tested with their magnetic couplings.

Work is continuing on in-line samplers and on the selection of flowmeters for Bi and salt service. Initially an electromagnetic flowmeter was selected for Bi and a thermal flowmeter for salt. However, tests showed them to be unpromising at such low flow rates. At present an orifice flowmeter shows the most promise and should be usable on both streams. It measures the change in pressure at a tap downstream from the orifice. A constant head (less friction losses in the pipe) is provided by the respective constant head tanks located at the upstream pressure tap, and a change in flow produces a variation in the liquid level of a standpipe located at the downstream orifice pressure tap. It is proposed to use a float and to measure the change in inductance of a coil as the float moves. Testing with water shows that even very low flows can be measured satisfactorily.

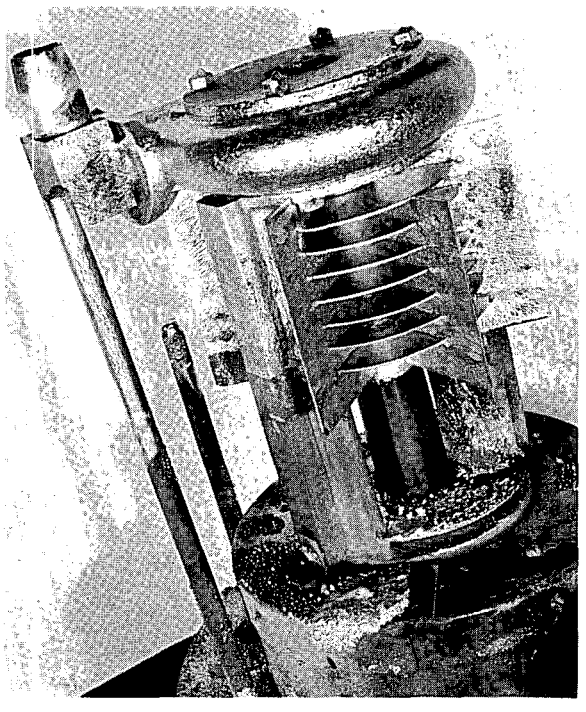

Figure 17. Pump baffles.

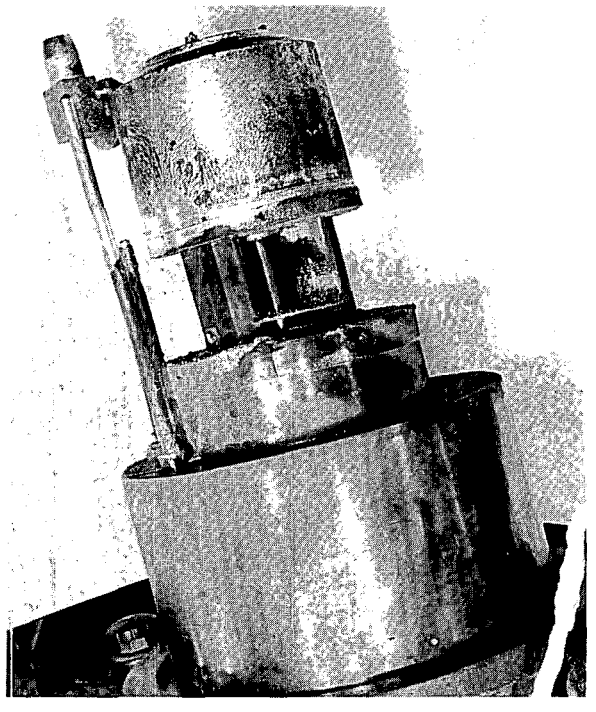

Figure 18. Pump baffles.

Pump Tests (Water)

The testing of liquid metal pumps in a water test rig was continued. In general, the water tests are used to determine pump characteristics, with various pumps and impeller arrangements, and to determine the effects of various can and baffle designs on pump characteristics.

A Lucite mock-up of the Ruthman pump can was made and proved useful in developing a baffle arrangement to minimize splashing in the pump. The baffle design adopted consisted of a series of horizontal discs and vertical plates mounted radially in relation to the shaft, all of which were surrounded by a deflector can. The baffles, shown mounted on a pump in Figures 17 and 18, are in the present pump in Loop G and were also tested in Loop H-1.

Additional work on the Ruthman pump consisted of testing impellers of different widths in order to verify the performance curves measured previously.

A test was made with a 3-hp, 1750-rpm Ruthman pump identical to that to be used in Loop N to determine whether the short circuiting of fluid directly from the discharge nozzle to the pump suction would cause undue splashing or turbulence in the pump can. No abnormal effects were noted.

Several runs were made with a Byron-Jackson pump to determine how performance, turbulence, and splashing were affected by the use of various sizes of pump cans.

EM Flowmeter Tests

An electromagnetic flowmeter designed specifically to measure flow rates in Bi systems was tested in Loop G. The unit was mounted in such a way that it can be removed from the pipe at all times except when flow measurements are being made. This feature prevents the trapping of corrosion products in the vicinity of the magnetic field. The size of the magnet was chosen to provide sufficient flux to allow for that lost in saturating the magnetic pipe.

During the test mechanical difficulties prevented the proper positioning of the magnet in relation to the pipe; as a result the full field strength could not be applied at the point of measurement. However, a strong signal was obtained even under these conditions. Since the magnet could not be positioned properly, no calibration of the flowmeter was obtained. At the next shutdown of the loop, the magnet will be removed and flux measurements made, and another attempt will be made to insert the meter in the loop and calibrate it.

Volatile Fluoride Project

PILOT PLANT DISSOLUTION STUDIES

Three additional dissolution runs, D-7, D-8, and D-9, were made in solutions of BrF_3 with batches of unirradiated natural uranium slugs of the type used in the BNL reactor. As in previous runs the UF_6 content of the solution was allowed to increase steadily, and the other parameters were held fairly constant: temperature = 120°C; flow rate through dissolver = 44 gpm; Br_2 concentration = $<$0.1 M%; and helium pressure = 175 to 180 psig. Only one slug was used in run D-7 to minimize the effect of changing UF_6 concentration; five slugs were used in each of the other runs in order to reach higher UF_6 concentrations quickly.

During these batch runs the Br_2 concentration was maintained at $<$0.1 M% by continuous regeneration of BrF_3 from BrF_5. The BrF_5 was added prior to each run, and the concentration decreased steadily throughout the run. This procedure improved the accuracy of the heat balance, since it eliminated compensation for heating the BrF_5 to 250°F.

The pressure on the solution was maintained near 175 psig with helium to suppress boiling at the slug surfaces and to prevent pump cavitation. The vapor pressure of the solution was approximately 40 psig. During these runs the specific gravity of the solution increased from 2.56 to 2.62.

Runs D-7 and D-8, made at about 3 M% and 3 to 4 M% UF_6, respectively, confirmed the fact that UF_6 does not significantly reduce the dissolving time in concentrations above 2 M%.

PILOT PLANT ACCIDENT

Run D-9, which was to be made in the 4 to 5 M% range, proceeded normally until the slugs were 79% dissolved, at 3.6 hr, when a series of explosions occurred within a 10-sec period in the dissolver section of the pilot plant. Prior to the

first explosion, there was no indication of any operational abnormality. The violent reactions involved 30 gal interhalogen mixture and 2½ lb natural uranium metal. The equipment was severely damaged, and four people received chemical burns, three slight and one serious. Although the conditions which initiated the accident have not been definitely established, the most probable cause appears to be that a slug fragment was lifted either to the vapor phase or to the liquid-vapor interface when the last slug height reading was taken with a retractable probe, and that ignition occurred within 1 or 2 min because of poor heat removal in the vapor phase.

Equipment damage effects indicated that local metal temperatures and pressures reached as high as 2500°F and 6000 psi, respectively. In addition to the bursting of the rupture disc on the dissolver, a rupture in the system occurred at one other point: a canned-rotor pump was blown wide open which had a bursting strength of $\approx$3500 psi. It is estimated that 374 lb interhalogens and 32 lb uranium as UF_6 were vaporized to the atmosphere.

In the design of the pilot plant, every precaution was taken to make it as safe as possible. Until the present accident, the possibility of an instantaneous reaction, with its accompanying high-intensity shock wave, was not known.

Reports on the accident issued by AEC and BNL investigating committees and by the BNL Volatility Studies Group, respectively, are:

AEC Office Memorandum on Explosion at BNL to K.E. Fields, General Manager, Washington, from Merril Eisenbud, Manager NYOO, June 7, 1957. (Committee Members: W.B. Harris, Charles J. Myerson, and Gordon E. Stubbings.)

Report of the Committee of Investigation on the Incident of May 15, 1957, J.B.H. Kuper, D.D. Jacobus, F.T. Miles, R.L. O'Connor, M.L. Perlman, S.M. Tucker, and C.J. Raseman, June 14, 1957.

Accident on Continuous Dissolver Pilot Plant of Fluoride Volatility Project on May 15, 1957, G. Strickland, F.L. Horn, R. Johnson, and O.E. Dwyer, BNL 452 (I-20), Revised August 20, 1957.

There was mutual agreement on the most probable cause of the accident, and the recommendations made fall into three categories: 1) suggested research to learn more about the chemical kinetics of uranium-interhalogen reactions; 2) suggested equipment design characteristics and operating procedures to eliminate foreseeable causes of violent chemical reactions; and 3) suggested features for such facilities for the protection of personnel in the event of an explosion.

Operation of the pilot plant in its present location, the semi-works area of the Hot Laboratory building, has been discontinued and the equipment is now being dismantled and stored for future use. A proposal for re-establishing the pilot plant in a new building has been submitted to the AEC.

EXPERIMENTAL DATA

Data for the nine runs are given in Table 7. A short discussion of the conditions for each run is given below.

Run D-1

Technical grade BrF_3, purchased from General Chemical Division, and purified to remove all traces of Br_2 and BrF_5 in the distillation section of the pilot plant, was used as the starting solvent. The charge of five slugs was added over a 23-min period as a precautionary measure. No BrF_5 was added to regenerate BrF_3; therefore, the Br_2 concentration steadily increased and colored the solution dark red. A separate regeneration run (R-1) was made before the start of Run D-2; at its conclusion no visual trace of Br_2 color remained.

Run D-2

This was a one-slug run, and the entire pilot plant was operated as a unit for the first time; that is, dissolution, regeneration, evaporation, and distillation proceeded simultaneously. The UF_6 concentration in the dissolver was maintained essentially constant by the continuous addition of BrF_3 to the dissolver while solution was being fed to the evaporator. The excess BrF_5 which remained after Run R-1 was used for regeneration. The analytical results showed that an improvement in the sampling technique and/or uranium analytical procedure (spectrophotometric) was necessary.

Run D-3

This was also made as a one-slug run to minimize the change of UF_6 concentration and thereby obtain an area vs time plot from the heat generation data. The attempt was not successful because of erratic operation of the heat exchanger differ-

Table 7

Summary of Batch Dissolutions in BrF_3 at 120°C

Run	D-1[g]	D-2	D-3	D-4	D-5
Batch type	Closed	Open	Closed	Closed	Closed
Slug charge[a]	5	1	1	5	1
Pressure, psig[b]	103 – 133	98 – 107	90 – 93	100 – 137	97 – 100
M% UF_6	0 – 1.1	1.08±0.18	0.73 – 0.95	1.03 – 2.06	2.06 – 2.31
M% BrF_5[c]	0	2.35 – 2.13	0.82 – 0.24	0.24 – 0.63	1.7 – 1.1
M% Br_2[d]	0 – 1.1	<0.1	<0.1 – 0.1	<0.1	<0.1
80% Dissolving time, hr[e]	7.3	3.6	3.3	4.0	2.7
100% Dissolving time, hr[f]	13.9	11.3	10.9	8.5	6.2

Run	D-6	D-7	D-8	D-9
Batch type	Closed	Closed	Closed	Closed
Slug charge[a]	5	1	5	5
Pressure, psig[b]	110 – 115	177 – 165	184 – 180	175
M% UF_6	2.08 – 3.13	2.97 – 3.21	3.03 – 4.23	3.91 – 4.41
M% BrF_5[c]	6.0 – 2.75	2.7 – 2.0	5.4 – 2.2	8.0 – 4.8[h]
M% Br_2[d]	<0.1	<0.1	<0.1	<0.1
80% Dissolving time, hr[e]	3.3	2.0	3.7	3.6
100% Dissolving time, hr[f]	10	7.3	9.3	9.0 est.[i]

[a]Unirradiated natural uranium BNL slugs, 1.10 in. in diameter and 4.0 in. long, 2.57 lb (1166 g).
[b]Dissolver was pressurized with helium to suppress boiling at the slug surfaces.
[c]Composition as determined by refractive index analysis: 99.6 M% BrF_5, 0.4 M% BrF_3.
[d]Estimated visually, except for Run D-1, by comparison with color standards.
[e]Based on heat data for five-slug runs and on characteristic dissolving curve for one-slug runs.
[f]Based on extrapolated slug height measurement.
[g]Starting solution was pure BrF_3, as determined by refractive index analysis and visual absence of Br_2 color; BrF_5 was not added for regeneration of BrF_3.
[h]Based on refractive index measurement; calculated concentrations, based on amount added, were 4.8 to 2.2.
[i]Estimated by comparison with slug height plot of Run D-8.

ential temperature controller. The initial UF_6 concentration was lower than that at the end of Run D-2, presumably because of venting losses during maintenance work. An improved sampling arrangement was installed, and it was found that more accurate uranium analyses could be obtained by the volumetric method.

Runs D-4 Through D-9

These runs were made in 5, 1, 5, 1, 5, and 5 slug batches for the reasons mentioned previously. During Run R-4, BrF_5 (used in regeneration) was added during the 3-hr period of maximum dissolution rate. In all succeeding runs, the BrF_5 was added prior to slug charging. Regeneration proceeded during the course of each run at temperatures of 160° to 165°C. The spectrophotometric uranium analyses for these runs were not consistent, and it was necessary to use the more time-consuming volumetric method preceded by elimination of the fluoride ion. This change and an improved sampling technique resulted in more accurate values by the end of Run D-6. Higher dissolver pressures were used for the last three runs to be certain of suppressing boiling as the solution became more volatile.

DISCUSSION OF RESULTS

The pilot plant work has been presented in a separate report, *Pilot Plant Fluorination of Uranium Fuel Elements by Bromine Trifluoride*, G. Strickland, F.L. Horn, and R. Johnson, BNL 457 (I-21), July 26, 1957.

A total of nine dissolution runs were made with solutions of BrF_3 and decanned BNL slugs [unirradiated, natural uranium, 1.10 in. in diameter and 4.0 in. long, 2.57 lb (1166 g)]. These runs were intended to supply information useful in programming continuous runs. Studies made at ANL (Mecham et al., 57-NESC-56, March 1957) showed that the rate of the dissolution reaction is

increased by temperature and also by the concentrations of the reaction products, UF_6 and Br_2, the former having the stronger effect. The purpose of the first series of BNL pilot plant runs was to determine the dissolving time of BNL slugs at 120°C vs UF_6 concentration.

The slug charge consisted of either 1 or 5 slugs. One-slug runs were made when the dissolving time was to be determined with a minimum change in UF_6 concentration, and five-slug runs when a large change in UF_6 concentration was desired. Since the dissolver system contained about 600 lb BrF_3, one slug corresponded to 0.25 M% UF_6. The Br_2 liberated during dissolution was reacted to BrF_3 by BrF_5 in a side loop maintained at 160° to 165°C. Slugs were fed to the dissolver through a lock system after prefluorination with BrF_5 vapor. Charging of the slugs was performed when the system was in equilibrium at the desired operating conditions.

The rate at which slugs dissolved was evaluated by two, and sometimes three, separate methods. First, a retractable probe was used to measure the total height of the slugs in the dissolver. These measurements were plotted in order to follow reaction rate during the course of a run. A five-slug charge resulted in random packing in the dissolver. When the slugs decreased in size, they settled to the plane of the support plate. After the shift, the height measurements were considered comparable to those for a single slug. Second, the rate of heat generation was calculated from measured values of the solution temperature differential across the heat exchanger, the flow rate, and a calculated value for the specific heat. Reliable heat data were obtained only for the five-slug runs. Third, dissolver solution samples were taken from a circulating sample stream, hydrolyzed, and analyzed for uranium content.

The uranium analytical data were correlated with the slug height and heat generation data to plot the following types of curves: % dissolved vs time, and % dissolved vs slug diameter. The accumulated data were then plotted as dissolving time vs M% UF_6. The BrF_3/BrF_5 ratio was determined by refractive index measurement with a cell (ANL-4941) which could be removed from the circulation line. BNL studies (*BNL Monthly Progress Report of Volatility Studies Group*, October 1956) had previously demonstrated this technique for known UF_6 concentrations and Br_2 concentrations below 0.5 M%. The Br_2 concentration was determined visually by means of color standards.

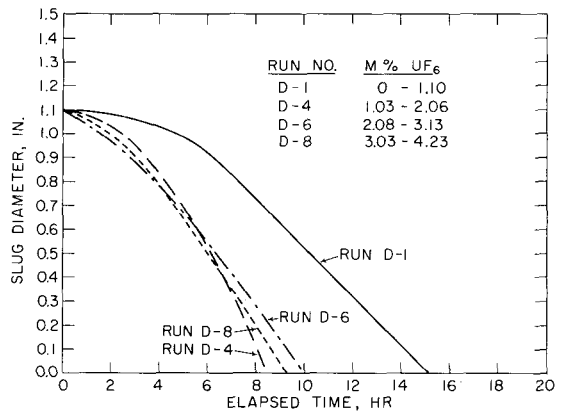

Figure 19. Slug diameter during dissolution (based on slug feeler height) for five-slug runs.

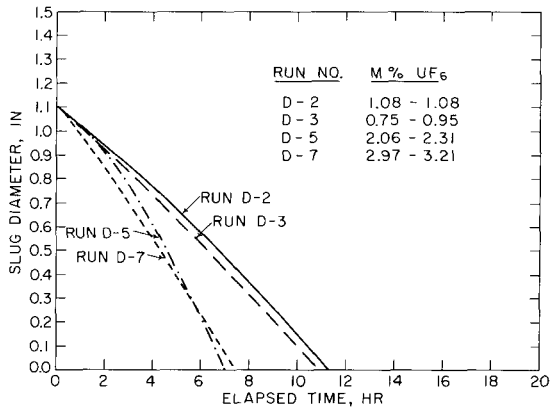

Figure 20. Slug diameter during dissolution (based on slug feeler height) for one-slug runs.

All nine runs were made at 120°C at a flow rate of 44 gpm through the dissolver and at a total pressure high enough (100 to 180 psig) to suppress boiling at the slug surfaces.

The heat data were used for determining dissolution rates. After the first run, it was found that when the slugs were expected to be 50% dissolved, based on slug diameter and equal longitudinal and radial penetration rates, they were actually 80% dissolved according to the heat data. This difference indicated that preferential attack occurred, and that it was largely longitudinal, because the slugs had to be considerably shorter to settle to the plane of the support plate as soon as they did. Preferential end attack had previously been observed in laboratory studies on similar

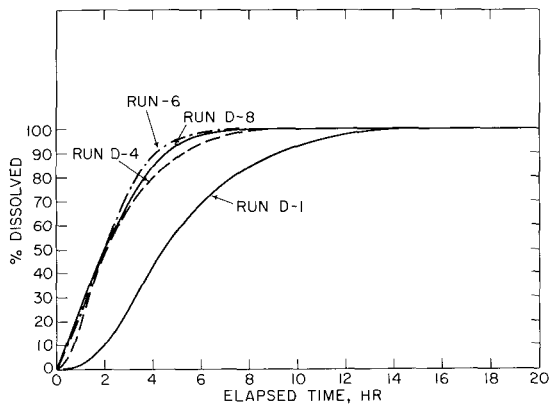

Figure 21. Amount of U dissolved (based on integrated heat) for five-slug runs.

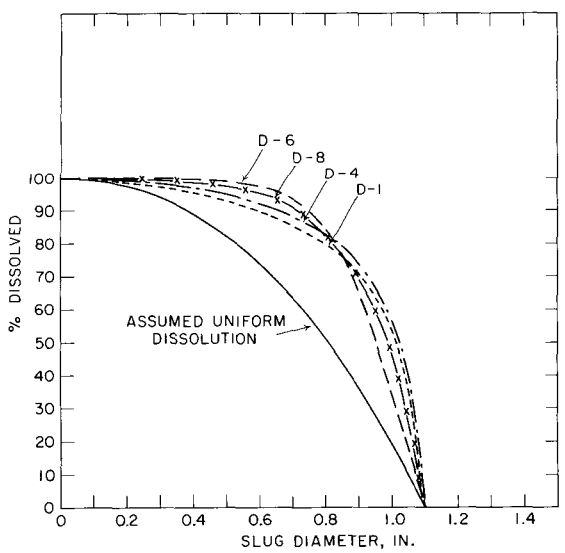

Figure 22. Characteristic dissolving of 4-in. U slugs in BrF_3 for five-slug runs.

slugs. The ends were penetrated in a rough conical-shaped pattern and the central core was porous. The slug was 92% dissolved and had a diameter of 0.48 in. For Run D-1, a slug having the same diameter was 93.5% dissolved.

It was later observed that the dissolution time for five-slug runs was greater than that for one-slug runs; hence an effect related to the local solution velocity must have existed. It was also evident that the manner in which the last 20% of a slug dissolved was subject to variation; therefore, the time for 80% dissolution was used for comparison.

The plot of slug diameter vs time for five-slug runs is shown in Figure 19, and for one-slug runs

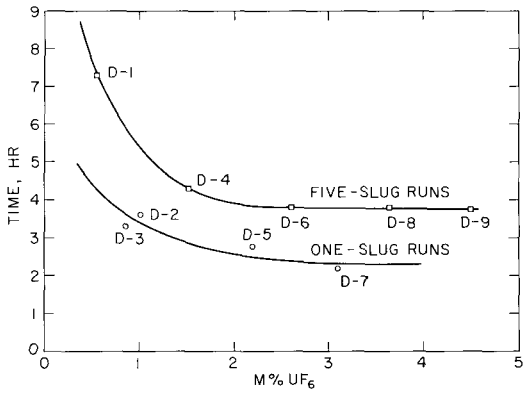

Figure 23. 80% Dissolving times (based on slug diameter and characteristic curve D-1) of BNL U slugs in BrF_3 at 250°F as related to M% UF_6.

in Figure 20. During Run D-1 the radial penetration rate gradually increased, along with the UF_6 and Br_2 concentrations, for the first 6 hr of dissolution and then remained constant at a value of 0.050 in./hr. The largest change in slope occurred in Run D-1, the catalytic effect of the reaction products being presumably the greatest. Since the Br_2 concentration was maintained at a much lower value in Run D-2, and the UF_6 concentration increased only slightly, it was shown that "catalytic" effect was mainly due to UF_6.

The rate of dissolution based on the heat data from five-slug runs is shown in Figure 21. The initial dissolution rate in pure BrF_3 (Run D-1) was very low, but as the UF_6 concentration increased, the rate rapidly accelerated to a maximum value at 3.25 hr, and then decreased because of reduced surface area. The initial slope of the other curves shows that the catalytic effect is reduced as the UF_6 concentration increases.

The relation between % dissolved and slug diameter is shown in the characteristic dissolving curves in Figure 22. The separation of the curve for equal longitudinal and radial penetration rates from the others shows the extent of preferential end attack. The irregular change of end attack from run to run was probably due to the particular slug packing arrangement and the fact that the probe measured the greatest slug rather than the average.

The time for 80% dissolution is related to the UF_6 concentration in Figure 23 for both classes of runs. The curves are based on the characteristic dissolving curve for Run D-1 and on the average

UF_6 concentration for each run. Compensation for the dilution effect introduced by the relatively high BrF_5 content during Runs D-6 and D-8 did not significantly affect the curve shape. In the five-slug runs, the effect of UF_6 on the dissolving time was very great in low concentrations and negligible in concentrations greater than 2 M%. The curve for one-slug runs was similarly drawn; the faster dissolving times indicate that the liquid streaming through the support plate holes may result in higher local dissolution rates for slugs resting on the plate. The upper slugs were subject to lower velocities and probably dissolved more slowly as indicated by the shallower initial slopes of the slug diameter curves for five-slug runs (Figure 19) compared with those for one-slug runs (Figure 20).

The manner in which a packed bed of slugs will dissolve in continuous operation was most closely approached in the five-slug runs, and the process information of importance in planning continuous runs was the effect of UF_6 concentration on dissolution time. This relationship for unirradiated BNL slugs at 120°C is shown for various percentages of dissolution in Figure 24. The time for 100% dissolution is based solely on heat data; whereas the other curves were based on slug diameter measurements used in conjunction with the heat data in order to reduce the variations introduced by each.

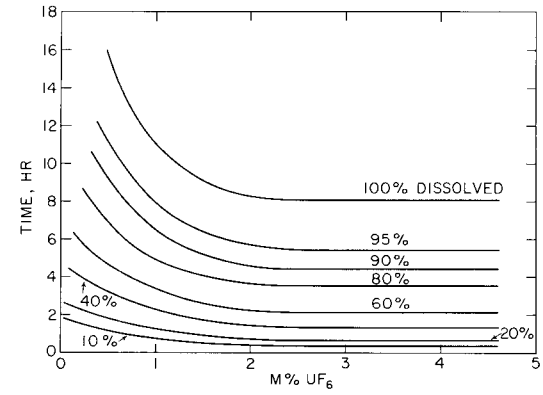

Figure 24. Partial dissolving times vs M% UF_6 at 250°F for BNL U slugs 1.1 in. in diameter and 4 in. long. (Based on Runs D-1, D-4, D-6, and D-8. For all four runs data from Figures 19 and 22 were used; for Run D-1 also data from Figure 21.)

Conclusions

The results of the eight pilot plant runs show that the slug dissolution time was approaching a constant value of 8 hr at UF_6 concentrations above 2 M%. Thus in continuous operation at the nominal addition rate of two slugs per hour, "steady state" conditions would be reached in 8 hr, and the dissolver would contain 16 slugs in various stages of dissolution. In view of this favorable reaction rate, the dissolver could readily accommodate sufficient metal to dissolve 6 to 8 slugs per hour and still have reserve heat exchanger capacity for emergency use.

On the basis of the limited results obtained, it is believed that a fluoride volatility pilot plant can be designed, constructed, and operated on the principles of continuous dissolution, evaporation, and distillation. Satisfactory equipment and instrumentation components were proven in operation with interhalogen solutions at the design temperatures and pressures.

Future Program

As mentioned previously, a proposal was submitted to the AEC for reconstruction of the pilot plant in a new building, and the pilot plant is now being dismantled. Laboratory-scale studies on uranium ignition and alloy fuel element dissolution have been planned. The ignition studies are related to the dissolver accident of May 15, and the dissolution studies had already been planned to determine the feasibility of using BrF_3 solutions for other fuels.

Fission Product Utilization

GAMMA IRRADIATION SERVICE

During the past quarter the following gamma sources were shipped:

To Whom	Type	Total Curies
Dept. of Agriculture (Hawaii)	8 Flat	480
Naval Powder Factory	Standard tubular	1330
Cities Service Co.	6 Flat	4800
du Pont	Standard tubular	1160
Dept. of Agriculture (Orlando, Fla.)	8 Flat	416
Pennsylvania Salt Mfg. Co.	Standard tubular	1440
General Electric Co.	Standard tubular	1000

The following sources were discharged from the reactor:

Cobalt No. 43	Flat	General Electric Co.
8 Flat	Flat	Dept. of Agriculture
1 Flat	Flat	Gamma Service

The following sources were inserted into the reactor:

Cobalt No. 49	Standard tubular	Mellon Institute
Cobalt No. 51	Standard tubular	B.F. Goodrich Co.

Three small tubular sources, one allocated to Minnesota Mining & Mfg. Co. and two to the AEC, were found to have defective casings. These were sent to Oak Ridge for recanning in stainless steel.

The following have made use of the gamma irradiation facilities during the past quarter:

OFF-SITE USERS

Socony Mobil Oil Company, Inc.
American Lecithin Company, Inc.
B.F. Goodrich Company
Picatinny Arsenal
Mellon Institute
Radiation Corporation of America
U.S. Naval Shipyard
Ruskin Research Institute
Rohm and Haas Company
Olin Mathieson Chemical Corporation
Fairchild Camera and Instrument Corporation
Princeton University
Aeroprojects, Inc.
Glenco Corporation
The Texaco Research Center of The Texas Company

ON-SITE USERS

Nuclear Engineering · Chemistry · Biology · Physics

Income from off-site work was $12,656; income from on-site work was $18,517.

FOOD IRRADIATION REACTOR STUDIES

Twenty runs have been completed in the slab and drum irradiators described in the previous quarterly report. About 70 items of data on dose distribution through various simulated food packages were taken per run. These data are now being evaluated.

Corrosion studies have been carried out on type 316 stainless steel in indium sulfate solutions of varying compositions at reflux temperatures. In all cases 0.5 wt % H_2SO_4 was present to preserve the chemical stability of the sulfate solution. Corrosion was found to be severe, but was the least for 15 wt % indium sulfate. Inhibitors reduced corrosion from 0.005 ipy to 0.002 to 0.003 ipy. Further study of 316 SS vs an inhibited sulfate solution at 70°C gave corrosion rates of the order of 0.00002 ipy. At 70°C, the proposed operating temperature of the FIR, 50 wt % indium sulfate solution with 0.5 wt % H_2SO_4 was found to exhibit acceptable corrosion rates on 302 and 316 SS; at 100°C these same systems showed a 1000 times greater corrosion rate.

Tests with indium nitrate in nitric acid at 70°C also give corrosion rates of the order of 0.00002 to 0.0003 ipy. Corrosion in this system at reflux temperature increases by a factor of less than 10. Current work involves the determination of a corrosion-time curve for the system 316 SS vs a solution containing 375 g indium (as nitrate) and 55.4 g nitric acid per liter of solution at 70°C [this solution is approximately 50 wt % $In(NO_3)_3$ and 5 wt % HNO_3].

The effect of prolonged gamma irradiation of this nitrate solution in the presence of type 316 SS at 70°C was investigated. Up to a total dose in the range of 140×10^6 rad (delivered at 2×10^5 rad/hr over a month), no evidence of excessive solution deterioration was observed. A slow initial increase in radiolytic gas pressure was observed, but this approached a fairly insignificant equilibrium value (6 to 8 psig) in the sealed container used in this experiment. In this experiment no enhanced corrosion of the stainless steel was observed.

A few simple in-pile irradiations were conducted to observe the effect of reactor radiations on the corrosion of 316 SS in the nitrate solution. Although these tests were far from conclusive, there was evidence to the effect that a corrosion rate in excess of that measured in the absence of such radiation might be encountered.

During the course of the determination of the time-corrosion behavior of type 316 SS in the nitrate solution, some instability of the solution has been noticed. A finely divided white precipitate appears after about 60 days at 70°C and after 7 days at reflux temperatures. This precipitate is thought to be the hydrolytically formed indium hydroxide. The same type of behavior has been subsequently noticed with indium sulfate solutions. The true identity of these precipitates, as well as the purity of the starting salts, is being investigated on the basis of their x-ray powder diagrams.

RADIATION RESEARCH STUDIES

Graft Copolymers

POLYETHYLENE-STYRENE. Further work has been done on the grafting technique which involves the pre-irradiation of a polyethylene polymer film in air or vacuum, and the addition of uninhibited styrene monomer. When the irradiations are performed in air the subsequent grafting process is favored by decrease in irradiation temperature, increase in dose rate, and increase in temperature of monomer addition. If the irradiations are performed in vacuum, the grafting process is affected in a similar manner except that higher grafting rates are favored by addition of monomer at lower temperature. The temperature range investigated was approximately 0° to 65°C. These results are consistent with the thesis that when irradiations are performed in air, peroxide links are formed which later decompose to peroxy free radicals which initiate graft copolymerization. Irradiation in vacuum produces stable free radical sites on the polymer which act as the loci for polymerization.

The shape of the grafting rate curves suggests that in the air irradiated case trapped free radicals may also be functioning as grafting sites.

Preliminary results on the effect of crystallinity indicate that the grafting process is more rapid with polymers of lower crystallinity.

RUBBER-STYRENE. Four different types of rubber (Hevea, Neoprene W, Paracril B, and Gr-S 1500) were swelled with styrene monomer and irradiated for various doses up to 15 megarad. The amount of styrene in the copolymer increased with exposure to about 60 to 70% in all cases at 15 megarad. (The products were highly cracked because of prolonged contact with the benzene solvent used to extract homopolymers of styrene, except in the case of Hevea rubber.) The shapes of the grafting curves were generally similar, all S-shaped, the major difference being in the length of the induction period. The swelling index (ml benzene/g sample) decreased with dosage for all series except the Neoprene, for which the swelling first increased and later decreased.

Radiation Catalysis

The dehydrogenation of cyclohexane was studied at 475° over alumina-molybdena catalysts. No significant difference was detected in the rate of dehydrogenation to benzene with unirradiated catalysts and with catalysts which had been irradiated for periods of up to 50 days in the BNL reactor at neutron fluxes of about 3×10^{12}, or with catalysts irradiated with a gamma dose of 50 megarad. It is quite possible that any radiation-induced catalyst changes were annealed out because of the high temperature at which the reaction was studied.

Attempts to detect radiation-induced changes will be extended by using electron magnetic resonance determinations and rates of conversion of *para* to *ortho* hydrogen. Because these measurements can be made at low temperature, a greater possibility should exist for detecting any change due to irradiation.

Comparison of Radiation Sources

The study of the efficiency of various types of radiation sources mentioned in the last report has been delayed because of increased emphasis on other projects.

Solid State Polymerization

It was reported last quarter that a detailed examination of gamma irradiated acrylamide failed to show the presence of any birefringence in the polymer product. This study has been extended to the following monomers, all of which are crystalline: methacrylamide, N-methylolacrylamide, N,N-methylenebisacrylamide, vinyl stearate, potassium acrylate, N-vinylcarbazole, and hexamethylcyclotrisiloxane. Each of these monomers was given an exposure of 100 megarad, and the products were examined for birefringence. In all cases except that of N-vinylcarbazole, there was no birefringence or merely strain birefringence. Appreciable birefringence was observed in the N-vinylcarbazole, but this proved to be due to unreacted monomer. Future study will be directed to explaining the failure of the polymer to be oriented and the fact that the crystals did not crack as might have been expected from the strain imposed by the volume change occurring during polymerization.

Fuel Element Dissolution Studies

Experimental work on aqueous head end processing of zirconium and Zircaloy containing fuel elements has led to an improved process, the Sulfex-F process, in which sulfuric acid with the addition of a small amount of HF is used as the

dissolution medium. The HF reduces the volume of the process fluid, eliminates sulfur formation, and minimizes to some extent the problem of the material of construction of the dissolver. A bench-scale dissolver of Hastelloy B has been constructed, and several runs on Zircaloy containing fuel elements have given dissolution rates > 300 mg/cm^2/hr. Experimental work is in progress on the chemical engineering aspects of the Sulfex-F process, the corrosion rate of promising dissolver construction materials, the removal and recovery of excess sulfate ion by Pb precipitation and electrolytic reformation, and the solvent extraction of uranium from sulfate containing systems. Reviews of aqueous head end treatment with details of the Sulfex-F process and of aqueous processing of other fuel elements from the Power Reactor Demonstration Program are given in BNL 3334, July 1957.

Waste Processing Development Studies

ENTRAINMENT. A 6-in. glass column for studying the entrainment of liquids in vapor streams has been constructed, and several test runs have been made. Some difficulty was encoutered in attempting to keep the column isothermal. Installation of a voltage regulator and an increase in condenser surface have improved this condition and have resulted in an increase in the range of boilup rates.

Runs are to be made with a standard NaCl solution. Preliminary analytical procedures with a flame photometer have sensitivities of $\pm 1\%$ at concentrations of 0.01 ppm NaCl. Attempts will be made to detect NaCl by neutron activation analysis.

XE-KR REMOVAL AND RECOVERY. For the past several months a research program has been in progress for developing an absorption-stripping system for removal and recovery of Xe and Kr from reactor and fuel processing plant purge gas streams on a continuous basis. The equilibrium solubilities of Xe, Kr, A, He, N_2, O_2, and air have been measured in various solvents. In general, the data show that the less the polarity of the solvent, the greater the solubility of the noble gas. Also, the heavier the noble gas, the greater the solubility in a particular solvent. The longer-chain saturated hydrocarbons (i.e., *n*-heptane and higher) appear to have appreciable capacities for Xe, of the order of 2 to 3 cc Xe per cc liquid solvent at room temperature and 1 atmos total pressure. Amsco 123-15, a kerosene base solvent, has been selected for further engineering studies because of the following characteristics: selectivity, relatively high flash point, low vapor pressure, relatively good radiation stability, and low cost. Table 8 summarizes the solubilities of various gases in liquid Amsco.

Table 8

Solubility of Gas in Liquid Amsco 123-15 at 15°C and 1 Atmosphere Pressure

Gas	Temperature, °C	cc Gas per cc Liquid
Xe	24	2.10
Kr	29	0.64
He	30	0.0
N_2	20	0.01
O_2	20	0.19

Measurements indicate that the solubilities of Xe and Kr in Amsco decrease at higher temperatures, so that the noble gases can be recovered from the solvent.

By a tracer method of analysis, with the use of pile-irradiated natural Xe and gamma scintillation counting, it has been possible to measure the equilibrium solubility of Xe in a gas mixture containing 1000 ppm Xe in N_2. The Henry's law constant has been found to be of the same order of magnitude at the low partial pressure of Xe as at 1 atmos. It is planned to establish equilibrium values for the system Xe-N_2-Amsco at lower concentrations of Xe, at various temperatures, and in the range at present found at processing plants.

Several preliminary runs with a 1-in.-diameter by 3-in.-high absorption column packed with a ¼-in. Raschig ring, and a feeding stream containing 969 ppm Xe in N_2, have indicated an H.T.U. of approximately 0.33 ft. With the help of the active tracer method of analysis, the variation of H.T.U. as a function of column capacity is being further investigated.

With the absorption column mentioned above and a mass spectrometric method of analysis, a preliminary run with a stream containing 5700 ppm Kr in N_2 gave an H.T.U. value of 0.74 ft. It is planned to determine equilibrium values for the system Kr-N_2-Amsco at concentrations below 500 ppm in the gas phase, and to establish H.T.U.

values as a function of the capacity of an absorption column, by using Kr^{85} in a radioactive tracer method of analysis.

Ultimate Waste Disposal

CORROSION STUDY ON EQUIPMENT FOR CALCINING ZIRCONIUM WASTES

A 500-hr corrosion experiment in which 50 alloy metals were exposed to actual operating conditions in the double kiln calciner was completed. All the specimens of the high temperature calciner have been mounted, polished, and lapped, and half have been etched and photographed. Several etching experiments were made to determine the amount of metal removed in varying lengths of time in order to make sure that the areas of the shell and core were not appreciably changed by etching. The maximum error resulting from etching was found to be $<1\%$ and in agreement with the error involved in the planographic measurement and the original machining of the specimens to 1/10,000 in.

SINGLE KILN CALCINER

Several new pieces of equipment have been designed to simplify the two-drum calciner so that operation as a single kiln unit may be studied. Previously some caking occurred in the pipes and equipment used to transfer powder from the first to the second kiln. In the one-kiln system this equipment will be eliminated and replaced with a simple powder settling chamber and collector.

A new absorption tower for the off gases has also been designed, and specimens have been ordered so that a preliminary determination of corrosion at the gas-liquid interface can be made.

A new solution feeder has also been designed, and drawings have been sent to the shop for fabrication.

The new equipment has been designed with the thought in mind that it will be used with a larger drum equipped with the more refined seals which are being considered for future calciners.

LONG CLAY COLUMN EXPERIMENT

Preparations are being made for a 15-ft clay column experiment with Sr^{90} as a tracer. The maximum column length used to date has been 4 ft. With the exception of Ru, which in anionic or nonionic form is not removed by the clay, the chief problem is adsorption of Sr. In this experiment 44 l feed solution containing 2 C Sr^{90} will be used. The equipment has been set up in the Hot Laboratory. Three 5-ft lengths of ½-in.-i.d. glass pipe connected in series will contain the clay columns. All tanks, tubes, and valves are stainless steel and are connected with Swagelok fittings.

LEACHING STUDIES

The purpose of this work is to determine the pickup of Sr by clay from a synthetic leach solution with respect to DF and volume. The leach solution is representative of what would be found in solution after leaching Al_2O_3 or ZrO_2-Al_2O_3 with pH 3.0 and pH 1.0 HNO_3, respectively, and contains 1.5×10^{-3} M Al^{+++}, 4.6×10^{-5} M Sr^{++}, and 7.0×10^{-5} M Cs^{+}, adjusted to pH 3.0 with HNO_3. The optimum pH for the clay is 4.5; therefore a second solution was prepared with the above concentrations of Al^{+++}, Sr^{++}, Cs^{+}, and acid, but neutralized from pH 3.0 to pH 4.5 with NaOH. Three 1-ft columns in series were set up for each of the two runs, and the solutions passed through at a rate of 2 ml/min. The solutions were spiked with Sr^{90}, and the flow continued until the first column was saturated as determined by $C/C_0=1$. The level of activity used was 10^{-5} dis/min/ml. The results of the pH 3.0 run showed a DF of $>10^{-3}$ from the system at 150 column volumes while the first column has a C/C_0 of 0.73. At saturation of the first column the DF from the system was 88 at 210 column volumes.

To overcome the effect on increasing pH of the effluent caused by the exchanged Ca and Mg from the clay, a hydrogen form of the clay was prepared by soaking the clay in 0.5 N HNO_3 and then washing with 0.1 N HNO_3 and water. The clay was then dried and extruded in the usual manner. A synthetic leach solution of pH 3.0 with a Sr^{90} tracer was passed through a single column. The results showed saturation of this column with Sr at 223 column volumes. Saturation of a single column of regular clay in the run with pH 3.0 leach solution occurred at 322 column volumes, while the pH 4.5 run showed saturation at 626 column volumes.

A column of vermiculite (Zonolite Co. product) was prepared, through which a solution contain-

ing 0.01 N Cs and 0.01 N $Sr+Sr^{90}$ tracer was passed. A rather rapid break-through of Sr was observed. It had been reported verbally by Dr. Amphlett (Harwell) that some vermiculites show a specificity for Sr. An attempt will be made to obtain some of this vermiculite from Harwell.

A series of experiments was started to determine the leaching characteristics of Al_2O_3 and ZrO_2-Al_2O_3 at elevated temperatures. Al_2O_3 and ZrO_2-Al_2O_3 are being leached in distilled water at 100°C. Initial results indicate that less than 3% of the Cs is removed from ZrO_2-Al_2O_3 with boiling distilled water, but 30 to 86% is removed from Al_2O_3. The inconsistency of results may be due either to surface adsorption on the oxides or to formation of colloids in the system.

Boiling water removes 30% of the Sr from ZrO_2-Al_2O_3, and about 70% from Al_2O_3. In order to obtain improved Cs removal, an attempt was made to use pH 3 HNO_3 at the boiling point as a leaching medium, but the acidity could not be maintained because the HNO_3 decomposed to oxides of nitrogen. Accordingly, a test was set up to compare the leaching action of pH 3 HNO_3 and pH 3 HCl at room temperature. Both the acids yielded approximately the same results; therefore, a series of experiments was begun with pH 3 HCl at boiling temperature as a leach. Scattered initial results indicate a removal of Cs from ZrO_2-Al_2O_3 in the range of 10 to 50%.

An investigation will be made to determine the effect of calcining temperature on the surface adsorption characteristics of the oxides.

FUEL ELEMENT DISSOLUTION STUDIES

A study was made to investigate the possibility of catalyzing the dissolution of fuel element materials in phosphoric acid in conjunction with the work on sulfuric acid. Results are given in Table 9.

The final product resulting from the dissolution of the PRDC element in the H_3PO_4-HF system was a black solution (possibly colloidal) which gave a black, hydrous precipitate upon the addition of water. A small amount of oxidizing agent (HNO_3, $KMnO_4$) was added to the solution, which then became a clear green, and no precipitate occurred upon the addition of water. The amount of oxidizing agent necessary may be equivalent to the amount of Mo in the solution.

The product obtained from the dissolution of Nb-U alloy in H_3PO_4-HF was also a black liquid, which gave a clear green solution upon addition of an oxidizing agent.

In the case of the dissolution of thorium oxide (this material was obtained from a thoria refractory crucible) the product was a clear, colorless solution. Addition of water to give a 2:1 dilution produced a white precipitate.

A brief study was made of the dissolution of Zircaloy-2 in the concentrated H_3PO_4-HF system. The dissolution rate was low, and the sample became coated with a thick white precipitate which stopped further action.

It is quite possible that H_3PO_4-HF solutions may be used in conjunction with H_2SO_4-HF solutions in equipment designed for the latter.

The lead dissolver has been pretreated by refluxing 55% H_2SO_4 solution in it for about 16 hr. Dissolution experiments with H_2SO_4-HF solutions following this pretreatment have produced almost clear solutions, whereas without pretreatment a precipitate (probably lead sulfate) was obtained.

Several experiments were performed to investigate the decrease in the dissolution rate of Zircaloy-2 in the H_2SO_4-HF system as the re-

Table 9

Dissolution of Fuel Element Materials in 85% H_3PO_4, 0.26 M in HF, at 170°C Reflux Temperature

Material	Volume, ml	Amount dissolved, g	Time, min	Rate, mg/cm²/hr
PRDC element (0.004-in. Zr clad), 10 wt % Mo-U alloy	100	9	75	2000
Nb-U alloy	100	3.4643	15	1700
Thorium oxide	75	7	135	300*

*Apparent surface area of porous material.

Table 10

Effect of $Zr(SO_4)_2$ on Dissolution Rate of Zircaloy-2 in 55% H_2SO_4, 0.26 *M* in HF (100 ml Solution at Reflux Temperature for 15 min)

Zr added initially as $Zr(SO_4)_2$, g	Zircaloy-2 dissolved, g	Average rate
0	2.0358	540
1.0	1.7681	470
2.64	1.1402	297

action proceeds. Results indicate that the decrease in rate is due to the increasing concentration of Zr in solution, which apparently results in a decrease in the amount of free fluoride available for attack on the Zircaloy sample. An experiment was performed in which various amounts of the salt, zirconium sulfate, were added to fresh solutions and the dissolution rate determined. Results are given in Table 10.

FLUORIDE REMOVAL

Because of the decrease in dissolution rate as more Zr goes into solution, it will probably be necessary to double the amount of HF in order to maintain adequate over-all rates. Therefore, it will be even more desirable to remove the fluoride in so far as possible from the final solution. Several experiments have shown that it is quite possible to remove fluoride by volatilization either as HF or H_2SiF_4, although complete removal has not yet been obtained.

FEED PRETREATMENT

Since one of the objectives in this work is to develop head end dissolution steps compatible with present solvent extraction processes, it would be highly advantageous to remove the bulk of the sulfate and replace it with nitrate ion prior to extraction. Waste handling would also be materially simplified. One of the simplest methods, chemically speaking, would be precipitation of Zr and U as the hydroxide and diuranate, respectively, with ammonia, followed by dissolution of the precipitate with nitric acid. Initial studies gave the following results:

1) U is precipitated quantitatively by ammonium hydroxide from a zirconium sulfate solution.

2) The resultant precipitate of zirconium hydroxide and ammonium diuranate is completely soluble in 6 *M* HNO_3.

3) When Zr and U were dissolved in a chloride system, 99% of the Cs remained in the filtrate upon precipitation with ammonia. If this occurs in the sulfate system, it may be of significant interest.

4) Sulfuric acid and ammonium hydroxide may be recovered easily from the filtrate by means of electrodeionization cells, the use of which is feasible in this instance because the short half-life, high specific activity fission products (Zr, rare earths) remain with the precipitate and are absent from the filtrate. While the recovery of these reagents would not be economically competitive with the purchase of fresh acid and base, it would be economically attractive because it would eliminate a source of radioactive waste.

The process and equipment development for a precipitation step in which enriched uranium drops out of solution presents many serious problems, most of them associated with criticality. In this instance, however, the end might well justify the means.

Possible designs for such a step include 1) in-line precipitation coupled with continuos discharge centrifuges, in which the amounts of uranium would be limited to an always safe mass, and 2) slab type precipitation vessels, where an always safe geometry is maintained. Work in the future will be done on both the chemistry and process design in order to determine feasibility.

Scientific Personnel

O.E. Dwyer, *Head,*
Chemistry and Chemical Engineering Division
C. J. Raseman, *Assistant to Head for Engineering*
F. Maslan, *Coordinator of LMFRE Program*

CHEMISTRY GROUP

R.H. Wiswall, *Leader*

S. Bookless
F. Bloch
B. Chu (summer visitor)
J. J. Egan
W.S. Ginell
R. J. Heus
H. Littman (summer visitor)
D.B. Marsland
D.E. Neil
J. Speirs

CHEMICAL ENGINEERING GROUP

Engineering Analysis Section (including Heat Transfer)

O.E. Dwyer, *Acting Leader*

A.M. Eshaya
F. Maslan
A. Friedland

Processing Section

F. Hill, *Supervisor*
H. Susskind, *Associate Supervisor*

G. Farber
L.E. Kukacka
L. Green
W.E. McNulty
F. Hoffmann
F. Salzano
H. Katz
E. Wirsing

Operations Section

R. J. Isler, *Supervisor*
C.H. Waide, *Assistant Supervisor*

W. Hansen
W.J. Johnson
W.F. Kenney
G.A. Schoener
J.H. Klein

Volatile Fluoride Project

G. Strickland, *Project Leader*

F. Horn
R. Johnson

CHEMICAL TECHNOLOGY GROUP

B. Manowitz, *Leader*

Radiation Research Section

D.S. Ballantine, *Supervisor*

G. Adler
A. Glines
P. Colombo
D. Metz

Gamma Irradiation Service Section

O.A. Kuhl, *Supervisor*
L. Galanter

Waste Processing Development Section

B. Manowitz, *Acting Supervisor*

C. Pierce
M. Steinberg
D. Richman
S. Zwickler

ULTIMATE WASTE DISPOSAL GROUP

L.P. Hatch, *Leader*

A. Abriss
J.J. Reilly
R. Domish
E.J. Tuthill
W.H. Regan

Mechanical Engineering Division

4-in. Utility Test Loop

The main purpose of the 4-in. utility test loop is to test equipment of the size to be used in the LMFRE, such as pumps, valves, heat exchangers, and instrumentation. In the primary section of the loop the molten U-Bi eutectic will be heated by an oil fired furnace and pumped through 4-in. pipe by a centrifugal pump, and will transfer its heat to the secondary section. In the secondary section the molten Bi will be heated in the heat exchanger, pumped through 4-in. pipe by a centrifugal pump, and cooled by an air blast.

During the report period the hold placed on work on Bi containing components was released from Catalytic Construction Co., Griscom-Russell, Byron-Jackson, and Foster Wheeler.

Breakdowns of charges for releasing the hold on Crane Co. and Chapman Valve Manufacturing Co. have been received and are being reviewed. The hold on all valves should be released during October. The breakdown of charges for releasing the hold on Westinghouse has not been received but is expected in October.

Meetings were held with Babcock and Wilcox personnel concerned with the 4-in. loop. On August 19, 1957 representatives of the company's design, service, and materials sections were given a description of the loop, and then the various components of the loop were discussed. The company's role in the inspection of loop components was clarified. When agreeable to the manufacturer, Babcock and Wilcox personnel will have an important part in inspecting Bi containing equipment.

On September 19, 1957 representatives of the Babcock and Wilcox system and components section met with Brookhaven personnel and company personnel in residence at the Laboratory to discuss changes which would be required to have 4-in. loop operation simulate the Phase I LMFRE design. Recommendations made subsequent to this meeting are under consideration.

R. Schomer of Babcock and Wilcox has requested that the fluid in the secondary section of the 4-in. loop be changed from Bi to Na. Consideration of this change has been shelved pending results from the study of the Na-Bi reaction and other hazards connected with the use of Na.

PRESSURE TRANSMITTER TEST

Bench testing of the Taylor and the Manning, Maxwell and Moore NaK-filled, diaphragm-sealed pressure transmitters was completed during this report period. The tests were satisfactory, and further testing was carried out in Loop H-1. The loop tests are described in the section on Loop H-1.

At the time the bench tests were discontinued, the transmitters had been cycled as shown in Table 11.

Table 11

Transmitter	Cycles	Pressure range, psig
Taylor	12,100	30 to 150
	4,011	30 to 200
	1,667	60 to 300
Manning, Maxwell and Moore	8,752	30 to 150
	1,667	60 to 300

Temperature=460°C (859°F).

HIGH SLIP MOTOR TEST

In order to determine the usefulness of a high slip motor, used in conjunction with a variable input voltage, in obtaining speed regulation of pump motors, a test stand was constructed according to a design specified by the Mechanical Engineering Division. The test results were satisfactory, and it is expected that motors of this type will be tried in Bi service.

FLANGE TEST FACILITY

A bench test assembly is under construction which will be used to determine the reliability of

flanges when subjected to temperature and pressure cycling.

High Velocity Loops 3 and 4

Originally six loops were planned in order to permit runs under a variety of conditions with U-Bi-Zr-Mg solution in both 2¼ Cr and 1¼ Cr. However, as the budget for fiscal 1958 was established, and as more information became available on the Babcock and Wilcox program, the decision was made to start with two loops, one of 2¼ Cr and one 1¼ Cr.

These loops are of the figure-eight type with a regenerative cooler preheating the cold fluid leaving the cooler by means of the hot fluid leaving the furnace. This system permits the development of a 75°C temperature difference between the hot and cold sections of the loop without excessive heat input on the furnace or output on the cooler.

The loops are constructed of ¾-in. schedule 40 alloy steel pipe, and the pump is capable of producing a flow velocity of up to about 12 ft/sec in this pipe size. The furnaces are of the conventional resistance-wire wound clamshell industrial type, electrically heated, of about 14-kw capacity. The exchanger (regenerative interchanger) is a shell and tube type with U tubes and shell. The cooler is a longitudinally finned alloy steel tube, cooled with air. The pump is a sump type, located at the top of the loop in such a manner that the free liquid surface existing at the top of the loop is in the pump sump. The loops are equipped with resistance type heater wires for preheating, and have a dump tank with emergency dump valves. The instrumentation is simple, its purpose being only to monitor operating conditions and to cause automatic shutdown in the event of certain emergency conditions.

All materials are on order, and construction will begin during the next quarter. The loops will be located in the metallurgy building.

Radiation Loop 1

During the report period work continued on all phases of the Radiation Loop, which is a figure-eight loop designed to operate at 75°C ΔT between the hot section (located in the BNL reactor) and the cold section, outlet of the cooler, located external to the reactor. The Bi-U^{235}-Zr-Mg fuel solution flows through the induction heated furnace and then to the hairpin loop and hot test section in the reactor. Final heating takes place in the reactor where 4 to 6 kw of fission heat is released. The fluid then flows through the hot side of the interchanger, through the cooler, cold test section, sampler, and pump, and back to the cold side of the interchanger and to the furnace.

The loop is made of 2¼ Cr – 1 Mo alloy steel, and contains ½-in. and ¾-in. standard weight pipe. The furnace is 60-r ac induction heated. The exchanger is a shell and tube type; the cooler is made of finned tubing; and the pump is a vertical centrifugal sump type so designed that in the event of pump failure the loop drains to the sump automatically without the need for any valves or other devices. Because the loop operates in the BNL reactor, it requires considerably more complicated instrumentation to provide for shutdowns of the reactor or shutdowns of the loop with the reactor running. The entire loop is radioactive and must be shielded with concrete blocks.

Various samples of alloy steel and graphite are located in the hot high flux region in the reactor, and others are located in the cold delayed neutron flux in the out-of-pile section.

The loop will have one pump, with a spare pump ready for installation if it should fail. Provisions have been made for remote installation of the pump. The first pump has already been successfully tested in Loop H-1.

Floor assembly of the loop is expected to begin in the reactor building during the next quarter.

EXPONENTIAL EXPERIMENT

Work has continued on the design of the appurtenances for these experiments including the parts of the source reactor and various rolling tables, control rod drives, shielding, etc., to make a complete operating facility. In addition, work was done on design and manufacture of a mixing mill for use by the fabricator of the exponential fuel foils.

Loop N

The contract for design and construction of this loop was placed with Catalytic Construction Co.,

and design is well under way. Manufacture of some components has begun. The Mechanical Engineering Division did liaison work in getting the job started, and checked the flow diagrams, piping, and vessel drawings.

PUMP TEST LOOPS

Layout of Loop H-2 was completed, and construction was begun. It will be used first to test a Findlay electromagnetic pump. The loop is made of ¾-in. and 1-in. alloy steel pipe for a capacity of about 10 to 20 gpm at 30 ft head.

MAGNETIC DRIVE

Exploratory work which was completed indicated that canned permanent magnet drives might be useful for driving pumps in hermetically sealed systems. A 10-hp drive is being designed for use on the salt pump on Loop N.

Hot Laboratory Division

L.G. STANG JR., Head, P. RICHARDS, Associate Head, G. SEARLES, E. DANIELS

Long-term tests of the Y^{90} milking system continue to be satisfactory. A simple rapid method has been found of assaying for Sr^{90} contamination in the milked product before administration to patients. New improved production processes now nearly completely developed will permit scaled-up production of Mg^{28} and F^{18}. The new I^{132} generator was further studied and put into satisfactory routine production. The alumina (used in this generator) forms the basis of a new improved purification process for the parent Te^{132}. A search for O^{20} by previously untried techniques has been started.

Development work in support of the radiochemical analysis service was done on colorimetric procedures for iodide, Cu, and Mg; conditions for the quantitative extraction of U; spectrographic procedures for Cu, Ta, and various corrosion products; a new method of assaying $BiCl_3$; and continued study of the polarography of U and Bi. Reports on incremental polarography, chronopotentiometry, and the separation of Mg^{28} will be issued.

The following total quantities of radioisotopes were shipped: 1331 mC I^{132} in 26 shipments; 5470 μC Mg^{28} in 32 shipments; 220 mC I^{133} in 13 shipments; and 9 units of F^{18} (the F^{18} and one of the Mg^{28} shipments were for use within BNL).

The BNL Model 4 Manipulator was partially mocked up satisfactorily and a scaled-down version of the Model 3 Manipulator was made. Design was begun on the new Metallurgical Cell.

Radioisotope Facilities Associated With a Research Reactor. L.G. STANG JR. Presented at Inter-American Symposium on Peaceful Application of Atomic Energy, Brookhaven National Laboratory, Upton, N.Y., May 13-17, 1957.

Associated with every reactor, regardless of type and size, must be some specialized equipment or facilities for handling the radioactive material which inevitably is produced in the reactor. In the case of very small low level reactors this equipment can be quite simple; in the case of reactors designed exclusively for power production the handling operations can be more or less routine and the facilities subject to some degree of automation. However, with most research reactors equipment and facilities must be provided for performing a wide variety of operations on radioactive material.

Typical operations, which will be described, include simple problems such as opening a container of radioactive material and more complex ones such as dismantling a piece of test equipment and performing physical tests on its components or chemically purifying a particular radioisotope. The bulk of this paper will be concerned with describing equipment and facilities for doing the various kinds of work encountered in handling radioactive material produced in a research reactor.

In this type of work advance planning and flexibility are two very important cornerstones. The fruits of insufficient advance planning of even the smallest details are sloppy and sometimes even hazardous work; the consequences of inflexibility are increased costs, lost time, and outright inability to handle unforeseen problems. Throughout this paper, planning and flexibility will be emphasized with concrete examples of good and bad facilities, equipment, and practices. At the same time it will be shown how a measure of judicious improvisation and ingenuity can also keep costs down.

In addition to the above points, the more or less conventional problems of ventilation, drainage systems for handling radioactive wastes, and appropriate layout of laboratory space will be briefly discussed.

The paper will conclude with a mention of the manpower problem, pointing out that there now exists a sufficient body of "know-how" described in the literature to permit those with little previous experience in the handling of radioactive material to design and operate hot laboratories. Some assistance in acquiring first-hand experience in this sort of work can be obtained from installations

now possessing hot laboratories, and, by way of illustration, the paper will describe Brookhaven's present efforts and potential capabilities in such training.

Special Radioisotope Development

W.D. TUCKER, Section Supervisor

Development of Methods for the Production of Certain Short-lived Radioisotopes. L.G. STANG JR., W.D. TUCKER, R.F. DOERING, A.J. WEISS, M.W. GREENE, AND H.O. BANKS JR.* Presented at the UNESCO Conference on the Use of Radioisotopes in Scientific Research, Paris, Sept. 9-20, 1957.

At the Brookhaven Hot Laboratory methods are being developed for producing radioisotopes which would be useful if they were available, or available in suitable form. Examples for which procedures have been completed include Mg^{28}, I^{132}, I^{133}, F^{18}, and Y^{90}. At Brookhaven these are reactor produced. This paper will describe unpublished recent results of this work.

Mg^{28}, 21-hr half-life, is a very important radioisotope for medical research and is the only isotope of Mg with a half-life long enough for practical use as a tracer. It is produced in specific activities of about 1 mC/g with a neutron flux of about 3×10^{12} n/cm^2-sec. The Brookhaven process involves irradiating 0.01-in.-thick foils of an alloy of natural Mg with Li enriched to 95% Li^6. The nuclear reactions are $Li^6(n,t)He^4$ and $Mg^{26}(t,p)Mg^{28}$. This paper will describe theoretical considerations involved in attaining the present high specific activity and will present details of the present routine production method.

I^{132}, 2.33-hr half-life, has been produced routinely at Brookhaven for the past four years. It is supplied as fission product Te^{132} contained in a "generator" from which the daughter iodine can be "milked" conveniently, as desired. Recently a new method of milking iodine from Te has been developed that is simpler and faster and reduces the stable Te contamination in the product solution to 0.1 μg/ml. Radiotellurium contamination is less than 5×10^{-3}%. Te^{132} is placed on a chromatographic alumina column and I^{132} removed as desired by passing 0.01 M NH_3 through the column. I^{132} yields are around 65%.

Because of the high ratio of average beta energy to average gamma energy of 21-hr I^{133}, its use in thyroid therapy is being explored by medical investigators. It is in routine use in conjunction with I^{131} in double-tagging experiments. A simple process has been developed which requires less than 0.5 hr and by means of which the fission product iodines produced in irradiated U_3O_8 are separated from U and other fission products. Necessary conditions of irradiation time and cooling time to maximize the amount of I^{133} over a practical period of use are discussed. The product contains about 85% I^{133} at time of use.

The 112-min F^{18} is the longest-lived radioisotope of fluorine and is produced by the $O^{16}(t,n)F^{18}$ reaction when Li_2CO_3 is irradiated in the nuclear reactor. A recently developed process for isolating the F^{18} reduces production time from 2 hr to 1 hr and increases the yield to two mC F^{18} per g Li_2CO_3 irradiated at a flux of 3×10^{12} n/cm^2-sec. The essential feature of the process, which results in very pure, high specific activity F^{18}, involves removal of radioactive contaminants by means of a cation exchange resin.

Because of the interest in the use of Y^{90} for intracavitary irradiation, a simple process has been developed whereby a clinical technician can easily and safely milk Y^{90} from Sr^{90} with virtually no Sr^{90} contamination. The Y^{90} solution, which is carrier-free, contains less than 10^{-6}% Sr^{90}. It is obtained by elution from a cation exchange resin on which Sr^{90} has been firmly fixed.

*Present address: The Martin Company, Baltimore, Md.

YTTRIUM-90

The long-term tests of the Y^{90} milking system have continued successfully, with Sr^{90} contamination of the milked product at around 4×10^{-7}%, a satisfactorily low value.

A simple rapid method of assaying for Sr^{90} contamination in the milked Y^{90} product before administration to patients has now been been developed which appears to be satisfactory. The method consists of passing a 5% aliquot of the product through a small auxiliary detector column of Dowex-1 resin in the OH^- form. This column precipitates Y locally as $Y(OH)_3$ and allows the Sr^{90} to pass through. This sample is counted first without added absorber and then with sufficient absorber to cut out all the Sr^{90} betas; by applying a factor to the second count to correct for the decrease in Y^{90} count, the Sr^{90} can be obtained as

the difference between the first count and the corrected second count. By this method the determination of *ca* 2μC Sr^{90} in the presence of 100 mC Y^{90} appears reliable, and the detection of 0.2 μC Sr^{90} may be possible. This method is almost ready for publication.

Several high activity Y^{90} sources have been prepared for others doing experiments in connection with the parity principle. R.F. Doering

MAGNESIUM-28

The rapidly increasing demand for Mg^{28} has required development of a new isolation process which will be more adaptable to scale-up and remote operation than the present process, which involves centrifuging $Mg(OH)_2$. A process has been nearly completed based on separation of Mg from Li by precipitation with 8-hydroxyquinoline, filtration, neutralization, and extraction of the organic reagent into chloroform, which leaves the Mg in the aqueous phase in high yield.

On a Li^6 recovery process, only a nominal amount of work was possible preparatory to measuring the cross section for the $Mg^{26}(t,p)Mg^{28}$ reaction. A. J. Weiss

IODINE-133

No further development or trouble-shooting was required on this process, as production ran smoothly.

FLUORINE-18

If a sufficiently large amount of F^{18} could be produced with no increase in cost, then the shipping range of this short-lived isotope could be widened. The irradiation of enriched $Li^6{}_2CO_3$, rather than natural Li_2CO_3, offers such a possibility, the Li^6 used being recovered from the waste from the Mg^{28} production prior to recovery and re-use in that process. However, the present purification process for F^{18} could not be scaled up because of limitations imposed by personnel exposure due to the considerable handling required.

A new isolation and purification process has been devised which eliminates these limitations and hence is capable of being scaled up. The process, based on the sorption of carrier-free radiofluoride on acid-treated alumina followed by elution with dilute caustic, gives a 95% yield and a product which has less than 50 ppm of other radioactive impurities (on an activity basis).

"Super-pure" F^{18} sources are also being prepared for others doing experiments in connection with the parity principle. A. J. Weiss

IODINE-132

The previously reported new type of iodine generator utilizing sorption of parent Te^{132} on alumina was further studied. These new generators are now in routine production and are eminently satisfactory. Some points of interest which have been discovered are: 1) Neither iodide nor iodate is eluted from acidified alumina; iodide but not iodate is eluted with 0.01 *M* NH_3 from neutral or basic alumina; some iodate is eluted with difficulty with 1 *M* NH_3. 2) Elemental iodine readily disproportionates on alumina. 3) The effect of *p*H during the growth of I^{132} on the valence of the iodine thus formed is obscure; but the data suggest that at high and low *p*H approximately 75% of the iodine is formed as iodide, while at intermediate *p*H the percentage formed as iodide is only 50% or less. 4) Sodium hydroxide (0.0001 *M*) can be used in place of 0.01 *M* NH_3 to elute I^{132}. 5) Retention of Te^{132} during placement on the alumina is nearly quantitative. 6) Te carrier can safely be added to the extent of 200 mg Te per 20 g alumina; Te in greater amounts may possibly increase the Te contamination of the product solution.

Alumina has also been used as the basis for a new process for separating Te^{132} from U and mixed fission products, which, when completely developed, is expected to be simpler and more rapid than the present one involving precipitations of elemental Te and of TeO_2.

M.W. Greene, A. Murrenhoff

SAMARIUM-151

Only a nominal amount of work was possible during this period on the problem of preparing a source of Sm^{151} for trial as a radiography source. Elution from a cation exchange resin with ethylenediaminetetraacetic acid is being investigated.

R.F. Doering

OXYGEN-20

In the belief that O^{20} may have a half-life long enough to make it practical for use as a radio-

active tracer for oxygen, a search for this highly desirable isotope was begun by use of a variation not known to have been previously tried by others. LiOH enriched in both Li^6 and O^{18} will be irradiated in the reactor in the hope of effecting the $O^{18}(t,p)O^{20}$ reaction. On the assumption that the half-life will be fairly short, only short irradiation times followed by immediate direct counting will be tried at first. By means of a multi-channel pulse height anlyzer, an attempt will be made to observe the characteristic 1.63-Mev gamma of the F^{20} daughter.

S. AMIEL

Radiochemical Analysis

H.L. FINSTON, Section Supervisor, S. ADLER, C. AUERBACH, M. KINSLEY, J. FORREST, L. VEPROVSKY, E. SELLECK, T. PRACH, M. PHILLIPS, C. BACHSMITH, M. WALTERS, M. ERICKSEN, T. ISHIDA, S. BRUCKENSTEIN, J. GLICKSTEIN

A detailed procedure for the colorimetric determination of iodide has been developed. Conditions for the quantitative extraction of mg and μg amounts of U have been determined. Spectrographic and colorimetric procedures for Cu have been devised. The technique of determining Pa^{233} by scanning a solid sample with a gamma spectrometer was checked and found to be satisfactory. A method for assaying $BiCl_3$ involving precipitation of the subcarbonate has ben developed. Studies of the polarography of U and Bi have continued. Emission spectroscopy techniques for the determination of Ta and various corrosion products have been established. A colorimetric procedure for the determination of Mg has been evolved. The final reports of the three summer visitors will be published in a subsequent report.

Hot Laboratory Operations

P. RICHARDS, Group Leader, E. J. KRIEDEMAKER

SPECIAL RADIOISOTOPE PRODUCTION

J. BARANOSKY, G. WALKER, V.S. WILLIAMS

Iodine-132

Nine production runs (Nos. 67 to 75 inclusive) were made during this period. Two of the runs were made in the record time of one day each. No difficulties were encountered in the chemical processing, although on one run difficulty was experienced in transferring the active slug from the reactor to the hot lab. Although the May 15th explosion elsewhere in the building hampered radioisotope production, no shipments were delayed as a result. The following shipments were made during this period:

Customer	No. of shipments	Total nominal activity (mC)
Esso Research and Engineering Co., Linden, N.J.	8	800
V.A. Hospital, Boston, Mass.	2	11
Mayo Clinic, Rochester, Minn.	9	90
Esso Standard Oil Company, Baton Rouge, La.	4	400
Georgetown Univ. Medical Center, Washington, D.C.	2	20
Industrial Nuclear Radiation Consultants, New Haven, Conn.	1	10
Total	26	1331

Most of the 10-mC shipments were the new type of generator, which customers have received enthusiastically; no difficulties have been reported thus far and none are anticipated.

Magnesium-28

Nineteen production runs were made during this period. The following shipments were made:

Customer	No. of shipments	Total nominal activity (μC)
University of Colorado, Denver, Colo.	13	2600
State University of New York, Brooklyn, N.Y.	7	1400
Massachusetts General Hospital, Boston, Mass.	4	200
Michigan State University, East Lansing, Mich.	1	500
University of Arkansas, Fayetteville, Ark.	3	420
Merck Institute, Rahway, N.J.	1	200
Albany Medical College, Albany, N.Y.	2	100
BNL Medical Department	1	50
Total	32	5470

No processing difficulties were encountered, but some of the cans enclosing the Li-Mg alloy came

out of the reactor with bowed lids. A number of new lids were measured, and some were found to be abnormally thin. Calculations indicated that the combined temperature and gas production effects should have produced pressures of only 10 to 12 psig, which does not seem excessive. However, switching to specially made thicker lids corrected the bowing condition.

Iodine-133

Eleven production runs were made during this period without incident, and the following shipments were made:

Customer	No. of shipments	Total nominal activity (mC)
Rosewell Park Memorial Institute Buffalo, N.Y.	11	120
Sloan-Kettering Institute, New York, N.Y.	2	100
Total	13	220

Fluorine-18

A total of nine units of fluorine-18 were made during this period for use at Brookhaven.

Table 12

"F" Waste Processing
Comparative figures on waste released to the sewer for the period

	Gal	Average activity level, C/ml	Total activity, mC
May – Sept.	1,842,155	1.6×10^{-11}	112.1
Jan. – April	1,734,395	2.47×10^{-11}	162.18

Waste Concentrator Operations

	Waste to evaporator	Concentrate to drums	Volume reduction	Activity in mC: Feed	Activity in mC: Distillate
May – Sept.	156,489	1,688	91.5:1	26,040	0.931
Jan. – April	115,635	991	116:1	25,736	0.217

Waste Sample Analysis

	"F" waste	Pile canal	Concentration	Misc.	Total
May – Sept.	256	45	130	37	468
Jan. – April	243	73	87	30	433

Waste Containers

	"D" waste	"A" waste	Total
May – Sept.	79	12	91
Jan. – April	67	10	77

Waste Inventory

	Gal start	Gal received	Gal to evaporator	Gal end
"D" Waste				
May – Sept.	148,140	189,045	153,100	184,085
Jan. – April	98,582	169,053	119,495	148,140
"A" Waste				
May – Sept.	3,570	125	0	3,695
Jan. – April	2,943	627	0	3,570

RADIOGRAPHY

A total of 569 radiographs were made during this period. Although the May 15th explosion elsewhere in the building hampered the radiography service, no disruption in service occurred as a result. Some special radiographs were made of a relief tank following the explosion to determine the amount of BrF_3 contained in the tank; this tank is a horizontal one, and the radiograph was made vertically, the amount of liquid being calculated from the width of the solution shown by the film. A number of the radiographs were for groups outside the Nuclear Engineering Department. J.C. Austin, H. Ruge

REMOTE CONTROL DEVELOPMENT AND STAFF SHOP OPERATIONS

Four motions of the BNL Model 4 Rectilinear Manipulator were mocked up and found to work satisfactorily. Additional motions will be added. A scaled-down version of the BNL Model 3 Manipulator was made for incorporation in a new setup for the production of Mg^{28}. Design was begun on the new Metallurgical Cell. In the meantime temporary equipment and shielding were being set up for performing some metallurgical tests on hot samples while the permanent Metallurgical Cell is being built.

A tremendous amount of work was done in cleaning up not only the shop but other areas in the building following the May 15th explosion.

Other items worked on during this period were: 1) special ventilation for and assembly of three 5-foot clay columns to be used by the Waste Disposal Group in experiments with 2 curies of Sr^{90}; 2) reconditioning of manipulators, periscopes, etc., damaged by the May 15th explosion; 3) design and construction of new types of lead shields for the 100-mC-size I^{132} generators; 4) improvements in the design of the electrical system of the remotely operated medical infusion pump; 5) new arc chamber sample holder for the emission spectrograph. A. J. Banslaben, C. Kiesling, L. Chirco, C. Petersen, C. Ruege, G. Uddman

LIQUID WASTE OPERATIONS

Liquid waste operations are summarized in Table 12. J. Baranosky, A. Macaulay, W. Austin, W.Gray, W. Schmitz

Metallurgy Division

LMFR Research and Development

FUEL AND BLANKET DEVELOPMENT

It has been reported previously that the liquid-plus-solid portions of the systems Th-Pb-Bi and Th-Bi offer a number of possibilities for dispersions of Th-rich intermetallic compounds in low-melting, low cross section liquids which might serve as fluid breeder-blanket materials. The following studies have been made on these systems during the last quarter.

Equilibrium Studies

TH-BI-PB SYSTEM. Work on the system has been continued to determine the composition, crystal structure, and temperature range of stability of the intermetallic compounds.

X-ray diffraction studies in the Th-Bi system have disclosed the existence of an intermetallic compound having a cubic structure in the neighborhood of 55 wt % Th. In the Th-Pb system, metallographic studies of specimens quenched after equilibrating at various temperatures have indicated that the compound $ThPb_3$ decomposes on heating by a peritectic reaction at 655°C rather than at 745°C as previously reported. The decomposition products are liquid lead containing approximately 0.07 wt % Th and an intermetallic compound containing approximately 40 wt % Th corresponding to the stoichiometric ratio Th_3Pb_5. X-ray diffraction studies of the compound $ThPb_3$ have indicated that at temperatures between 450°C and the peritectic the Th and Pb atoms are randomly distributed in the face-centered cubic lattice. Metallographic evidence supported by x-ray diffraction indicates that this compound is capable of holding a considerable amount of Th in solid solution. The Th solubility decreases with increasing temperature.

TH-BI-TE SYSTEM. Results previously reported indicated that small additions of Te to the Th-Bi alloys lowered the solubility of Th in liquid Bi and decreased the rate of isothermal particle growth at 800°C in Th-Bi dispersions. In order to examine more closely the effects of Te additions upon the Th-Bi system, a series of filtration experiments were carried out. Alloys containing 10 wt % Th and additions of 1.0, 0.50, 0.25, and 0.10 wt % Te were filtered at 1000°, 800°, 600°, and 500°C. Filtrates and residues were submitted for chemical analysis. The results of filtrations at 1000°C are shown in Table 13.

Table 13

Wt % Te in alloy	Analysis of 1000°C filtrate	
	Wt % Th	Wt % Te
0	6.87	0
0.10	6.51	0.0013
0.25	5.33	0.0082
0.50	0.99	0.248
1.00	0.25	0.51

Analytical results from the filtrations at lower temperatures showed no Te detectable in the filtrates, and a relatively small effect, if any, of alloy Te content upon the Th solubility. Because these results are questionable, the lower temperature filtrations will be repeated with greater care to insure alloying.

Thorium-Bismuth Dispersions

PRODUCTION BY QUENCHING AND REHEATING. It has been reported previously that dispersions of fine platelets of $ThBi_2$ in Bi are produced by rapid quenching of Th-Bi solutions, and that such dispersions containing more than 3 wt % Th are not fluid in the temperature range 300° to 500°C. Reheating to higher temperatures causes the platelets to thicken without increasing in diameter; equiaxiality is approached at a rate which increases with temperature. Such treatment restores fluidity to the dispersions. There has been some evidence that the degree of equiaxiality necessary for high fluidity increases with the Th content of the dispersions. A series of experiments was conducted to determine the degree of equi-

axiality necessary for high fluidity in a 10 wt % Th dispersion and the heat treatment required to produce it. Alloys containing 5 wt % Th were heated to 1000°C to dissolve the Th and then quenched by pouring into graphite crucibles held at 300°C. This treatment produced platelets approximately 1 μ thick by 60 μ in diameter. Specimens were then reheated to 800° or to 900°C, held for 5 to 30 min, and then cooled to 300°C with agitation to keep the solid particles suspended and thus prevent precipitation of platelets. The specimens were then held at 300°C for 1 hr without agitation to allow the particles to settle, and then allowed to freeze. Each specimen was sectioned vertically and examined to determine the height of the settled layer. Specimens which had settled sufficiently were sectioned horizontally to remove enough of the supernatant free Bi to leave an alloy containing 10 wt % Th. Specimens which had settled to less than 10% Th were sectioned just above the settled layer, and the composition was calculated by subtracting the weight of Bi removed.

Each of the concentrated alloys was tested for fluidity in the temperature range 300° to 500°C by observing the time required for a 10-g sample to flow through a 1/16-in. diameter hole in graphite, a time of less than 2 sec indicating satisfactory fluidity.

The specimens were examined metallographically to determine the particle size and shape. The results are shown in Table 14.

On the assumption that dispersions which had not settled to 10% Th would not be fluid if concentrated to 10%, these results indicate that a particle diameter-to-thickness ratio of no greater than 5:1 is necessary for fluidity in a 10 wt % Th dispersion. This ratio can be achieved by heat treatments of 5 min at 900°C or 20 min at 800°C.

Production by Electrolysis of Fused Salts. Twelve dispersions ranging in weight from 6 to 10 lb were received from Horizons Inc. which had been prepared by electrodeposition of Th upon molten Bi cathodes from supernatant mixtures of fused Na, K, Ca, and Th chlorides. Examination disclosed that in all but three of the ingots the salt content was very much higher than the representative value reported by Horizons (0.20 wt % Cl). The salt inclusions, which were visible to the naked eye on a freshly polished surface, were distributed throughout the part of the ingot containing the $ThBi_2$ particles as discrete droplets or as a lacy structure. The tops of these ingots were rough and contained adherent salt. Of the three ingots containing no gross salt inclusions, one had been electrolyzed at a low current density for a much longer time than any of the others with some stirring during electrolysis but not during cooling, another had been stirred during the first hour only of an abnormally long cooling period (14 hr) after electrolysis, and the third had been electrolyzed and cooled without stirring. This last ingot contained a few plates of $ThBi_2$ but no equiaxed particles, which indicated the necessity for stirring. The polished surfaces of metallographic specimens of all three ingots became wet on standing in air, which indicated the presence of some hygroscopic salt. Chemical analyses of these specimens for chlorides have not yet been received. Several of the ingots had pieces of quartz adhering to the sides from the containers in which they were prepared. When the quartz was chipped off, it was observed that a thin layer of salt had penetrated between the alloys and the

Table 14

Heat treatment		Composition,	Flow time	Average particle size, μ	
Temperature, °C	Time, min.	wt % Th	at 300° to 500°C, sec	Diameter	Thickness
800	5	7.65	1.4	55	5
	15	8.93	1.4	55	10
	20	10.00	1.4	55	11
	30	10.00	1.5	55	12
900	5	10.00	1.5	55	12
	30	10.00	1.7	80	30

container to an average depth of 1¼ in. from the top of the ingot.

Metallographic examination of the ingots disclosed that $ThBi_2$ particles in alloys produced with stirring were of satisfactory size and shape. Clusters of particles were usually associated with droplets of salt. In every case in which electrolysis had been continued beyond depletion of Th in the salt, the alloy contained plates of calcium bismuthide.

A top-to-bottom section of a representative ingot (474-23) was washed to remove surface salt, weighed, and then heated at 600°C for 72 hr without agitation in a graphite crucible. After cooling, the ingot was washed and reweighed. It was found that 11.5 wt % salt (corresponding to 6.9 wt % chloride) had been removed. Microexamination of the resulting ingot revealed that some salt was still present. Salt removal was less complete in a similar specimen heated at 600°C for 72 hr with slow stirring. In both experiments, the inside walls of the graphite crucibles were completely wetted by the molten salt.

Production and Behavior of Dispersions Containing Tellurium. Preliminary experiments previously reported have indicated that minor additions of Te may inhibit particle growth in Th-Bi dispersions. Various methods for adding Te to the dispersions have been studied. Heating admixtures of Th, Bi, and Te to produce dispersions by the exfoliation method or additions of straight Te to ready-made dispersions have resulted in nonuniformity. Uniform dispersions were produced for the preliminary experiments by first preparing a Te-Bi alloy having twice the desired Te concentration, and Th-Bi dispersion having twice the desired Th concentration, and then heating equal weights of each together at 500°C for 2 hr with stirring. This method produced particles which had approximately the same shape and maximum dimensions as the original $ThBi_2$ particles, but many of which were hollow and filled with Bi. This may indicate that Te additions bring a compound richer in Th into equilibrium with the liquid. After these dispersions were heated for 16 to 18 hr at 800°C, there was no increase in the maximum dimension of the particles. The number of particles having the maximum dimension had increased, the smallest particles had disappeared, and the hollow particles had been mostly filled in.

Two additional dispersions containing 5 wt % Th, 0.050 wt % Te and 5 wt % Th, 0.025 wt % Te were prepared in the manner described above. After heating for 16 hr at 800°C, the maximum particle dimension in the dispersion containing 0.050 wt % Te remained constant at 60 μ; the maximum dimension in the dispersion containing 0.025 wt % Te increased from 60 to 70 μ. These results may be compared with a previous observation that in a 5 wt % Th dispersion without Te subjected to the same treatment the maximum particle dimension increases from 60 to 120 μ. Because this method of production produces hollow particles which are not ideal for particle growth studies, other methods were tried.

An alloy of 5 wt % Th, 0.1 wt % Te, balance Bi was heated at 1000°C for complete solution and then quenched by pouring into a cooled graphite crucible. This treatment produced a dispersion of very fine platelets (<50 μ in diameter by <1 μ thick) in Bi. The dispersion was not fluid when reheated to 300° to 500°C. Specimens cooled with agitation after heating to 700°, 800°, and 900°C for 5 min were fluid at 300° to 500°C. The effects of these treatments upon the average particle size are shown in Table 15.

Two dispersions containing 10 wt % Th, 0.10 wt % Te, balance Bi were produced by adding 0.01-in.-thick Th chips and 325-mesh Th powder to previously prepared Te-Bi alloys and heating at 500°C. The progress of the reaction was followed by periodic cooling and microscopic examination. In the dispersion produced with Th powder, the Th had reacted completely in 30 min, yielding solid equiaxed particles most of which were less than 15 μ in diameter but a few of which reached 30 μ. In a specimen of this dispersion heated at 800°C for 16 hr, the largest particles grew to 55 μ in diameter. In the dispersion produced with Th chips, complete reaction of the Th was achieved after 6 hr. The reaction was ob-

Table 15

		Average particle size, μ	
Temperature, °C	Time, min	Diameter	Thickness
700	5	25	3
800	5	30	5
900	5	40	12

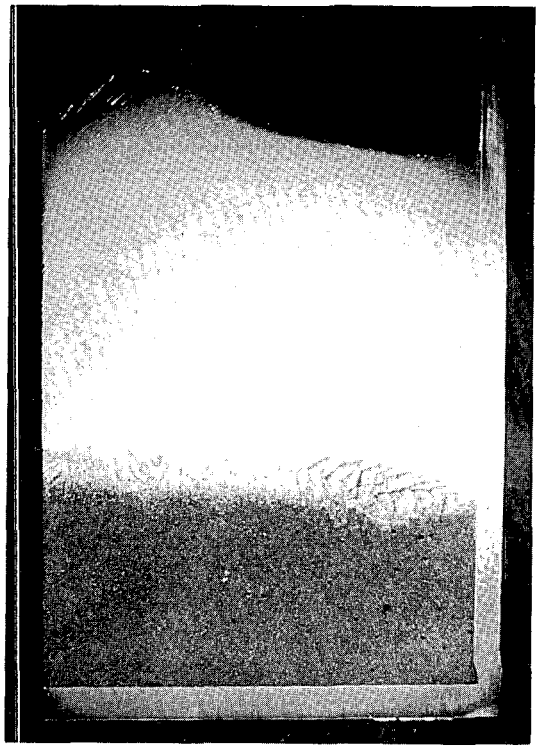

Figure 25. Settled Th-Bi alloy.

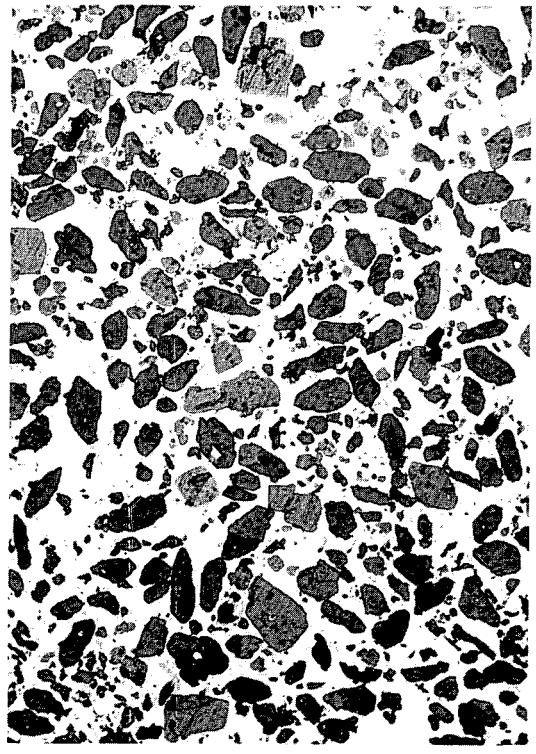

Figure 26. Settled Th-Bi alloy, 150×.

served to proceed by exfoliation of an intermediate reaction product, yielding solid exquiaxed particles up to 40 μ in diameter. Heating this dispersion at 800°C for 16 hr caused the maximum particle dimension to increase to 55 μ. J. Bryner

Preparation of Thorium-Bismuth Slurries from Thorium Chips. The method in use for the preparation of batches of equiaxed Th-Bi slurry 1 kg or larger is to add washed Th powder to a stirred Bi bath heated at 500° to 600°C. The reaction is carried out under helium, and the dispersion is then degassed by stirring under vacuum. This method is adequate for engineering experiments and holds promise for use in very large systems requiring ton quantities of slurry. However, at present Th powder is not readily obtainable; therefore, it seemed prudent to investigate other methods of slurry preparation suitable for engineering experiments.

It was decided to attempt to scale up the technique used to prepare 50 to 100-g alloys by the exfoliation reaction of Th chips with Bi. Th chips, 140 g, and 1860 g filtered Bi were loaded into a 2½-in.-i.d. steel crucible and put into a steel pot containing a furnace and connections to a gas-vacuum manifold. The system was evacuated, filled with 3 psig He, and heated to 550°C. A 2-in.-diameter two-blade stirrer was pushed into the center of the melt at 350°C and rotated at 500 rpm. After 2 hr at 550°, the alloy was cooled to 400°, the stirring was stopped, and the system was evacuated overnight. On the following day the alloy was stirred at 500 rpm for 1 hr under vacuum, and the particles were then allowed to settle for 1 hr before the alloy was cooled to room temperature.

Figure 25 shows a photograph of a part of the ingot. Some small gas pockets may be seen mixed in with the solids, but the top of the alloy is very clean. Figure 26 shows a representative photomicrograph of the alloy taken at 150×. The particles are nearly equiaxed, and the largest particle diameter is about 75 μ.

It is of interest to note in Figure 25 that the solids settled to 36% of the alloy height. Chemical analysis of the alloy has shown it to contain 7.4% Th; therefore, the average Th concentration in the settled layer was 20.6%. This is about the same

Th concentration as was found in the plugged section of Slurry Loop 1 and is to be compared with a maximum of 15% Th which is found in settled layers of alloys in capsules. It seems likely that the Th chips on the bottom of the crucible reacted quickly and formed a viscous mass that was not disturbed by the stirring action, which was directed up and away from the bottom of the crucible.

A portion of the ingot was heated at 500°C for 2 hr under vacuum and was gently stirred with a rod for a few minutes. Examination of the cooled alloy showed no porosity, and the settled height of the solids was now 42% of the alloy height, from which a Th concentration of 17.6% can be calculated for the settled layer. Thus, it would appear that under certain conditions a slurry containing 20% Th could occur, but once it had been redispersed it would not settle to as high a concentration unless the conditions which led to its formation were repeated.

It appears that large batches of slurry may be prepared by the reaction of Th chips in Bi or by the addition of chips to a Bi bath. If the Th and Bi are to be mixed together from the start, it is necessary to be sure that the mixing is adequate to prevent the formation of a viscous layer containing a high concentration of Th.

M. Brodsky

Behavior of Dispersions in Croloy 2¼ Capsules. A series of capsule experiments has been started to develop information which may be used to predict or to explain the behavior of Th-Bi dispersions in larger-scale circulating systems. The first experiments have been conducted in capsules of Croloy 2¼ steel because this material is being used in the Th slurry loop now under construction. Because Zr additions have proved beneficial in inhibiting mass transfer by Bi solutions circulating through a temperature differential in Croloy systems, duplicate experiments were run with and without Zr additions.

Two Croloy crucibles containing alloys of 1 wt % Th in Bi and 1 wt % Th, 0.025 wt % Zr in Bi were heated to 800°C for 2 hr to dissolve the Th, and then cooled rapidly by directing a stream of air at a spot on the crucible wall. The crucible and contents were sectioned vertically through the cooled spot and polished for metallographic examination. In both specimens the alloy was observed to contain small platelets of $ThBi_2$ uniformly distributed. There were platelets touching the crucible walls, but the concentration near the walls and in the region of the cooled spot was no greater than in the center of the alloy. There was a thin layer (1 to 2 μ thick) of unidentified material at the interface between the alloys and the crucibles. Autoradiographs showed that this layer contained Th in the alloy containing no Zr, and that the layer was probably richer in Th than the $ThBi_2$ platelets. In the alloy that contained Zr the layer did not contain Th and is presumed to be zirconium nitride. The results of these experiments showed that there is no tendency for $ThBi_2$ to plate out on Croloy during precipitation on cooling, and that the rate of nucleation at the Croloy-Bi interface is not detectably greater than in the bulk of the alloy.

Two Croloy crucibles containing alloys of 1 wt % Th in Bi and 1 wt % Th, 0.025 wt % Zr in Bi were heated to 800°C for 2 hr and then allowed to cool slowly in the furnace. The crucibles with contents were sectioned vertically and examined metallographically. The alloys contained large plates of $ThBi_2$. The plates had settled out of the top central portion of the ingot, leaving plates adhering to the walls which were larger on the average than those which had settled. Interfacial layers like those in the first two experiments were observed. These results indicate that $ThBi_2$ plates which are nucleated at the walls tend to adhere to the walls, and that the presence or absence of Zr does not affect this tendency.

A dispersion of equiaxed particles of $ThBi_2$ in Bi containing 5 wt % Th, 0.025 wt % Zr was loaded into a 2½-in.-long, ⅝-in-i.d. Croloy crucible, and the top was closed with a press-fit steel frit. The crucible was heated under vacuum to 600°C for 1 hr and cooled to 300°C, then inverted and held at 300°C for 1 hr, and then cooled. This treatment allowed the particles to settle to what had been the top of the crucible, leaving Bi at what had been the bottom. The crucible with contents was sectioned lengthwise and polished for metallographic examination. The individual $ThBi_2$ particles were observed to adhere to the crucible walls in the region from which they should have settled. It could not be determined whether the particles became stuck to the walls during the heating at 600°C or during cooling to 300°C.

An identical specimen was tumbled end over end at 20 cycles/min during heating to 500°C for

1 hr and cooling to 300°C, and then stopped in the upright position and held at 300°C for 1 hr to allow the particles to settle before cooling. The crucible with contents was sectioned lengthwise and polished for metallographic examination. A few individual $ThBi_2$ particles were observed to adhere to the crucible walls in the region from which they should have settled. The number of adhering particles was very much less than in the previous case. No $ThBi_2$ plates were observed. The results of this experiment indicate that the tendency of the particles to adhere to the walls during heating at 600°C or during cooling to 300°C can be decreased by keeping the particles in motion.

J. BRYNER

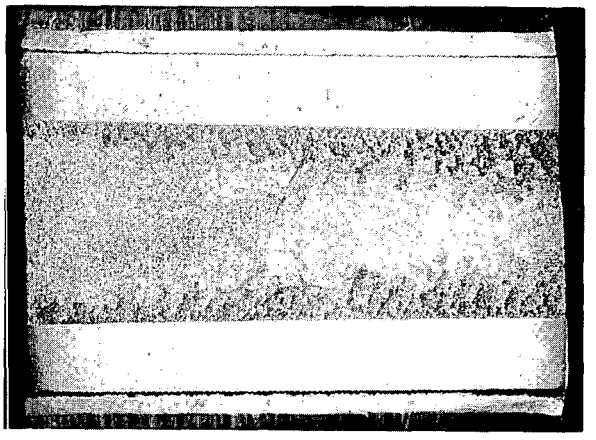

Figure 27. Cooler section.

Slurry Loops

Dispersions of $ThBi_2$ in Bi have been shown to have desirable properties for a breeder blanket in capsule and batch experiments, but little is known about their behavior in pumped systems, particularly those having a temperature gradient. It is possible that as the slurry is pumped through a temperature differential, thorium bismuthide which is dissolved in the hotter regions will precipitate on the cool region walls rather than on the suspended particles. Slurry Loops 2 and 3 have been constructed to determine this tendency for deposition on walls. These loops should also yield information about other matters such as particle growth, erosion by $ThBi_2$ particles, and corrosion of pipes by Th-Bi alloys.

SLURRY LOOP 2. Slurry Loop 2 was made of ½-in. schedule 80 Croloy 2¼ pipe and contained 7 kg 7% Th-Bi slurry. A small amount of irradiated Th was used to permit the observation of plug formation by radioactivity determinations. The loop plugged after running at 0.7 to 1.0 ft/sec for 4 hr isothermally and then for 10 hr with a temperature gradient. The major part of the gradient operation was with 425° and 500°C bulk slurry extreme temperatures (375° to 525° film temperatures). The slurry was pumped with a Croloy impeller driven by means of a magnetic coupling. Two short power failures had occurred before the loop finally plugged.

After all attempts had failed to recirculate the slurry, the insulation and heater windings were removed and the gross gamma activity was determined as a function of loop position. The highest activity regions were the vertical cooler section and the top and bottom horizontal sections. On sectioning, a good correlation was obtained between gamma activity and Th content.

The samples were polished and examined by the methods used for naturally radioactive alloys with a few additional precautions to prevent overexposure, spread of contamination, etc. $ThBi_2$ particles seemed to have been concentrated along the walls of the entire cooler section. The region near the center of the cooler was filled with particles completely across the pipe. Figure 27 shows a portion of the cooler section which was above the center of the cooler and which was not full of particles. The build-up of particles towards the center of the cooler can be seen as dark areas in the photograph. High magnification studies of the polished samples showed many particles to be touching the steel wall. There is no way, however, of knowing how firmly the particles were attached to the wall while the slurry was moving.

Figures 28, 29, 30, and 31 show photographs of particles in the loop at 150×. Figure 28 is a photomicrograph of the slurry before it was added to the loop, and Figures 29, 30, and 31 were taken of particles found in the cooler section after the loop plugged. Figure 29 is typical of most of the slurry in the loop, while Figures 30 and 31 show isolated areas. The very large particles in Figure 31 were probably formed after the loop had plugged and when areas adjacent to the cooler were heated above 600°C.

There was no sign of erosion or corrosion on the pump impeller or on the walls of the highly turbulent areas around the impeller. Microscopic

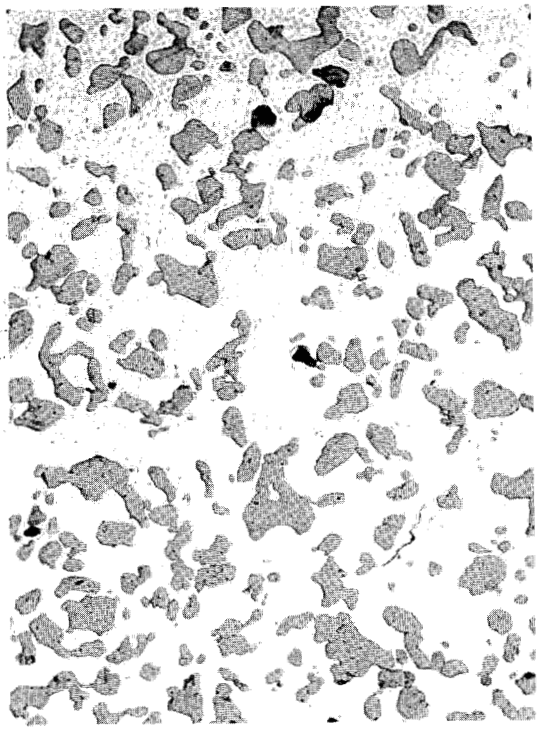

Figure 28. Slurry before addition to loop.

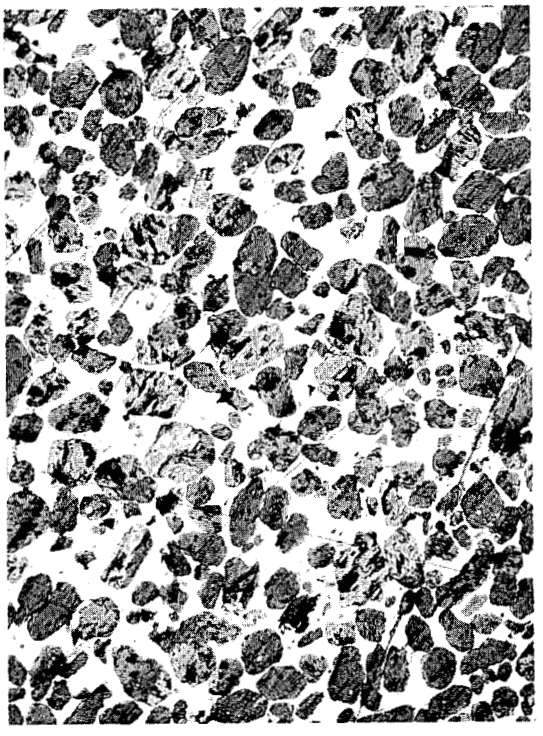

Figure 29. Particles found in cooler section after loop plugged, typical area.

Figure 30. Particles found in cooler after loop plugged, isolated area.

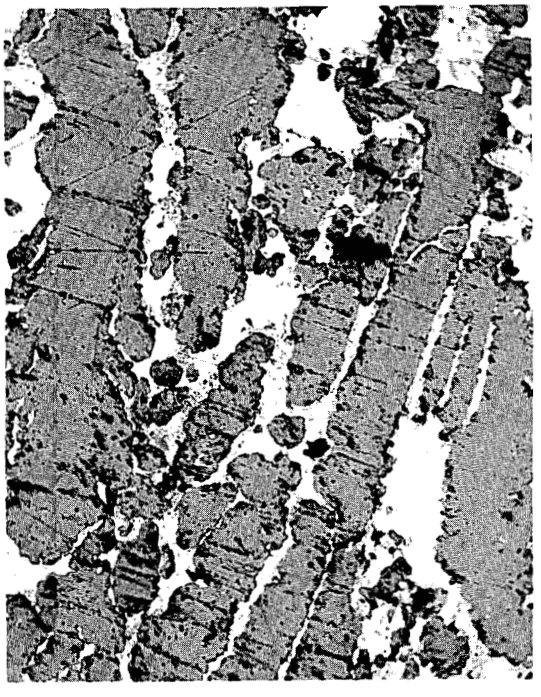

Figure 31. Particles found in cooler after loop plugged, isolated area.

examination of the steel walls of the loop showed evidence of slight corrosion on the pipe adjacent to the main furnace and nowhere else. The temperature in this section had reached 650°C and remained above 600° for 1 hr.

Because of the power shutdown during the operation, it is difficult to determine the cause of the initial deposition of $ThBi_2$. It seems likely that the initial deposition took place during the first power shutdown, because the first indication of an increase in the counting rate at the finned cooler was found immediately after the power was restored. It is possible, however, that deposition had already begun but not to the extent needed for its detection by the counting technique. In the latter case the power failure would have merely accelerated the plug formation.

It is hoped that a careful control of operating conditions in Slurry Loop 3 and capsule experiments, which will almost duplicate the conditions in a pumped system, will yield information about the nature of $ThBi_2$ deposition. Once the mechanism of deposition becomes understood, it may be possible to take proper preventive measures.

M. Brodsky

Slurry Loop 3. The construction of Slurry Loop 3 is nearly completed. This loop is also constructed of ½-in. schedule 80 Croloy 2 ¼ pipe, and the same type of impeller pump as that used in Slurry Loop 2 has been installed. The loop has been designed to pump 7% Th-Bi at a velocity of 1 ft/sec through a maximum bulk slurry temperature difference of 60°C. A dump tank has been included in the loop, and the slurry level in the loop will be maintained by a pressure differential between the loop and the dump tank. Activated Th will again be used to observe the build-up of $ThBi_2$ on pipe walls. It is hoped that radiography of the loop after a dump will also show the presence of any deposited material.

The initial operations will be carried out with Bi containing 300 ppm Zr and 200 ppm Th in solution. After all equipment has been shown to be operating properly during isothermal operation, a gradient will be applied to the loop to permit the calibration of the pump by means of heat balance calculations. The solution will then be returned to the dump tank, and the slurry will be prepared by the addition of Th powder to the stirred Bi. The loop will then be operated with slurry under isothermal conditions for 2 weeks, after which it will again be dumped to permit sampling of the slurry for the determination of the effect of pumping on the particles. This will be followed by a gradient run with extreme bulk temperatures of 440° and 460°C (427° to 467° film) until information is obtained on the tendency of $ThBi_2$ to precipitate on walls.

M. Brodsky and A. J. Romano

CORROSION STUDIES AND ENGINEERING TESTS

Pumped Loops

Two pumped loops are now being run by the Metallurgy Division to study the variables which affect the corrosion and mass transfer of container materials by liquid U-Bi. Such variables as materials, welds, liquid composition, ΔT, T_{max}, flow rate, and inhibitors can be studied.

Although the flow rate in these loops is about one fourth that proposed in present LMFRE designs, it is still greater by a factor of 200 than that attained in the sample thermal convection loops. LMFRE velocities can be attained by using test sections of small diameter. These loops are designed in such a way that the hot test section and finned cooler can be removed and new sections inserted, so that several runs can be made with one loop.

Two more loops, HVL 3 and HVL 4, have been designed and soon will be under construction which will be capable of circulating U-Bi through a temperature differential up to 150°C at flow rates up to 12 gpm.

High Velocity Loop I – Run 5. The purpose of this run is to study the corrosion and mass transfer in a circulating Bi system containing 250 ppm Zr and 350 ppm Mg and operating with a 75°C bulk Bi temperature differential. After 500 hr of temperature differential operation, 1000 ppm U will be added to the system.

The layout and construction of the loop in this run are similar to those of runs 1 to 4. The entire loop including all components is made from 1¼ Cr – ½ Mo steel. The piping in this run is ¾-in. schedule 40 pipe except for the furnace test section and the pump cell.

The loop is being pumped with a GE electromagnetic pump, and the flow can be maintained at 1.60 gpm. At this flow rate the velocity in the furnace test section is about 1.6 ft/sec. The pump itself is mounted in a vertical position with

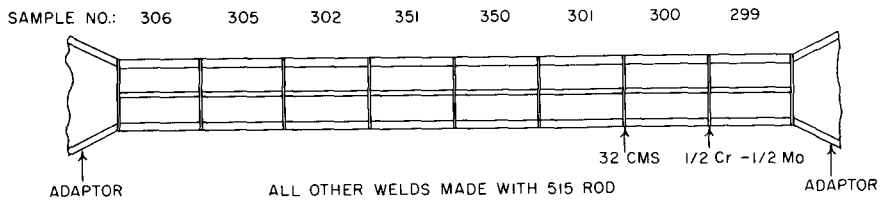

Figure 32. HVL I test section.

the direction of flow downward into the sump tank.

The furnace section contains 8 corrosion specimens each of which is ½-in. IPS. All the corrosion samples are located at the outlet end of the furnace section (see Figure 32). The following corrosion samples were included:

1) No. 306: Bar No. 001, 1¼ Cr – ½ Mo, annealed at 1650°F for 1 hr.
2) No. 305: Bar No. 001, 1¼ Cr – ½ Mo, stress relieved at 1325°F for 1 hr.
3) No. 302: Bar No. 012, 1¼ Cr – ½ Mo, oil quenched, tempered at 1325°F for 2 hr.
4) No. 351: Bar No. 068, 1¼ Cr – ½ Mo, normalized at 1750°F for ½ hr, tempered at 1325°F for 1 hr.
5) No. 350: Bar No. 068, 1¼ Cr – ½ Mo, stress relieved at 1325°F for 1 hr.
6) No. 301: Bar No. 012, 1¼ Cr – ½Mo, normalized at 1750°F for 1 hr, tempered at 1325°F for 2 hr.
7) No. 300: Bar No. 012, 1¼ Cr – ½ Mo, annealed at 1650°F for 1 hr.
8) No. 299: Bar No. 012, 1¼ Cr – ½ Mo, stress relieved at 1325°F for 1 hr.

All welds in the furnace test section were made with 515 weld rod with inert arc except for the transverse weld between samples No. 300 and No. 301 which is made from CMS 32 and the transverse weld between No. 299 and No. 300 which is ½ Cr – ½ Mo. The adaptors are both from bar No. 002, 1¼ Cr – ½ Mo, ¾-in. IPS swaged to ½-in. pipe.

Construction of the loop was completed in late July, and final insulation and wiring were completed in August. On August 9 heat was applied to the system and the piping and welds were stress relieved in place at 700°C for 1 hr. A series of conditioning runs was then performed on the loop, and the system was ready for start-up. At this time 350 ppm Mg and 250 ppm Zr were added to the system. On Sept. 12 a temperature differential of 75°C based on the bulk Bi temperatures was applied to the system, and a flow rate of 1.6 gpm was maintained. The furnace temperature was maintained at 520°C (bulk Bi) and the cooler temperature at 445°C (bulk Bi). Under the present conditions the over-all film drop in the finned cooler is 17°C and that in the furnace is 1°C. This indicates that the film temperatures are 521° and 428°C in the furnace and cooler respectively.

As of Sept. 21, the loop has operated for 170 hr at a temperature differential of 75°C, and no deposition is detectable by radiographic inspection of the finned coolers. The loop is sampled periodically for liquid Bi. Results from these samples show no change in composition and hence indicate stability of the additives.

High Velocity Loop II – Run 1A. The purpose of this run is to study the corrosion and mass transfer in a circulating Bi system containing 350 ppm Zr and 350 ppm Mg operating at a temperature differential of 75°C based on Bi film temperatures. After 113 hr of temperature differential operation, 1000 ppm U was added to the system.

The piping in this run is made from 2¼ Cr – 1 Mo steel pipe except for parts of the furnace test section. This loop is pumped with a Callery 25-30 electromagnetic pump, and the flow is maintained at 1.7 gpm. At this flow rate the velocity in the furnace test section is about 1.7 ft/sec.

The furnace section contains 17 corrosion specimens located at the hot end of the furnace. The following corrosion samples (see Figure 33) were included in this run:

1) No. 258: 2¼ Cr – 1 Mo, longitudinal weld made by inert arc with 521 rod.
2) No. 259: 2¼ Cr – 1 Mo, longitudinal weld by inert arc with 502 rod.
3) No. 260: 1¼ Cr – ½ Mo, longitudinal weld by inert arc with 515 rod.
4) No. 261: 2¼ Cr – 1 Mo, transverse weld by inert arc first pass and metal arc second pass (sample submitted by Babcock and Wilcox).

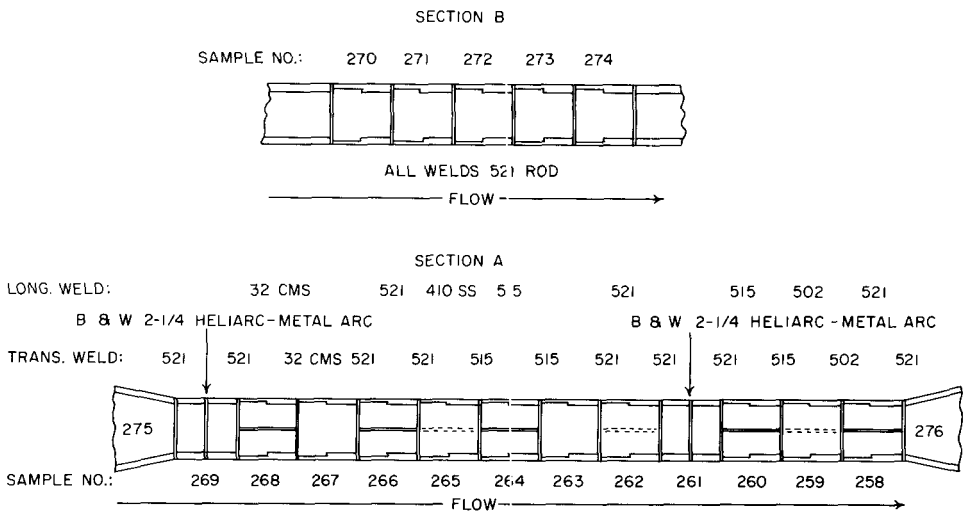

Figure 33. HVL II test section.

5) No. 262: 2¼ Cr – 1 Mo, heat treated in dry H_2 at 1925°F, cooled 50°F/hr to 1250°F, air cooled. Weld by inert arc and 521 weld rod.
6) No. 263: 2¼ Cr – 1 Mo, heat treated in dry H_2 at 1925°F, rapidly cooled to 1250°F, cooled 200°F/hr to room temperature.
7) No. 264: 1¼ Cr – ½ Mo, heat treated in dry H_2 at 1925°F, cooled 50°F/hr to 1250°F, air cooled. Longitudinal weld by inert arc with 515 rod.
8) No. 265: 12 Cr (type 410), longitudinal weld by inert arc with 410 rod.
9) No. 266: Composite of 12 Cr and 2¼ Cr – 1 Mo, longitudinal welds by inert arc with 521 weld.
10) No. 267: 2¼ Cr – 1 Mo, heat treated in dry H_2 at 1925°F, cooled to 1250°F at 50°F/hr, air cooled.
11) No. 268: Bessemer steel, longitudinal weld by inert arc with CMS 32 rod.
12) No. 269: 2¼ Cr – 1 Mo, transverse weld by metal arc (sample submitted by Babcock and Wilcox).
13) No. 270: 2¼ Cr – 1 Mo, annealed at 1750°F, furnace cooled 50°F/hr.
14) No. 271: 2¼ Cr – 1 Mo, normalized from 1900°F, air cooled 2000°F/hr and tempered at 1250°F.
15) No. 272: 2¼ Cr – 1 Mo, normalized from 1750°F, air cooled 2000°F/hr and tempered at-1250°F.
16) No. 273: 2¼ Cr – 1 Mo, normalized from 1600°F, air cooled 2000°F/hr and tempered at 1250°F.
17) No. 274: 2¼ Cr – 1 Mo, oil quenched from 1750°F and tempered at 1250°F.

After assembly, the entire loop including the test section was stress relieved at 700°C (1300°F) for 2 hr.

A temperature differential of 75°C based on film temperatures was applied to the system on March 23. The loop was dumped at 500, 750, and 1250 hr of operation for radiographic inspection of the furnace test section. No corrosion or deposition was detectable at this time. This concluded 1250 hr of operation at 520° (film) and 445°C (film) temperature differential with only the finned cooler used to remove the heat.

At this time it was decided to use two finned coolers to remove the heat at the same differential but to lower the film drop. On May 29 the loop was filled and run for another 1250 hr. The loop had now run at 75°C film temperature differential for 2500 hr and no corrosion or deposition had been detected.

On July 29 the loop was restarted and a new differential of 75°C based on bulk Bi temperatures was applied to the system. Under these conditions the film ΔT was about 95°C. After running several hundred hours at the new differential, slight deposition was noted in the coldest end of the finned coolers. The loop was dumped at 3500 hr and examined radiographically. No corrosion was

detectable on examining the radiograph taken of the furnace test section, and there was no appreciable gain in deposition in the finned cooler.

The loop was filled and started on September 11 and is now running at 75°C bulk Bi temperature differential. As of September 20 the total running time of this loop is 3710 hr. Sampling of liquid Bi shows no change in the composition of the additives.

HIGH VELOCITY LOOPS 3 AND 4. Two new high velocity loops are being designed which are to be built and operated in the metallurgy building. They will use Gibbs-Ruthman mechanical centrifugal pumps capable of delivering 11.5 gpm at a head of 38.5 ft.

The design of the loops has been fixed and final prints are being drawn up. One loop will be made of 2¼ Cr – 1 Mo steel and the other of 1¼ Cr – 1 Mo steel. Both these loops are expected to be operated with a bulk temperature differential of 75°C.

A. J. ROMANO

Thermal Convection Loops

These tests are considered useful in selecting materials for U-Bi containment, in studying the effects of variables on corrosion and precipitation, and in demonstrating the effectiveness of inhibitors. Thermal convection loops can be used to study most of the variables encountered in U-Bi corrosion. The most important limitation is the flow rate, which is about 0.05 ft/sec, on the order of 200 times lower than in the proposed LMFR installation. To date 40 thermal convection loop tests have been completed.

As of September 20, 1957, 19 thermal convection loops are in operation, in which the following variables are being studied: ΔT; maximum temperature of hot leg; four types of steel; heat treatment of 2¼ Cr – 1 Mo steel; loop cleaning procedure; effect of Be insert; effect of fission products; and Zr concentration. The status of each of the operating loops is shown in Table 16.

Table 16

Status of Thermal Convection Loops as of September 20, 1957

Loop	Material of construction	Pretreatment	Additive, ppm			Temperature, °C		Hr of operation	Radiographic inspection		Remarks
			Mg	Zr	U	Hot leg	Cold leg		Hot leg	Cold leg	
33	2¼ Cr – 1 Mo	H_2 fired, acid cleaned	350	250	1000	550 550	535 440	644 14,557	Pitting at weld and pipe	Slight ppt.	Pitting at the weld has penetrated about 75% of thickness. The rate of penetration in the last 3000 hr has been very slow. Will continue to operate loop to see if pitting will perforate pipe.
39	RH 1081	Acid cleaned, H_2 fired	350	250	1000	550 550 550	550 510 415	906 815 4,372	No corrosion	No ppt.	RH 1081 is a low-Mn, 0.30-C steel with 0.30 Ti. This loop has operated with no evidence of corrosion or ppt. in spite of the high Ti content.
40	2¼ Cr – 1 Mo	H_2 fired, acid cleaned	350	250	1000	550 550 550 600 600 600 600	550 510 450 600 550 525 500	1,032 647 1,004 192 5,043 2,346 293	No corrosion	Slight ppt.	This loop indicates that high (600°C) hot temperature does not increase corrosion. In fact the higher temperature appears to have improved the protective film formation.
41	2¼ Cr – 1 Mo	H_2 fired, acid cleaned	350	250	1000	525 525 525	525 405 405	532 1,136 7,139	Slight pipe corrosion	Slight ppt.	Incipient corrosion was observed after about 5000 hr of operation at 120°C ΔT.
42	2¼ Cr – 1 Mo	H_2 fired, acid cleaned	350	250	1000	550 550 550	550 510 450	331 841 7,960	No corrosion	Slight ppt.	Comparison of this loop with 41 indicates that ΔT is more important factor in causing pitting than higher temperature of the hot leg.

Table 16

Status of Thermal Convection Loops as of September 20, 1957

Loop	Material of construction	Pretreatment	Additive, ppm			Temperature, °C		Hr of operation	Radiographic inspection		Remarks
			Mg	Zr	U	Hot leg	Cold leg		Hot leg	Cold leg	
43	2¼ Cr – 1 Mo	H_2 fired, acid cleaned	350	250	1000	500 500 500	500 460 400	738 938 7,018	No corrosion	Slight ppt.	
44	2¼ Cr – 1 Mo	H_2 fired, sandblasted	350	250	1000	525 525 525	525 485 415	650 1,417 5,185	No corrosion	Slight ppt.	No apparent detrimental effect of cleaning by sandblasting has been observed.
45	2¼ Cr –1 Mo	Sandblasted, H_2 fired	350	250	1000	525 525 525	525 485 400	650 554 6,794	Slight weld corrosion	Slight ppt.	This loop confirms the result of Loop 41.
46	2¼ Cr – 1 Mo	H_2 fired, nitrided	350	250	1000	550 550 550	550 510 425	573 504 6,581	No corrosion	Slight ppt.	This loop was nitrided to about 0.015-in. deep Zr, and U concentration has been dropping in this loop.
48	2¼ Cr – 1 Mo	H_2 fired, acid cleaned	350	250	1000	550 525 525	550 485 425	549 1,032 5,969	No corrosion	Slight ppt.	
49	1¼ Cr – ½ Mo	H_2 fired, stress relieved at 720°C, acid cleaned	350	250	1000	550 525 525	550 485 425	932 1,007 5,334	No corrosion	Slight ppt.	This loop is made of 1¼ Cr – ½ Mo steel. The result will be compared with Loop 48.
50	½ Cr – ½ Mo	H_2 fired, stress relieved at 720°C, acid cleaned	350	325	1000	550 500 500	550 460 405	890 1,175 4,703	No corrosion	Slight ppt.	Results will be compared with Loops 48 and 49.
51	1¼ Cr – ½ Mo	Stress relieved at 720°C, sandblasted	350	325	1000	550 500 500 550	550 460 400 440	1,413 1,504 963 2,422	No corrosion	Slight ppt.	
53	2¼ Cr – 1 Mo	Normalized from 1750°F, sandblasted	350	325	1000	550 550 500	550 510 400	813 2,331 1,441	Slight pipe corrosion	Slight ppt.	The loop was normalized from 1750°F.
54	2¼ Cr – 1 Mo	Annealed from 1650°F, sandblasted	350	325	—	550	550	4,416	Pitting at pipe and weld	No ppt.	The loop was annealed from 1650°F. Severe pitting was observed under isothermal condition; progress of pitting appears to have stopped.
55	2¼ Cr – 1 Mo	Normalized from 1750°F, sandblasted	350	325	—	550 550 525	550 510 430	1,762 2,114 125	No corrosion	No ppt.	This loop should be identical to 53 (made from same lot of steel).
56	2¼ Cr – 1 Mo	Normalized from 1750°F, sandblasted, W/Be insert	350	325	—	550 550	550 510	3,431 481	No corrosion	No ppt.	To study corrosion of Be and its effect on a U-Bi steel system.
57	2¼ Cr – 1 Mo	Annealed from 1650°F, sandblasted	350	350	—	550 600 700 550 550 550	550 600 700 550 510 415	984 620 123 145 869 99	Pipe corrosion	No ppt.	This loop corroded during isothermal operation as did Loop 54.
58	2¼ Cr – 1 Mo	Normalized from 1750°F, sandblasted	350	325	—	550	550	2,952	No corrosion	No ppt.	About 1500 ppm of various fission products was added to study their effect on corrosion.
59	2¼ Cr – 1 Mo	Normalized from 1750°F, sandblasted	350	325	550	550	550	955	No corrosion	No ppt.	Same as 58 but will be run at different ΔT.

During the last quarter, the following corrosion information has been observed in thermal convection loop operation:

1) Pitting appears to have stopped before penetrating the pipe. This was observed in Loops 33 and 54.

2) Higher hot leg temperature does not increase the rate of corrosion; it is possible that it improves the chance of formation of a protective film. This is illustrated in Loops 40 and 42.

3) A low Mn, 0.30 C, 0.30 Ti steel (Loop 39) was found to be exceptionally resistant to U-Bi. Since the presence of Ti should tie up any N in the steel, it is believed that a protective film of ZrC is being formed. A ZrC film has been found on this steel when exposed to static Zr inhibited Bi.

4) Pitting was observed in Loops 54 and 57 while they were operating under isothermal conditions. Both these loops were fabricated from the same lot of pipe, which chemical analysis has shown to be of nominal 2¼ Cr – 1 Mo composition except that its carbon content was 0.19% instead of 0.15% max. Further study will be made on this to determine why this lot of pipe is less resistant to Zr inhibited U-Bi.

During the period covered by this report, the following two loop tests were completed:

1) Loop 18. This was a 2¼ Cr – 1 Mo steel loop containing molten Pb. The loop was discontinued after 27,765 hr of test because of inability to maintain circulation after a power failure. The loop is being sectioned for metallographic examination, after which a report will be issued.

2) Loop 47. This loop was fabricated from 2¼ Cr – 1 Mo steel, and then nitrided by gas nitriding to a depth of 0.015 in. This loop operated for 6718 hr before it was shut down because of a rupture in the hot leg resulting from an attempt to restart the loop after an electrical winding failure. A detailed report will be issued after metallographic examination.

Miscellaneous Corrosion and Uranium Stability Test

During this quarter, three convection pot tests and 17 tube tests to study the U stability were completed. Most of these tests have been in operation in excess of 20,000 hr. The results generally indicate that U concentration can be maintained if one or more of the following oxygen "getters" are added to the Bi: Mg, Th, Ca, Ti, or Zr. A report on this series of tests is being prepared.

J. Chow

Bearing Test Apparatus

During the past quarter the bearing test apparatus was modified to incorporate a dc canned motor drive. One run was completed in which materials such as Mo, TiC, Rex AA, and Stellite 90 were contacted for a long period of time.

The bearing test consists of contacting a rotating cylinder of one material against a flat specimen of the same or a different material in liquid Bi containing 300 ppm Zr and 350 ppm Mg at 450°C. Specimens are evaluated on a relative basis with regard to wear, surface damage, and coefficient of friction.

All previous runs made with the bearing tester were of 15-min duration and with an applied load of 34 lb. Results of these runs indicated materials such as Stellite 90, Rex AA, TiC with 1020 and 2¼ Cr – 1 Mo steel binders, and Mo to be promising for use in U-Bi. It was felt that such runs were too short to show any corrosion effects, and the calculated bearing pressures were much higher than those encountered in bearing design.

In an attempt to evaluate the effect of longer runs and lower bearing pressure, a run was set up in which the time of contact would be 100 hr and the bearing load 15 lb. Mo was chosen as cylinder material, and Rex AA, Stellite 90, TiC (1020 binder), and TiC (2¼ Cr – 1 Mo binder) were the flat stationary specimens.

Results of this run are shown in Table 17. The condition of the samples is shown in the photograph in Figure 34. It can be readily seen that severe wear had taken place on the Mo cylinder, probably because the Mo was much softer than any of the flat specimens (R_b73 vs R_c45 to 60). In this type of test the initial bearing pressure is extremely high because of the line contact. As wear takes place on the flat specimen, this pressure decreases. In this run, because the Mo was the cylinder, the high bearing pressure and hence greater wear existed through the entire 100-hr contact period.

Inspection of the samples under high magnification revealed the presence of corrosion pits in the contact area of both TiC specimens (Figure 35). Since no other corrosion tests have been performed on this material, it is difficult to determine the added effect of surface rubbing; possibly it re-

Table 17

Rotating Specimen

Material	Hardness Initial	Hardness Final	Surface roughness, μ in. RMS Initial	Surface roughness, μ in. RMS Final	Wear depth, Mls	Surface appearance
Mo	R_b73	R_b70	15	100	0.083	Scoring, transfer of material
"	"	"	"	"	0.044	Fairly smooth, some transfer
"	"	"	"	"	0.030	Fine scoring
"	"	"	"	"	0.038	Fine scoring

Stationary Specimen

Material	Hardness Initial	Hardness Final	Surface roughness, μ in. RMS Initial	Surface roughness, μ in. RMS Final	Wear surface area	Bearing load, lb.	Surface appearance	Coef. of friction
Rex AA	R_c60	R_c60	9	40/150*	0.197	15	Half smooth, half fine scoring	0.137
TiC+1020	R_c45	R_c35	3	175	0.220	15	Fine scoring, corrosion pits in contact area	0.133
Stellite 90	R_c60	R_c60	4	60	0.153	15	Some scoring	0.136
TiC+ 2¼ Cr – 1 Mo	R_c45	R_c43	4	300	0.241	15	Very deep scoring, corrosion pits in contact area	0.140

*Contact area of specimen moved with wear of cylinder. Fine scoring received at start of run and then smooth wear was encountered.

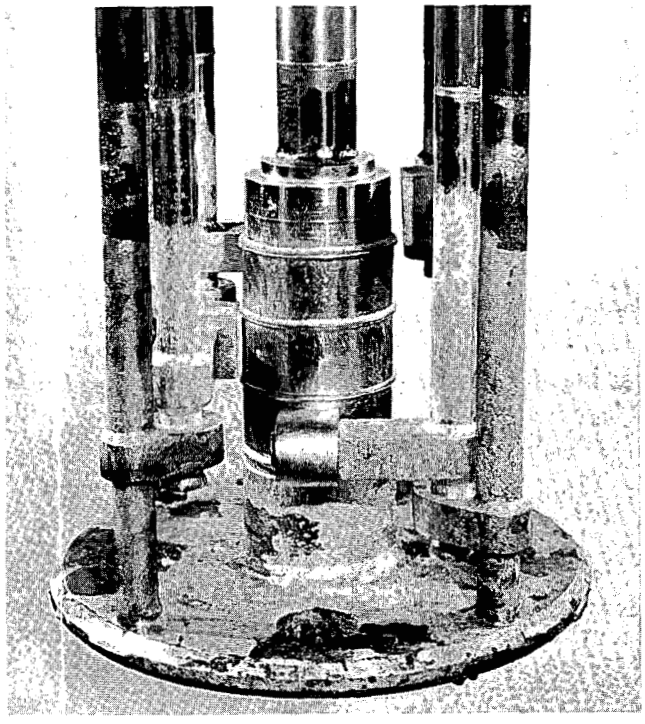

Figure 34. Bearing test apparatus.

Figure 35. TiC specimen from bearing test.

moves any protective surface films which might form, or hastens wetting of the specimen by the Bi in the area of contact, so that the onset of corrosion occurs earlier here than at other parts of the specimen. Future long runs will be made with the harder material as the cylinder. C. KLAMUT

Metallographic and X-Ray Studies

LIQUID METAL THERMAL CONVECTION LOOPS. *Loop 19.* The purpose of this loop was to study corrosion and mass transfer of 2¼ Cr – 1 Mo steel in U-Bi with Zr alone as the inhibitor. However, Zr was shown to drop consistently from 400 ppm to 195 ppm in 2375 hr of operation. After 3848 hr of operation 350 ppm Mg, 1000 ppm U, and 150 ppm Zr were added to the system. Thereafter the loop operated for 9882 hr at a 90°C differential without any noticeable loss in additives. After 13,552 hr of operation, the loop was shut down for metallographic examination.

The loop was fabricated of 2¼ Cr – 1 Mo steel ½-in. schedule 90 pipe and was welded by the inert arc process with a 502 (4 to 6 Cr) filler rod. The loop was cleaned by acid pickling followed by H_2 firing.

A temperature differential of 55°C (550° to 495°) was applied 25 hr after filling and maintained for 3700 hr. The temperature differential was then increased to 90°C (550° to 460°) for 9882 hr.

A thorough metallographic investigation was performed on Loop 19 (Lambda) to determine the extent of corrosion, soundness of the welds, general loop condition, and inhibition by ZrN. Sectioning revealed no evidence of plugging in the cold region. Minute amounts of Fe-Cr were randomly distributed in both the hot and cold legs. The general loop condition was good. No indication was found that any appreciable amount of corrosion had taken place. All welded joints were sound and suffered no ill effects during operation. Attempts to find a ZrN layer on any portion of the system proved unsuccessful.

Loop 35. The purpose of this loop was to study corrosion and mass transfer of a typical 2¼ Cr – 1 Mo steel in U-Bi inhibited with 250 ppm Zr and 350 ppm Mg operating at a 150°C temperature differential.

This loop was fabricated of a 2¼ Cr – 1 Mo steel and contained U-Bi to which 250 ppm Zr and 350 ppm Mg had been added. All welds were performed by the inert arc process with a bar 502 (4 to 6 Cr) filler rod. The corrosion sample was machined from bar stock and hardened by quenching in oil from 1700°F. The loop was cleaned by acid pickling followed by H_2 firing.

The loop operated isothermally (550°C) for 935 hr and with a 135°C (550° to 415°) temperature differential for 4369 hr before being shut down for metallographic examination.

Liquid metal samples taken during operation showed the Zr concentration to be stable for 2000 hr and to drop consistently thereafter. One hundred ppm and 133 ppm were added respectively after 3643 hr and 4478 hr of operation. Other additives remained stable throughout the test.

Loop 35 was completely sectioned and polished. Visual inspection revealed a partial plug covering 3 to 4 in. at the bottom of the cold leg. The precipitate, though not sufficient to stop the flow completely, filled over half the diameter of the pipe.

The entire hot leg exhibited trans and intergranular corrosion. The most severe attack was noted at the "tee." The welds in this area showed considerable corrosion, as did the standard sample inserted 3 in. below the "tee."

Grin 25. The purpose of this loop was to study the effect of AGHT graphite inserted in the hot leg on corrosion and mass transfer in a 2¼ Cr – 1 Mo steel thermal convection loop.

The loop was fabricated of a commercial 2¼ Cr – 1 Mo steel, ½-in. schedule 40 pipe and welded with 502 (4 to 6 Cr) welding rod. An AGHT graphite insert and corrosion sample were included in the hot leg. The corrosion sample was machined from bar stock and oil quenched from 1750°F. The loop was acid cleaned prior to welding and then H_2 fired at 550°C.

A 40°C temperature differential (550° to 510°) was applied to the loop 1 hr after filling and maintained for 526 hr of operation, after which it was increased to 105°C (550° to 445°) for 14,560 hr; the loop was then shut down for metallographic examination.

Recovery of U added to this loop was poor. Of the 1000 ppm added, 850 ppm was recovered; however, this concentration remained stable for the duration of the test. Mg and Zr losses were also experienced. The Mg dropped from 340 ppm to 200 ppm and the Zr from 350 ppm to 175 ppm, which necessitated an addition of 50 ppm at 13,400 hr of operation.

After 13,400 hr of operation, Loop 25 was sent to Metallography for examination. Precipitation had occurred at the bottom of the cold leg. The precipitate covered only a small portion of the surface in this area. Severe inter and transgranular corrosion was found at the "tee" and on the wall just below the "tee." The welds in this area were also attacked, but welds in other portions of the loop were sound. The machined 2¼ Cr – 1 Mo test bushing exhibited no corrosion. The AGHT graphite bushing showed considerable Bi penetration but only slight erosion. The presence of graphite in the loop did not appear to increase the rate of corrosion. Similar loops run without graphite show the same general appearance when examined.

NHF 28. The purpose of this loop was to study corrosion, mass transfer, and stability of additives in a 2¼ Cr – 1 Mo steel loop which had not been H_2 fired.

The loop was fabricated of a 2¼ Cr – 1 Mo steel ½-in. schedule 40 pipe and welded by the inert arc process with a bar 502 (4 to 6 Cr) filler rod. The standard sample was machined from bar 2¼ Cr – 1 Mo stock and heat treated by oil quenching from 1700°F. The loop was acid cleaned.

Immediately after filling with Bi, 250 ppm Zr and 350 ppm Mg were added. After 709 hr of operation, 1000 ppm U were added. The loop was placed on a 40°C (550° to 510°) temperature differential immediately after filling and operated at this ΔT for 1428 hr. The temperature differential was then increased to 100°C (550° to 450°) for 9500 hr, after which the loop was shut down for metallographic examination.

Liquid metal samples taken during the test showed a slight drop in Mg. The U concentration remained the same throughout the test, and the Zr dropped slightly. Fifty-one ppm was added after 8413 hr of operation; however, similar drops in Zr content have been observed in these experiments when corrosion and precipitation occur.

As in the previous loops, a small build-up of Fe-Cr plug material was found at the bottom of the cold leg. The areas subjected to the greatest amount of corrosion were the "tee" and just below the "tee." Welds in these areas were also attacked. The machined 2¼ Cr – 1 Mo test bushing revealed no corrosion.

General Loop Remarks. 1) The walls of all 2¼ Cr – 1 Mo loops show decarburization on both the o.d. and i.d. 2) U-Bi, Mg-Bi, and Zr-Bi particles are found uniformly distributed throughout the loops. 3) The i.d. of all pipe walls exhibits an irregular condition due to the pretreating chemical cleaning operation.

Loop H Welds. Two weld failures were noted during the operation of Loop H. In each instance the welds exhibited cracking through the weld material and large masses of Fe_2O_3 on the outer surface of the pipe. This oxide may be formed by a mechanism similar to that encountered in Cr-Mo steels in the presence of a small amount of oxidizing agent. In this instance Bi_2O_3 acting in this manner could react with the steel surface to form the Fe_2O_3. The latter compound was identified by x-ray diffraction.

Examination of Special Heats from Babcock and Wilcox. Fourteen samples were submitted to Metallography for photomicrographs of representative structures and the measurement of the decarburized layer at the i.d. of the pipe. Decarburization ranged from 0.002 to 0.064 in. on a piece of 1¼ Cr – ½ Mo pipe. A complete chart is

Table 18

Specimens Forwarded to U.S. Steel

Specimen	Loop	Material	Location in Loop	Condition
1	Grin	2¼ Cr – 1 Mo	Top of hot leg	Severely pitted
2	Grin	2¼ Cr – 1 Mo	Bottom of hot leg	Good
3	Lambda	2¼ Cr – 1 Mo	Center of hot leg	Excellent
4	HVL – Run 2	2¼ Cr – 1 Mo, nitrided	Adjacent to right-angle bend sample No. 238	Excellent
5	Loop G	1¼ Cr – ½ Mo	From hot test section	Excellent
6	Loop G	521 weld	Weld No. 6 from hot test section	Excellent
7	Bess	Bessemer steel	Center of hot leg	Excellent

available, along with the various structures, in Metallurgy Memo 693.

Selection and Preparation of Electron Diffraction Specimens for U.S. Steel. Various specimens from the loops that have been examined were sent to U.S. Steel for electron diffraction studies (Table 18). Most samples taken from loops which were run at 550°C maximum reveal no layer formations when examined with standard microscopic and x-ray diffraction techniques. It was felt that electron diffraction methods might help identify surface layers.

Electron diffraction results have been obtained from U.S. Steel. The patterns were all different, but none match the patterns of ZrN or ZrC. A possible identification has been reported of the pattern from Sample 1 as $Zr(NO_3)_4 \cdot 5H_2O$ or Fe_4N. The remaining six patterns could not be identified. Patterns of UC, UC_2, UN, UN_2, UFe_2, and U_3Bi_5 that are not in the ASTM index have been sent to U.S. Steel to aid in the identification work. O.F. Kammerer and J. Sadofsky

Miscellaneous Test Work

Thermal Cycling of BNL Natural Uranium Elements. Inspection of the three 30-slug fuel

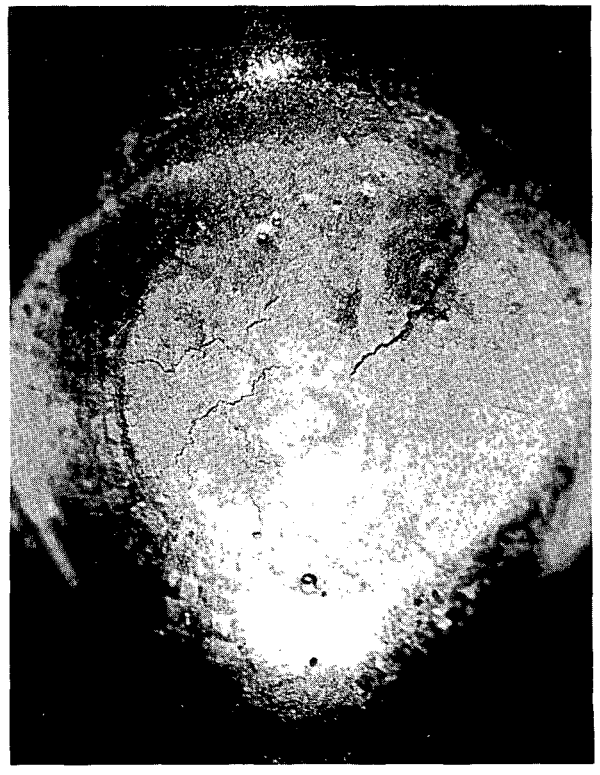

Figure 36. Cracks in weld.

Table 19

Cycling Test Results

Run No.	Element	No. of cycles	Type of weld	Welding rod	Condition of welds at start	Results
1	A	108	Penetration	2S	Cracked	No crack progression
	B	108	Tight bridge	2S	Satisfactory	No cracks developed
	C	108	Penetration	2S	Cracked	No crack progression
	D	108	Tight bridge	2S	Satisfactory	No cracks developed
2	E	200	Penetration	2S	Cracked	No crack progression
	F	200	Penetration	2S	Cracked	No crack progression
	G	200	Penetration	2S	Cracked	No crack progression
	H	200	Penetration	2S	Cracked	No crack progression
3	I	217	Penetration	43S	Satisfactory	Satisfactory
	J	217	Penetration	43S	Satisfactory	Satisfactory
	K	217	Penetration	43S	Satisfactory	Satisfactory
	L	217	Penetration	43S	Satisfactory	Satisfactory
4	M		Tight bridge	2S	Satisfactory	Still under test
	N		Tight bridge	2S	Satisfactory	
	O		Tight bridge	2S	Satisfactory	
	P		Tight bridge	2S	Satisfactory	

elements cycled 655 times from 400° to 40°C showed no major physical or dimensional changes. Maximum elongation was approximately 0.065 in., and volume increase was 2 cc.

These elements were then cycled from 470° to 50°C. After 210 cycles only very slight elongation and volume changes occurred. At no time was there evidence of physical damage such as "pimpling," excessive fin sag, or any wall irregularities. This test has been discontinued to permit cycling of the enriched uranium BNL elements.

Thermal Cycling of Enriched BNL Fuel Elements. Minute cracks were observed on the welds of many recently received "windmill" elements fabricated by the Sylvania Electric Co. for service in the BNL reactor (Figure 36). These cracks occurred on welds which penetrated the 61St end rings and in which the welding rod had been 2S Al. Occasional cracks were found on any "bridge" welds or penetration welds made with 43S welding rod.

Bridge welds were of two types. A "loose bridge" weld closes the gap across the floating end ring, and a "tight bridge" weld butts the rigid end ring without actual penetration into the ring. Elements of each type were thermally cycled from 385° to 40°C to determine progression of cracked welds and possible crack formation on bridge or 43S welds. The "floating" end rings and their "loose bridge" welds are not listed as no cracks occurred. Cycling test results are given in Table 19.

The results of runs made thus far indicate that the cracks present in the "as received" elements do not appear to propagate under thermal cycling. Modified end ring joints with a "tight bridge" weld or a 43S filler rod do not show cracks in the "as received" condition, and these joints stand up well under thermal cycling. Mechanical tests performed on the thermally cycled elements by the Reactor Operations Group have shown that the "cracked weld" elements are not as strong as the modified end ring designs.

F. Iseli and C. Klamut

FUNDAMENTAL CORROSION STUDIES

Surface Reaction Studies

To obtain qualitative, rapid information on the corrosion resistance and film formation properties of various steels, a program on surface reactions is being carried out at elevated temperatures (600° to 800°C).

Previous results on six 2¼ Cr – 1 Mo steels containing various N to Al ratios from 28 to 0.19 (Table 20) indicated that the x-ray diffraction intensity patterns for ZrN films formed on these steels were proportional to these N/Al ratios. Similar studies on pure Fe indicated that high Mg and low Zr concentrations had the same protective effects as saturated Zr. To check further the effects of various N/Al ratios and high Mg concentrations, and to see whether thorium nitride films would inhibit corrosion, these same steels and a Bessemer steel were contacted with 1) Th-Bi solution, 2) Th-Zr-Bi solutions, and 3) high Mg-Bi solutions. The results are reported below.

Magnesium-Steel Reactions. The six steels listed in Table 20 were contacted with a 2.34% (by wt) Mg in Bi solution for 200 hr at 693°C. At the end of this time, the adherent Bi was removed and the samples were examined. Metallographic

Table 20

% Composition

No.	C	Mn	P	S	Si	Cr	Mo	Al (tot)	Al (sol)	N (tot)	N/Al*
1	0.10	0.40	0.014	0.014	0.21	2.36	1.03	0.007	0.003	0.042	28
2	.14	.55	.012	.013	.27	2.40	1.05	.007	—	.050	1.3
3	.13	.69	.012	.014	.29	2.48	1.02	.008	—	.010	2.15
4	.13	.63	.014	.012	.32	2.57	1.13	.14	—	.013	0.19
5	.09	.40	.011	.010	.26	2.35	0.99	.40	—	.056	0.28
6	.11	.07	.010	.010	.24	2.42	1.00	.094	.062	.049	1.6

*N/Al is obtained from the total N and the soluble Al. For the steels that lack the soluble Al analyses the N/Al ratio is a minimum.

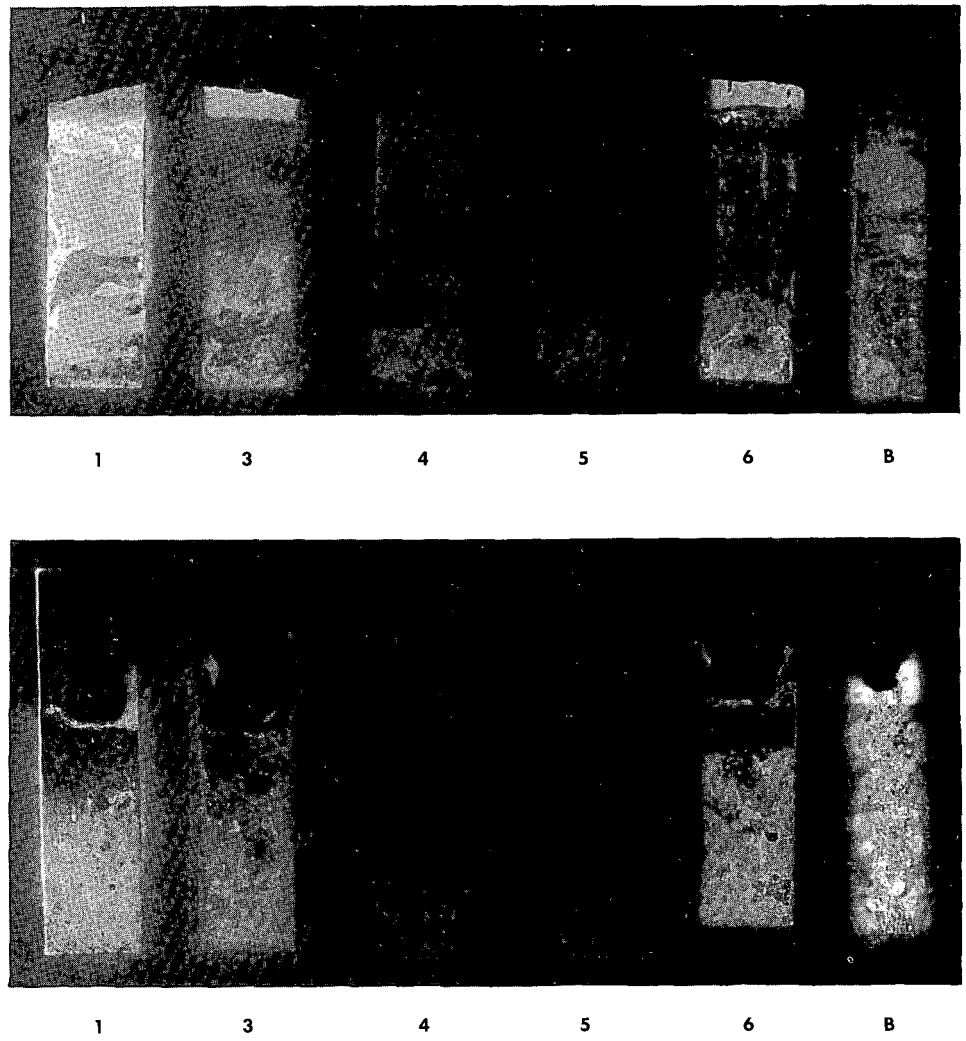

Figure 37. Autoradiographs of steels contacted with Th-Bi.
Top, polished sides; bottom, etched sides.

examination showed that all six steels were wetted above the liquid level interface and that slight uniform intergranular attack had taken place. No detectable surface deposits were found by x-ray examination.

THORIUM-STEEL REACTIONS. Steels No. 1, 3, 4, 5, and 6 (Table 20) and a Bessemer steel were contacted with 0.55% Th in Bi for 185 hr at 689°C.

Visual observation indicated no corrosion on any of the samples. The patterns obtained by x-ray diffraction are at present unidentified, although the intensities vary directly with the N/Al ratios. This indication that the Th in the surface deposit is in some way tied up with N is borne out by further data obtained by beta counting and by autoradiographs of the samples. Figure 37 shows a 65-hr exposure of the six dipsticks. It can be seen that both the polished and the acid-etched (1:1 HNO_3-H_2O) faces show approximately the same relative intensities as the N/Al ratios, viz., 1, Bessemer, 6, 3, 4, and 5, respectively. The beta-gamma counts (2 min) obtained are given in Table 21.

THORIUM-ZIRCONIUM-STEEL REACTIONS. A duplicate set of the above six steels (1, 3, 4, 5, 6, and Bessemer) were contacted with 0.17% Th and 280 ppm Zr in Bi for 190 hr at 699°C. None of the steels showed any attack. The Bessemer steel and No. 1, 6, and 3 produced ZrN films, but no

Table 21

Beta-Gamma Counts
(Background=37)

Stock	Polished face	Etched face
No. 1	285	148
No. 3	142	107
No. 4	69	68
No. 5	61	64
No. 6	151	180
Bessemer	237	260

detectable deposit could be found on No. 4 or 5. It is noteworthy that these latter 2 steels form ZrC under other conditions (June 1957 Progress Report) and have never formed ZrN.

STEEL-COMPARISON STUDIES. Preliminary results have been obtained from a program designed to distinguish between the corrosion resistance of various steels and between different heats of the same steels.

Two 1¼ Cr – ½ Mo, three 2¼ Cr – 1 Mo, one 1081, one Bessemer, one mild steel, and No. 1 and 4 (Table 20) were contacted with 1110 ppm U, 440 ppm Mg, and 221 ppm Zr for 216 hr at 700°C. Only the two 1¼ Cr – ½ Mo steels and one of the 2¼ Cr – 1 Mo steels showed some attack at the liquid level interface. However, because of the geometry of the experiment, these three steels may have had metal contacts different from those of the adaptor pins. The experiment is being repeated with this condition corrected.

X-ray and metallographic examinations of the sections of the steels immersed below the liquid level have shown that none of the steels were attacked. The two 1¼ Cr – ½ Mo steels gave ZrC layers, Bessemer gave a ZrN layer, the three 2¼ Cr – 1 Mo gave ZrC layers, 1081 and No. 4 gave ZrC layers, No. 1 gave a ZrN layer, and the mild steel showed nothing. D. SCHWEITZER

Nitrogen and Aluminum Analyses

During the previous report period a series of 2¼ Cr – 1 Mo steels with the same N/Al ratio of 2 were contacted with Zr-Bi solutions for various times (20 to 200 hr) and temperatures (680° to 820°C). The results indicated that when ZrN films were formed the total N contents of the steels were depleted a maximum of about 20%.

A similar program was undertaken to determine the effect of various N/Al ratios on the depletion of N in 2¼ Cr steels under various time, temperature, and additive conditions. Steel No. 1 had an initial total N of 0.042%. The results on this steel (N/Al=28) are given in Table 22. These results are significantly different from those obtained with standard 2¼ Cr – 1 Mo steels (N/Al=2) run under similar conditions. The high N/Al steels not only have lost more than 90% of the total N but also end up with a lower residual N content than the standard 2¼ Cr steels.

D. SCHWEITZER

Solubility Studies

Recent results have indicated that the solubility of U in Bi is lowered by the presence of 100 ppm or more of Zr. In order to clarify the problem, a study of the ternary U-Zr-Bi system is being carried out. As a first step in this program, the solubility of U in Bi was rechecked and found to be lower than that reported by D. Bareis. The results of the investigation to date are reported below.

URANIUM IN BISMUTH. The solubility of U in Bi was measured over the temperature range 295° to 687°C. Samples were equilibrated from 5 to 40 hr. The temperature was measured at the time the sample was taken by a thermocouple placed in contact with the top of the graphite sampler. The equilibration temperatures for six random samples were rechecked by placing the thermocouple in a graphite shield and immersing the couple in the melt immediately after taking the sample. Four of these temperature rechecks

Table 22

Melt composition	Time, hr	Temperature, °C	Total N	N as AlN	Al (sol)	Al (insol)
1) 500 ppm Zr+1.5% Mg in Bi	288	705	0.0039	0.0002	0.003	0.012
2) 500 ppm Zr in Bi, no Mg	260	715	.0039	.0002	.003	.010

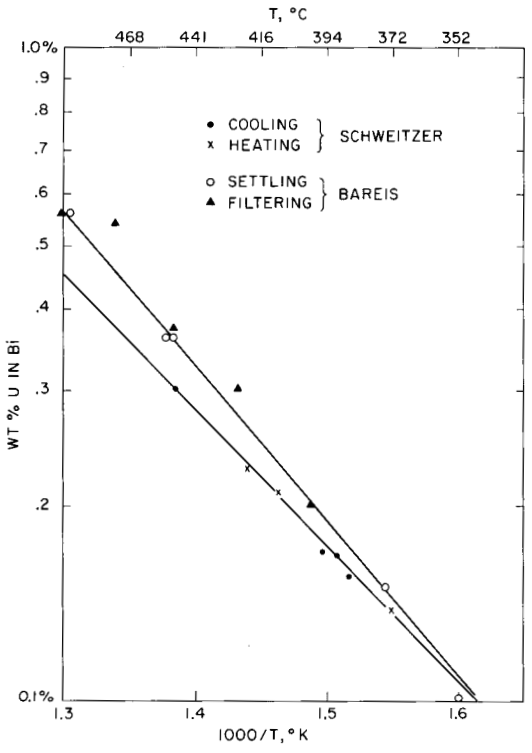

Figure 38. Solubility of U in Bi.

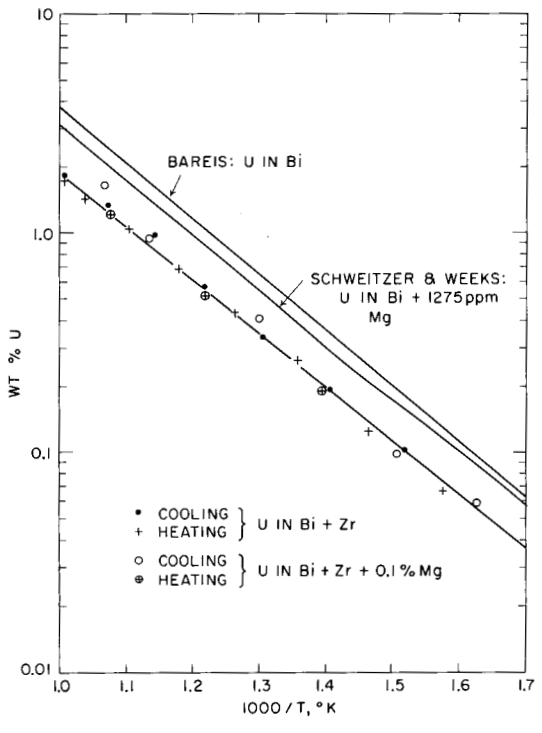

Figure 39. Solubility of U in Bi saturated with Zr.

Table 23

Uranium Solubility from Curves of Figure 38

Schweitzer		Bareis	
Temperature, °C	U solubility, %	Temperature, °C	U solubility, %
350	0.105	350	0.107
360	.118	360	.123
370	.134	370	.140
380	.149	380	.159
390	.167	390	.181
400	.185	400	.205
410	.205	410	.230
420	.227	420	.259
430	.251	430	.290
440	.276	440	.324
450	.303	450	.360

Table 24

Uranium Solubility Data (Experimental, Schweitzer)

Temperature, °C	% U	Temperature, °C	% U
449	0.300	370	0.138
395	.168	419	.226
345	.084	386	.155
295	.044	490	.209
320	.062	390	.167

were identical with those by the original method, and the other two showed maximum differences of 4°C. At the end of the run the freezing point of the U-Bi solution was determined to be 271.3± 0.3°C. A further check on temperature calibration was made by placing a bare thermocouple in a well drilled in the bottom of the crucible containing the U-Bi solution. This was compared both to the thermocouple used in the normal sampling procedure and to a bare thermocouple encased in a quartz tube and immersed in the melt. At 675° and at 410°C all three thermocouples read alike to within 4°C.

In the range from 295° to 500°C the values obtained from 2½ cycles of cooling and heating can be expressed by the equation

$$\log_{10}(\text{ppm U}) = 6.33 - (2062/T).$$

The average deviation from the straight line where the deviation (in %) is defined as the absolute value of

Table 25

Temperature, °C	U solubility, %			Zr solubility, %	
	In Bi*	In Bi**	In Bi+Zr	In Bi	In Bi+U
700	3.15	2.6	1.65	0.69	0.68
650	2.25	1.9	1.19	.48	.44
600	1.58	1.03	0.84	.32	.30
550	1.04	0.86	0.56	.20	.175
500	0.59	0.47	0.36	.125	.100
450	0.360	0.303	0.215	.071	.060
400	0.205	0.185	0.120	.036	.033
350	0.107	0.105	0.061	.017	.016

*From D.W. Bareis
**From D. Schweitzer

$$\frac{\text{line value} - \text{experimental value}}{\text{line value}} \times 100$$

was found to be less than 2%.

Figure 38 shows a plot of this data in the temperature range 350° to 500°C and a similar plot of the data obtained by D. Bareis. Table 23 gives the interpolated data from both plots. Experimental data are listed in Table 24.

A plot of the solubility data of U in Bi from 500° to 700°C does not appear to follow the straight line obtained at the lower temperature but curves up toward higher concentrations. At present insufficient data are available to describe accurately the high temperature portion of the solubility curve.

Effect of Saturated Zirconium and 1000 ppm Mg on the Uranium Solubility. The mutual solubility of U and Zr in Bi has been measured over the temperature range 325° to 700°C. The U solubility was appreciably decreased by saturating the Bi with Zr. Only a slight decrease was noted in the Zr solubility; typical values obtained are given in Table 25.

The data, obtained by both heating and cooling to the equilibration temperatures, can be approximated to within analytical error (±5%) by the equation

$$\log_{10}(\text{wt \% U}) = 2.74 - (2460/T) \quad \text{(Figure 39).}$$

The addition of 1000 ppm Mg had no additional effect on the U or Zr solubility. The absence of an effect due to Mg is substantiated by previous work in which the solubility of U was determined in the presence of 1275 ppm Mg. At that time the U values were reported as lower than those of Bareis, and the decrease in the U solubility was attributed to the Mg. However, these former results agree very well with the normal U solubility obtained in this laboratory.

J.R. Weeks

Solubility of Uranium for Fixed Amounts of U, Zr, and Mg. A series of experiments has been started to investigate the conditions for precipitation of U and Zr from Bi melts as they are cooled. A predetermined amount of U and Zr (and occasionally Mg) is dissolved in a graphite crucible at a temperature well in excess of that required for complete solution of U and Zr. The melt is then cooled in increments, and the liquid metal is sampled with a filtration technique at each temperature. When the freezing point of Bi is reached, the melt is reheated in increments and again sampled at each temperature. The results of two such experiments are shown in Figures 40 and 41.

Figure 40 shows the results obtained when 250 ppm Zr, 1500 ppm U, and 350 ppm Mg were added; these are listed in Table 26. Figure 41 shows the results obtained when 580 ppm Zr and 1420 U were added; these are listed in Table 27. Other experiments with excess U present and either 250 ppm Zr and 300 ppm Mg or 500 ppm Zr and 300 ppm Mg gave U solubility results similar to that obtained in the absence of Zr with less than a 10% decrease in U solubility between 350° and 500°C (Figure 42; Table 28). A careful study of the U-Zr-Bi ternary system is required before these results can be interpreted.

J.R. Weeks

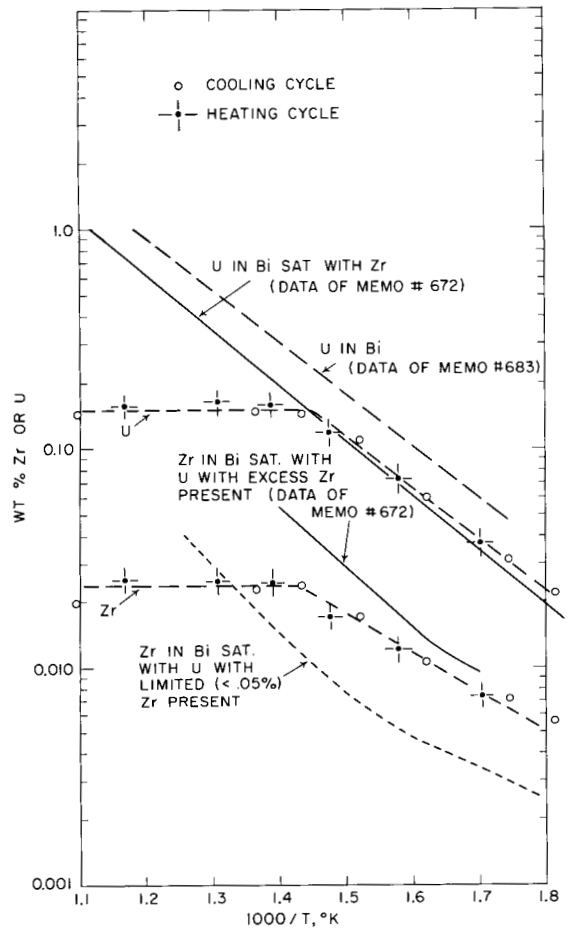

Figure 40. Solubility data from cooling a Bi melt containing 220 ppm Zr, 1500 ppm U, and 340 ppm Mg.

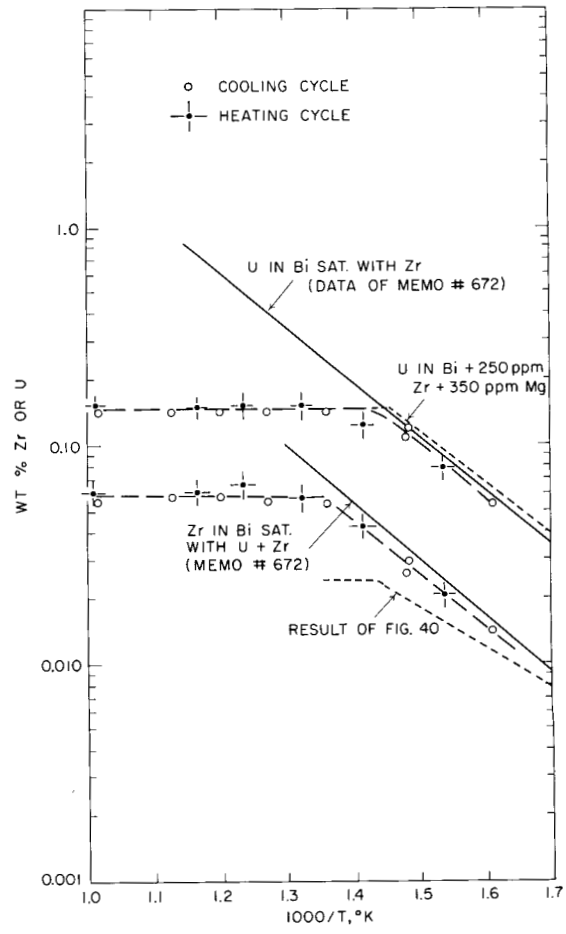

Figure 41. Solubility data from cooling a Bi melt containing 580 ppm Zr and 1420 ppm U.

Table 26

Data for Figure 40
(1500 ppm U, 250 ppm Zr, and 350 ppm Mg in H_2 fired Bi in graphite crucible)

Sample	Equilibration time, hr	Temperature, °C	1000/T, °K	ppm U	ppm Zr	ppm Mg
S-745	42	640	1.095	1450	198	344
S-746	5	459	1.366	1480	226	332
S-747	17	424	1.434	1440	235	—
S-748	5	384	1.521	1090	169	—
S-749	65	344	1.621	600	106	341
S-750	5	300	1.745	310	71	—
S-751	17	279	1.811	220	56	—
S-752	5	314	1.703	370	74	350
S-753	17	360	1.579	720	120	—
S-754	5	404	1.476	1180	171	—
S-755	17	447	1.388	1590	241	335
S-756	5	491	1.308	1630	249	—
S-757	17	583	1.168	1655	252	330

Table 27

Data for Figure 41
(1420 ppm U and 580 ppm Zr in H_2 fired Bi in graphite)

Sample	Equilibration time, hr	Temperature, °C	1000/T, °K	ppm U	ppm Zr
S-761	90	711	1.016	1430	555
S-762	4	615	1.126	1420	585
S-763	17	560	1.200	1430	585
S-764	5	513	1.272	1410	555
S-765	17	461	1.362	1420	540
S-766	5	400	1.485	1180	295
S-767	23	402	1.481	1090	258
S-768	5	348	1.610	540	141
S-769	17	378	1.536	780	207
S-770	5	432	1.416	1220	430
S-771	65	483	1.323	1520	580
S-772	5	537	1.234	1520	660
S-773	17	586	1.164	1500	610
S-774	5	718	1.009	1520	610

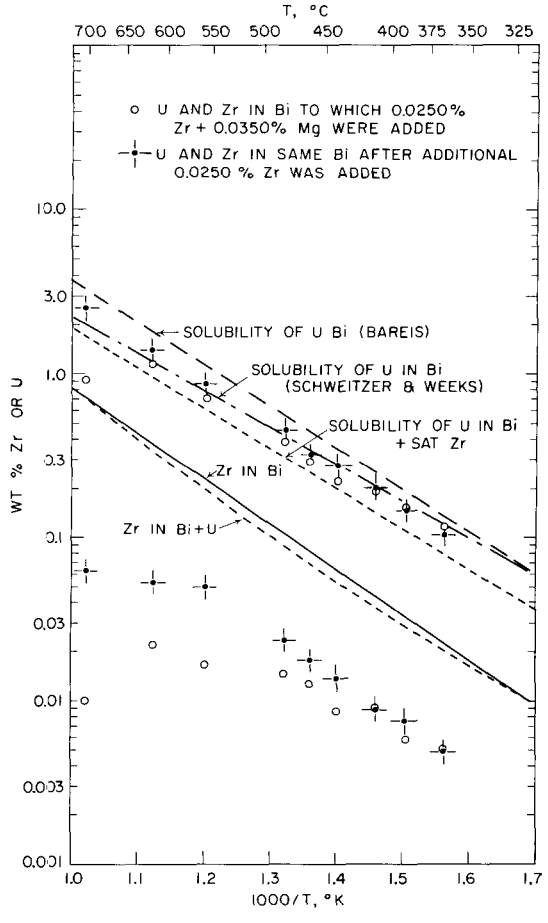

Figure 42. U-Zr solubility effects in Bi.

Table 28

Solubility of U in Bi to Which 250 ppm Zr and 350 ppm Mg Had Been Added

Temperature, °C	Equilibration time, hr	% U	ppm Zr	ppm Mg
706	18	0.92	100	283
462	5	0.293	129	297
413	18	0.193	91	300
367	9	0.118	51	300
392	36	0.152	58	290
441	5	0.222	85	286
484	18	0.39	146	281
553	5	0.71	163	274
617	4	1.14	220	260
250 ppm additional Zr added at this point				
617	20	1.40	530	249
462	5	0.32	177	255
413	18	0.198	96	257
367	5	0.103	48	266
392	16	0.149	75	266
441	48	0.278	138	262
484	5	0.46	233	255
553	18	0.87	500	251
706	5	2.54	625	254

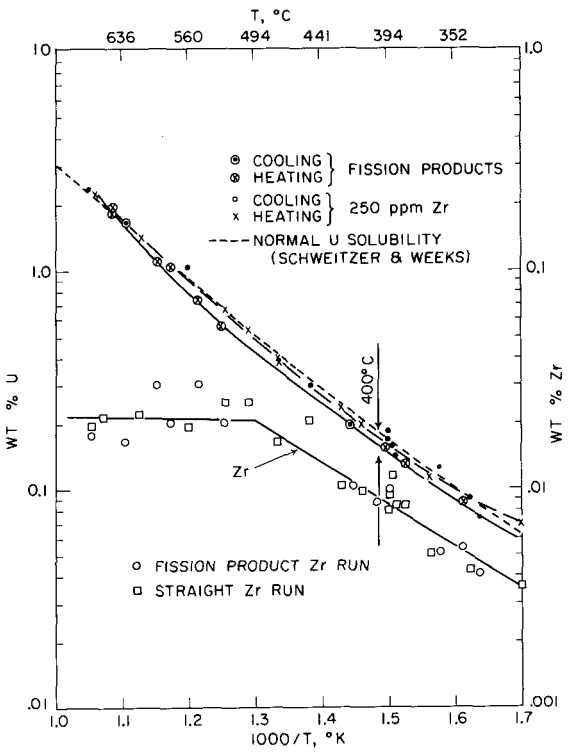

Figure 43. Solubility of U in Bi+250 ppm Zr, and in Bi+250 ppm Zr+350 ppm Mg+120 ppm fission products. Excess U present at all times.

Solubility of Uranium in the Presence of Fission Products. The solubility of U in the presence of 250 ppm Zr, 350 ppm Mg, 60 ppm Nd, 15 ppm Sm, 15 ppm Sr, 10 ppm Cs, and 8 ppm Ru is shown in Figure 43 along with the solubility of U in the presence of 250 ppm Zr. The latter data are in excellent agreement with the run described in the previous section (U in presence of 250 Zr+350 Mg) both for U and for Zr (Figure 41). Therefore the difference in the U solubility curves shown in Figure 43 is due to the fission products and not to the Zr or Mg. The analytical data for both runs are listed in Tables 29 and 30.

D. Schweitzer

Solubility of Mn in Bi. The solubility of Mn in Bi over the range 330° to 500°C can be expressed by the equation

$$\log_{10}(\text{wt \% Mn}) = 3.79 - (2168/T) \quad \text{(Figure 44).}$$

D. Schweitzer

Radiation Effects

LMFR PROGRAM

BNL Capsule Program

The capsule development was undertaken so that samples of steel or graphite in contact with

Table 29

Data for Figure 43
Solubility of U in the presence of 250 ppm Zr, 350 ppm Mg, and 120 ppm fission products

Sample No.	Temperature, °C	U, ppm	Zr, ppm	Mg, ppm	Cs, ppm	Sr, ppm	Rare earths, ppm Nd+Sm	Ru, ppm
1	502	none	none	303	<2	3.3	70 – 100	8
2	672	16,400	170	361	20	19	"	"
3	629	16,300	167	344	13	19	"	"
4	399	1,500	87	364	<3	17	"	"
5	578	10,200	215	324	7	16	"	"
6	420	1,940	104	328	<3	13	"	"
7	395	1,470	73	365	<3	14	"	"
8	362	1,240	51	349	<3	14	"	"
9	338	750	41	362	<3	14	"	"
10	304	550	27	348	<3	14	"	"
11	348	870	54	324	<3	<2	"	"
12	383	1,340	84	307	<3	<2	"	"
13	396	1,500	98	310	<3	3.5	"	"
14	525	5,500	212	290	<3	3.5	"	"
15	549	7,300	316	304	7	7	"	"
16	595	10,900	312	285	<3	<2	"	"
17	648	19,600	262	268	—	—	"	<3
18	649	18,400	257	276	17	20	"	<3

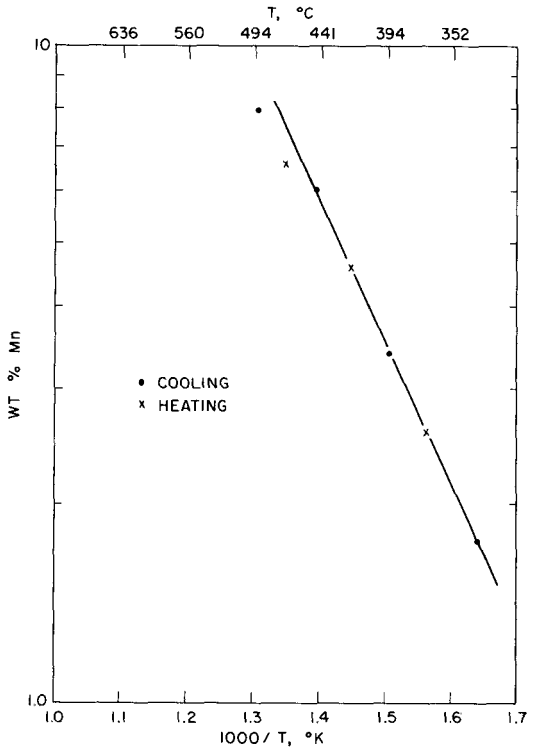

Figure 44. Solubility of Mn in Bi.

the U-Mg-Bi-Zr solutions could be exposed to neutrons and fission products in the temperature range 300° to 700°C. These samples are examined for corrosion and physical property changes.

The design which has been evolved appears to be satisfactory. The capsule consists of two stainless steel cylinders, one inside the other, with the annular space between them evacuated. The inner can contains the U-Bi solution with inhibitors inside a graphite cylinder. The capsules are evacuated through a nickel tube which is sealed off under vacuum. Pending examination in the hot cell it appears that nickel tubing can be sealed off and remain tight during irradiation. A laboratory mock-up of this design for calibration purposes is in progress. The status of the capsules since the last progress report is indicated in Table 31.

The capsule's design is now complete, and samples can be irradiated in large numbers when hot cell facilities are available. More than ten capsules have been irradiated but not yet opened for metallurgical examination. Therefore, every effort is being made to complete the intermediate

Table 30

Solubility of U in Presence of 250 ppm Zr
(Added 16.4 g U to 407 g Bi in graphite crucible. After removal of 250 g of samples, 250 g additional Bi were H_2 fired into the crucible, and 200 ppm Zr added to the melt.)

Sample	Equilibration time, hr	Temperature, °C	1000/T, °K	ppm U	ppm Zr
U-15	66	734	0.993	26,400	205
U-16	5.5	678	1.051	23,900	198
U-17	18	561	1.198	10,500	206
U-18	5	450	1.383	2,930	208
U-19	19	395	1.497	1,660	92
U-20	5.5	344	1.621	890	40
U-21	18	292	1.770	520	30
U-22	6	316	1.697	690	36
U-23	18	368	1.560	1,130	50
U-24	5	425	1.432	2,370	104
U-25	18	475	1.336	3,900	167
U-26	18	614	1.127	14,000	230
U-27	5	389	1.510	1,400	81
U-28	18	412	1.460	1,960	98
U-29	5	394	1.499	1,820	78
U-30	18	671	1.059	17,700	226
U-31	23	671	1.059	21,500	216
U-32	41	671	1.059	22,500	212
U-33	5	502	1.290	5,400	252
U-34	18	523	1.256	6,600	—
U-35	5	392	1.504	1,530	250

Table 31

Status of Capsules

Capsule No.	Concentrations, ppm U	Mg	Zr	Sample	Max. Bi Temperature °C	Exposure days
20	4000	190	160	Graphite G with ZrN-ZrC layer	580	10
21	4000	190	160	Morgan Crucible EY9	700	20
22	4000	190	160	Morgan Crucible EY9	680	42
23	4400	350	250	1¼ Cr Steel 2¼ Cr Steel	550	In the pile since Aug. 24

hot cell so that more samples can be irradiated and examined. J. MILAU

Radiation Effects Loop 1

The purpose of this loop is to study the corrosion and physical changes of LMFR materials under radiation, high velocity, and temperature conditions that may exist in the LMFRE. This is a cooperative project between Babcock and Wilcox and BNL. BNL's responsibilities are to construct and fabricate the in-pile portion, shielding, sampler, velocity gage, mass transfer deposition gage, pump control panel, and shielding. Babcock and Wilcox is to fabricate the out-of-pile portion which includes the containment box, heater exchanger, cooler, furnace, and melt dump tank. The status of the BNL work is described below.

DEPOSITION GAGE. A method is desired for determining the quantity of material deposited on the cold leg of the in-pile loop. Radiography is not suitable because of the radiation present in the loop. Ultrasonic methods were considered, but several problems were encountered which would require extensive development. It was concluded that emphasis should be placed upon developing an instrument which would measure thickness magnetically. The Instrumentation Division has cooperated with the radiation effects group to design such an instrument. The gage will measure the reluctance of a magnetic circuit containing the pipe. It consists of an iron yoke, the pipe to be measured, a dummy pipe, a detector coil, and a pair of primary coils. The schematic arrangement is shown in Figure 45.

A and *B* are the measured pipe and dummy pipe with their axes perpendicular to the plane of the paper. Coils *C* and *D* are the primary coils placed around the iron yoke *F*. A voltage from an oscillator produces a current in the primary coils such that a magnetic field is produced around the yoke and pipes in the direction indicated by the arrows. It may be seen that the magnetic fields in the center of the yoke buck each other, and no voltage may be detected in the detector coil *F*. When a deposit is formed in the pipe, there will be an unbalance in the magnetic fields and the net field in the center will not be zero. A voltage will then be produced in the detector coil. This voltage is amplified and sent to a phase detector where it is read on a dc voltmeter. A block diagram of the circuit is shown in Figure 46.

FLOW GAGE. A gage is desired for measuring the flow of liquid Bi in the radiation (in-pile) loop without utilizing pressure trans-

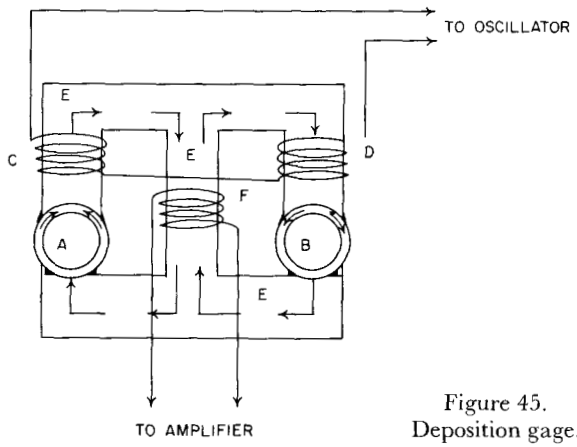

Figure 45.
Deposition gage.

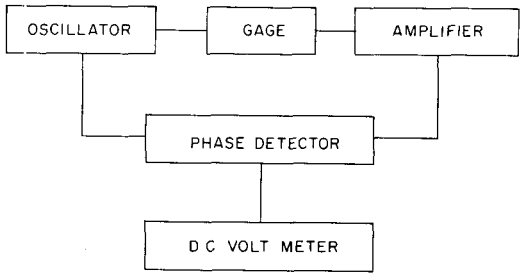

Figure 46. Detector circuit.

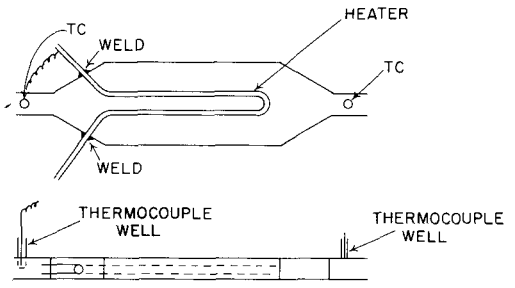

Figure 47. Flow gage.

mitters or bellows, which have created difficulties in previous loops. A type of flow gage utilizing the measurement of the time of passage of a thermal pulse was investigated, but experimentation on a water system indicated that a heat pulse sharp enough to observe could not be readily generated.

Measurements of water flow were made by a heat balance method and compared to measurements by a calibrated rotometer. The range of 1 to 9 gpm was covered. If temperature measurements are taken 1 min after a change of flow rate, a 5% deviation is found. If, however, about 10 min is allowed to elapse after a change in flow rate, the accuracy is better than 2%.

Based upon the mock-up in water, a flow gage for the radiation loop has been designed. The heater element consists of a U-shaped nichrome element surrounded by MgO insulation with a 2¼ Cr Croloy tube swaged over the insulation. The element is welded to a section of pipe as shown schematically in Figure 47. The film temperature at 6 gpm and 1000 watts is calculated to be somewhat less than 15°F above the bulk liquid Bi temperature. It is planned to put this device in Loop H and compare it with the flow measuring device already in this loop. A.E. Roswell

Test Section for Radiation Loop. The test sections of the loop are for the purpose of determining the effect of U-Bi solution on the properties of reactor materials. The Bi solution will have additions of Mg and Zr as corrosion inhibitors. These should form protective layers on the steel and graphite and thus reduce the rate of corrosion as demonstrated in out-of-pile loops. It is conceivable that the layer may be damaged or flake off because of the fission recoil particles and neutrons, which would reduce the protection. The rate of corrosion will then depend on the rate of formation of a new layer. But corrosion is not the only property to be investigated. The tensile and impact strength of the steel will also be tested for effects of exposure to neutrons, fission recoils, and Bi corrosion. The tensile bars are 1¼ in. long and 0.100 in. minimum diameter, and the impact bars are a modified charpy bar with 0.1 in. root diameter and 3/16 in. o.d.

The test materials are 2¼ Cr and 1¼ Cr Croloy normalized at 1750°F and tempered at 1350°F. Others are annealed at 1650°F. Be (QVM) rods will also be placed in the test section, as well as types of the most impervious graphite. The corrosion test assembly will be a sample tube com-

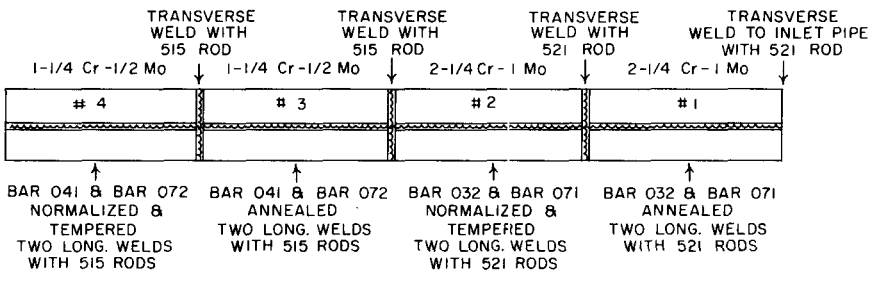

Figure 48. Corrosion test assembly, Radiation Loop 1. After making transverse welds, stress relieved at 1325°F for 1 hr, finish machined to 59/64 in. o.d., ¾ in. i.d., 12⅜ in. long.

posed of segments welded together as shown in Figure 48.

The test sections are composed of tube samples that contain the impact and tensile specimens. The velocity across the surfaces will be 7 to 8 ft/sec because of the constriction of cross sectional area by samples. The same test sections will be placed in three positions in the loop. These are high temperature (475°C), high flux in the center of the pile; high temperature, low flux in the hold-up tank; and low temperature (400°C), no flux.

PUMP. The out-of-pile test will be for at least 500 hr and should start in early October.

SAMPLER. A Lucite mock-up has been made and remotely operated successfully in the laboratory. It is expected that the prototype will permit remote sampling of the loop.

ZrC Layer Study

This is an effort to understand the rate of growth, adherence, and thermal stability of ZrC layers on graphite. An apparatus for evaporation of Zr on graphite was completed and tested. A Zr wire wound furnace was used to evaporate the Zr. The Zr did not adhere to the graphite, and it is felt that this was because the graphite had not been previously degassed. Graphite will be heated in this apparatus by passing current through the specimen, and then Zr wil be evaporated onto the clean graphite.

Graphite samples have been placed in a Zr-Bi solution at 1250°C for 38 to 194 hr. No coherent, uniform layer has been formed as yet. This method of layer deposition will be continued with different graphites, outgassing procedures, and deposition times. M. BASCHE

Hot Facilities

INTERMEDIATE FACILITY. One of the most important projects in the group's effort is to construct and equip a facility for the metallographic examination of irradiated samples from the capsules and loop. The intermediate cell is under construction and should be capable of opening and examining the capsules several weeks after removal from the reactor.

A remotely controlled cutoff device has been completed and will be tested when a plastic wheel guard is complete. An inverted stage microscope has been adapted for use in the facility and is ready for installation as soon as the construction work on the cell is complete.

The cell has been modified and extended to allow the mechanical testing equipment to be placed in it. A small overhead crane was constructed and is ready for installation. Windows for the facility were ordered and are in transit. A small elevator for specimen introduction is complete and in position in the cell. Electrical, plumbing, and air services are being installed. A specimen mounting press was received and is at present being modified for remote operation. Special manipulator arms are being designed for loading the mounting press.

HIGH LEVEL METALLURGICAL FACILITY. The Architectural Planning Group is working out preliminary cell design at the present time. A preliminary layout of equipment in the cell is complete. M. BASCHE

Graphite Development

Graphite for use in an LMFR should be stable to radiation and absorb little fuel or fission products. A screening program for the purpose of selecting a graphite that meets the above requirements is in progress.

The long-term Bi penetration tests indicate that the graphites take on approximately 0.3 to 0.5 g Bi per cc graphite in 1200 hr. This value has been nearly constant after the first 800 hr. Bi and water transmission studies through graphite have been started this quarter.

Since a certain amount of fuel absorption will have to be tolerated with the graphites now available, it was considered essential to measure the diffusion of U into graphite by means of a Bi or Bi solution carrier. This was accomplished by first impregnating graphite with only Bi or with Bi containing additions of Mg and/or Zr. After a maximum or near maximum amount of the Bi solution had been impregnated at a given pressure, U was added to the solution and the graphite allowed to soak for a given period of time. The amount of U which diffused into the graphite was measured by sectioning the graphite and analyzing for U concentration as a function of distance from the surface of the graphite. In order to accelerate the diffusion process, a 200-psi impregnation pressure was used to bring about a near maximum amount of penetration. The greater absorption results in exposing a larger graphite

surface area, which, it was hoped, would facilitate the measurement of a uranium-graphite reaction.

The experimental setup consisted of a vacuum-pressure chamber accessible through a ball valve and a Wilson seal for the loading of the Bi solution, additions of U, and sampling of the solution. The solution was contained in a graphite crucible at the center of which was suspended, by means of a Mo rod, a 1-in. diameter by 1⅜-in.-long graphite specimen, which was then completely submerged in the Bi solution.

The procedure followed the pattern of first vacuum outgassing the graphite assembly at 600°C for a period of 40 hr followed by loading of the Bi solution at 550°C. After loading, a 200-psi helium pressure was applied to the chamber to cause penetration into the graphite. After the graphite had been allowed to soak for approximately 90 hr, the U was added, and the 200-psi pressure and 550°C temperature were maintained for the duration of the experiment.

In the first experiment, a specimen of EY9 Morgan graphite and a container of 237 Great Lakes graphite were used. The Bi solution contained 390 ppm Mg, and 1000 ppm U was added at the proper time.

The U concentration in the graphite was obtained from slices of the graphite taken at varying distances from the graphite-melt interface. The thicknesses of the graphite slices cut off are listed in Table 32. The ppm U and Mg and the % Bi in the graphite as a function of distance from the interfaces are listed in Table 33. The U concentration in the graphite specimen was found to be less than in the melt solution and decreased from the interface inwards. The U concentration in the graphite container is lower at the interface than was expected.

An estimate of the diffusion coefficient of U was made by the equation given by R.M. Barrer (*Fusion In and Through Solids*, p. 32, University Press, Cambridge, England, 1941) for the diffusion into a circular cylinder when the concentration of the diffusing element on the surface of the cylinder is kept at a constant value. For a first approximation only the first term of the equation was used. An apparent value for D of 3.66×10^{-7} cm^2/sec was obtained, which is greater than the diffusion coefficient in most solid metal systems but considerably smaller than could be expected in liquid Bi; e.g., the diffusion coefficient of Au in Bi at 500°C is 5.2×10^{-5} cm^2/sec.

The second experiment was performed exactly as was the first, but Mg was not added to the melt. The graphite specimen was made from Great Lakes type HLM graphite, which absorbs less Bi than the EY9 graphite used in the first experiment.

The U concentration and the % Bi in the graphite are listed in Table 34 as a function of distance from the graphite-melt interfaces. It is worthy of note that the U concentration near the surface of the specimen has built up to a value considerably greater than that initially in the melt, and the concentration gradient with distance is much

Table 32

Thicknesses of Graphite Slices

From graphite sample	
Specimen No.	Thickness, in.
1	1/16
2	1/16
3	1/16
4	1/8
5	3/8 dia. core
From graphite container	
Crucible No.	Thickness, in.
6	1/16
7	1/16
8	1/16
9	1/16
10	1/8

Table 33

Specimen No.	Distance, in.	% Bi	ppm Mg	ppm U
1	0.0312	32.2	1,150	900
2	.0937	30.5	1,050	840
3	.1562	29.6	750	810
4	.250	28.0	800	760
5	.500	26.0	820	740
Crucible No.				
6	.0312	1.47	780	380
7	.0937	1.28	700	350
8	.1562	1.02	≈5,000	870
9	.2187	1.47	900	740
10	.3125	1.70	780	440

Table 34

Specimen No.	% Bi	ppm U
1	16.35	5,600
2	16.87	2,630
3	16.38	460
4	16.78	70
5	17.78	30
Crucible No.		
6	2.74	14,300
7	0.304	5,100
8	0.085	1,700
9	0.070	2,800
10	0.047	2,400

steeper than was found with Mg present in the solution. The U concentration in the graphite container was also found to have increased to an abnormally high value near the surface. This high value for the U/Bi ratio near the interfaces may be explained by assuming that U reacted with the impurities present on the graphite surfaces. Although some uranium oxide was found on the surface of the melt which was not present with the Mg additions, the influence of the Mg in solution is seen from the U build-up in the graphite when Mg is absent.

Irradiation of Impervious Graphites

The stability of graphite to radiation must be determined before the selection for LMFR use can be made. The properties of greatest interest are growth, thermal conductivity, physical strength, corrosion, and coefficient of thermal expansion. Certain types of impervious graphite are now being irradiated at 400°C at the MTR in a capsule designed and built by Nuclear Development Associates. This work is being performed under a subcontract with BNL. The capsule now being irradiated was loaded Aug. 5, 1957 and will remain for 2 to 3 cycles, after which it will be returned to NDA for withdrawal of samples, foil activity determination, and thermal conductivity and growth tests. R. Bourdeau

Capsule for Horizontal Beam Hole in MTR

Another capsule, designed for the purpose of irradiating a large number of graphite samples at a controlled temperature, will be inserted into a beam hole in the MTR. This capsule may be placed closer to the core than the one now used by NDA, which means that the gamma heating is about 10 w/g or a total of about 9 kw in the vicinity of the sample chamber. Tests conducted as detailed in the previous report showed that the section containing the sample chamber can transfer the gamma heat to the water coolant. The original plan was to maintain temperature control by using electrical heaters inserted into some of the samples, but this method has not proved feasible. A new concept of temperature control has now been envisioned which eliminates all high voltage leads in the capsule, i.e., that solid to solid thermal conductance is a function of the gas. By changing the gas in the chamber from helium to argon (or nitrogen) a large thermal barrier is placed between the graphite and the Al which results in an increased graphite temperature. Thus, when the gamma heat is increased by an increase of pile power, a higher concentration of helium will be forced into the sample chamber for better heat transfer.

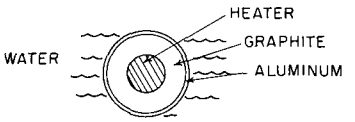

Figure 49.

A test was conducted to determine how well the temperature might be controlled by this system. An Al can is placed in a container of water. Inside the Al can is a graphite core with a resistance heater imbedded (Figure 49). Helium and argon and mixtures of both were introduced into the can, and the temperature drops between the graphite and the can were measured as a function of power, gas pressure, and tightness of fit between the graphite and Al. With 0.005 in. between the graphite and Al, with nitrogen the conductance was found to be 150 Btu/hr-ft^2-°F, and with helium, 560. At 0.025-in. separation, the conductance is found to be 70 and 200 Btu/hr-ft^2-°F with nitrogen and helium respectively. These values indicate that this system is capable of controlling temperature over a wider range than a system with heating elements. Further tests will be performed to establish a system of valves which can control the mixture of gases in the capsule.

A.E. Roswell

BNL Pile Studies

Two further air samples were taken in fuel channel B-3-6 which contained the old type of fuel. No evidence of Xe was found in either case. It is concluded that the high count derived from the first test must have been caused by a leaky fuel element. This view is substantiated by the fact that the element ruptured the day after the Xe-air sample was taken. This study had indicated that the new type of U-Al elements do emit measurable amounts of Xe. The amount of measured activity at this time is not serious according to the Health Physics Division. Further tests will be conducted when the pile contains more U-Al fuel elements. J. MILAU AND R.A. MEYER