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MASTER

CONTINUOUS URANIUM MONITORING OF
A LIQUID METAL FUEL REACTOR

Report to
BABCOCK AND WILCOX COMPANY
ATOMIC ENERGY DIVISION

January 3, 1958
C-61041

ARTHUR D. LITTLE, INC.

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Arthur D. Little, Inc.

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January 3, 1958

Babcock and Wilcox Company
Atomic Energy Division
Lynchburg, Virginia

Gentlemen:

C-61041

We submit herewith the final report covering our feasibility study of the problem of continuous uranium monitoring in a liquid metal fuel reactor experiment. We shall be glad to answer any questions that may arise concerning our findings.

We have enjoyed performing this study for you, and have appreciated the cooperation received from the staff of Babcock and Wilcox at all times. We hope we may look forward to a continuing association with your company on the LMFRE project.

Respectfully submitted,

Arthur D. Little, Inc.

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I. ASSIGNMENT

On August 19, 1957, the Babcock and Wilcox Company authorized Arthur D. Little, Inc., to proceed with a feasibility study of continuous uranium monitoring in a liquid metal fuel reactor experiment. It was agreed that this study should include a careful review of the available data related to the problem and analyses of the various possible methods of performing the measurement. Such analyses were to consider as thoroughly as possible the chemical, physical, nuclear and electrical properties of the solutions encountered and the environmental conditions anticipated at the site of operation of the reactor experiment. It was specified that the end product of the study should be a report identifying the various monitoring systems considered and the one system considered to be most feasible as a result of the study. Finally, it was agreed that the report would include: (1) appropriate technical comparisons between the recommended system and the others considered, (2) economic advantages and disadvantages of the recommended system, (3) a comprehensive estimate of the steps required to develop the recommended system through to the fabrication and delivery of a prototype device, and (4) the estimated cost of each step.

The following specifications for a prototype uranium monitoring device were set forth in our agreement with the Babcock and Wilcox Company:

The prototype system must be capable of indication and control of uranium 235 concentration over a range of 10 to 2000 parts per million. The operating temperature will be between 750° and 1200° F. The instrument must have an accuracy of $\pm 2\%$ with a minimum response time. The uranium monitored will be either the reactor fuel stream (i.e., an enriched $\geq 90\%$ in a bismuth plus 500 parts per million zirconium-and-magnesium solution, and all the fission products in various concentrations) or the reactor fuel stream in an alkali and alkaline earth halide solution. The various isotopes of uranium will also be present with the U-238 content varying up to a maximum 15% of the total uranium solution.

In discussions with Babcock and Wilcox representatives during the period in which the feasibility study was being performed, the following modifications of the above specifications have been mutually agreed upon:

1. The accuracy requirement, originally specified to be $\pm 2\%$ over the entire concentration range, was established to be ± 10 ppm over the entire range of 10 to 2000 ppm.

2. It was agreed that the study would not be limited to examination of means of measuring the isotopic concentration of U-235, but that possible methods of measuring total uranium concentration would also be considered, with preference assigned to isotopic analytical methods if promising ones could be found.

3. By the reference to two kinds of uranium solutions in the specification quoted above, it was understood that, if possible, an instrument is desired that could be employed for continuous monitoring of uranium in either a liquid-metal-fuel stream or a fused-salt chemical-processing stream. After the specification was drafted, the Babcock and Wilcox Company decided not to attempt continuous fused-salt processing in its liquid-metal-fuel reactor experiment. It was then agreed that primary emphasis should be placed, in this study, on monitoring of uranium in liquid bismuth solution. At the same time, it was agreed that the original objective was still a desirable one, from the viewpoint of future liquid-metal-fuel reactor technology, and that flexibility of instrument design should be regarded as an important consideration, for that reason.

4. The phrase "minimum response time" was specified to mean less than 6 seconds, in the case of liquid-metal-fuel monitoring. The reason for this is that a measurement within the time of transit of liquid metal fuel from the heat exchanger outlet to the reactor inlet is desired.

II. SUMMARY

Many types of measurement systems have been reviewed for appropriateness to the task of continuous uranium monitoring of a liquid-metal fuel reactor. Of these, the three general classes of neutron methods, X-ray methods, and paramagnetic susceptibility methods have been selected for detailed evaluation, primarily for the case of liquid-fuel stream monitoring. In addition, the present state of development of electrochemical and spectroscopic methods for application to fused-salt monitoring has been assessed.

A. CONCLUSIONS

1. There is no feasible method based on neutron detection that could be made insensitive to fission products in the liquid fuel stream.

2. A method employing the expected delayed neutron flux as a neutron source shows promise of feasibility. In this method the main fuel pipe is surrounded by a thick layer of graphite, and the ratio of fast to thermal neutron counting rates at an appropriate position within the graphite is measured.

3. A second method employing the delayed neutron flux as a neutron source shows promise of feasibility. In this method two pipe segments are surrounded by reflector material, one of them with thermal neutron absorbent at the pipe-reflector boundary, and detection is based upon the ratio of thermal neutron fluxes at appropriate positions within the reflector.

4. Of the several possible methods based on neutron attenuation, one shows promise of feasibility. In this method both incident and detected neutrons are thermal, and a layer of fuel solution of thickness one foot or more is required.

5. A method based on irradiation of fuel solution with thermal neutrons and detection of fast neutrons of fission origin appears to have at least marginal feasibility.

6. Liquid fuel monitoring based on X-ray absorption measurement is at best marginally feasible.

7. The spectrum of fission product photons emerging from U-Bi solution may be expected to show structure, due to quantum interactions with the constituents of the solution, that might prove applicable to uranium analysis. We recommend that this spectrum be investigated experimentally.

8. A continuous measurement of paramagnetic susceptibility can be achieved with 4-second response time. A signal is thus provided that is proportional to uranium concentration within the specified limits of accuracy. Buildup of paramagnetic fission products over a one-year period at 20 Mw without reprocessing would contribute only about 6% of the uranium signal at 1200 ppm. Dissolved zirconium would contribute to an extent that is uncertain, but may be as high as 20%. Dissolved iron at 8 ppm would contribute a maximum of 10% of the uranium signal. (The absence of ferromagnetic particles would be essential.) Other paramagnetic corrosion products might contribute to a small, unevaluated extent. If we assume that rapid fluctuations in concentrations of paramagnetic species other than uranium will not take place, the concentration of uranium would be known by correction of the signal for interfering substances on the basis of periodic batch analyses. Correction to isotopic U-235 concentration could be carried out similarly.

B. RECOMMENDATION

Of the methods examined for liquid-fuel monitoring we find the paramagnetic susceptibility method most promising, and recommend its development to the stage of prototype instrument construction. In deciding on this selection we have been strongly influenced by the fact that the neutron methods mentioned above would provide information very similar to that available from core instrumentation. (See Section IX for discussion.)

The prototype instrument we recommend would not be applicable to fused-salt stream monitoring. We find that the methods of chronopotentiometry and absorption spectrophotometry offer substantial promise of providing a solution to this problem. We have not attempted to evaluate the applicability of the methods described in (2) - (7) above to fused-salt monitoring, but it is our opinion that of these only X-ray absorption shows promise for this application.

III. DISCUSSION

In this section we will attempt to set forth the view of the uranium monitoring problem that we have developed in the course of this study. The purpose of this discussion is two-fold. First, it is intended to indicate the factual and conceptual frame of reference within which we have drawn our conclusions, so that these conclusions may themselves be better evaluated. Second, it is hoped that our thoughts about the purpose of and specifications for a continuous uranium monitoring system may prove helpful to the Babcock and Wilcox Company in reaching future necessary decisions on this subject.

A. ENVIRONMENTAL CONDITIONS OF OPERATION

Our information concerning liquid-metal-fuel reactors in general, and LMFRE in particular, has been obtained by personal interviews with the personnel of Babcock and Wilcox and of Brookhaven National Laboratory (BNL), and by the study of unclassified reports and published literature⁽¹⁻¹⁰⁾. We have keyed our thinking particularly toward the LMFRE reference design described in reports BAW-1019 and BAW-1017^(1, 2).

The operation of LMFRE will be based on continuous circulation of highly enriched U-235 fuel ($\geq 90\%$) dissolved in liquid bismuth at a concentration of about 1000-1500 ppm, through an unclad graphite matrix containing 226 channels, each 1.5 inches in diameter. The critical mass in this assembly is about 3.3 kg of U-235, and the volume of the out-of-core portion of the circulating system is such that a total fissionable material inventory of about 80 kg is anticipated. The reactor is designed for operation at 20 MW power level, and at this level a reactor outlet temperature of 885°F and a temperature rise across the core of 135°F are expected.

The main components of the primary circulating system are, in sequence, the core, a degassing system for volatile fission product removal, and a heat exchanger. The entire circulating system will be enclosed by croloy-2-1/4 steel, containing 2.00-2.50% chromium, 0.30-0.60% manganese, 0.90-1.1 % molybdenum, and minor amounts of carbon, sulfur, phosphorus, silicon and nickel⁽¹¹⁾. Main fuel piping will be 12 inches in diameter, shielded by between 5-3/4 - 6-3/4 feet of barytes concrete. At 20 MW operation, rate of liquid bismuth flow will be about 14×10^6 pounds per hour, corresponding to a linear flow velocity of about 8 ft/sec in the 12-inch pipe segments of the system. Transit times at this flow rate from the core outlet are 2.0 sec to the degasser inlet, 19.9 sec to the heat exchanger inlet, and 26.6 sec to the reactor inlet. The complete cycle time is 37.4 sec. The time required for flow from heat exchanger outlet to reactor inlet is thus 6.7 seconds less the heat exchanger transit time, which is unknown to us.

The position that has been selected for continuous monitoring of liquid-metal fuel is immediately beyond the heat exchanger outlet, and we are informed that an 8 x 10 x 12 foot space will be available at this position to accommodate the necessary access and equipment. Monitoring of the main stream itself, requiring access through the very thick shielding, or, alternatively, monitoring of solution flowing through a small bypass stream, imposing much less stringent shielding requirements, may be considered. It is the condition of the liquid-fuel stream at this position that is of primary interest to this study.

We assume that the temperature of the liquid bismuth at the heat exchanger outlet will be identical to that at the reactor inlet, reported to be 750°F (400°C) at steady 20 MW operation. This also corresponds to the lower temperature of the range 750-1200°F specified by Babcock and Wilcox for operating conditions. We infer that temperatures as high as 1200°F are not likely to be encountered, particularly at the heat exchanger outlet, except in extraordinary circumstances, but that the instrument should be capable of withstanding such temperatures for brief intervals without damage. For practical operating conditions we will assume a liquid bismuth temperature of 400-500°C (750-930°F). (A reactor outlet temperature of 975°F is reported to correspond to 33-1/3 MW operation.)

The liquid-bismuth stream will contain uranium, when the reactor first becomes critical, at a concentration somewhere in the vicinity of 1000 ppm. As reactor operation continues and fission products form, the concentration will be made larger to compensate for poisoning effects. The initial charge of uranium will consist of approximately 90% U-235, the rest largely U-238. The U-238 concentration will build up slowly as U-235 is burned up, and will undergo occasional stepwise alterations when fresh fissionable material is added. In addition to U-238, the isotopes U-234 and U-236 will also be present initially at small concentrations. The U-236 concentration will build up slowly due to radiative thermal neutron capture in U-235, to an extent estimated to give about 30 ppm after 2 years' operation. The U-234 concentration, like that of U-238, will increase slowly due to U-235 burnup. In addition to these uranium isotopes, small concentrations of neptunium and plutonium isotopes, particularly Pu-239, will develop very slowly.

The liquid-bismuth stream will contain approximately 350 ppm of magnesium metal, added as an oxygen-getter and also to repress uranium extraction if fused-salt reprocessing is used. The stream will also contain up to 350 ppm of zirconium metal, added as a corrosion inhibitor. Finally, it will contain all of the fission products. The volatile fission products should be largely removed by the degasser unit, but the efficiency of this operation has not been fully evaluated, and we will assume that small concentrations of volatiles will remain. The concentrations of these fission

products should quickly reach fixed, steady-state values, but occasional changes in degassing efficiency may result in fluctuations. As for the remaining fission products, those of very short half-life will reach steady-state concentrations quickly. The concentrations of the remainder will increase slowly with time, and will undergo rapid alteration only when batches of fuel are removed from the stream for chemical processing and fresh fuel is introduced.

In addition to the above constituents, dissolved iron will be present in the liquid-bismuth stream, as a result of corrosion of croloy. The solubility of iron is reported to be about 6 ppm at 400°C and around 20 ppm at 500°C⁽¹³⁾. The possibility that entrained iron may be present in excess of solubility has been indicated by experience with a stainless steel in-pile loop⁽⁹⁾. However, from extensive experience with croloy loops, it appears that a concentration of 6-8 ppm of iron may be reasonably anticipated, and that while small amounts of entrained, particulate iron may be present in the stream, the total amount of iron in this form should be negligible⁽¹⁴⁾. In addition to iron, small concentrations of other corrosion products, particularly manganese and molybdenum, may be expected, although these will probably also be negligible.

The fuel stream will carry delayed neutron emitters at steady-state concentrations. It has been estimated⁽¹²⁾ that each cm³ of solution will emit 5×10^8 neutrons per second at the heat exchanger outlet at 20 MW power. This quantity will be sensitive to changes in power level. In addition to the delayed neutron background, there will be a very large background of gamma radiation, ranging from an estimated 4×10^{10} photons/cm³-sec in the energy group 0.1-0.4 Mev, to 1.79×10^8 at 2.8 Mev⁽¹⁵⁾. This background cannot be accurately predicted in advance, and will vary with time as fission products buildup and as batches of fuel are removed for chemical processing.

We have not attempted to evaluate in detail the environment of a possible fused-salt-stream monitoring device. Since continuous chemical processing is not contemplated for LMFRE, physical details such as length of time since processed fuel left core, pipe diameter, etc., are not known. However, we have familiarized ourselves with the general nature of fused-salt processing^(7, 9, 16, 17) so that we could assess the present state of development of analytical methods potentially applicable to salt-stream monitoring. We assume that the processing stream will contain NaCl-KCl-MgCl₂ ternary eutectic at a temperature between 400-500°C. The uranium concentration will be between 10-2000 ppm, and rare-earth fission product concentrations will be substantially higher than in the liquid-bismuth stream. There may be no neutrons present from delayed neutrons, if the stream is sufficiently aged, but a substantial neutron background from polonium α

particle bombardment of chlorine may be expected. The intensity of gamma radiation will be substantially less, on a volume basis, than that of the fuel stream, but still very large. The density of the molten eutectic mixture is 1.90 g/cm^3 at 420°C (18), very much smaller than the liquid-bismuth density of about 9.8 g/cm^3 .

B. PURPOSE OF MONITORING INSTRUMENT

The purpose of monitoring uranium concentration in the liquid-bismuth stream cannot be stated in a clearcut fashion. Three general areas of application have been identified in our discussions with Babcock and Wilcox personnel: startup control, operation control, and safety.

(a) Startup. Reactor startup will be carried out, we understand, by first circulating pure bismuth, then adding Mg and Zr at appropriate concentration levels, and finally adding U-235. Fuel additions will be made in increments, so that stepwise concentration changes should be observed in an external monitoring instrument. Indication of approach to criticality would be obtained from reactor core instrumentation. For the first startup operation, at any rate, the critical fuel concentration will not be known with sufficient accuracy to give out-of-core monitoring a primary role in control. On the grounds that concentration should be well known at all times during startup from fuel inventory at the admission system, we could therefore argue that continuous monitoring during startup is unnecessary. At the same time, the possibility of unexpected oxidation leading to phase separation and uranium deposition at some position in the system must be contended with. The use of galvanic cell measurements sensitive to magnesium concentration (see Section VIII) should serve to indicate the presence of unexpected oxygen leaks, but there may be other sources of uranium loss that would require direct uranium measurement for detection. We conclude that while monitoring during startup is not strictly necessary, an independent check on the disposition of uranium as it is added would be a valuable source of comfort to operating personnel, and that the information derived from such measurements on LMFRE would contribute greatly to the experiment.

(b) Operation. When the reactor has been brought to full power operation, occasional increases in uranium concentration will be necessary to compensate for burnup and for fission product poisoning. Fluctuations in uranium concentration are therefore to be anticipated from this source, as well as from inhomogeneities in the fuel stream and from possible interactions between uranium and system components. It may be argued that a continuous concentration signal could be usefully coupled to the control rod drive system, to anticipate reactivity additions, and to a uranium addition system to replenish the fuel when lowered concentration makes this necessary. We do not believe that either application is a valid one for LMFRE. Because

of the expected negative temperature coefficient of the reactor, reactivity additions of the order expected from operational concentration fluctuations should present no problem. Burnup of fuel at 20 MW will not be rapid, and uranium addition could not be accomplished quickly enough to warrant an attempt at automatic control even if this seemed desirable. Although the situation may well be different for future high power LMFR plants, we conclude that continuous monitoring would not be capable of performing a valuable routine operational control function in LMFRE.

As an experiment, LMFRE will be designed to develop as much new information as possible about the behavior of liquid-metal-fuel systems. Short and long term changes in uranium concentration, as measured independently of core reactivity, could be an important item of information. On this basis, we believe that an attempt to monitor uranium concentration continuously is more than justified. Feasibility demonstration for possible future application in full scale power plants is a further item of justification.

(c) Safety. As we have said above, the negative temperature coefficient of LMFRE should be able to take care of increases in fuel concentration of the magnitude expected in ordinary operation. Relatively large reactivity additions can be accommodated without damage, but there must be some critical increment of reactivity that would have catastrophic consequences. We do not know how large a surge of fuel concentration would be required to produce a disaster, but we assume that it must be a significant fraction of the critical mass. Since the ratio of fuel inventory to critical mass will be very large, however, it is conceivable that quantities of uranium corresponding to "disaster threshold" size could become deposited somewhere in the system. As has been pointed out to us by Babcock and Wilcox personnel, with a concentration measurement to $\pm 2\%$ on a total inventory of 80 kg, over an extended period, deposition of more than a critical mass could conceivably take place without the knowledge of the reactor operators. If substantial portions of such a mass should later become dislodged and entrained in the fuel stream, a potentially dangerous situation would exist. If the mass were to break off as chunks of diameter greater than 1.5 inches, the chunks would not gain entry to the core. A large number of particles of smaller size would therefore be required to produce a catastrophe. Other possible sources of dangerous concentration surges are failure in the addition system, and oxygen leakage leading to separation of uranium oxide from the solution phase, accumulation, and subsequent entrainment.

We are not in a position to evaluate the probability of occurrence of the hazardous events described above. If they are thought even remotely probable, appropriate steps should be taken to make sure that the presence of dangerously high fuel concentration is known in advance of entry to the reactor, with sufficient time left over for appropriate automatic remedial

action. We are not sure, however, that the instrument specified in our agreement with Babcock and Wilcox would be a complete answer to this problem. As will be brought out in subsequent sections, it does not appear feasible to perform a monitoring measurement on the main fuel stream itself, so that the instrument would undoubtedly be built around a bypass stream of smaller diameter. Chunks of fuel of appreciable size would have little chance of entering such a bypass, because of streaming of material past the opening. Dangerous surges of very fine particulate matter would probably be detectable, and we assume that entrained uranium oxide might be more likely to pass through as a fine sludge than as chunks.

We conclude that continuous monitoring would provide a partial answer to the problem of detecting surges of particulate uranium fuel, and would thus contribute to safety of the reactor's operation. We feel that the problem of chunk detection, if real, is separable from the problem of liquid-fuel concentration monitoring. It should be approached, in our opinion, either by application of special engineering provisions for the filtering or trapping of chunks, or by the design of a special chunk-detecting instrument, or by both means.

Our general conclusion about the purpose of continuous uranium monitoring of the LMFRE fuel stream may be summarized as follows:

- (1) it would be useful, though not necessary, during reactor startup;
- (2) it would be highly desirable from an experimental research point of view during reactor operation, although not an operational necessity for the reactor;
- (3) it could play a significant and highly desirable, though incomplete, role in ensuring the safety of operation of the reactor.

C. SPECIFICATIONS FOR LIQUID-FUEL MONITORING

The specifications set forth in our agreement with Babcock and Wilcox require high accuracy ($\pm 2\%$) over a wide concentration range (10-2000 ppm), and small response time (< 6 sec). In the light of the threefold purpose described in the preceding paragraphs:

- (a) The very low concentration range would be of interest only during startup, and high accuracy would not be necessary until concentrations approaching the critical value were reached. For this reason the more realistic specification of ± 10 ppm was agreed upon, stressing accuracy in the higher concentration region. Rapid response time would have no particular virtue in the startup application, in our opinion.

(b) To aid in the gathering of useful experimental data during steady reactor operation, high accuracy would be desirable, but we cannot see that rapid response time would be necessary.

(c) For application of a uranium monitor as a safety device, accuracy would not have great importance, but the entire validity of the application would depend upon rapid response time.

An instrument capable of serving all three areas of purpose should therefore perform according to the specified requirements, even though these may contain mutually self-contradictory elements when viewed in the light of one purpose area alone. For a given method high accuracy and rapid response time may turn out to be mutually exclusive, for example; if a decision were made to adopt such a method, an order of preference would have to be assigned to the three purposes. Ideally, however, the selected method will be capable of satisfying the requirements for all three.

D. ISOTOPIC AND TOTAL URANIUM CONCENTRATION SIGNALS

Since U-235 will be the fuel in LMFRE, it is the concentration of this isotope alone that is the subject of interest in continuous monitoring, and an ideal instrument will provide an isotopic concentration signal directly. However, if this should not be feasible, a concentration signal corresponding to total uranium would be almost as useful. The rate of alteration of the uranium isotopic ratios due to U-235 burnup will not be rapid. We are informed that periodic batch analyses of the fuel stream, by mass spectrometry, are planned. If the total uranium concentration is known, periodic calculations of U-235 concentration from the isotopic ratios obtained in these analyses may be made. From knowledge of the burnup rate, at steady operation, an adequate approximation to the isotopic concentration could be maintained between batch analyses, on a continuous basis. Another source of alteration of uranium isotope ratios will be periodic additions of uranium. We assume that mass spectrometric analyses may be coordinated with such operations.

E. FUSED-SALT MONITORING

The principal purpose of monitoring of a fused-salt processing stream, we believe, would be to maintain an inventory of uranium losses from the processed fuel. For this purpose high accuracy would be desirable, and since the concentration range of interest would be much lower than for the primary fuel stream, the instrumental problem would be somewhat different. We do not believe that rapid response time would be essential to this measurement, although it would be valuable if feasible.

REFERENCES, SECTION III

- (1) Report BAW-1019, "LMFRE Reference Design Report," Aug., 1957.
- (2) Report BAW-1017, "LMFRE Preliminary Hazards Evaluation," July, 1957.
- (3) Report BAW-2, "LMFRE Technical Feasibility Report," June 30, 1955.
- (4) "The Preliminary Design of LMFRE," BNL Nuclear and Mechanical Engineering Division, April 30, 1956.
- (5) Miles, F. T., and C. Williams, "Liquid Metal Fuel Reactor," Paper 8/P/494, International Conference on the Peaceful Uses of Atomic Energy, Geneva, July, 1955.
- (6) Williams, C., and F. T. Miles, Chem. Eng. Prog. 50, No. 11, 245 (1954).
- (7) Raseman, C., and J. Weisman, Chem. Eng. Prog. 50, No. 12, 153 (1954).
- (8) Atherton, J. E., et al., Chem. Eng. Prog. 50, No. 12, 23 (1954).
- (9) Raseman, C. J., H. Susskind and C. H. Waide, Paper 57-NESC-27, 2nd Nuclear Engineering and Science Conference, Philadelphia, March, 1957.
- (10) BNL Staff, "LMFRE Power Reactor Systems," Nucleonics 12, No. 7, 11-42 (1954).
- (11) Letter from C. H. Anderson to F. T. Bonner, Oct. 16, 1957.
- (12) Thomas, G. R., Personal Communication, Sept., 1957.
- (13) Data from B and W Research Center, May 3, 1957.
- (14) Klamut, C., Personal Communication, Oct., 1957.
- (15) Letter from G. R. Thomas to F. T. Bonner, Sept. 30, 1957, and Personal Communication, Oct., 1957.
- (16) Bareis, D. W., R. H. Wiswall and W. E. Winsche, Chem. Eng. Prog. 50, No. 12, 228 (1954).
- (17) Dwyer, O. E., A. I. Ch. E. Jour. 2, No. 2, 163 (1956).
- (18) Letter from O. E. Dwyer to H. W. Hoffman, April 25, 1956.

IV. ANALYTICAL METHODS

In this section we shall discuss the preliminary screening process on which we based our decisions as to methods deserving detailed evaluation.

A. ISOTOPIC METHODS

Since an ideal instrument would yield a U-235 concentration signal directly, it is appropriate first to consider possible isotopic analytical methods. The specific properties on which such analyses may be based are characteristic alpha decay energies, characteristic gamma spectrum, isotopic mass, nuclear spin (7/2), fine structure in uranium emission spectrum, and high thermal neutron fission cross-section.

(a) Alpha counting could not be adapted to continuous measurement, since minimum self-absorption is required, and protracted sample preparation procedures would be necessary.

(b) Gamma spectroscopy would be virtually impossible to perform in the presence of the very large fission product gamma background anticipated.

(c) Mass spectrometry would necessarily be a batch sampling process, with substantial time devoted to sample preparation.

(d) Nuclear magnetic resonance absorption. Since the characteristic radiation involved in NMR measurements would penetrate to negligible depth in liquid U-Bi solution, we do not believe that reliable measurements could be made by this method. Its applicability to fused salt-stream analysis may warrant further study, however.

(e) Emission spectroscopy for isotopic analysis of uranium is reported to be possible at high precision⁽¹⁾. The method is intrinsically limited to batch analyses, however.

(f) Neutron attenuation. A beam of neutrons on traversing the liquid fuel stream will lose intensity because of absorption in various nuclear species, predominantly U-235. The method would be complicated by the anticipated background, and would not provide direct information if the primary beam were thermal; but it appears worthy of further consideration.

(g) Prompt fission gamma detection. The gamma rays produced in fission have higher energies than most fission product decay gammas, hence uranium analysis by thermal neutron irradiation combined with high energy

photon detection could be considered. Very high energy gammas are also produced in simple radiative neutron capture processes, however, and there may also be some very high photon decay energies emitted by fission products of very short half-life. The complexity of this situation would make it very difficult to relate counting rate to uranium concentration.

(h) Prompt fission neutron detection. A source of thermal neutrons could be employed to cause fission in the fuel stream. Detection of fast neutrons, of energy in excess of those in the delayed neutron groups, would provide a means for detecting fission and at the same time discriminating against the large delayed neutron background. Neutron-absorbing fission products would interfere. A method based upon fission to fast neutrons may also be considered.

(i) Moderation of fission neutrons. A segment of fuel-bearing pipe could be surrounded by moderator, and a source of thermal neutrons appropriately placed to cause fission in the fuel. Some fission neutrons would become thermalized in the moderator and return to the stream to cause further fission. The increased flux could be employed as an indicator of U-235 concentration in the stream. The use of a zero-power reactor for analytical measurements, including uranium isotope ratio determination, has been reported^(1, 2) An immediate objection that may be raised is that the delayed neutron background will be very large and may mask the multiplication effect. However, we may consider employing this flux itself as our primary neutron source. Another objection is that variable and unknown concentrations of high cross-section fission products are expected to be present in the stream, so that the U-235 concentration would not be measured on a direct basis. This objection is serious, but the method is worthy of further evaluation.

(j) Fission product detection. The possibility of subjecting the fuel stream to known thermal neutron flux at the point of analytical interest, then quantitatively measuring the amount of some fission product produced by the irradiation may be considered. The fission product nuclide selected would have to have a half-life short in comparison with the transit time from core to heat exchanger outlet, if preliminary cleanup of the stream were to be avoided. For continuous detection it must have a gamma decay energy greater than that of any other fission product, to avoid interference from the very large gamma background. No suitable candidate is to be found in existing data, but it has been suggested⁽³⁾ that one or more of the very short-lived isotopes of krypton may have gammas of energy greater than 3 Mev; the decay energetics of very short-lived fission products have not been completely explored. We feel that while the method is interesting, any further discussion of it would be entirely speculative at this time.

From the above discussion it can be seen that we are left with several neutron methods which seem to warrant further scrutiny. Because of this limitation on isotopic concentration measurement, it is necessary to consider means of measuring total uranium concentration.

B. TOTAL URANIUM METHODS

The properties that may be considered as possible bases for continuous total uranium measurement fall in the categories of specific chemical properties of uranium, specific physical properties of uranium, and bulk properties of U-Bi or fused-salt solutions.

Specific chemical properties, in general, cannot be observed in the absence of chemical changes. For that reason we may immediately eliminate all standard chemical uranium analyses on the ground that their application would be intrinsically discontinuous. On the same grounds we may eliminate from consideration for liquid fuel monitoring any physicochemical analytical techniques that depend upon uranium in oxidized form. This would include colorimetry, fluorimetry, and absorption spectrophotometry, for example. While rapid means of converting uranium metal to suitable oxidized form for such measurements may be visualized, continuous operation would require continuous reduction and return of metal to the fuel stream, which would be a very formidable problem. Uranium will be present in oxidized form in a fused-salt process stream, however, and methods of this sort may be given serious consideration for process stream monitoring. Electrochemical methods, based either on the electrode potentials of oxidation-reduction systems containing uranium, or on current-voltage characteristics of uranium-containing systems under electrolysis, may also be considered for fused-salt systems.

Specific physical properties of uranium and bulk solution properties that we have considered for monitoring application are enumerated below.

(a) X-ray fluorescence. When an X-ray beam containing radiation of the critical frequency for interaction with uranium K-shell electrons is incident upon U-Bi solution, X-radiation characteristic of transitions from outer shells to the K-shell will be emitted. An immediate objection is that such fluorescence radiation will probably be strongly absorbed in bismuth, since the two elements are relatively close in atomic number.

(b) X-ray absorption. X-radiation of wave length corresponding to the K- or L-absorption edge of uranium would be strongly absorbed in photoelectric interaction with uranium atoms. Such radiation would also be absorbed, at smaller cross-section, by bismuth. In a U-Bi solution, then, the discrete absorption in uranium at K- or L-edge wave length would be super-

imposed upon the continuum of bismuth absorption. Since the anticipated concentration of uranium is small, however, the height of the peak above background absorption must also be expected to be small. Superimposed on this difficulty is the discouragingly large background of gamma radiation, much of it in the same energy region as the necessary incident radiation. At the same time, the method would provide a convenient means of continuous measurement, without direct access to fuel, and it therefore seems worthy of detailed evaluation.

(c) Electron paramagnetic resonance. This method would involve even smaller penetration depth in U-Bi solution than the method of nuclear magnetic resonance.

(d) Bulk paramagnetic susceptibility. Uranium, an actinide element containing three 5f electrons, is paramagnetic, while bismuth is diamagnetic. Continuous measurement of the bulk magnetic susceptibility of the fuel solution could therefore yield information closely related to the total uranium concentration. The method would be complicated by the presence of iron, zirconium, and paramagnetic fission product atoms. It would probably not be applicable to fused-salt monitoring because of the expected enhancement of lanthanide rare earth fission product concentrations.

C. CONCLUSIONS

While we cannot guarantee that we have thought of everything worth thinking of, we do not believe that we are likely to have missed any promising methods in the screening process described above. As a result of the process we are left with three general measurement types to consider for liquid-fuel monitoring: neutron methods, X-ray methods, and magnetic susceptibility methods. We therefore select these for the detailed evaluations given in succeeding sections. Of the three, neutron and X-ray methods could prove applicable to molten-salt monitoring as well as fuel-stream measurement, while magnetic susceptibility probably would not be. Methods which may be feasible for fused-salt monitoring but not directly applicable to liquid fuel have been identified above as being either electrochemical or optical in nature. These will also be evaluated below, in less detail than the other methods because our stronger emphasis is placed on liquid-bismuth monitoring, and also because the present state of development of these methods for application in fused salts is not sufficiently advanced to permit an attempt at detailed evaluation.

Of the three methods for fuel-stream monitoring which remain in our list, the X-ray method is in principle capable of providing information that would be directly and unambiguously related to uranium concentration. Most neutron methods would be subject to the vagaries of fluctuating fission product

concentrations in the stream. A magnetic susceptibility signal would reflect zirconium, corrosion product, and some fission product concentrations, as well as uranium, and the effects of possible fluctuations in these concentrations require careful assessment.

REFERENCES, SECTION IV

- (1) Lovett, J. E., and J. O. Roberts, Nucleonics, 15, No. 7, 72 (1957).
- (2) Nucleonics, 15, No. 6, 134 (1957).
- (3) Manowitz, B., Personal Communication, Nov., 1957.

V. NEUTRON METHODS

In considering neutron counting as the basic measurement for uranium analysis, we should first find out if the accuracy requirements can be met on a statistical basis. The highest limit of accuracy in the specification is 2000 ± 10 ppm, or 0.5%; this would require 4×10^4 total counts. Instrumentally, this requirement could easily be met within one second. The processes involved must, of course, be assumed to be random.

One may consider external neutron sources for the measurement, e. g., Ra-Be or Po-Be, which yield between $10^6 - 10^7$ total neutrons per second per curie. Ra-Be is a somewhat more efficient source than Po-Be, but on the other hand, there will be very large quantities of polonium available at the operating site of LMFRE. Since there will be a very large flux of delayed neutrons at the heat-exchanger outlet position, any method based on use of an external source will require a large source and means of discriminating against this background. As an alternative to using an external source, then, we may inquire whether an analysis may be based on the expected delayed neutron flux itself.

We take 5×10^8 neutrons/sec-cm³ to be the volume source value for delayed neutrons at the heat exchanger outlet in a pipe 12 inches in diameter⁽¹⁾. We assume that there may be uncertainty in this value, however, because of possible removal of delayed neutron precursor nuclei at the degasser unit, to an extent unknown to us. It can be shown that essentially zero thermal neutrons of core origin will arrive at the heat exchanger outlet position by diffusion down the pipe or by "entrainment" in the moving liquid. It can also be shown that while the slowing down time for neutrons in the delayed groups in bismuth is short in comparison with the characteristic times of interest, the number that actually get down to thermal energy before escaping from the pipe is negligible. Therefore, without moderator, the effective multiplication factor in the pipe is essentially zero. Since nearly all neutrons leak out with very little slowing down or capture, the neutron current at the surface of a pipe 15.25 cm in radius will be

$$\frac{\pi \times (15.25)^2 \times 1 \times 5 \times 10^8}{2 \pi \times 15.25 \times 1} = 3.8 \times 10^9 \text{ neutrons/cm}^2\text{-sec.}$$

A. THERMAL AND FAST FLUXES NEAR A REFLECTED PIPE

Let us next examine the consequences of placing an infinite graphite reflector around the 12-inch fuel-bearing pipe. For this purpose we have developed a two-group calculation with a source term, assuming the neutron source fast and uniform. Because of the very extended nature of this calculation, it will be shown here only in outline*. The equations are:

$$\left. \begin{aligned}
 D_{fc} \nabla^2 \phi_{fc} - \Sigma_{fc} \phi_{fc} + \frac{k}{p} \Sigma_{sc} \phi_{sc} + S &= 0 \\
 D_{sc} \nabla^2 \phi_{sc} - \Sigma_{sc} \phi_{sc} + p \Sigma_{fc} \phi_{fc} &= 0 \\
 D_{fr} \nabla^2 \phi_{fr} - \Sigma_{fr} \phi_{fr} &= 0 \\
 D_{sr} \nabla^2 \phi_{sr} - \Sigma_{sr} \phi_{sr} + p_r \Sigma_{fr} \phi_{fr} &= 0
 \end{aligned} \right\} \quad (1)$$

where the symbols have their usual significance⁽²⁾, and the subscripts s and f refer to "slow" and "fast," the subscripts c and r to "core" and "reflector."

For the reflector, solutions are found of the form

$$\left. \begin{aligned}
 \phi_{fr} &= F K_0(\kappa_{fr} r) \\
 \phi_{sr} &= F \frac{\Sigma_{fr} p_r}{D_{sr} (\kappa_{sr}^2 - \kappa_{fr}^2)} K_0(\kappa_{fr} r) + G K_0(\kappa_{sr} r)
 \end{aligned} \right\} \quad (2)$$

*The complete details of this calculation are retained in our files and may be made available as an addendum to this report, if desired.

where the constants F and G are determined by the boundary conditions at the core-reflector interface, and where

$$\left. \begin{aligned} \kappa_{fr} &= \sqrt{\frac{\Sigma_{fr}}{D_{fr}}} = \frac{1}{\sqrt{\tau_s}} , \\ \kappa_{sr} &= \sqrt{\frac{\Sigma_{sr}}{D_{sr}}} = \frac{1}{L_r} . \end{aligned} \right\} \quad (3)$$

For the core,

$$\left. \begin{aligned} \phi_{fc} &= A I_0(\zeta r) + C I_0(\nu r) \\ \phi_{sc} &= S_1 A I_0(\zeta r) + S_2 C I_0(\nu r) \end{aligned} \right\} \quad (4)$$

where A and C are constants, ζ and ν are defined by the equations

$$\left. \begin{aligned} -\zeta^2 &= \frac{1}{2} \left\{ -\left(\frac{1}{\tau_c} + \frac{1}{L_c^2}\right) + \sqrt{\left(\frac{1}{\tau_c} + \frac{1}{L_c^2}\right)^2 + \frac{4(k_\infty - 1)}{\tau_c L_c^2}} \right\} \\ \nu^2 &= \frac{1}{2} \left\{ \left(\frac{1}{\tau_c} + \frac{1}{L_c^2}\right) + \sqrt{\left(\frac{1}{\tau_c} + \frac{1}{L_c^2}\right)^2 + \frac{4(k_\infty - 1)}{\tau_c L_c^2}} \right\} \end{aligned} \right\} \quad (5)$$

and

$$\left. \begin{aligned} S_1 &= \frac{D_{fc}}{\tau_c D_{sc}} \frac{p}{(\mu^2 + 1/L_c^2)} \\ S_2 &= \frac{D_{fc}}{\tau_c D_{sc}} \frac{p}{(-\nu^2 + 1/L_c^2)} \end{aligned} \right\} \quad (6)$$

The boundary conditions are that the fast and slow fluxes and fast and slow currents are equal on the two sides of the core-reflector interface, and that solutions are finite at the center of the core and at infinity. The following set of boundary condition equations was found:

$$\begin{aligned}
 H + A I_0(\zeta a) + C I_0(\nu a) &= F K_0(\kappa_{fr} a) \\
 S_4 H + S_1 A p I_0(\zeta a) + S_2 C I_0(\nu a) &= F S_3 K_0(\kappa_{fr} a) + G K_0(\kappa_{sr} a) \\
 D_{fc} \left[A \zeta I_1(\zeta a) + (\nu I_1(\nu a)) \right] &= - F \kappa_{fr} D_{fr} K_1(\kappa_{fr} a) \\
 D_{sc} \left[A \zeta S_1 I_1(\zeta a) + S_2 C \nu I_1(\nu a) \right] &= - F S_3 \kappa_{fr} D_{fr} K_1(\kappa_{fr} a) \\
 &\quad - G \kappa_{sr} D_{sr} K_1(\kappa_{sr} a)
 \end{aligned} \tag{7}$$

where

$$\begin{aligned}
 H &= \frac{S \tau_c}{(1 - k)} \\
 S_3 &= \frac{D_{fr} p_r}{D_{sr} (\tau_r / L_r^2 - 1)} \\
 S_4 &= p \frac{D_{fc}}{D_{sc}} - \frac{L_c^2}{\tau_c}
 \end{aligned} \tag{8}$$

and where $\underline{a}$ refers to the actual radius of the core.

The four equations (7) are to be solved for A, C, F, and G so that the fast and slow fluxes may be evaluated. Employing the values of nuclear parameters shown in Table 1 and assuming a U-235 concentration of 1120 ppm by weight, we obtain the following values:

$$\begin{aligned}
 G &= 56.5 \\
 F &= 825.4 \\
 C &= 8335 \\
 A &= -132.4
 \end{aligned}$$

TABLE 1NUCLEAR PARAMETERS

$$N(\text{Bi}) = \frac{\rho N_o}{A} = \frac{9.8 \times 6.03 \times 10^{23}}{209} = 2.83 \times 10^{22} \text{ cm}^{-3}$$

$$N(\text{U}^{235}) \text{ at } 1120 \text{ ppm} = 1.12 \times 10^{-3} \times \frac{209}{235} \times N(\text{Bi}) = 2.82 \times 10^{19} \text{ cm}^{-3}$$

$$\sigma_a(\text{U})(\text{slow}) = 687 \text{ barns}$$

$$\sigma_s(\text{Bi})(\text{slow}) = 9.0 \text{ barns}$$

$$\sigma_a(\text{Bi})(\text{slow}) = 0.032 \text{ barns}$$

$$\Sigma_a(\text{core}) = N(\text{Bi})\sigma_a(\text{Bi}) + N(\text{U})\sigma_a(\text{U}) = 0.0203 \text{ cm}^{-1}$$

$$\Sigma_s(\text{core}) = N(\text{Bi})\sigma_s(\text{Bi}) = 0.254 \text{ cm}^{-1}$$

$$\Sigma_s(\text{reflector}) = 0.331 \text{ cm}^{-1}$$

$$D_{fc} = 1.292 \text{ cm}$$

$$D_{sc} = 1.310 \text{ cm}$$

$$D_{fr} = 1.068 \text{ cm}$$

$$D_{sr} = 0.903 \text{ cm}$$

$$L_c = 8.03 \text{ cm}$$

$$L_r = 50.2 \text{ cm}$$

$$\tau_c \approx 9000 \text{ cm}^2$$

$$\tau_r = 350 \text{ cm}^2$$

$$k_\infty = 2.89 \times 10^{-5}$$

TABLE 1 (Continued)

$$p_c = 1.46 \times 10^{-5}$$

$$p_r \approx 1$$

$$\epsilon \approx 1$$

$$\kappa_{fr} = 0.0534 \text{ cm}^{-1}$$

$$\kappa_{sr} = 0.0199 \text{ cm}^{-1}$$

$$\eta(\text{U}^{235}) = 2.08$$

$$\xi(\text{Bi}) = 0.00954$$

Returning to equation (2), we then evaluate the ratio of fast to slow neutron fluxes at the boundary between core and reflector and find it to have the value

$$\left[\frac{\phi_{fr}(a)}{\phi_{sr}(a)} \right]_{1120 \text{ ppm}} = 3.31 \quad (9)$$

This result indicates that a reflector is capable of providing a very substantial flux of slow neutrons. For the absolute values of the fluxes at the boundary we find

$$\left. \begin{aligned} \phi_{fr}(a) &= 2.3 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1} \\ \phi_{sr}(a) &= 6.95 \times 10^{10} \text{ cm}^{-2} \text{ sec}^{-1} \end{aligned} \right\} \quad (10)$$

Next it is appropriate to inquire about the sensitivity of the ratio expressed in (9) to U-235 concentration. The two-group calculation was therefore repeated for an atomic concentration of uranium 1.5 times that assumed above (~1680 ppm). For the flux ratio in this case we find

$$\left[\frac{\phi_{fr}(a)}{\phi_{sr}(a)} \right]_{1680 \text{ ppm}} = 4.08 \quad (11)$$

This indicates a sensitivity of fast-to-slow flux ratio to concentration of about 0.5% per 1% change in uranium concentration over this interval.

The above calculations indicate that a uranium concentration measurement based on fast-to-slow flux ratio in a reflector may be feasible. A graphite reflector extending about 50 cm along the pipe and an equal distance radially outward would probably be sufficient. Since the fluxes are so large, however, a more compact situation may be visualized. If the method were to be given serious consideration a more refined calculation would be necessary, and questions of optimization would require a detailed design study. Difficult technical problems, including the protection of counting equipment against the expected gigantic gamma ray background, would have to be overcome. Finally, although the presence of fission products has not been taken into explicit account in these calculations, the flux ratio would reflect the effects of fission product poisoning as well as uranium concentration.

B. THERMAL FLUX IN A REFLECTED PIPE WITH PERFECT NEUTRON ABSORBER AT THE BOUNDARY

The thermal flux in the reflected assembly described above obviously could not be employed alone as a measure of uranium concentration, because of changes in delayed neutron flux with changes in reactor power level. It is for this reason that a flux ratio measurement has been considered. The detection of fast neutrons in the presence of a large gamma background is not straightforward, however, and we may consider another kind of ratio measurement based entirely on thermal neutrons. In this method there are two reflected segments of pipe. At the core-reflector boundary of one segment a perfect absorber of thermal neutrons (e. g. , boron) is placed so that new fission neutrons are not formed. The two segments are assumed geometrically distinct.

The two-group calculation employed in (A) has been adapted for analysis of this new case by alteration of boundary conditions. The slow flux in the core, and the slow flux in the reflector, are both equated to zero. The other two boundary conditions employed in (A) remain unchanged.

Again for a pipe of radius 15.25 cm, a uranium concentration of 1120 ppm, and at positions in the reflectors somewhat removed from the boundaries themselves (but not optimized), we find for the ratio of thermal fluxes with and without absorber:

$$\left[\frac{\phi_{sr}(\text{no abs.})}{\phi_{sr}(\text{abs.})} \right]_{1120 \text{ ppm}} = 5.94 \quad (12)$$

For the case of 1.5 times the above atomic concentration, we find

$$\left[\frac{\phi_{sr}(\text{no abs.})}{\phi_{sr}(\text{abs.})} \right]_{1680 \text{ ppm}} = 7.50 \quad (13)$$

The sensitivity to uranium concentration is again about 0.5% per percentage change in [U] .

This method would also result in a measurement sensitive to fission product as well as uranium concentration. It would have the advantage over the fast-to-slow flux ratio method that detection would be based entirely on thermal neutrons. It would have the disadvantage that two pipe segments would be

involved, hence would require more space. Also, the delayed neutron populations would be slightly different, although probably to a constant and predictable extent. Possible effects of shielding materials have not been taken into account, and optimization for best sensitivity has not been studied.

If either of these methods involving a reflected pipe assembly should be given serious consideration, the possibility of a criticality occurrence would require careful review. If sizable chunks of uranium could somehow become entrained in the stream, the critical condition at the reflected position could conceivably be met.

Methods based on application of the delayed neutron flux would not, of course, be applicable during the reactor startup period. The use of an external source during this period could be considered.

C. NEUTRON ATTENUATION

A beam of neutrons of intensity I_0 incident upon a plane slab of fuel will emerge with a reduced intensity, I . We will now estimate the extent of this neutron attenuation, and its sensitivity to uranium concentration in the fuel stream. Four cases may be distinguished: the incident neutrons may be slow or fast, and the slab thick or thin compared with the diffusion length for neutrons in bismuth.

1. Fast Neutrons Incident

Fast neutrons incident upon a thin sample are attenuated according to one of the exponential relationships:

$$I = I_0 e^{-\Sigma_T x} \text{ for "good" geometry} \quad (14)$$

$$I = I_0 e^{-\Sigma_a x} \text{ for "poor" geometry} \quad (15)$$

In "good" geometry, both the incident and detected beams are well collimated, so that scattered neutrons do not reach the detector. Therefore, the measured attenuation of the beam depends upon both absorption and scattering, or upon the total macroscopic cross section, Σ_T . In "poor" geometry, the detector picks up the scattered neutrons, and therefore attenuation of the beam is a function of the absorption cross section, Σ_a , only. In the considerations

below we will assume that the source consists of neutrons of energy greater than the maximum for the delayed groups (0.6 Mev), but less than the inelastic scattering threshold for bismuth (0.9 Mev). (If a more complete analysis were desirable, the effects of inelastic scattering could be taken into account.)

To evaluate Σ_T and Σ_a for fast neutrons, we use the appropriate values of σ_T and σ_a , dropping σ_a for bismuth because of its very small value:

$$\begin{aligned}\Sigma_T &= N(U) \sigma_T(U) + N_{Bi} \sigma_T(Bi) \\ &= 2.82 \times 10^{19} \times 6.6 \times 10^{-24} + 2.825 \times 10^{22} \times 5.2 \times 10^{-24} \\ &= 1.860 \times 10^{-4} + 0.1470 = 0.1472 \text{ cm}^{-1}\end{aligned}\tag{16}$$

$$\begin{aligned}\Sigma_a &= N(U) \sigma_a(U) \\ &= 2.82 \times 10^{19} \times 1.18 \times 10^{-24} = 3.34 \times 10^{-5} \text{ cm}^{-1}.\end{aligned}\tag{17}$$

(These values refer to 1120 ppm of U^{235} .) From the above we see that Σ_T would have little sensitivity to uranium concentration in small path length, and that Σ_a is so small that very little attenuation would be observable in the case of poor geometry. When we consider a pipe diameter of the order of centimeters, we must apply a diffusion calculation.

Let us now suppose that the pipe diameter a is larger than a diffusion length, and that a neutron source is located on one side of the pipe. We will assume that the source is isotropic, and that the neutrons are not slowed down appreciably in the fuel solution. In this case, neutron diffusion theory is applicable, and the flux, ϕ , of neutrons leaking out of the pipe on the opposite side from the source is given by the solution to the equations

$$D \nabla^2 \phi - \Sigma_a \phi + S = 0 \tag{18}$$

$$D \frac{\partial^2 \phi}{\partial x^2} - \Sigma_a \phi = 0 \tag{19}$$

where D is the diffusion constant for neutrons in the solution and S is the flux from the source. The source is oriented so that the neutrons are incident along the z axis of a cylindrical coordinate system. Equation (19) has the solution:

$$\phi = Ae^{-\kappa z} + Ce^{+\kappa z} \quad (20)$$

where $\kappa = \sqrt{\frac{\Sigma_a}{D}}$.

The neutron current, J_- , in the $(-z)$ -direction is zero; in the $(+z)$ -direction, J_+ is just half the flux from the isotropic source. From diffusion theory

$$J_- = \frac{\phi}{4} + \frac{D}{2} \frac{\delta \phi}{\delta z} = 0 \quad (21)$$

$$J_+ = \frac{\phi}{4} - \frac{D}{2} \frac{\delta \phi}{\delta z} = \frac{S}{2} \quad (22)$$

Solving (21) and (22) simultaneously, with ϕ as given by (20), we can evaluate the constants A and C in terms of the source S . Finally, the flux $\phi(a)$ after the neutrons have passed through a centimeters of fuel is:

$$\phi(a) = \frac{-2 D \kappa S}{-(1/2 + D \kappa)^2 (e^{\kappa a}) + (1/2 - D \kappa)^2 (e^{-\kappa a})} \quad (23)$$

The numerical values of the constants are

$$D = \frac{1}{3 \Sigma_{tr}} \approx \frac{1}{3 \Sigma_s} = \frac{1}{3 \times 0.147} = 2.27 \text{ cm.} \quad (24)$$

$$\kappa = \sqrt{\frac{\Sigma_a}{D}} = \sqrt{\frac{3.34 \times 10^{-5}}{2.27}} = 3.84 \times 10^{-3} \text{ cm}^{-1}. \quad (25)$$

If κa is small compared to unity, $e^{\pm \kappa a} \approx (1 \pm \kappa a)$ and:

$$\frac{\phi(a)}{S} \approx \frac{1}{1 + \frac{a}{4D}} \quad (26)$$

Thus, for a less than $1/\kappa$ (≈ 260 cm), the emergent flux is independent of uranium concentration.

If κa is equal to one, the approximate expression (26) is no longer valid. Retaining the first three terms in the power series expansion of the exponential:

$$\frac{\phi(a)}{S} = \frac{2D}{2D + a [1/2 + 2(D\kappa)^2]} \quad (27)$$

Since $D\kappa \ll 1$, $1/2 + 2(D\kappa)^2 \approx 1/2$, and once more, the emergent flux is roughly independent of uranium concentration.

It is thus seen that κa must be made substantially greater than unity if sensitivity to uranium concentration by this method is to be achieved. This would mean providing a fuel path length considerably greater than 8.5 feet. Equation (23) may be applied to find the ratio of two fluxes $\phi(a)$ and $\phi'(a)$:

$$\frac{\phi(a)}{\phi'(a)} = \frac{\kappa}{\kappa'} \left[\frac{(1/4 + D^2 \kappa'^2) \sinh \kappa' a + D \kappa' \cosh \kappa' a}{(1/4 + D^2 \kappa^2) \sinh \kappa a + D \kappa \cosh \kappa a} \right] \quad (28)$$

For uranium concentrations differing by 1%, $\frac{\kappa}{\kappa'} = 0.99$; therefore let us seek the value of a for which $\frac{\phi}{\phi'} = 1.01$. To have this requirement met the bracketed quantity in Equation (28) must equal 1.02. The quantity κ' may be eliminated by use of the relation

$$D \kappa' = D \kappa (1 + 0.005). \quad (29)$$

We find ultimately that

$$1/4 \kappa a - 0.045 = \tanh \kappa a \quad (30)$$

A graphical solution of this equation shows that the appropriate conditions are met when $\kappa a = 4$, or $a \approx 30$ feet. We conclude that the method is not feasible. It is the only neutron method we are aware of that would be insensitive to fission products if it were feasible.

2. Thermal Neutrons Incident

For the case of thermal neutrons, we will begin by considering the thick slab case, assuming from the outset that a thin slab would provide little sensitivity. The general considerations are the same as those for fast neutrons, but the values of the constants are different. This time, for 1120 ppm of U-235:

$$\kappa = 0.1247 \text{ cm}^{-1} \text{ (based on } \Sigma_a \text{ value in Table 1)}$$

$$D = 1.310 \text{ cm (see Table 1)}$$

$$D\kappa = 0.1632 .$$

This time it is clear that the condition $\kappa a \gg 1$ will be much more readily met, since a must be only 8 cm for $\kappa a = 1$. The condition for 1% detection that $\kappa a = 4$, as shown above, is met in this case when $a = 32$ cm, or about one foot. This is an entirely reasonable path length, since it is nearly identical to the planned fuel-bearing pipe diameter. The method therefore appears feasible, and could be quite accurate. In principle, one would expect no background interference from the large flux of delayed neutrons if the detection were based on a strictly thermal absorption process, and the source strength requirement would not be inordinately large. In practice, however, we suspect that moderation in shielding materials might lead to a serious background problem. The method would be sensitive to fission products.

D. FISSION RATE COUNTING WITH AN EXTERNAL THERMAL SOURCE

In either "good" or "poor" geometry, we could base our measurement on the detection of fission neutrons of energy in excess of the maximum for the delayed groups, using an external source of thermal neutrons. This

method would assure discrimination against the large neutron background. For this case we develop a nondiffusion calculation, which should be valid for thicknesses up to a few centimeters.

Imagine a beam of thermal neutrons incident upon a stream of flowing U-Bi solution in a pipe of diameter $\underline{a}$. The thermal flux at distance $\underline{x}$ within the pipe is given by

$$\phi(\underline{x}) = S e^{-\Sigma \underline{x}} \underline{a} \quad (31)$$

The number of neutrons with energy between E and $(E+dE)$ produced in a layer of thickness dx at $\underline{x}$ is

$$n(E, \underline{x}) dE dx = \Sigma_f \phi(\underline{x}) \nu(E) dE dx, \quad (32)$$

where $\nu(E)dE$ is the number of neutrons with energy between E and $(E+dE)$ emitted in a single fission event.

The number of neutrons with energy between E and $(E+dE)$ produced after the beam has traversed path length $\underline{a}$ is given by

$$n_a(E)dE = \frac{\Sigma_f}{\Sigma_a} S (1 - e^{-\Sigma \underline{a}}) \nu(E)dE \quad (33)$$

If we take the angular distribution of fission neutrons to be isotropic, a counter which subtends solid angle $\Delta\Omega$ at the sample will receive

$\frac{1}{4\pi} \Delta\Omega$ of the neutrons produced. If $\varepsilon(E)$ is the fractional counter efficiency for detection of neutrons of energy E , and E_0 is the detection threshold, then the neutron counting rate (C) will be given by

$$C = \int_{E_0}^{\infty} n_a(E) \varepsilon(E) \frac{\Delta\Omega}{4\pi} dE. \quad (34)$$

The energy spectrum of U^{235} fission neutrons is accurately represented by the relation (3).

$$\nu(E)dE = e^{-E} \sinh \sqrt{2E} dE, \quad (35)$$

where

$$\int_0^{\infty} \nu(E)dE \approx 2.5. \quad (36)$$

Therefore,

$$C = \frac{\Delta \Omega}{4\pi} \frac{\Sigma_f}{\Sigma_a} S (1 - e^{-\Sigma_a a}) \int_{E_0}^{\infty} e^{-E} \sinh \sqrt{2E} \bar{\epsilon}(E) dE \quad (37)$$

The last integral cannot be exactly evaluated. For a detector we must consider the necessity for distinguishing fast neutrons from gammas in a large background of the latter. For such a device, as described by Hornyak⁽⁴⁾, we may take $\bar{\epsilon}(E) = 0.02$.

Taking $\Sigma_a = 0.0203 \text{ cm}^{-1}$ and $\Sigma_f = 0.0164 \text{ cm}^{-1}$, and $\bar{\epsilon}(E) = 0.02$, and letting $a = 5 \text{ cm}$, Equation (37) becomes

$$C = 0.0064 S \Delta \Omega \int_{E_0}^{\infty} e^{-E} \sinh \sqrt{2E} dE \quad (38)$$

The value of E_0 required is about 0.65 Mev, just in excess of the maximum neutron energy in delayed groups. We are not certain about the value of the integral in this equation, but note that $\nu(E)$ has its maximum value at about $E = 2 \text{ Mev}$. Let us take 0.1 as an approximation to the integral and further assume a geometry such that $\Delta \Omega = 0.1$. Then

$$C = 6.4 \times 10^{-5} S \quad (39)$$

To achieve a counting rate of 10^4 sec^{-1} , we then see that a source strength of

$$S = \frac{10^4}{6.4 \times 10^{-5}} = 1.56 \times 10^8 \text{ sec}^{-1} \quad (40)$$

would be required. This would mean a source of the order of 100 curies, which would be just within the bounds of reason.

We thus see that a method based on fission neutron detection with an external thermal source appears marginally feasible. To evaluate just how feasible this method is would require a considerably more detailed analysis than that given above. In particular, diffusion theory should be applied to the case of thick absorbing path. The method would be sensitive to fission product poisons.

In addition, one should consider three sources of background signals in the neutron counters. In the first place, it is conceivable that a certain small fraction of the delayed neutrons emitted by fission products will diffuse back into the fuel stream after becoming thermalized in the biological shield surrounding the fuel pipe. They will then tend to cause fission in U^{235} nuclei, and give rise to fast fission neutrons which are identical with the ones emitted as a result of external source irradiation.

A second cause of background signals is to be attributed to neutrons emitted in fast fission of U^{235} caused by delayed neutrons. Although the fast fission cross section of U^{235} at the maximum delayed neutron energy of 0.6 Mev is only about 1.2 barns, which is several hundred times smaller than the slow neutron fission cross section, the delayed neutron flux is itself very intense.

A third cause of background arises from gamma-ray pulses which are not strongly enough rejected by pulse-height discrimination following the Hornyak neutron counter, and by pile-up of small gamma-ray pulses.

The first of these sources of background can be minimized by preventing back-diffusion of thermalized neutrons with a boron shield, and the third by filtering the observed fast neutrons with a bismuth or lead filter which would eliminate the gamma-ray background. The second source of background counts is somewhat more difficult to deal with. We could profit here by chopping the incident neutrons and using narrow-band amplification and lock-in detection to reduce the influence of the background.

E. CONCLUSIONS

Our calculations in this section have been rather approximate, and have not attempted to deal with all the complexities of the methods considered. Specifically, the effects of fission product poisons have been neglected, and the uranium present has been assumed to consist entirely of U^{235} . While neglecting U^{238} makes little difference, fission product poisoning is a significant factor, and may be a strongly variable one, to an extent dependent on the consistency of operation of the degasser unit and on fluctuations in reactor power level. We have not succeeded in finding an analytical method based on neutrons that would be independent of fission product concentration.

Within the limitations described above, we have identified four neutron methods that show some promise of feasibility. Two of these are based on the delayed neutron flux, with use of a reflector for thermalization.

A third one is based on thermal neutron attenuation with an external source, and the fourth on fission neutron detection. All of these methods would present very formidable technical problems. The least promising, in our opinion, is the method based on fission neutron counting. We believe that the neutron methods showing greatest promise are those based on use of a reflected assembly. Further remarks on the possible use of these methods may be found in Section IX.

REFERENCES, SECTION V

- (1) G. R. Thomas, personal communication, September, 1957.
- (2) Glasstone, S. and M. C. Edlund, The Elements of Nuclear Reactor Theory, (Princeton: D. van Nostrand Co., 1952), pp. 238-247.
- (3) Hughes, D. J., Pile Neutron Physics (Cambridge: Addison-Wesley Publishing Co., Inc., 1952).
- (4) Hornyak, W. F., Rev. Sci. Inst. 23, 264 (1952).

VI. X-RAY METHODS

X-ray methods that seem to hold some promise for continuous uranium monitoring in the LMFR are (1) X-ray absorption in the neighborhood of the uranium K or L edge, (2) uranium X-ray fluorescence, and (3) detailed analysis of the X-ray emission spectrum of the fuel stream.

A. X-RAY ABSORPTION AT THE URANIUM K EDGE

In Figure 1, absorption cross sections in units of cm^2/g are plotted against the energy of incident photons for both bismuth and uranium⁽¹⁾. The curve for bismuth was constructed by extrapolation of the given curves for thallium and lead (Figure 2)⁽¹⁾. The curves for bismuth and uranium are summed graphically in Figure 1. Clearly, if the bismuth and uranium were present in equal concentrations, there would be a marked absorption peak at the K_α edge for uranium. In a mixture containing 1g Bi and 0.001g U, the total absorption cross section would jump 0.00392 cm^2 out of 3.66 cm^2 at the uranium K_α edge. The problem is whether this small peak is detectable under practicable conditions.

The simplest possible experimental design⁽²⁾ is outlined in Figure 3. A is a source of X rays, whose continuous energy spectrum includes components in the region of the uranium K_α line (0.1163 mev)⁽¹⁾. The X-ray beam is passed through the sample at B and the emergent radiation is incident upon a double crystal monochromator at C. The latter is oscillated to span a small energy region about the uranium K_α line. The monochromatic beam is picked up by a scintillation counter at D. Ideally, we would record a certain number of counts per second, I , at 0.1162 mev and a reduced number, $I - \Delta I$, at the K edge itself. The quantity, ΔI , would provide a direct measure of the uranium concentration. For reasons to be discussed in a later portion of this section, the simple design of Figure 2 would require very extensive modification if the method were to be used.

(a) X-Ray Absorption Coefficients⁽³⁾. If an X-ray beam of intensity I_0 passes through x centimeters of matter of absorption coefficient μ , the emergent beam has intensity I given by:

$$I = I_0 e^{-\mu x} \quad (1)$$

Here, μ has units of cm^{-1}

FIGURE 2
ENERGY VERSUS CROSS SECTION (2)

FIGURE 3

SCHEMATIC DIAGRAM OF ABSORPTION APPARATUS

In tables of absorption constants, an absorption coefficient a^μ , expressed in units of cm^2/atom , is usually given. The relationship between a^μ and μ is:

$$\mu = \frac{\rho N a^\mu}{A} \quad (2)$$

where N is Avogadro's number, A is the atomic weight, and ρ the density of the material in question.

Our system is essentially a solution of p parts per million (ppm) of uranium ($10 \leq p \leq 2000$) in liquid bismuth. The absorption coefficient for the mixture is:

$$\mu = N \left[\frac{\rho_{\text{Bi}} a^\mu_{\text{Bi}}}{A_{\text{Bi}}} + \frac{\rho_{\text{U}} a^\mu_{\text{U}}}{A_{\text{U}}} \right] \quad (3)$$

where ρ_{Bi} and ρ_{U} are not the tabulated densities of the elements but the number of atoms of each element per cc multiplied by the weight of a single atom. Therefore:

$$\mu = n_{\text{Bi}} a^\mu_{\text{Bi}} + n_{\text{U}} a^\mu_{\text{U}} \quad (4)$$

where n_i is the number of atoms of element i per cc. In general, a^μ is a function of the energy of incident photons.

At the K_α edge for uranium (0.1163 mev), the atomic absorption coefficient for bismuth is $a^\mu_{\text{Bi}} = 1270$ barns, while that for uranium rises abruptly from 342 barns just before the K edge to 1890 barns just at the edge. Furthermore:

$$n_{\text{Bi}} = 2.93 \times 10^{22} \text{ atoms/cc}$$

$$n_{\text{U}} = (2.6 \times 10^{16}) (p) \text{ atoms/cc}$$

Therefore, the absorption coefficient for the mixture becomes μ_{K-} just before and μ_K just at the uranium K edge:

$$\begin{aligned}\mu_{K-} &= (2.93 \times 10^{22}) (1270 \times 10^{-24}) + (2.6 \times 10^{16} p) (342 \times 10^{-24}) \\ \mu_K &= (2.93 \times 10^{22}) (1270 \times 10^{-24}) + (2.6 \times 10^{16} p) (1890 \times 10^{-24}) \\ \mu_{K-} &= 37.21 + 0.00889 \times 10^{-3} p \\ \mu_K &= 37.21 + 0.0491 \times 10^{-3} p\end{aligned}\tag{5}$$

Taking $p = 1000$ ppm:

$$\begin{aligned}\mu_{K-} &= 37.21_g \\ \mu_K &= 37.25_g\end{aligned}\tag{6}$$

(b) Size of the X-ray Tube. For bismuth, the K_α edge is at 0.09052 mev; for uranium, it is at 0.1163 mev⁽¹⁾. For analytical purposes, it would be useful to obtain the absorption curves for the solutions under study from about 0.1000 mev to 0.1330 mev.

The continuous energy spectrum from an X-ray tube of voltage V exhibits a sharp minimum wave length, $\lambda_{\min}$, or maximum energy, $E_{\max}$, given by (4):

$$eV = hc/\lambda_{\min} = h \gamma_{\max} = E_{\max}\tag{7}$$

where e is the electronic charge, h is Planck's constant, c is the velocity of light, and $\gamma_{\max}$ is the frequency corresponding to $\lambda_{\min}$. Substituting $E_{\max} = 0.1330$ mev into (7), we find that the minimum voltage X-ray tube whose spectrum includes a component in the energy range of interest is 133.2 kilovolts. In all subsequent discussion, we shall assume an X-ray tube of 150 kilovolts.

High voltage X-ray tubes (up to 300 kv), to be operated continuously at currents of 5 to 25 milliamperes, are commercially available from General Electric at a cost of from \$15,000 to \$30,000. These are therapy tube units and the price can vary considerably, depending upon the exact conditions under which the equipment is used.

(c) X-ray Tube Efficiency. Only a small fraction of the total energy applied to the cathode is converted to X-ray energy. Quantitatively, the efficiency ϵ of a cathode-ray tube operated at voltage V with a target material of atomic number Z is:

$$\epsilon = \frac{\text{X-ray energy}}{\text{Cathode-ray energy}} = 1.1 \times 10^{-9} ZV \quad (8)$$

The formula is accurate to about $\pm 20\%$. With a tungsten target ($Z = 74$), the efficiency of a 150 kv X-ray tube run at 10 milliamps is $\epsilon = 0.0122$. Therefore, the total X-ray energy emerging from the tube is $(0.0122)(1500) = 18.3$ joules/sec. For our experiment, we will be interested only in that fraction of the total X-ray energy in the range 100 to 133 kev. From the calculation in Appendix I, it is seen that 0.1 of the energy in the X-ray beam is in the desired range; i. e., the total useful flux is about 1.8 joules/sec. Taking an average energy per photon of 112 kev, we find that this corresponds to 1.0×10^{14} photons/sec.

For geometrical reasons, only a small fraction of the total useful flux is usable. If the monochromator face, C , has a surface area of w square centimeters and lies 1 cm from the source, A , then the detector subtends a solid angle of $w/1^2$ steradians at the source, and intercepts a fraction $f(w/1^2)$ of the energy of the X-ray beam. The usable I_0 then becomes:

$$I_0 = (1.0 \times 10^{14})f(w/1^2) \quad (9)$$

In Table 2, approximate values are given for the percentage of the intensity of the X-ray beam within viewing range of the counter at several small $\sqrt{w/\ell}$ ratios. The table was compiled by graphical integration of a theoretical plot ⁽⁵⁾ of X-ray intensity vs angle of emission for a thin target X-ray tube. It is assumed, of course, that the sample will be placed so as to receive the maximum possible flux.

TABLE 2

FRACTIONAL X-RAY INTENSITY AS A FUNCTION
OF THE ANGLE INTERCEPTED BY THE DETECTOR

$\frac{\sqrt{W}}{l}$ Radians	$\frac{\sqrt{W}}{l}$ Degrees	Fraction	%
0.0100	0.57	0.0086	0.86
0.0200	1.14	0.013	1.3
0.0500	2.9	0.041	4.1
0.0833	4.9	0.066	6.6
0.100	5.7	0.0792	7.9
0.150	8.6	0.117	11.7

(d) Calculation of Sampling Tube Diameter. From (1), with the values of μ given by (6), we see that the intensities of the transmitted X-ray beam before and after the uranium K_{α} edge are respectively:

$$I_{K^-} = I_0 e^{-37.219x}$$

$$I_K = I_0 e^{-37.259x} \quad (10)$$

for a uranium concentration of 1000 ppm. In Table 3, we have recorded I_{K^-}/I_0 and I_K/I_0 for path lengths x from 0.1 to 0.8 cm.

The anticipated gamma-ray background from fission products in the fuel stream is 4.0×10^{10} photons/cc/sec, on a volume source basis, in the energy range 0.1 to 0.4 mev⁽⁶⁾. This is an estimated value that relies on information not directly applicable to a circulating fuel system⁽⁷⁾, and may be considerably in error. It is, however, the best value available. Assuming that the energy of the photons is distributed uniformly over the range mentioned, there will be a flux of 3.2×10^9 photons/cc/sec in the region 0.100 to 0.133 mev.

For accurate analysis, the signal must ordinarily be of at least comparable intensity with the background, and preferably, an order of magnitude greater. By means of a chopper on the influx side and a lock-in amplifier in the detector circuit, it might be possible to detect a signal 100 times or so less than the background.

The background depends directly upon the area subtended by the detector face. The incident intensity, and therefore, the signal, are also affected by the area of the detector face, but in a different way from the background. Unfortunately, complete optimization of the geometry is not amenable to simple analysis. An increase in the power of the source by means of increased voltage or increased current or both would also enhance the signal. Finally, the signal-to-noise ratio should be improved as the diameter of the sampling tube decreases. Since the only concern at present is whether the X-ray absorption method is feasible, it will suffice to assume a sampling tube of 0.2 cm diameter. If the method were to be attempted experimentally, this matter would require more detailed consideration.

TABLE 3

ABSORPTION AS A FUNCTION OF PATH LENGTH FOR
A URANIUM CONCENTRATION OF 1000 PPM

<u>x cm</u>	<u>$\frac{I_K}{I_0} = e^{-37.219x}$</u>	<u>$\frac{I_K}{I_0} = e^{-37.259x}$</u>
0.1	2.419×10^{-2}	2.409×10^{-2}
0.2	5.850×10^{-4}	5.804×10^{-4}
0.3	3.846×10^{-5}	3.800×10^{-5}
0.4	3.422×10^{-7}	3.368×10^{-7}
0.5	8.282×10^{-9}	8.118×10^{-9}
0.6	2.002×10^{-10}	1.955×10^{-10}
0.7	4.842×10^{-12}	4.709×10^{-12}
0.8	1.171×10^{-13}	1.134×10^{-13}
1.0		

(e) Sample Calculation. For demonstration purposes, let us consider the case:

Area of the monochromator face = $w = 1 \text{ cm}^2$

Distance from source to monochromator = $\ell = 7 \text{ cm}$

Distance from sample to monochromator = $n = 5 \text{ cm}$

Diameter of sampling tube = $x = 0.2 \text{ cm}$

X-ray tube of 150 kv run at 10 milliamp.

We will ignore the geometric losses between the monochromator and counter.

Since $\sqrt{W}/\ell = 0.142$, we see from Table 1 that roughly 11% of the X-ray energy from the source will be utilized. From (9):

$$I_0 = (0.11) (1.0 \times 10^{14}) = 1.1 \times 10^{13} \text{ photons/sec} \quad (11)$$

From Table 2, the number of photons reaching the counter per second due to the signal is, just before and just at the K edge:

$$\begin{aligned} I_{K-} &= 6.435 \times 10^9 \text{ photons/sec} \\ I_K &= 6.384 \times 10^9 \text{ photons/sec} \end{aligned} \quad (12)$$

with a uranium concentration of 1000 ppm. Superimposed upon this is a background of about 3.2×10^9 photons/cc/sec. These photons are emitted in all directions. Those going backward will not be detected. Furthermore, the counter will pick up radiation from a volume of $(1) (0.2) (0.2) \text{ cc} = 0.04 \text{ cc}$. Therefore, we will assume a background of $0.04 \times 0.5 \times 3.2 \times 10^9 = 6.4 \times 10^7$ photons/sec. Since the dead time of a scintillation counter is about 10^{-9} seconds, the emergent radiation would have to be attenuated. This would be easy to do by interposing an appropriate thickness of lead between sample and detector.

However, if we are to obtain sufficient accuracy in the allotted time of six seconds, we cannot attenuate the beam arbitrarily. In general, the concentration of uranium is p parts per million, and we want to detect

p to ± 10 ppm. We want to do this by making a measurement just before the uranium K edge and one just after the edge. If I is the number of photons emerging per second just before the uranium K_{α} edge, and $(I - \Delta I)$ is the number emerging just at the K_{α} edge, then we must be able to detect p or ΔI to $\pm 1000/p\%$; i. e., ⁽⁸⁾

$$\Delta I \pm \frac{10 \Delta I}{p} \quad (13)$$

Since ΔI is small, compared to I, $I - \Delta I$ and I are practically equal, and the error in each measurement must be no greater than half the allowable error in their difference. That is, we must detect I to $\pm 5 \Delta I/p$, or:

$$I \pm \frac{500 \Delta I}{p} \% \quad (14)$$

In other words, we must make M counts both before and after the K edge such that:

$$\frac{\sqrt{M}}{M} = \frac{5 \Delta I}{I p} \quad (15)$$

$$\sqrt{M} = \frac{p I}{5 \Delta I} \quad (16)$$

$$M = \frac{p^2 I^2}{25 (\Delta I)^2}$$

The time required to make M such counts is:

$$t = \frac{p^2 I^2}{25 (\Delta I)^2} \leq 6 \quad (17)$$

Since:

$$I = I_0 e^{-\mu x} \quad (18)$$

$$\Delta I = I_0 \left[e^{-\mu_1 x} - e^{-\mu_2 x} \right] = I_0 e^{-\mu_1 x} \left[1 - e^{-x(\mu_2 - \mu_1)} \right] \quad (19)$$

If $(\mu_2 - \mu_1)$ is small compared to one:

$$\Delta I = I_0 e^{-\mu_1 x} \left[x (\mu_2 - \mu_1) \right] \quad (20)$$

$$\frac{\Delta I}{I} = x (\mu_2 - \mu_1) \quad (21)$$

$$M = \frac{p^2}{x^2 (\mu_2 - \mu_1)^2} \quad (22)$$

$$t = \frac{p^2}{x^2 (\mu_2 - \mu_1)^2 I} \leq 6 \quad (23)$$

From equation (5), $(\mu_2 - \mu_1) = 0.04 \times 10^{-3} p$ with $\mu_2 = \mu_K$ and $\mu_1 = \mu_{K-}$ of equation (5). Finally:

$$I x^2 \geq 4.1 \times 10^6 \quad (24)$$

With $x = 0.2$ cm, the emergent radiation, I , must be greater than 1.0×10^8 photons/sec. In the present example, then, we could only attenuate the beam by a factor of 60 in order to obtain the desired accuracy in the allotted time, provided, of course, that we were able to get 100% counting efficiency. Nonetheless, 10^8 counts per second is staggeringly large even for a scintillation counter.

The amount of absorption, ΔI , varies approximately linearly with concentration, as can be seen from the following considerations. From (1) and (5):

$$I_{K-} = I_0 e^{-37.21x} e^{-0.00889 \times 10^{-3} p x}$$

$$I_K = I_0 e^{-37.21x} e^{-0.0491 \times 10^{-3} p x}$$

Since the third factor is small over the entire range $10 \leq p \leq 2000$,

$$I_{K-} \approx I_0 e^{-37.21 x} (1 - 0.00889 \times 10^{-3} p x)$$

$$I_K \approx I_0 e^{-37.21 x} (1 - 0.0491 \times 10^{-3} p x)$$

$$\Delta I \approx I_0 e^{-37.21 x} (0.040 \times 10^{-3} p x)$$

(f) Conclusions and Discussion. It must be emphasized that the above calculation is rough. The geometry is over-simplified. The efficiency of an X-ray tube is not known with great accuracy. A theoretical expression, with at best semi-quantitative validity, was used for the energy distribution of X-radiation. An even poorer theoretical curve was used to estimate the angular distribution of the energy from an X-ray tube. The anticipated background flux was calculated; the experimental flux may be very different.

On the basis of this very approximate calculation, the X-ray absorption method looks just about marginally feasible. However, the needed flux of 10^8 photons/sec is formidable. The background is likely to be enormous, and even in the absence of background, we would be looking for an exceedingly small nick in the absorption curve. The need for a sampling tube, at the most several millimeters in diameter, is highly discomfiting. It would probably necessitate the use of an electromagnetic pump, which would increase the cost of the instrument appreciably. In view of the gross estimates which had to be made in the present feasibility calculation, only experimentation, in the last analysis, could prove whether the method would work or not. Since such development work would be very costly, and by no means certain of success, this method is not recommended for the liquid-metal solution. It might be more feasible for the fused salt, where bismuth does not interfere.

If, in spite of the uncertainties, development work should be attempted, careful thought would have to be given to optimum experimental design.

Strictly speaking, (1) holds only for a monochromatic X-ray beam. If we work close to the maximum energy limit of the X-ray tube spectrum, then the low energy components can be removed by a determinable thickness of lead absorber. Because of the high background, it would probably be necessary to analyze the efflux radiation in some detail. The double crystal monochromator could be oscillated to scan the energy region from 0.1000 to 0.1330 mev, so that the only radiation reaching the counter is in the desired range. It would also be necessary to do a pulse height analysis on the output from the counter.

B. X-RAY ABSORPTION AT THE URANIUM L EDGE

The L_3 edge for uranium is at 0.01720 mev, the L_1 edge at 0.02181 mev. At 0.02 mev, the total photon cross section for lead is 24,700 barns/atom; that for bismuth would, of course, be slightly higher. This means that the diameter of the sampling tube would have to be even smaller than that required at the K edge for appreciable radiation to emerge. L-absorption, though it would require less costly equipment, would therefore be even less practical than K-absorption.

C. X-RAY FLUORESCENCE

The L_3 edge for uranium is at 0.01720 mev; the L_1 edge is at 0.02181 mev, and the K edge is at 0.1163 mev. Therefore, the principal fluorescence X-radiation from uranium would be expected to have energies of 0.0991 and 0.0945 mev. The K-absorption edge for bismuth is at 0.0905 mev, and the cross section at 0.0991 is about 2000 barns/atom. This is substantially higher than the cross section in bismuth for uranium K-edge radiation, with the result that bismuth would be virtually opaque to uranium fluorescence radiation of this energy. The depth in solution from which radiation would emerge would be very restricted, and the total intensity at the wavelength of interest very small. When the background radiation is considered in addition to these difficulties, the method appears quite unfeasible. The situation for fluorescence radiation due to L-shell excitation is even worse, because the L edges of uranium and bismuth have less energy separation than their K edges.

D. DETERMINATION OF URANIUM CONTENT BY MEASURING THE SPECTRUM OF THE EMITTED PHOTONS

In considering the nature of the fission product gamma background in relation to characteristic X-ray detection, we were led to some speculation about the history of photons during their emergence from a liquid U-Bi stream. For reasons now to be set forth, we believe it probable that the emergent gamma spectrum should show structure as a result of interactions with Bi and U. It is conceivable that this structure could be applicable to uranium concentration measurement.

The fission products in the liquid bismuth produce throughout the volume of the liquid a large output of gamma rays, covering a wide energy spectrum. The probable fate of a given photon depends on its energy. A photon of energy above 1.02 mev can be annihilated by pair production; the resultant positron will itself yield two photons of about 0.5 mev. Photons of energy above 1 mev are also subject to inelastic collisions with electrons

(Compton scattering), which would result in a large flux of photons of degraded energy, probably in a continuum. Photons of energy below 1 mev are also subject to Compton scattering, at cross section which decreases with energy. At energies considerably less than 1 mev, annihilation by photoelectric interaction with bound electrons becomes the predominant process of interaction.

Primary photons on their way out of the liquid solution would thus be subjected to two processes: annihilation, and energy degradation. The primary photons that finally emerge from the surface would probably represent a small fraction of the initial source photons, to an extent conditioned by the diameter of the containment pipe. They should also be expected to cover a much narrower energy spectrum than when formed.

Still considering only primary photons, we would expect the total spectrum of emergent radiation to be a broad continuum, narrowed as described above. However, in the lower energy range, where annihilation probability is relatively great for energies near the K-, L-, and M- absorption edges of absorbing atoms, we believe that the emergent spectrum should show superimposed absorption lines. These would correspond to quantum interactions between bound electrons and primary photons, primary photons that have been degraded by scattering, positron annihilation gammas that have been degraded, and some secondary and tertiary photons.

The secondary photons that will emerge from the liquid-bismuth stream will consist largely of fluorescent X-rays arising from readjustment of the electron shells in atoms ionized in the processes described above. These photons would start out with sharply defined energies, the emission lines lying at energies slightly lower than those of corresponding absorption lines. On their way out of the solution they may be subject to some Compton scattering, which would tend to broaden the lines and perhaps to shift them to slightly lower energies. They would also be subject to further photoelectric annihilation which would give rise to tertiary photons. The depth within the pipe from which emergence of fluorescence radiation can be expected is of course sharply limited by the high absorption coefficients discussed earlier in this section, and a depth appreciable for analytical purposes may not be expected. However, the absorption lines described in the previous paragraph should correspond to substantial depths.

From the above discussion we believe it reasonable to assume that the spectrum of radiation emerging from fission-product containing U-Bi fuel solution should show recognizable structure, containing both absorption and emission lines. The structure should contain lines characteristic of both uranium and bismuth, and of other elements present. The principal constituents of the stream, in addition to these, have atomic numbers very much

smaller than 92, and would therefore not be expected to provide interference with the characteristic uranium lines. One may then think of the possibility of a U-Bi ratio measurement based on the relative intensities of lines characteristic of these two elements. Whether the intensities themselves would be adequate for the measurement, and whether their heights would be sufficient to achieve good sensitivity, cannot be estimated at this time. The complexity of the physical situation and the multiplicity of processes involved are such that theoretical analysis would require major effort, although many of the pertinent data are probably available. The simplest way to evaluate the method would probably be by experimental investigation. It should not be difficult to simulate the primary photons in a sample of bismuth at room temperature containing a concentration of uranium in the range of interest. Measurement of the spectrum of the emitted photons could be performed with a standard X-ray crystal spectrometer.

The idea here proposed is entirely speculative, and not presently subject to confirmation or denial, as far as we know. We feel confident that some discrete structure would be observed in the experiment described above, if executed with sufficient care and precision. Whether the intensities of the expected peaks would be high enough to permit analysis with sensitivity and precision cannot be predicted. The simplicity of the measurement, if measurement should prove feasible, would have substantial advantages. We believe that the appropriate experiment should be performed.

REFERENCES, SECTION VI

- (1) G. W. Grodstein, "X-Ray Attenuation Coefficients from 10 kev to 100 mev," NBS Circular 583, April 30, 1957. The Bi-curve was interpolated.
- (2) C. M. Davisson and R. D. Evans, Phys. Rev. 81, 404 (1951).
- (3) I. Kaplan, Nuclear Physics, Addison-Wesley, Cambridge, Mass., 1955, Chap. 15.
- (4) A. H. Compton and S. K. Allison, X-Ray in Theory and Experiment, D. Van Nostrand Co Inc., New York.
- (5) Handbuch der Physik, Band XXX, Rontgenstrahlen. Springer-Verlag, Berlin (1957), Ch. 1 by Werner Schaafs, Ch. 5 by S. T. Stephenson.
- (6) G. R. Thomas, Personal Communication, Oct. 1957.
- (7) G. R. Thomas, letter to F. T. Bonner, Sept. 1957.
- (8) G. Friedlander and J. W. Kennedy, Nuclear and Radiochemistry, J. T. Wiley and Sons, Inc., New York (1955), Ch. 9.

VII. PARAMAGNETIC SUSCEPTIBILITY METHOD

A. INTRODUCTION

For the determination of the amount of uranium present in liquid bismuth, it is very suggestive to consider a measurement of the magnetic susceptibility of the liquid metal stream. Uranium is a paramagnetic substance; its paramagnetic susceptibility is largely independent of the physical environment of the uranium atoms, or their state of ionization, as in the case of the rare earths. On the other hand, bismuth is diamagnetic, and its susceptibility is temperature-independent above its melting point. Moreover, bismuth is almost a semi-conductor; it has a larger electrical resistivity than any other metal. As a result, the skin depth which characterizes the penetration of an a-c magnetic field into the metal is very large; thus, we can consider using a low-frequency a-c bridge method for measuring the susceptibility of the liquid metal stream.

To judge the usefulness of the method, we must consider the background signal that arises from the presence of paramagnetic impurities in the liquid bismuth, from the use of a paramagnetic metal (tantalum) as a container for the stream, from eddy currents in the liquid bismuth and in the containing tube, and from other causes. These and related questions are now discussed in turn.

1. The Magnetic Susceptibility of Uranium

It is now well established⁽¹⁾ that the paramagnetic behavior of uranium is due to the presence of three unpaired 5f electrons, the electron shell structure of uranium outside the closed radon shell being $5f^3 6d^1 7s^2$. In salts in which the uranium atom exhibits a valence of three or less, and in solutions in which the most highly ionized state of the uranium is U^{3+} , uranium has a susceptibility corresponding to a magnetic moment per atom of 3.1 Bohr magnetons. Due to the high degree of dilution of the uranium in the liquid bismuth, corresponding to a mean distance between uranium atoms of 35 Angstrom units at a concentration of 1000 ppm, we would expect the uranium to have a susceptibility given by Curie's Law:

$$\kappa_v = \frac{N_v \mu_{eff}^2}{3 kT} \quad (1)$$

Here N_V is the number of uranium atoms/cm³, χ_V is the susceptibility in ergs/gauss² - cm³ (e.m.u./cm³), μ_{eff} is the effective magnetic moment per atom in ergs/gauss, and T is the absolute temperature. Deviations from Curie's Law due to dipole-dipole interactions are generally negligible for interatomic distances greater than 4 or 5 Angstrom units⁽²⁾. Setting

$$N_V = N_O d_u / M_u \text{ with } d_u = 10^{-6} \eta_u d_{\text{Bi}} = 1.00 \times 10^{-5} \eta_u \frac{\text{gr}}{\text{cm}^3}$$

where

$$N_O = \text{Avogadro's number} = 6.025 \times 10^{23} \text{ atoms/mole};$$

$$d_u = \text{density of uranium in grams/cm}^3;$$

$$d_{\text{Bi}} = \text{density of bismuth} = 10.0 \text{ gr/cm}^3;$$

$$\eta_u = \text{concentration of U in Bi by weight, in parts per million};$$

$$M_u = \text{gram atomic weight of U-235} = 235 \text{ grams/mole},$$

we get

$$N_V = 2.55 \times 10^{16} \eta_u \text{ atoms/cm}^3.$$

On the other hand,

$$\mu_{\text{eff}} = 3.1 \mu_O$$

where

$$\mu_O = 1 \text{ Bohr magneton} = 0.927 \times 10^{-20} \text{ ergs/gauss},$$

so that

$$\mu_{\text{eff}}^2 = 8.65 \times 10^{-40} \text{ ergs}^2/\text{gauss}^2.$$

Substituting these values, as well as $k = 1.38 \times 10^{-16}$ ergs/deg K in (1), we get

$$\chi_{V_u} = \frac{5.31 \eta_u \times 10^{-8} \text{ e.m.u./cm}^3}{T} \quad (2)$$

2. The Magnetic Susceptibility of Bismuth

The magnetic behavior of bismuth is discussed by Van Vleck⁽³⁾ and Bozorth⁽⁴⁾. Above the melting point, the susceptibility per mole is -7.3×10^{-6} e.m.u., while it has a value of -200×10^{-6} e.m.u./mole just below the melting point. The susceptibility above the melting point corresponds to -3.5×10^{-7} e.m.u./cm³. Its value is independent of temperature above the melting point.

3. The Paramagnetic Susceptibility of Iron

We shall assume that iron is present in a dissolved state in liquid bismuth, and not in the form of macroscopic particles. This assumption is discussed in detail later on. In a state of true solution, the iron would be expected to be a paramagnetic substance obeying Curie's Law, given by (1). We shall assume that the magnetic behavior of the iron in our case will be similar to its behavior in aqueous solution, for which

$$\mu_{\text{eff}} = 5.33\mu_0 \text{ for Fe}^{++}$$

and

$$\mu_{\text{eff}} = 5.94\mu_0 \text{ for Fe}^{+++}. \text{ These values are in approximate accord}$$

with the theoretical spin-only values⁽³⁾. We shall take the worst case from our point of view which is $\mu_{\text{eff}} = 5.94\mu_0$ as representative of iron dissolved as a paramagnetic impurity in liquid bismuth. Setting

$$M_{\text{Fe}} = 56 \text{ grams/mole}; d_{\text{Fe}} = \eta_{\text{Fe}} \times 1.00 \times 10^{-5} \text{ gr/cm}^3$$

where η_{Fe} = ppm of iron (by weight) present in liquid bismuth, we get for the number of iron atoms/cm³

$$N_V = 1.07 \eta_{\text{Fe}} \times 10^{17} \text{ cm}^{-3}.$$

Furthermore, $\mu_{\text{eff}}^2 = 30.5 \times 10^{-40} \text{ ergs}^2/\text{gauss}^2$, so that the paramagnetic susceptibility becomes

$$\chi_{\text{Fe}} = \frac{7.87 \eta_{\text{Fe}} \times 10^{-7}}{T} \frac{\text{e.m.u.}}{\text{cm}^3}. \quad (3)$$

4. The Susceptibilities of the Rare Earth Fission Products

The rare earth fission products produced in appreciable quantity are the following^(5,6): Tb, Eu, Gd, Pm, Sm, Pr, Nd and Ce. Table 4 lists the computed build-up of these elements as a function of time of operation at 20 MW without processing, as well as the effective magnetic moments of their trivalent ions, taken from Van Vleck.⁽³⁾

If we assume a bismuth inventory of $200 \text{ ft}^3 = 5.58 \times 10^7$ grams, then 1 gram of a rare earth represents a concentration in parts per million by weight of $\eta_e = 0.018$. If we assume 1 year of operation without processing and an absolute temperature of 700 K (430 C), then the susceptibilities that we would predict from Curie's Law, by the same procedure used for uranium and iron previously, are listed in Table 5.

Thus the total contribution of all the rare earths after one year's operation without processing is only

$$4.12 \times 10^{-9} \frac{\text{ergs/gauss}^2}{\text{cm}^3},$$

as compared to

$$109 \times 10^{-9} \frac{\text{ergs/gauss}^2}{\text{cm}^3}$$

for 1430 ppm of uranium, or the rare earth contribution to the susceptibility is about 4 percent of the uranium contribution. (This is neglecting promethium, whose susceptibility has not been measured. Its contribution, however, would be expected to be negligible--of the order of 0.1%.)

From the data of Table 5, it is evident that we can neglect Tb, Eu and Sm, and concentrate on the other four rare earths. Combining Tables 4 and 5 we then compute an increase in susceptibility as a function of time as shown in Figure 4 at an absolute temperature of 700 K.

The total susceptibility due to the rare earth elements as a function of time τ (in months) at 700 K can be written approximately

$$\kappa_v = 0.323 \times 10^{-9} \tau \frac{\text{e.m.u.}}{\text{cm}^3}$$

or at an arbitrary temperature T,

TABLE 4

COMPUTED BUILD-UP OF RARE EARTH FISSION PRODUCTS
AS A FUNCTION OF TIME WITHOUT PROCESSING

	<u>Mass at</u> <u>3 mos.</u>	<u>Mass at</u> <u>6 mos.</u>	<u>Mass at</u> <u>9 mos.</u>	<u>Mass at</u> <u>12 mos.</u>	<u>μ_{eff}/μ_0</u>
Ce	250.7 gr	468.8 gr	688.0 gr	860.0 gr	2.10
Pr	55.9	118.9	180.8	240.0	3.41
Nd	169.6	365.0	583.0	810.0	3.45
Pm	26.3	42.2	52.3	59.0	Not known
Sm	24.1	62.8	107.8	156.0	1.63
Eu	2.92	4.53	5.36	5.8	3.2
Gd	2.26	8.40	16.2	25.0	7.86
Tb	0.035	0.134	0.282	0.46	9.8

FIGURE 4

MAGNETIC SUSCEPTIBILITY PER UNIT VOLUME OF
 THE FOUR MOST IMPORTANT RARE EARTH FISSION PRODUCTS
 (ABSOLUTE TEMPERATURE = 700°K)

TABLE 5

PREDICTED SUSCEPTIBILITIES OF THE RARE EARTH FISSION
PRODUCTS AFTER ONE YEAR OF OPERATION WITHOUT PROCESSING

	η_e (ppm)	$\kappa_v \times 10^9 \left(\frac{\text{e.m.u.}}{\text{cm}^3} \right)$
Ce	15.5	0.872
Pr	4.31	0.557
Nd	14.6	2.15
Pm	1.06	
Sm	2.81	0.0886
Eu	1.04	0.125
Gd	0.45	0.317
<u>Tb</u>	<u>0.0083</u>	<u>0.0089</u>
U	1430	109
(for comparison)		

TABLE 6

SUSCEPTIBILITY OF METALLIC ZIRCONIUM
AS A FUNCTION OF TEMPERATURE

<u>Temperature (°K)</u>	$\kappa_{v_{Zr}} \times 10^6$
200	1.28 e.m.u./gr
400	1.32
600	1.41

$$\kappa_{ve} = \frac{2.16 \times 10^{-7}}{T} \tau \frac{\text{e.m.u.}}{\text{cm}^3} \quad (4)$$

5. The Magnetic Susceptibility of Zirconium

The magnetic susceptibility of metallic zirconium is known and its values are listed in Table 6. (7)

From the very slow variation of the susceptibility with temperature, we would suspect that the measured values mostly represent free electron paramagnetism. It is likely that the atomic paramagnetism, if present at all, is largely "quenched" by the crystalline field in the solid metal. No measurements of the magnetic susceptibility of zirconium salts, or of zirconium ions in solution, have been reported. (8, 9)

Nevertheless, we would predict zirconium to be paramagnetic in solution; its electron shell structure outside the krypton closed shell is $4d^2 \cdot 5s^2$. The two 4d electrons, according to Hund's Rule, should tend to have parallel spins, forming a 3F_2 ground state. If we assume that the two 5s electrons are both detached in metallic solution, we would probably expect to find spin-only paramagnetism, with an effective magnetic moment given by

$$\mu_{\text{eff}} = \sqrt{4S(S+1)} \mu_0 = 2.83 \mu_0 \text{ for } S = 1.$$

On the other hand, if only one of the 5s electrons is detached in solution, the orbital moments may not be quenched, giving rise to an effective moment (10)

$$\mu_{\text{eff}} = g \sqrt{J(J+1)} \mu_0$$

where g is the Lande splitting factor, which has a value of $2/3$ for $S = 1$; $L = 3$; $J = L - S = 2$. Then $\mu_{\text{eff}} = 1.63 \mu_0$.

We have no sound basis for distinguishing between these two possibilities.

For a spin-only susceptibility (principal ion Zr^{++}), we then have from Curie's Law, by arguments similar to the ones used previously,

$$\kappa_{vZr} = \frac{1.10 \eta_{Zr} \times 10^{-7}}{T} \frac{\text{e.m.u.}}{\text{cm}^3} \quad (5)$$

For the orbit-plus-spin susceptibility (principal ion Zr^{+}), we have, on the other hand,

$$\kappa_{vZr} = \frac{3.65 \eta_{Zr} \times 10^{-8}}{T} \frac{\text{e.m.u.}}{\text{cm}^3} \quad (6)$$

where η_{Zr} = ppm of Zr in Bi, by weight.

The influence of zirconium on the net susceptibility of our liquid metal stream is therefore uncertain. This is an important point because zirconium occurs in the stream both as an additive substance and as a fission product. We shall discuss this question in more detail later on.

6. The Susceptibilities of Other Paramagnetic Fission Products

Aside from the rare earths, a number of other fission products of high yield are paramagnetic. These fission products are characterized by a type of paramagnetism arising from an incompletely filled d-shell. For this reason, it is considerably more difficult to predict their susceptibilities in metallic solution than was the case for the rare earths.

The most important of the d-shell type fission products are the following:

Mo (350 grams after 12 mos. without processing);

$$\mu_{\text{eff}} = 3.6 \mu_0 \text{ for Mo}^{+++} \quad (\text{Van Vleck})$$

Ru (340 grams after 12 mos. without processing);

$$\mu_{\text{eff}} = 2.0 \mu_0 \text{ for Ru}^{+++} \quad (\text{Selwood; Bates})$$

Zr (750 grams after 12 mos. without processing);

$$\mu_{\text{eff}} \text{ not known.}$$

Yttrium (Y^{+++}) is almost certainly diamagnetic, and so is Pd^{++} (Van Vleck).

The other elements that can be suspected of paramagnetism have too small a yield to be of importance. We shall omit a discussion of zirconium for the reasons stated previously. Using a procedure similar to the one outlined for the rare earths, we can predict a susceptibility variation as a function of time (in months) without processing for molybdenum and ruthenium given by Figure 5 at an absolute temperature of 700 K (430 C).

The total susceptibility of molybdenum and ruthenium combined can be written

$$\kappa_{vd} = 0.167 \times 10^{-9} \tau \frac{\text{e.m.u.}}{\text{cm}^3}$$

where τ = number of months without processing. For an arbitrary temperature T , this becomes

$$\kappa_{vd} = \frac{1.17 \times 10^{-7}}{T} \tau \frac{\text{e.m.u.}}{\text{cm}^3} \quad (7)$$

7. The Magnetic Susceptibility of Tantalum

One possible system for containment of the liquid metal stream consists of using tantalum tubing, as we shall see later on. Tantalum itself is paramagnetic, and the susceptibility of the metal as a function of temperature is well known.

Measurements have been reported by Kriesman ⁽¹¹⁾ and Asmussen and Soling ⁽¹²⁾. The results of these measurements are summarized in Figure 6.

We can describe the variation of susceptibility with temperature by the formula

$$\kappa_{vTa} = (14.28 - 0.00113T) \times 10^{-6} \text{ e.m.u./cm}^3 \quad (3)$$

8. The Resistivity of Bismuth

The electrical resistivity of bismuth changes with temperature as indicated in Figure 7. These values are for pure bismuth and would be expected to be affected by impurities, as is the case for mercury. Mercury is similar to liquid bismuth in having a relatively high electrical resistivity.

FIGURE 5
MAGNETIC SUSCEPTIBILITY OF Mo AND Ru
(ABSOLUTE TEMPERATURE = 700°K)

FIGURE 6

THE MAGNETIC SUSCEPTIBILITY OF METALLIC
TANTALUM AS A FUNCTION OF TEMPERATURE
(FROM C.J. KRIESMAN, REV. MOD. PHYS. 25, 122-126, 1953)

FIGURE 7
RESISTIVITY OF BISMUTH AS A FUNCTION OF TEMPERATURE

In the case of mercury, the increase in conductivity caused by the addition of impurities is usually attributed to the increase in the number of ionic charge carriers. Effects of this type, however, are small for impurity concentration much less than one percent.⁽¹³⁾ In the case of the liquid bismuth reactor stream, the total concentration of all additives, including uranium, zirconium, magnesium, dissolved iron and fission products, will never exceed 3000 ppm, or 0.3%. For this reason, the change in the resistivity of liquid bismuth caused by impurities does not seem to be an important problem. Nevertheless, in view of the uncertainty connected with this question, we are proposing a magnetic susceptibility device designed to minimize the influence of the signal arising from eddy currents in the bismuth stream.

The resistivity change of bismuth with temperature above the melting point can be represented by the following equation

$$\rho = [128.9 + 0.055 (t - 300)] \times 10^{-8} \text{ ohm-m} \quad (9)$$

where t is the temperature in degrees C.

9. The Resistivity of Tantalum

The electrical resistivity of tantalum also enters into the analysis of the signal derived by use of an a-c method, if the bismuth stream is made to flow through tantalum tubing. The resistivity as listed in a number of handbooks is shown in Figure 8. The slope of the straight line drawn through the experimental points is consistent with the known temperature coefficient of resistivity of tantalum at room temperature.⁽¹⁴⁾ It is therefore safe to assume that the relation between temperature and resistivity is indeed a linear one, as is true approximately in the case of copper.

The curve of Figure 8 can be described by the equation

$$\rho = [24.6 + 0.043 (t-300)] \times 10^{-8} \text{ ohm-m} \quad (10)$$

where t = temperature in °C.

FIGURE 8
RESISTIVITY OF TANTALUM AS A FUNCTION OF TEMPERATURE

B. ANALYSIS OF PROPOSED METHOD

In order to measure the magnetic susceptibility of the liquid bismuth stream, we propose to use a self-balancing mutual inductance bridge method. In this method, a primary coil is used to produce a low-frequency alternating magnetic field in a region of space traversed by tubes carrying the flowing bismuth stream. The tubes themselves are surrounded by secondary coils. The a-c signal picked up in the secondary coils is a function of the magnetic permeability of the material flowing through the tubes. The signal is also affected by the permeability of the tubes themselves and by eddy currents produced both in the liquid metal stream and in the tubes, as we shall now see.

1. Analysis of Signal Obtained in a System with Cylindrical Geometry

We shall assume that we have a primary coil in the form of a solenoid having n turns per meter. The magnetic field at the center of the solenoid carrying a current of i amperes is then given in m.k.s. units by

$$H = n i \text{ ampere turns/meter.} \quad (11)$$

If the secondary coils are short compared to the primary and are located near the center of the primary coil, the field at the surface of the bismuth-carrying tubes will be axial and uniform, and its intensity will be given by the expression just written.

The magnetic induction at a given point inside the secondary coil will be given by

$$B = \mu \mu_0 H$$

where $\mu = 1 + 4\pi \kappa_v$

is the local permeability and $\mu_0 = 4\pi \times 10^{-7}$ henry/meter is the permeability of free space. (Note that we are expressing the magnetic susceptibility per unit volume in e.m.u., in agreement with conventional usage. All other quantities are expressed in m.k.s. units.) The e.m.f. induced in a secondary of N turns is then

$$E(t) = N \frac{d\phi}{dt} = \mu_0 N \frac{d}{dt} \left[\int_A \mu H dA \right] \quad (12)$$

where we integrate over the area A of the secondary coil. In general, both μ and H are functions of spatial coordinates. If we use a system of cylindrical coordinates consisting of a z -axis in the direction of the axes of the cylindrical primary and secondary coils, and a radial distance r , as illustrated in Figure 9, then the statement made previously implies that

$$H = H_z(r, t);$$

that is, the magnetic field has a z -component only, which is a function of r alone. In view of the fact that the magnetic permeabilities of the bismuth solution and the surrounding tubes are different, we can regard μ as a function of r , so that $\mu = \mu(r)$. Under the conditions of the measurement made here, μ differs from unity by an amount of the order of 10^{-6} , so that if we write $\mu(r) = 1 + 4\pi\kappa_V(r)$, then $4\pi\kappa_V(r) \sim 10^{-6}$.

The magnetic field $H_z(r, t)$ differs from its value $H_0 e^{j\omega t}$ at the surface of the bismuth-carrying tubes on account of the eddy currents induced in the liquid bismuth and tubing walls. However, the difference between $H_z(r, t)$ and $H_0 e^{j\omega t}$ is a very small fraction of $H_0 e^{j\omega t}$ in our case, as we shall show later on. (This is a result of the fact that the tubes that we propose to use have a radius which is a small fraction of a skin depth.) If we write

$$H_z(r, t) = h_z(r) e^{j\omega t} = H_0 e^{j\omega t} \left\{ 1 - \left[1 - h_z(r)/H_0 \right] \right\}$$

then $1 - h_z(r)/H_0$ is very small compared to unity. (We shall see later that the real part of $1 - h_z(r)/H_0$ is never larger than 10^{-6} , while its imaginary part is of order 10^{-3} .) In the integrand of (12), we are therefore justified in neglecting a term of the type $4\pi\kappa_V(r) [1 - h_z(r)/H_0]$, which corresponds to the product of two small quantities. Equation (12) then becomes

$$E(t) = \mu_0 N H_0 j\omega e^{j\omega t} \left[4\pi \int \kappa_V(r) 2\pi r dr + \frac{1}{H_0} \int h_z(r) \cdot 2\pi r dr \right] \quad (13)$$

Our next step is to find the form of $H_z(r, t) = h_z(r) e^{j\omega t}$. In general, H_z is given by a solution of the skin effect equation

FIGURE 9
SECTION THROUGH AXIS OF FLOW TUBE

$$\nabla^2 \vec{H} = \sigma \mu_0 \frac{\partial \vec{H}}{\partial t}$$

where σ is the local electrical conductivity of the medium in which $\vec{H}$ is defined. Under the conditions specified above, this becomes

$$\frac{d^2 h_z}{dr^2} + \frac{1}{r} \frac{dh_z}{dr} - \sigma \mu_0 j \omega h_z = 0, \quad (14)$$

This can be written in terms of the variable $s = r \sqrt{\sigma \mu_0 j \omega}$,

$$\frac{d^2 h_z}{ds^2} + \frac{1}{s} \frac{dh_z}{ds} - h_z = 0.$$

The general solution to this equation is

$$h_z(s) = G_1 I_0(s) + G_2 K_0(s) = G_1 I_0(r j^{1/2} \sqrt{\sigma \mu_0 \omega}) + G_2 K_0(r j^{1/2} \sqrt{\sigma \mu_0 \omega}) \quad (15)$$

where I_0 and K_0 are modified Bessel functions of the first and second kinds, respectively, of zero order, as defined by Sneddon⁽¹⁴⁾ and McLachlan⁽¹⁵⁾ G_1 and G_2 are constants of integration fixed by boundary conditions.

Strictly speaking, for an exact solution of the eddy-current problem, we should define two solutions, one of which is valid in the region $0 \leq r \leq R_1$, while the other one applies to the region $R_1 \leq r \leq R_2$, where R_1 and R_2 are the inner and outer radii of the tantalum tube, respectively. The four constants of integration (two for each solution) would then be defined by the requirements that $h_z(r)$ must be finite at $r = 0$, that its value at the surface of the tantalum is H_0 , and that $h_z(r)$ and its derivative with respect to r be continuous at $r = R_1$, the boundary between the two regions. To avoid this rather laborious procedure, we shall derive upper limits to both solutions by the following procedure.

In the presence of the tantalum tubes, the alternating magnetic field to which the liquid bismuth is exposed is smaller than would be the case if the tantalum tubes were absent. We can therefore derive an upper limit to the bismuth-eddy-current contribution by ignoring the presence of the tantalum and setting $h_z(R_1) = H_0$ at the surface of the bismuth. To get

an upper limit to the tantalum contribution, we replace the hollow tantalum tubes by tantalum rods of the same diameter.

For both metals we can then discard the second term of (15) which corresponds to a solution that diverges at $r = 0$. We then have

$$h_z(r) = H_0 \frac{I_0(j^{1/2} c r)}{I_0(j^{1/2} c R)} \quad (16)$$

in both cases, where we set $c_{Bi} = \sqrt{\omega \mu_{Bi} \mu_o \sigma_{Bi}} = \sqrt{\omega \mu_o \sigma_{Bi}}$

and $R = R_1$, for the bismuth contribution, and

$$c_{Ta} = \sqrt{\omega \mu_{Ta} \mu_o \sigma_{Ta}} \approx \sqrt{\omega \mu_o \sigma_{Ta}}$$

and $R = R_2$ for the tantalum. (The quantity $\sqrt{2}/c$ is the skin depth as usually defined.)

If we use the definition^(14, 15)

$$I_0(j^{1/2} c r) = \text{ber}(c r) + j \text{bei}(c r), \text{ then}$$

$$h_z(r, t) = H_0 \frac{\text{ber}(c r) + j \text{bei}(c r)}{\text{ber}(c R) + j \text{bei}(c R)} \quad (17)$$

The ber and bei functions have been tabulated.⁽¹⁶⁾ For small values of x , the following expansions are valid^(14, 15, 16):

$$\text{ber } x = 1 - \frac{(x/2)^4}{(2!)^2} + \frac{(x/2)^8}{(4!)^2} - \dots \quad (18)$$

$$\text{bei } x = \frac{(x/2)^2}{(1!)^2} - \frac{(x/2)^6}{(3!)^2} + \dots \quad (19)$$

If we assume that $c R$ is small (and of course $c r \leq c R$ always), that is, if the radius of the tube is small compared to the skin depth $\sqrt{2}/c$, it is sufficient to use the first two terms of (18) and the first term of (19). (This holds to a very high degree of approximation in our case.)

We then have

$$\text{ber}(c r) = 1 - (c r)^4/64$$

and

$$\text{bei}(c r) = (c r)^2/4.$$

To this degree of approximation, (16) becomes

$$h_z(r) = H_0 \left[1 - \frac{(c r)^4}{64} - \frac{3}{64} (c R)^4 + \frac{c^4 (r R)^2}{16} + j (c^2/4) (r^2 - R^2) \right] \quad (20)$$

This is now in a form suitable for use in our analysis. Substituting in (13), integrating and adding the eddy-current contributions due to tantalum and bismuth, we obtain

$$\begin{aligned} E(t) = \mu_0 N H_0 j \omega e^{j \omega t} & \left\{ \pi R_1^2 \left(4 \pi \sum_{\ell} \kappa_{v \ell} \right) + \pi (R_2^2 - R_1^2) 4 \pi \kappa_{v \text{Ta}} + \right. \\ & \pi R_2^2 \left[1 - \frac{1}{48} (c_{\text{Bi}} R_1)^4 \frac{R_1^2}{R_2^2} - \frac{1}{48} (c_{\text{Ta}} R_2)^4 \right] - j \left[\frac{(c_{\text{Bi}} R_1)^2}{8} \frac{R_1^2}{R_2^2} + \right. \\ & \left. \left. \frac{(c_{\text{Ta}} R_2)^2}{8} \right] \pi R_2^2 \right\} \quad (21) \end{aligned}$$

The eddy-current contributions to the signal are represented by the last four terms, two of which are real and negative, while the other two are imaginary. We understand that in view of the approximation made earlier, these terms represent upper limits to the size of the actual eddy-current signal.

The actual signal is represented by the real part of $E(t)$. If we set $E(t) = e^{j\omega t} (u + jv)$, then $\text{Re } E(t) = u \cos \omega t - v \sin \omega t$. The signal in the secondary coil therefore has a component $u \cos \omega t$ in phase with the applied field $H_0 \cos \omega t$, and a component $-v \sin \omega t$ which is 90° out of phase with the applied field. As can be seen by inspection of (21), the eddy currents in the liquid bismuth and in the tantalum contribute to both u and v . We shall term the contribution to v the diamagnetic contribution of the eddy current; it is represented by the last two terms of the first square bracket. The contribution to u we shall term the "out-of-phase signal," in the sense that this signal is out of phase with the paramagnetic signal, although it is in phase with the applied field, as stated above. u is represented by the second square bracket.

We intend to use an electronic system which is sensitive only to $v \sin \omega t$, and which does not respond to $u \cos \omega t$ at all. This is accomplished by means of a phase-sensitive ("lock-in") detector which follows the narrow-band amplifier used to amplify the signal from the secondary coil. (This is a standard technique employed in many instruments, as for example in infra-red spectrometers.) From now on, we shall concern ourselves only with the part $v \sin \omega t$ of $E(t)$ which is in phase with the paramagnetic signal, and we shall ignore the "out-of-phase" component $u \cos \omega t$. v can be written

$$v(t) = \mu_0 N H_0 \omega \pi \left\{ R_1^2 \left(4\pi \sum_{\ell} \kappa_{v\ell} \right) + (R_2^2 - R_1^2) 4\pi \kappa_{vTa} + R_2^2 \left[1 - (1/48) (c_{Bi} R_1)^4 \frac{R_1^2}{R_2^2} - (1/48) (c_{Ta} R_2)^4 \right] \right\} \quad (22)$$

where the κ_v 's are given by (2) through (8) and

$$\kappa_{vBi} = -3.5 \times 10^{-7} \text{ e. m. u. / cm}^3.$$

Equation (22) expresses completely the information concerning the paramagnetic susceptibility of uranium obtainable by means of an a-bridge method.

We shall now discuss the design of the system in more detail.

C. DESIGN OF COILS AND FLOW TUBES

In a mutual inductance bridge, as we shall demonstrate later on, the signal from the coil containing the sample is "bucked" with the signal from another mutual inductance, that is, the two signals are put in opposition until a null condition is obtained. For the purpose of making an accurate measurement, it is desirable to consider the following arrangement. A series of tantalum tubes wrapped with secondary coils, as in Figure 9, are placed inside the primary coil. One half of these tubes has the liquid metal stream flowing through them while the other half, though filled with pure bismuth, is blocked off at both ends. The signals from all the open tubes are placed in opposition to the signals from the closed ones in such a way that the net signal is zero when the open tubes are also filled with pure bismuth.

A possible arrangement of a total of 22 tubes (3/8-inch O. D.) placed inside a 4-inch I. D. primary coil structure is shown in Figure 10. The advantage of this arrangement is that for tantalum tubes of identical dimensions and for a condition of thermal equilibrium in the entire system, the paramagnetic signal from the tantalum, as well as the diamagnetic signals from the eddy currents in the tantalum and from the diamagnetism of the bismuth, will tend to cancel. The diamagnetic signals from the eddy currents in the bismuth cancel only to the extent that the electrical conductivities of the pure and "contaminated" bismuth are the same. The possible difference between these two conductivities has been taken into account explicitly in what follows.

If we let v' = signal obtained from the open tubes and v'' = signal obtained from the closed tubes, then the net signal is $v_o = v' - v''$, which can be written

$$v_o = N \mu_o \omega H_o \pi R_1^2 \left[4\pi (\kappa_{v_u} + \kappa_{v_{Fe}} + \kappa_{v_{2r}} + \kappa_{v_e} + \kappa_{v_d}) - \frac{1}{48} (\mu_o \omega)^2 (\sigma_{Bi}^{1^2} - \sigma_{Bi}^{2^2}) R_1^4 \right] \quad (23)$$

where

σ_{Bi}^1 = electrical conductivity of the contaminated bismuth stream flowing through the open tubes;

BLOCKED TUBES, TANTALUM WALL

OPEN TUBES, TANTALUM WALL

SCALE 1:1

FIGURE 10
SECTION THROUGH MANIFOLD

σ_{Bi} = electrical conductivity of the pure bismuth in the closed tubes.

To evaluate the second term in the square brackets, let us assume the dimensions indicated in Figure 10. We shall also assume that we are using an alternating field having a frequency of 13 cycles/sec.

Then setting

$$\mu_o = 4\pi \times 10^{-7} \text{ henry/m}$$

$$\omega = 2\pi \times 13 \text{ cycles/sec}$$

$$\sigma_{\text{Bi}} = 7.75 \times 10^5 \text{ mhos/m [Equation (8)]}$$

$$R_i = 0.150 \text{ inches} = 3.8 \times 10^{-3} \text{ m}$$

we get

$$\frac{1}{48} (\mu_o \omega)^2 \sigma_{\text{Bi}}^2 R_1^4 = 2.7 \times 10^{-8}$$

This is only about 3% of the uranium signal at 1000 ppm and 700 K. In view of our previous discussion of the conductivity of liquid bismuth in the presence of impurities, we would not expect σ_{Bi} to differ from σ'_{Bi} by a large amount. For example, in the unlikely case that the impurities would increase the bismuth conductivity by 10%, we could write the term

$$\sigma_{\text{Bi}}'^2 - \sigma_{\text{Bi}}^2 \approx 0.2 \sigma_{\text{Bi}}^2.$$

The second term in the square brackets of (23) would then amount to 0.6×10^{-8} , or 0.6% of the uranium signal at 1000 ppm, which would be just detectable. These considerations lead us to the suggestion that the second term of (23) be ignored from now on.

Setting $H_o = n i_o$ in accordance with (11), where n = turns/meter of primary coil and i_o = peak current in the primary, we can then write

$$\begin{aligned} v_o = N n \mu_o \omega i_o \pi R_1^2 (6.68 \eta_{\mu} + 98.9 \eta_{\text{Fe}} + 4.58 \eta_{2r} \\ + 41.8 \tau) \times 10^{-7} (1/T) \end{aligned} \quad (24)$$

for the output signal in volts, where we have used the magnetic susceptibilities of the components of the bismuth stream given by (1) through (7). (The effects of the rare earths and of the d-shell type fission products have been added to obtain the last term in the parentheses.) We have used the unquenched susceptibility of zirconium given by (5). As before η_u , η_{Fe} and η_{Zr} refer to the concentrations (in parts per million by weight) of uranium, iron and zirconium in liquid bismuth, and τ is the time of operation without processing in months. *

To make a comparison of the relative importance of the different contaminants, let us set

$$\eta_u = 1200 \text{ ppm}$$

$$\eta_{Fe} = 8 \text{ ppm}$$

$$\eta_{Zr} = 350 \text{ ppm}$$

$$\tau = 12 \text{ mos.}$$

Then the contributions of uranium, iron, zirconium and the fission products are in the ratio $100 \div 9.8 \div 20 \div 6.2$, that is, the iron contributes about 10%, zirconium 20% and the fission products 6% of the uranium signal. From this argument, it is apparent that the most important criterion for the workability of the method depends on three things: the degree to which the solubility of iron in the liquid bismuth stream is kept at or below the limit of solubility (10 ppm), the magnitude of the susceptibility of zirconium, and the degree to which the zirconium concentration in the stream tends to stabilize.

2. Details of Design

If we consider the uranium alone and assume a concentration of $\eta_u = 1200 \text{ ppm}$, we can deduce the size of the uranium signal. Let

*It should be noted that (24) indicates that the interpretation of the signal v_o in terms of the concentration of the contaminants is a function of the absolute temperature T . It is therefore necessary to accompany the susceptibility measurement by a temperature measurement. An accuracy of $\pm 5^\circ \text{C}$ would be sufficient.

$$N = 1000$$

$$n = 1000 \text{ turns/meter} = 10 \text{ turns/cm}$$

$$\omega = 2\pi \times 13 \text{ sec}^{-1}$$

$$i_o = 10 \text{ amperes}$$

$$R_1 = 3.8 \times 10^{-3} \text{ m}$$

$$T = 700 \text{ K}$$

Then

$$v_o = 5.32 \times 10^{-8} \text{ volts.}$$

If the secondary consists of 1000 turns of anodized No. 38 aluminum wire (diameter 0.004 inches), the coil can be wound in a single layer over a length of 5 inches. The total length of the coil wire would be about 100 feet and it would have a resistance of 305 ohms at 430 C. If eleven such coils are put in parallel, and the combination is then put in series opposition with another set of eleven coils, having the same number of turns but wound around closed tantalum tubes as suggested previously, the total resistance of the combination would be 55 ohms. This is the resistance across which the signal v_o is developed.

To evaluate the sensitivity of the amplifier needed to amplify a signal of this size, we may refer to the Beckman Model 14-K Breaker Amplifier. This amplifier has a bandwidth of about 1 cycle/sec and it employs a 14 cycle/sec modulation system, which is comparable with the 13-cycle/sec modulation proposed above. Observation shows that a 0.1 μ -volt signal developed across a 20-ohm source at 300 K can be amplified with this circuit in such a way that the noise in the output signal amounts to about 0.5% of the total output signal. The noise referred to the input then amounts to 5×10^{-10} volts. By using a 1/4 cycle bandwidth (corresponding to a response time of about 4 seconds), but operating with a 50-ohm input resistance at 700 K, we would expect to get about the same noise figure, which is one percent of the figure quoted above for the uranium signal. From this point of view, the design of the primary and secondary coils proposed above meets the requirements of a uranium monitoring system both as regards sensitivity and response time, to the extent that these are limited by the characteristics of the electronic circuits employed.

It should be emphasized that we have a considerable amount of flexibility as far as the design of the secondary coils and of the primary coils and current are concerned. By increasing the current in the primary,

or by increasing the number of turns in the secondary coils, we can obtain a larger signal, if needed. However, for the present we shall restrict our discussion to the design outlined above.

A sketch of the entire system of tubes and coils, as proposed above, is shown in Figure 11. As can be seen from this sketch, we expect to be able to include the entire assembly of flow tubes and coils in a steel pipe of 12 inches I. D. The 3/8-inch diam tantalum flow tubes are 12 inches long; at each end, they are welded to 3/4-inch diam tantalum tubes in such a way that the whole assembly is about 24 inches long. The 3/4-inch diam tantalum tubes in turn are welded to a tantalum flange which is sealed to a steel flange by means of a metal gasket. The space between the tantalum tubes and the larger steel housing is filled with dry argon under pressure. (This is to avoid the oxidation of tantalum which occurs at high temperatures in air.)

This construction results in a hermetic seal of the tantalum tube system. If a failure of the metal gasket seal should occur, the space ordinarily filled with dry argon will fill up with liquid bismuth. This would make the monitoring device inoperative, but it would not interfere with the operation of the reactor as a whole.

A problem is connected with the lead-throughs required to bring the primary and secondary leads out through the wall of the steel housing. The insulation on these lead-throughs must withstand the radiation background. At the same time, they must be constructed in such a way that the insulating material is not attacked by liquid bismuth, should a failure of the gasket occur, as described above. We do not feel now that we have a solution to this problem.

As for the insulation on the coils themselves, our feeling at the moment is that anodized aluminum wire would constitute a good solution. It is also possible to anodize the tantalum by well-known techniques^(17, 18), producing an insulating film of Ta_2O_5 on the surface of each tube. We intend to investigate the relative advantages of these different possibilities in detail.

3. Analysis of Liquid Metal Flow

If we assume that the mass transport of liquid bismuth through the 12-inch diam tube leading to the reactor inlet amounts to 1.42×10^7 lb/hr, and if we take a value of 1.25 centipoise for the viscosity of liquid bismuth and a value of 625 lb/ft^3 for its density, we would expect a pressure drop of 0.045 lb/in^2 per foot length of tubing⁽¹⁹⁾. Over a 10-ft length of the 12-inch diam tubing, we would then expect a pressure drop of 0.45 lbs/in^2 .

PRIMARY COIL:

100 TURNS OF #12 ANODIZED AI WIRE
SINGLE LAYER; TOTAL LENGTH: 10 INCHES;
DIAMETER: 4 INCHES.

SECONDARY COILS:

TOTAL NUMBER OF COILS: 22; 1000 TURNS/COIL;
#38 ANODIZED AI WIRE; LENGTH OF EACH
COIL: 5 INCHES; DIAMETER OF EACH
COIL: 3/8 INCH.

FIGURE 11

FLOW TUBE SYSTEM

Let us assume that a bypass line is connected to the main flow tube at two points which are 10 feet apart. If we could arrange our system in such a way that the entire pressure drop over this distance along the main tube is applied to the tantalum manifold of Figure 11, then the flow through each of the 0.300-inch diam. tantalum tubes would be about 900 lb/hr, which corresponds to a flow velocity of $0.2 \text{ ft/sec} = 2.4 \text{ in/sec}$. This flow would be just sufficient for the required response time of the monitoring instrument. (It would take 6 sec for the bismuth to flow through the 12-inch length of the small tube.)

This argument, however, is unrealistic because the requirement that most of the pressure drop in the bypass line occur across the tantalum manifold implies that we have a constriction in the bypass line at the location of the manifold; that is, the remainder of the bypass line must have a large diameter. The flow velocity through the remainder of the bypass would then necessarily be extremely small.

We would like to propose the following solution to this problem. The tantalum manifold itself is bypassed in order to achieve quick transport of the liquid bismuth stream to the manifold entrance. The pressure drop across the manifold is then only a certain fraction of the pressure drop across the 10-foot distance in the main tube. We therefore need to increase the pressure drop in the main tube by some means. For this purpose, we would like to propose that a flow obstruction be placed into the main pipe between the places where the bypass line enters and leaves, such that the total pressure drop between these two points is increased to about 6 lb/in^2 .

A sketch of a bypass system based on these suggestions is shown in Figure 12. We have assumed that the bypass tubing has a diameter of 4 inches. Under these conditions, the linear flow velocity through the bypass line is about as fast as the flow through the main tube, so that substantially no delay occurs in transporting the bismuth stream to and from the tantalum manifold.

4. Electronic Circuits

To record the signal from the secondary coils, we propose the use of a self-balancing mutual inductance bridge, as outlined in Figure 13. The current in the primary coil is derived from a small ac generator driven by a synchronous motor. The secondary circuit consists of a closed loop, as shown in the diagram. In this circuit, signals of opposite sign are derived from the secondary coils wound around the open and closed tantalum tubes. To correct for any small differences between the

FIGURE 12
 PROPOSED FLOW SYSTEM
 (ARROWS INDICATE DIRECTION BISMUTH FLOW)

OPEN TUBES CARRYING
LIQUID BISMUTH STREAM

FIGURE 13

SCHEMATIC DIAGRAM OF PROPOSED ELECTRONIC SYSTEM

signals obtained from the two sets of coils when all the tubes are filled with pure bismuth, two small correcting mutual inductances wound in opposite directions are provided.

Furthermore, a coupling transformer T_1 having a large step-up ratio is placed in series with the secondary coils. (We plan to use here a transformer of the same type used in the Perkin-Elmer Model 21 Infrared Spectrometer.) The stepped-up signal is amplified further with a fairly wide-band high-gain ac amplifier. The output signal from the ac amplifier is fed back into a feedback loop leading through a phase-shifting network back to the small mutual inductance T_2 . T_2 is wound in such a way that the current flowing through the feedback loop produces a signal in opposition to the signal from the secondary coils. The system is then self-balancing to the extent that the output from the ac amplifier tends to annul the signal that the amplifier sees at its input. The degree to which the null condition is maintained depends on the gain of the amplifier. (This system of self-balancing through a feedback loop is widely used in dc amplifiers used for current integration (20).)

The narrow-band tuned amplifier which follows the high-gain amplifier essentially has applied to its input a signal which is proportional to the current flowing in the feedback loop. This amplifier would be tuned to the modulation frequency (13 cycle/sec) with a band width of about $1/4$ cycle/sec. Its output is then fed into a synchronous rectifier. The rectification is synchronized with a signal derived from the primary circuit current generator. In this way, we achieve "lock-in" detection of that part of the signal which is in phase with the signal from the paramagnetic components in the bismuth stream. The dc output of the synchronous rectifier is then displayed on a recorder.

(Circuits which have some similarity to the one proposed here, but which are based on a somewhat different principle of operation have been described by Pacault and his collaborators (21, 22) and by Efferney, Parsons and Bockris (23). A general discussion of mutual inductance bridge methods of measuring paramagnetic susceptibilities is found in the DeKlerk's chapter in the new addition of the Handbuch der Physik (24) and in an article by L. D. Roberts and collaborators (25).)

D. GENERAL EVALUATION OF METHOD; LIMITATIONS OF ANALYSIS CARRIED OUT ABOVE

It is appropriate at this point to summarize the results of the discussion of the magnetic susceptibility method of uranium detection. We have seen that by means of the arrangement outlined in Figure 11 we are able to obtain an ac signal proportional to uranium concentration. The

amplitude of the signal is such that a concentration of 1200 ppm of uranium in liquid bismuth should be measurable to an accuracy of $\pm 1\%$ of the concentration. The response time of the circuit that we have proposed is approximately four seconds; the flow time of the bismuth stream through the tantalum tubing is also about 4 seconds, provided the flow obstruction shown in Figure 12 is chosen so that the pressure drop from the inlet to the outlet of the bypass line is at least 6 lb/in^2 . To this extent, the proposed system meets the requirements that have been specified for the uranium monitor.

We have seen that appreciable concentration signals result from dissolved iron and zirconium in the liquid bismuth stream. The paramagnetic signal is very sensitive to small concentrations of iron, and satisfactory operation can probably not be achieved unless the iron passing through the detector is in the dissolved state, at or below the solubility limit (~ 10 ppm). In experiments with a stainless Type 347 in-pile loop some evidence for the presence of corrosion-product iron in excess of solubility has been adduced. (25) We understand that the analyses leading to this result were performed without filtering, and that therefore the presence of particulate iron may be inferred. (26) No evidence of radiation acceleration of corrosion was observed in the in-pile loop experiment. (25) Extensive experience with out-of-pile croloy loops has been gained at BNL, and we are informed that analytical measurements, both with and without filtration, have never indicated an iron concentration in excess of 6-8 ppm. (27) In one instance, however, iron particles were found at the polar faces of an electromagnetic pump. The total quantity, corresponding to 2000 hours of operation, was said to be small. (27) While the poor reproducibility of the results reported in (25) raised some doubt about the high iron concentration reported, we have the impression that croloy is less subject to corrosion by degranulation than stainless, and that the problem of particulate iron is not a serious one. Even small traces of ferromagnetic material would be damaging to paramagnetic susceptibility analysis, however, and we propose that a fairly powerful permanent magnet be placed near the entrance to the sampling tubes to collect any particulate iron that might be present.

There is uncertainty attached to the value of the paramagnetic susceptibility of zirconium in liquid metal solution, as we have seen. This would form a necessary subject of experimental investigation, and it is even possible that zirconium could turn out to be diamagnetic under the conditions of interest. Assuming that it is not, however, the important question is the stability of the zirconium concentration. We have the impression that rapid changes in zirconium concentration should not be expected.

We have ignored in our analysis three possible corrosion products other than iron, all of which are paramagnetic. These elements are molybdenum, manganese and chromium. Because molybdenum and manganese are present in croloy at such low concentration, we do not believe that they will contribute significantly to the signal. Although a steady concentration of 32 ppm of chromium has been reported in a stainless 347 loop, we have no information about chromium removal in croloy. If iron remains at a low value of croloy, however, chromium should be correspondingly smaller. Chromium contribution to the signal remains a problem requiring investigation.

It should be emphasized that the computed susceptibilities of paramagnetic elements employed in our calculations are all uncertain to some extent. This uncertainty arises because we do not accurately know the states of ionization and/or chemical combination of these elements to be expected in liquid metal solution, and both factors affect the degree to which the atomic orbital movements are quenched. If the paramagnetic elements should be present in atomic form, their susceptibilities would be less than the values computed above. However, we must expect some electron loss from metallic atoms in liquid metal solution, unless their valence electrons are involved in covalent chemical combination. In the latter case, of course, the susceptibilities may be reduced, partially or completely. In the cases of iron and zirconium, we have made the worst possible assumptions in computing susceptibilities.

For uranium and the rare earths, which contain electrons in f-orbitals, our predicted susceptibilities are much less uncertain than in the cases of transition elements whose paramagnetism is due to unpaired electrons in d-orbitals, since quenching of orbitals does not take place in these elements. The magnetic moment of a uranium atom, for example, is virtually independent of state of ionization up to U^{+3} . If more than three electrons are removed by ionization, or are paired by covalent combination, the susceptibility of uranium, of course, decreases. In tetravalent salts, e. g., UCl_4 , the susceptibility is about 10% smaller than in trivalent compounds. (8) Uranium becomes diamagnetic in hexavalent form, e. g., uranyl salts. We do not know the state of ionization or of chemical combination of uranium. The thermodynamic evidence of high heat of solution and small activity coefficient of uranium in bismuth solution⁽²⁸⁾ clearly indicates some interaction between the two elements. The detailed nature of this interaction is presently an unresolved problem, as far as we know; several solid-phase U-Bi compounds have been identified⁽²⁹⁾, but the liquid-phase problem is much more complex. Experience with the Mg-Bi system indicates a net loss of conduction electrons,⁽³⁰⁾ and we may assume that the U-Bi case may be similar. Despite the unknown factors, we believe it is inconceivable that the uranium susceptibility in liquid bismuth

could be less than that corresponding to its trivalent state, and that the uncertainty in our computed values of signal corresponding to uranium is small.

E. PROPOSED DEVELOPMENT PROGRAM

We can divide the work necessary to develop a working uranium monitor based on the magnetic susceptibility principle into a number of steps. These steps do not necessarily have to be followed in the order indicated, but can be carried out simultaneously to some extent.

1. Design and Construction of Electronic Circuits

This step is listed first in order of priority because the magnetic susceptibility measurements described below require a working electronic system. In the actual detailed design of the circuits, we intend to make use of the services of members of our electronics group and of the facilities of our instrument shop. We do not anticipate any particular difficulty in this part of the program. The estimated time required to develop a working electronic system is about three months.

2. Investigation of Materials Problems

This investigation can be carried out simultaneously with the design of the electronic circuits. It is necessary to develop a reliable high-voltage insulation coating on the wire to be used on the primary and secondary coils. The coating must retain its insulating properties under the conditions of temperature and radiation flux to be encountered in actual operation. As stated previously, our feeling at the present time is that both anodized aluminum wire and a tantalum oxide film on tantalum tubes seem to offer promise. However, many other possibilities exist and should be investigated in detail so that the most favorable possible selection may be made.

We must also study methods of achieving reliable, corrosion-free joints between tantalum and croloy. We have been informed that welds of satisfactory appearance between these two metals can be made. (32) There is corrosion danger at dissimilar metal joints, however, and it is possible that a more favorable joint could be made by use of a third metal as a gasket material. A more satisfactory solution might be found in the employment of a ceramic material.

The resistance of tantalum to liquid-bismuth corrosion should be studied thoroughly. In our design, we are proposing the use of 3/8-inch O. D. tubing with approximately 1/32-inch wall. Obviously, an essentially negligible corrosion rate would be necessary. If this should not be the case, other metals can be considered, particularly tungsten. (33)

Other materials problems (described below) are associated with the handling of liquid bismuth in possible experiments to be carried out.

It is difficult to predict the length of time that would be required for these materials investigations, but a six-month period, beginning at the start of the development program, would seem reasonable.

3. Magnetic Susceptibility Measurements

These would be designed to determine the magnetic susceptibilities of the various additives, corrosion products, and fission products in liquid metal solution. It would be our intention to concentrate on uranium and zirconium in this study. Preliminary measurements might be carried out employing mercury as a room-temperature liquid metal solvent. Mercury has a number of physical properties in common with liquid bismuth; e. g., it is diamagnetic and has a large electrical resistivity. Measurements on liquid bismuth solutions would be essential, however.

This investigation could be begun as soon as the construction of the electronic circuitry is completed. We estimate that it would require about six months for completion.

4. Final Design and Construction of the Instrument

By the final design of the instrument we mean principally the design of the coils and tantalum tube manifold, and possible refinements in the electronic circuits. In the design of the manifold, we would call on the services of metallurgists in our own company, and would also expect to seek the cooperation of the Fansteel Metallurgical Corporation. Fansteel has had extensive experience with the construction of complicated manifolds made of tantalum, such as the ones that are widely used in the chemical industry. We anticipate that actual fabrication of the tantalum tube manifold would be carried out by Fansteel.

The other part of the construction would consist of the assembly of the primary and secondary coils. In this work, a method of fastening the secondary coils to the tubing on which they are wound would have to be

chosen. A support for the primary coils must be designed. A solution to the very difficult problem of bringing leads through the croloy housing, insulating them from the housing in a manner that is electrically reliable, and at the same time guaranteeing the gas-tightness of the seal, must be found.

We feel that our design responsibility should stop with the tantalum tube manifold, and that the steel structure to which the manifold is to be attached, the steel housing, and the design of the bypass line should be the responsibility of the Babcock and Wilcox Company. However, we would, of course, be ready to cooperate in any way that would be helpful in this connection.

We estimate that the final design and construction phase just outlined could be accomplished in about three months, and that it could begin about six months after the start of the development program.

5. Testing of the Instrument

Testing of the completed instrument should be planned for coordination with an appropriate liquid bismuth loop experiment at Brookhaven National Laboratory or, possibly, at Lynchburg or Alliance. Such testing would logically take place during the final three months of the program.

REFERENCES, SECTION VII

- (1) Bleaney, B. , "Paramagnetism of the Actinide Group, " Disc. Farad. Soc. No. 19, p. 112 (1955).
- (2) Bates, L. F. , Modern Magnetism, Cambridge University Press (1951).
- (3) VanVleck, J. H. , The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, p. 92 (1932).
- (4) Bozorth, R. M. , Ferromagnetism, D. Van Nostrand, New York (1951).
- (5) Lock, C. J. L. , Fission Product Formation in a Homogeneous Power Reactor, Atomic Energy Research Establishment Tech. Rep. No. A. E. R. E. C/R 1715 (1956).
- (6) Memorandum from T. C. Engelder, Lynchburg, to W. R. Foley, Lynchburg (May 3, 1957), File No. 600-0046-32-29 B.
- (7) Hampel, C. R. , Rare Metals Handbook, Rheinhold, New York (1954).
- (8) Selwood, P. W. , Magnetochemistry, Interscience, New York (1943).
- (9) Bowers, K. D. , and J. Owen, "Paramagnetic Resonance," Repts. on the Progress of Physics, XVIII, pp. 304-74 (1955).
- (10) See Reference 2.
- (11) Kriessman, C. J. , "High Temperature Magnetic Susceptibility of V, Nb, Ta, W, and Mo, " Rev. Mod. Phys. 25, p. 122 (1953).
- (12) Asmussen, R. W. , and H. Soling, "Magnetic Properties of the Elements Tantalum, Niobium and Rhenium," Acta. Chem. Scand. 8, pp. 563-68 (1954).
- (13) Prof. Carl Wagner, Massachusetts Institute of Technology, Private Communication.
- (14) Sneddon, I. A. , Special Functions of Mathematical Physics and Chemistry, Oliver and Boyd, London (1956).
- (15) McLachlan, N. W. , Bessel Functions for Engineers, Oxford University Press (1934).

- (16) Dwight, H. B. , "Bessel Functions for A. C. Problems, " Trans. Am. Inst. Elect. Engrs. , 48 , p. 812 (1929).
- (17) Young, L. , "Anodic Oxide Films on Tantalum Electrodes, " Trans. Far. Soc. 50 , p. 153 (1954).
- (18) Vermillyea, D. A. , "Formation of Anodic Films on Cathodes, J. Electro. Chem. Soc. , 101 , p. 389 (1954).
- (19) Perry, John H. , Chemical Engineer's Handbook, McGraw-Hill, New York (1950).
- (20) Higinbotham, W. A. , and S. Rankowitz, "A Combined Current Indicator and Integrator," Rev. Scient. Inst. , 22 , p. 688 (1951).
- (21) Pacault, A. , B. Lemanceau and J. Jousset-Dubien, "New Method of Measurement of Magnetic Susceptibilities," Comptes Rendus 237 , pp. 1156-58 (1953).
- (22) Jousset-Dubien, J. , B. Lemanceau and A. Pacault, "Electronic Apparatus for the Measurement of Magnetic Susceptibilities," J. Chim. Phys. 53 , pp. 198-205 (1956).
- (23) Efferney, M. G. , D. F. Parson and J. O'M. Bockris, "Investigation of the Heterodyne Beat Method of Measurement of Magnetic Susceptibility," J. Sci. Inst. 32 , p. 99 (1955).
- (24) DeKlerk, D. , "Adiabatic Demagnetization," Handbuch der Physik, XV, Springer Verlag, Heidelberg (1956).
- (25) Erickson, R. A. , L. D. Roberts and J. W. T. Dabbs, "Mutual Inductance Bridge and Cryostat for Low Temperature Magnetic Measurements," Rev. Scient. Inst. 25 , p. 1178 (1954).
- (26) Raseman, C. J. , H. Susskind and C. H. Waide, Chem. Eng. Progress 53 , No. 2, p. 92-F (1957).
- (27) Susskind, H. S. , Personal Communication, Oct. 1957.
- (28) Klamut, C. , Personal Communication, Oct. 1957.
- (29) Egan, J. J., and R. H. Wiswall, Nucleonics 15 , No. 7, p.104 (1957).
- (30) Battelle Memorial Institute, Report 1000.

- (31) Prof. C. Wagner, Personal Communication, Nov. 1957.
- (32) Heus, R. J. , Personal Communication, Nov. 1957.
- (33) Lyon, R. N. , Liquid Metals Handbook (USAEC, June, 1952) p. 176.

VIII. ELECTROCHEMICAL AND OPTICAL METHODS FOR FUSED-SALT APPLICATION

In Section IV we reached the conclusion that electrochemical and optical methods of analysis, while not applicable to liquid-metal fuel monitoring on a continuous basis, could appropriately be considered for application to fused-salt monitoring. In this section we will present an evaluation of the present state of development of the several methods in this category that seem to offer the greatest promise of applicability. Of the various available techniques based on electrochemical processes, potentiometry and two variations of voltammetry, called polarography and chronopotentiometry, are under investigation at BNL and elsewhere for LMFR application. (In our considerations of potentiometry below, we take up the possibility of liquid fuel as well as fused-salt monitoring.) The optical method that appears to offer most promise is absorption spectrophotometry.

A. POTENTIOMETRY

The electromotive force of a reversible galvanic cell is a direct measure of the free energy of the chemical (oxidation-reduction) process which may occur within the cell if current is withdrawn. Voltage measurement of such cells is generally made in a manner such that actual current drain is so low that the characteristics of the cell cannot be altered by electrolysis. Cells are composed of two reversible electrodes, or half-cells, each of which may consist of a metal dipping into electrolyte containing its own ions, a metallic solution (e. g., an amalgam) in contact with electrolyte containing ions of the more electronegative element, an inert metal dipping into electrolyte containing ions in two valence states, or some other arrangement appropriate to the process under study. Conventionally, the electrolyte employed in galvanic cell measurements is an aqueous solution, but nonaqueous conducting solutions have been employed and, more recently, high-temperature galvanic cell measurements have been carried out employing fused-salt electrolytes. Galvanic cell measurements constitute a powerful method for the acquisition of fundamental thermodynamic data.

A variety of thermodynamic quantities important to LMFR technology have been determined by Egan and Wiswall⁽¹⁾ by a high-temperature galvanic cell method. For example, a cell containing uranium metal and liquid U-Bi alloy electrodes, with LiCl-KCl eutectic containing 5% UCl₃ as electrolyte, was employed for determination of the activity coefficient and free energy of mixing of uranium metal in bismuth at 500°C. This cell may be represented in standard notation as

The EMF of the cell is expressed by the relation

$$-n \mathcal{F} \mathcal{E} = RT \ln f_U N_U, \quad (1)$$

where n represents the number of electrons involved in the oxidation-reduction process (in this case, $n = 3$); $\mathcal{F}$ the Faraday constant; $\mathcal{E}$ the EMF; f_U the activity coefficient of uranium in the alloy; N_U the mole fraction of uranium in the alloy. The activity coefficient for uranium, under the conditions investigated, was found to have the surprisingly low value of 1×10^{-5} .

We could consider the use of a cell similar to that described above for measurement of the concentration of uranium in liquid-bismuth fuel. The only difference from the above case would be the presence of Mg, Zr and fission product ions in the liquid alloy electrode. In principle the EMF of the cell should be responsive to uranium concentration, and the effects of the added Mg and Zr on the activity coefficient of U could be empirically determined. Although LiCl is very much more stable than MgCl_2 , the free energies of formation of these two compounds are sufficiently close together that from equilibrium considerations⁽²⁾ some transfer of magnesium from the alloy to the salt phase may be anticipated. A strong tendency of magnesium to extract into LiCl-KCl eutectic from bismuth solution has, in fact, been observed⁽³⁾. Again, although MgCl_2 is more stable than UCl_3 , the free energy difference is, in this case, very small; it must therefore be expected that a uranium electrode in contact with salt containing magnesium ion would quickly develop a film of magnesium metal, and exhibit the electrochemical characteristics of a magnesium electrode.

The utility of a uranium electrode in ternary NaCl-KCl- MgCl_2 eutectic would be even worse than the above case, because of the greater concentration of MgCl_2 . It has been suggested⁽⁴⁾, however, that auxiliary electrolysis could be employed to strip magnesium from a uranium electrode, and that if EMF measurements were then made at zero electrolysis current, the values might be indicative of uranium concentration in the fuel stream. Various concentration cells could be considered, but we are informed that these have been carefully reviewed at BNL and that none with promise of uranium concentration responsiveness has been found⁽⁵⁾.

Potentiometric measurements employing magnesium electrodes dipping into ternary eutectic which is also in contact with liquid fuel are capable of providing a sensitive indication of magnesium concentration in the fuel⁽¹⁾. Such measurements should play an important role in LMFR process control. We conclude that it is likely to be the only process application of potentiometry to LMFR systems containing magnesium.

B. POLAROGRAPHY

The current which passes through an electrochemical cell is a function of the applied voltage, and the current-voltage characteristics of the cell may be made dependent upon the rates of processes occurring at the electrodes. Voltammetry is the study of such current-voltage characteristics, and polarography is a traditional analytical form of voltammetry in which dropping-mercury electrodes are employed⁽⁶⁾.

When a readily reducible substance is present in an electrochemical cell, its concentration in oxidized form at the cathode surface quickly drops to a value that is negligible in comparison with its bulk concentration in the cell. Thus, a concentration gradient is established at the electrode, and current is determined by the rate at which reducible material is transferred across this gradient to the electrode. Mass transfer to the electrode may also be affected by convection due to stirring or to density or temperature gradients, and by migration of ionic species under the applied electric field. When no stirring is employed, and electrolysis time is short, convective transfer may be virtually eliminated. If a substantial concentration of nonreducible ions (called supporting electrolyte) is present, migration is also negligible. In these circumstances, mass transfer of reducible species is virtually controlled by diffusion, and the limiting diffusion current observed is a direct measure of the bulk concentration of reducible substance. In the dropping-mercury electrode of conventional polarography, a fine capillary of narrow bore (0.02-0.05 mm) is in contact with the electrolyte, and a head of mercury establishes a constant drop time. The cathode surface thus expands and is continuously refreshed during the formation time of a drop. The anode conventionally used is a pool of mercury of large area at the bottom of the cell. For this kind of cell the limiting diffusion current (i_d) and concentration of reducible substance (C_o) are related by the Ilkovic equation,

$$i_d = 7.082 \times 10^4 n m^{2/3} t^{1/6} C_o D^{1/2}, \quad (2)$$

in which n represents the number of electrons involved in the electrochemical change, m the mass flow rate of mercury in the capillary, t the drop time and D the diffusion coefficient of the ionic species of interest. In practical polarographic measurements, the working electrode potential is measured as a function of current; the resulting curve is wave-like, and exhibits a plateau region in the higher potential region, corresponding to the limiting diffusion current. The appropriate current-potential equation is

$$E = E_{1/2} + \frac{RT}{n} \ln \frac{i_d - i}{i}, \quad (3)$$

where $E_{1/2}$, the so-called half-wave potential, corresponds to $\ln \frac{i_d - i}{i} = 0$.

Polarographic measurements are applicable to fused-salt electrolyte, and the method should in principle be possible for the measurement of uranium concentration in a fused-salt processing stream. It could not be applied to a liquid-metal fuel stream without an intermediate chemical transformation. Work on fused-salt polarography has been carried out at BNL, and at Carter Laboratories and the University of New Hampshire under BNL subcontract. In these studies, dropping-bismuth electrodes have been employed (also liquid Bi-Pb solution, at Carter Laboratories). Because of difficulties encountered in establishing steady flow, and because of a serious problem of plugging in capillaries of very narrow bore, the relatively large bore size of 0.075 mm has recently been adopted at BNL. Polarographic measurements have been carried out using dropping-bismuth cathodes, bismuth-pool anodes, LiCl-KCl eutectic at 450°C as supporting electrolyte, and Pb^{++} as reductant species⁽⁸⁾. The measurements have verified the validity of equations 2 and 3, above, for this system. In particular, the observation of direct proportionality between i_d and C_0 demonstrates the potentiality of polarography as an analytical method for fused-salt systems.

When two or more reducible components are present, they will reduce in order of their oxidation potentials, and successful analysis depends upon complete separation of the corresponding waves, so that diffusion currents may be individually evaluated. Egan has reported good separation of Pb^{++} and Zn^{++} in LiCl-KCl eutectic, but experiments with Pb^{++} - Cd^{++} mixtures have not led to adequate separation. No polarographic measurements of uranium in fused-salt solution are known to us. The practical case of uranium concentration measurement in a fused-salt processing stream would be complicated by the presence of bismuth, which reduces just before uranium and, if present at substantial concentration, could mask the uranium limiting diffusion current. It is conceivable that this problem could be handled by chemical complexing of bismuth, to alter its order of reduction with respect to uranium, as has been accomplished in aqueous systems⁽⁹⁾.

Derivative polarography, in which improved resolution is achieved by differentiation of current-potential curves during mercury drop formation, has been applied to uranium and bismuth analysis in aqueous systems at BNL⁽⁹⁾. The method is in principle applicable to fused-salt systems, but has not been tried.

Polarography may be considered as a possible analytical method for uranium analysis of fused-salt streams. The present state of development of polarography for this purpose is not sufficiently advanced to permit detailed evaluation. Continuous polarographic measurement would not be possible: since stirring of the cell must be avoided to prevent convective

mass transfer, intermittent flow of eutectic through the cell would be required. However, rapid scanning techniques can be applied to polarographic measurement; thus, if intermittent transfer of material at reasonable rate could be arranged, conveniently small delay times between analyses might be possible.

In summary, we believe that polarography has some promise, for fused-salt stream analysis only. The present state of its development for this purpose is rudimentary, and the technical problems requiring further investigation, particularly the problem of adaptation for operation in a sealed system, are formidable. We conclude that it is less promising for fused-salt stream analysis than other methods.

C. CHRONOPOTENTIOMETRY

A modification of voltammetry which has been receiving recent attention as an analytical method is based on constant current electrolysis and has been named "chronopotentiometry" by Delahay and Mamantov⁽¹⁰⁾. A reducible substance present in solution containing supporting electrolyte, unstirred to eliminate convective mass transfer, is brought in contact with an electrode of substantial area, which may be a mercury pool or a metallic disc. During constant current electrolysis, the concentration of reducible substance at the electrode surface, controlled by diffusion from the bulk solution, decreases steadily. As this concentration approaches zero, the potential of the working electrode undergoes rapid change. The total electrolysis time required to produce this rapid change, called "transition time," is the basic measured quantity of chronopotentiometry. Its measurement requires that the working electrode potential be followed continuously, which is accomplished by means of a third, reference electrode and suitable potentiometer circuit.

The theory of chronopotentiometry has been reviewed in detail by Delahay and Mamantov(op. cit.), who provide the following relation between transition time (τ) and bulk concentration (C):

$$\tau^{1/2} = \frac{n F \pi^{1/2} D^{1/2} C}{2 i_0} , \quad (4)$$

where i_0 represents the constant current density applied. Delahay and Mamantov also treat the case of two reducible constituents, which give two transition times. In this case the second transition time (τ_2) is related to the concentration of the second substance (C_2) by the equation

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{n_2 F \pi^{1/2} D_2^{1/2} C_2}{2 i_0} . \quad (5)$$

The validity of these relationships and the utility of chronopotentiometry as an analytical method has been demonstrated experimentally by Reilley, Everett and Johns⁽¹¹⁾. These investigators have studied the potential-time characteristics of aqueous systems containing Pb^{++} , Cd^{++} , and Zn^{++} individually, and Pb^{++} and Cd^{++} together, over the concentration range 5×10^{-5} -- 1×10^{-2} molar, under current densities such that transition times ranged from 4 to 60 seconds. Both mercury-pool and platinum-disc electrodes were used. Laitinen and Ferguson⁽¹²⁾ have applied chronopotentiometry to the analysis of Bi, Cd, Ag, and Cu, and to the mixtures Bi-Ag and Bi-Cu, in fused LiCl-KCl eutectic at 450°C , employing current densities such that transition times were between 1 and 5 seconds. The working electrode used in this study was a 1-cm, square platinum foil, and a Pt-PtCl₂ reference electrode was employed. The feasibility of the method in fused-salt systems is clearly demonstrated by this investigation, and an accuracy of $\pm 2.6\%$ is claimed.

Experimental work on chronopotentiometry in aqueous systems has been carried out at BNL⁽¹³⁾. A single fused-salt experiment has been carried out, in which an attempt was made to reduce UCl_3 at a molybdenum-disc cathode⁽¹⁴⁾. No transition corresponding to the expected uranium reduction was observed in this experiment, although when polarity was subsequently reversed, an anodic oxidation transition was observed. This single observation on uranium chronopotentiometry remains unexplained, and further experimentation employing platinum-foil electrodes is proceeding at the present time.

The state of development of chronopotentiometry for uranium analysis in fused-salt systems is thus not very advanced at this time. The method appears to have considerable promise, however, discounting the single discouraging experiment reported at BNL. Chronopotentiometry offers many advantages over polarography for the purposes of interest to LMFR technology, and we believe that its development for process applications should take precedence over the latter. Among these advantages is the greater reported range of concentration sensitivity. We estimate 10 ppm of uranium in ternary KCl-NaCl-MgCl₂ eutectic to represent a concentration of about 10^{-4} molar, which may lie on the edge of detectability for dropping-bismuth polarography, but should lie well within the range of accurate resolution for chronopotentiometry. Another advantage is that chronopotentiometry can be applied to oxidation as well as reduction. It is conceivable that it could be applied to the analysis of uranium in liquid-bismuth solution by making a fixed quantity of liquid-metal fuel the anode in a cell, followed by polarity reversal and cathodic reduction. Its most likely application, however, is in fused-salt analysis.

Like polarography, chronopotentiometry cannot be made continuous. It is obvious from equation 4, however, that transition times may be made arbitrarily short by increasing current density. The limiting transition time for 0.01 molar solution of reducible substance is reported to be about 1 millisecond⁽¹⁵⁾. Thus, with oscilloscopic detection chronopotentiometric measurements may be carried out in minimal time intervals. The requirement that the electrolyte must be at rest, so that intermittent flow would be necessary, would impose a much more severe limitation upon frequency of analytical results, but we do not believe this would be serious for fused-salt monitoring.

D. ABSORPTION SPECTROPHOTOMETRY

Of the various possible optical methods for detecting uranium, absorption spectrophotometry appears to be the only one with promise for continuous LMFR process application. It could not be considered for direct application to the liquid-metal fuel stream without intermediate chemical processing of the uranium metal, but it is very likely that it could be used for fused-salt monitoring. Emission spectroscopy could be employed for liquid-metal analysis, and is even capable of yielding isotopic ratios⁽¹⁶⁾, but would be applicable only on a batch-sample basis.

A modification of the Beckman DU spectrophotometer for high-temperature use has been described by Sundheim and Greenberg⁽¹⁷⁾. Absorption spectrophotometric measurements on fused-salt systems have been carried out in the laboratories of B. R. Sundheim at New York University, H. Haendler at the University of New Hampshire, D. Gruen at ANL, and W. Ginell and C. Auerbach at BNL. Although numerous technical difficulties have been encountered, the method has shown considerable promise as an investigative and analytical technique.

Sundheim has performed a single experiment on uranium dissolved in fused nitrate⁽¹⁸⁾. Very strong absorption was observed, and the color of the solution was bright red. The oxidation state of uranium in this experiment was uncertain, but it is believed that it may have been + 4.

Haendler has performed a series of experiments in which UCl_3 is formed directly in ternary NaCl-KCl-MgCl_2 eutectic by reaction between uranium metal and lead chloride⁽¹⁹⁾. The uranium salt formed in this manner is presumed to be UCl_3 . The resultant fused-salt solutions show strong absorption in the ultraviolet, between 600 and 240 millimicrons, in general agreement with the U^{+3} U.V. absorption spectrum reported by Klixbull-Jorgenson⁽²⁰⁾ for concentrated HCl solution. The solutions are reported to

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have a brownish, rather than red, color. A sharp peak is observed in the U. V. at about 260 mμ, although Haendler is not certain that it is ascribable to uranium. The solution is observed to have relatively high transmittance in the red end of the visible, which slopes off toward the blue. All of these measurements have been carried out in quartz optical cells, and employing a Perkin-Elmer instrument with chopped beam, specially adapted for work in the visible and ultraviolet.

Although only in its earliest development stages, it seems clear to us that absorption spectrophotometry in fused-salt systems has strong potential for LMFR process application. It cannot be given quantitative evaluation in the absence of experimental data which have not yet been developed. There are several possible sources of technical difficulty associated with the method, which include the following:

1. Etching of quartz cells by fused-salt mixtures, reducing their optical transmittance. This difficulty has plagued most experimental programs on fused-salt spectrophotometry. However, it is probable that the difficulty is largely due to traces of moisture, and could be eliminated entirely in a sealed monitoring system in an operating plant. Also, it is possible that other serviceable optical cell materials, showing less tendency to etch, could be found.

2. Radiation damage to the optical cell is an unevaluated source of difficulty. Quartz loses its transparency on prolonged exposure to gamma radiation. However, it can be annealed, and its transparency restored, at temperatures between 200-300°C. Since the operating range of a fused-salt monitoring system would be well in excess of this range, it seems probable that little or no opacity would develop due to radiation damage. If not, other cell materials, such as titania and alumina, could be investigated.

3. Concentration measurement in absorption spectrophotometry is based on the Beer-Lambert law

$$I = I_0 e^{-\epsilon \ell c} ,$$

where I represents transmitted light intensity, I_0 initial intensity, ℓ absorbing path length, c concentration of absorbing substance, and ϵ , called extinction coefficient, is a characteristic constant for the absorbing substance at given incident wave length. While there is no question of the validity of this relation for fused-salt systems, it has generally been observed that extinction coefficients are very large. Coefficients as high as 10^5 have been observed in alkali halide systems by Sundheim, and Haendler reports that the extinction coefficient of U^{+3} in ternary eutectic ranges between 500 and

1500 in the U. V. This means that very short light paths and very dilute solutions must be used; Sundheim has used optical cells offering path lengths less than 1 mm. Since the concentration of uranium anticipated in process fused-salt solution is small, dilution presumably would not be a problem. However, it is possible that the concentration range in which accurate measurements could be made without controlled dilution may turn out to be inadequate.

4. Interference from other components of a complex mixture is always a source of complication in analysis of a single constituent by absorption spectrophotometry. For example, it is conceivable that traces of chromium, as a corrosion product, could turn out to absorb strongly in the same wave-length region as uranium. Whether interference will be a problem and, if so, whether it can be overcome, can only be answered by empirical observation, since absorption data obtained on aqueous systems cannot be directly applied to fused-salt systems.

The technical problems enumerated above indicate that a substantial development program is needed. Provided all of them can be met satisfactorily, absorption spectrophotometry will offer a simple, convenient, and truly continuous method of monitoring uranium in a fused-salt stream. For continuous operation, the method offers the advantage over chronopotentiometry that measurements can be made on a moving stream. The possible limits of accuracy of the method over the concentration range of interest cannot be evaluated at this time.

REFERENCES, SECTION VIII

- (1) Egan, J. J. and R. H. Wiswall, Jr., Nucleonics 15, No. 7, 104 (1957).
- (2) Bareis, D. W., R. H. Wiswall and W. E. Winsche, Chem. Eng. Progress 50, No. 12, 228 (1954).
- (3) Raseman, C. J., H. Susskind and C. H. Waide, Paper No. 57-NESC-27, 2nd Nuclear Engineering and Science Conference (1957), page 13.
- (4) B. R. Sundheim, Personal Communication, Nov. 1957.
- (5) D. Marsland, Personal Communication, Nov. 1957.
- (6) See Kolthoff and Lingane, "Polarography," 2nd Ed. (New York: Interscience, 1953), for complete description of the method.
- (7) Delahay, P., "New Instrumental Methods in Electrochemistry " (New York: Interscience, 1954), page 64.
- (8) J. J. Egan, Personal Communication, Nov. 1957.
- (9) J. Glickstein, Personal Communication, Aug. 1957.
- (10) Delahay, P., and G. Mamantov, Anal. Chem. 27, 478 (1955).
- (11) Reilley, C. N., G. W. Everett and R. H. Johns, Anal. Chem. 27, 483 (1955).
- (12) Laitinen, H. A., and W. S. Ferguson, Anal. Chem. 29, 4 (1957).
- (13) BNL Hot Lab Monthly Progress Report, July 1957, Appendix.
- (14) W. Ginell and C. Auerbach, Personal Communication, Nov. 1957.
- (15) BNL Hot Lab Monthly Progress Report, July 1957, Appendix, page 3.
- (16) Lovett, J. E. and J. O. Roberts, Nucleonics 15, No. 7, 73 (1957).
- (17) Sundheim, B. R. and J. Greenberg, Rev. Sci. Inst. 29, 703 (1956).
- (18) Sundheim, B. R., Personal Communication, Nov. 1957.
- (19) H. Haendler, Personal Communication, Nov. 1957.
- (20) Klíxbull-Jorgenson, C., Acta. Chem. Scand. 10, 1503 (1956).

IX. DISCUSSION OF RECOMMENDATION

We recommend that an instrument based on paramagnetic susceptibility measurement be developed for application to the liquid-fuel stream of LMFRE. To explain fully the basis for this recommendation, we must resume a discussion of the purpose of continuous uranium monitoring begun in Section III.

We assume that continuous measurements of the mean temperature of the reactor will be made during operation. Therefore, the reactivity of the fuel will be known with a much higher degree of accuracy than could be achieved by measurements at any position outside the core. We also assume that a record of the reactor power level will be continuously maintained, and that quantities of uranium added to the fuel stream, and of solution withdrawn, will be accurately known. From this information the concentration of uranium at any time should in principle be calculable, although it is true that if uranium should deposit anywhere in the system the calculations would be in error. For routine reactor operation we do not believe that external monitoring could provide useful information that would not be available, at a higher level of accuracy, from reactor core instrumentation.

Aside from routine operation, the purposes of external monitoring that we have identified earlier are (1) concentration indication during startup, (2) safety, and (3) development of information of an experimental research nature. The startup application, in our opinion, would be valuable but not necessary. The safety objective, as we have stated, seems to us to be separable from the kind of instrument under discussion here. Chunks of uranium metal, with density nearly twice that of liquid bismuth, should settle rapidly despite the expected turbulence, and it should not be difficult to arrange means of preventing them from entering the core. Very fine particles of uranium might be more difficult to cope with. Uranium oxide, with density less than that of liquid bismuth, would be readily carried along in the stream. Oxidation of uranium would be preceded by oxidation of magnesium, however, and continuous electrode potential measurements should be capable of indicating a dangerous oxidizing situation before uranium oxide formation could set in. At any rate, the safety problem is one of detecting very large surges in fissionable material concentration. An instrument designed to detect them would properly sacrifice accuracy in favor of extremely rapid response time, and the measurement should be effected across an entire cross section of main liquid-fuel stream piping, rather than across a bypass stream. These requirements might best be met by one of the neutron methods discussed in Section V.

The main justification for an instrument of the kind specified, in our opinion, is therefore the experimental aspect of the reactor. We believe that this reason alone is a very persuasive one. LMFRE will be the prototype of an important power reactor class, and its operational system will be extremely complex. It will be important to gain a maximum amount of information about the behavior of this system in long-term operation, and the long- and short-term fluctuations in uranium concentration that the proposed instrument could follow would be a valuable component of the knowledge to be gained. From this point of view it would be desirable to make the instrument one which provides information clearly separable from that available from core instruments.

In Section VI we have seen that X-ray detection of total uranium concentration in liquid bismuth is a very questionable proposition. The neutron methods that appear feasible from our presentation in Section V are all sensitive to fission product poison concentrations. The measurements they would provide would thus essentially be a reflection of fuel reactivity, rather than uranium concentration. We therefore turn to the paramagnetic susceptibility method, whose probable feasibility we have demonstrated analytically in Section VII.

The paramagnetic susceptibility measurement is not an ideal one in terms of the specified requirements. It measures total uranium rather than fissionable material, and it is also subject to interference from fission products. This interference would be at a low level, however, and would have the virtue, from the point of view we have set forth above, of representing a complex of fission product concentrations different from that of the thermal neutron case. This type of measurement would also be subject to interference from zirconium and from corrosion products. Because of corrosion products, it would probably not have great value for concentration indication during reactor startup unless equilibrium values of corrosion product concentrations should be established very quickly during the operational stages before uranium addition.

Despite its drawbacks, we feel that the method using a paramagnetic susceptibility instrument is the best available selection within the framework of our previous discussion. We may also argue that the use of this principle in LMFRE would be a significant experimental trial of a measurement technique not previously attempted in reactor technology as far as we are aware.

The basis for our selection will require careful review. Since we have had no association with the over-all design problems of LMFRE,

it is possible that very persuasive operational arguments have escaped our attention. It may be that continuous fuel reactivity measurement on the fuel stream, despite its apparent duplication of information available from core instrumentation, would have more value than the composite signal we propose, for reasons unknown to us. If this should be the case, the neutron methods discussed in Section V should be given serious consideration.

The problem of fused-salt stream monitoring cannot be met by a magnetic susceptibility method, since uranium concentrations would be low and rare earth fission product concentrations relatively high. In our judgment this problem is sufficiently different from that of fuel-stream monitoring that the two should be given separate treatment. X-ray detection might be possible, although substantial development work would be required. We believe that one or the other of two methods already under development at BNL and elsewhere, chronopotentiometry and absorption spectrophotometry, will provide the ultimate practical answer to the problem of fused-salt monitoring.

APPENDIX I

FRACTION OF X-RAY ENERGY IN THE RANGE E_1 TO E_2

According to Kramers⁽⁵⁾, the average energy per electron, $I_\nu d\nu$, between frequencies ν and $(\nu + d\nu)$ from a thick target X-ray tube is:

$$I_\nu d\nu = \frac{8 \pi e^2 h}{3 \sqrt{3} \ell m c^3} Z (\nu_0 - \nu) d\nu$$

where e is the charge, m the mass of an electron, c is the velocity of light, $\ell \approx 6$, h is Planck's constant, and Z is the atomic number of the target material. The average energy in the region ν_1 to ν_2 is:

$$\int_{\nu_1}^{\nu_2} I_\nu d\nu = \frac{8 \pi e^2 h Z}{3 \sqrt{3} \ell m c^3} \left[\nu_0 (\nu_2 - \nu_1) - 1/2 (\nu_2^2 - \nu_1^2) \right]$$

The frequency ν_0 is the maximum frequency of the continuous energy spectrum from the X-ray tube.

The fraction Q of the total X-ray energy in the range ν_1 to ν_2 is:

$$Q = \frac{\int_{\nu_1}^{\nu_2} I_\nu d\nu}{\int_0^{\nu_0} I_\nu d\nu} = \frac{\nu_0 (\nu_2 - \nu_1) - 1/2 (\nu_2^2 - \nu_1^2)}{\frac{\nu_0^2}{2}}$$

$$Q = \frac{2(\nu_2 - \nu_1)}{\nu_0} - \left(\frac{\nu_2^2 - \nu_1^2}{\nu_0^2} \right)$$

Since $\nu = \frac{E}{h}$

$$Q = \frac{2(E_2 - E_1)}{E_0} - \frac{(E_2^2 - E_1^2)}{E_0^2}$$

Substituting $E_2 = 133$ kev, $E_1 = 100$ kev, $E_0 = 150$ kev:

$$Q = 0.440 - 0.341 = 0.099 \approx 0.1$$