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REPROCESSING OF URANIUM FUELS BY SELECTIVE OXIDATION-REDUCTION REACTIONS IN A FUSED SALT-LIQUID METAL SYSTEM

by

Sidney John Stephenson Parry

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

Major Subject: Nuclear Engineering

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Dean of Graduate College

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I. INTRODUCTION

Since the advent of the nuclear age, which dates from 1942 with the construction and operation of the first self-sustaining nuclear reactor, one of the goals of the scientific research performed in this field has been the application of this new energy source to the production of useful, economic power for civilian uses. Since the primary aim of all the initial investigations was the development of an atomic weapon, the insertion and realization of this new goal, which has required an even larger effort than the original weapons development, has taken some time. Thus, it was not until December, 1951, that electricity was first generated by the heat of a nuclear reactor in the EBR I, Experimental Breeder Reactor No. I, at Arco, Idaho. Since that time, several experimental and two completely commercial power reactors have been completed in the U.S. However, in the U.S.S.R. and the U.K., the demand for weapons material has been such that the several power plants built in these countries are run as both plutonium production and power sources. Because of this dual nature of the reactors, the economics of the plants have been adjusted so as to make the plants justified from a cost viewpoint. In the U.S., the government, through the A.E.C., does buy fissionable isotopes produced in power reactors; however, such purchases are not the prime economic factor in the operation of the U.S. plants. From these statements it can be seen that in thw U.S. power reactors must be economical, ultimately as power sources and not as production reactors, excluding those breeder plants in which new fuel for the reactor is generated.

The Shippingport Plant, which started operation in December, 1957, is one of the commercial operating plants for which operating costs are generally available (1). These costs are presented in Table 1.

Table 1. Power costs for the Shippingport Power Plant in mils/KWH

	Mils/KWH
Capital investment	22.7
Fuel charges	43.4
Operating costs	3.3
	69.4
Less fuel credit	5.0
Total power cost	64.4

When this figure of 64.4 mils/KWH is compared to a figure of 7 to 8 mils for conventionally fueled plants, it is obvious that this plant is not competitive economically. However, it must be remembered that this plant was not designed for economic power production, but was constructed to provide a plant from which operating conditions and plant criteria could be evaluated. Regardless of the purpose of the plant, it is apparent that a major cost in nuclear power plants is the total fuel charge, i.e., fuel charges less fuel credits. Recently, it has been estimated that a total fuel cost of 2 mils/KWH must be reached to obtain competitive power costs (2).

In addition to the power costs from the Shippingport Plant, we have available estimated costs of certain reactor types as of today and probable costs in the future (3). A summary of the pertinent data is given in Table 2. The columns in Table 2 refer to several reactor types as follows: PWR - pressurized water (light) reactor, BWR - boiling water (light) reactor, OMR - organic moderated reactor, SGR - sodium graphite reactor, GCR - gas cooled reactor, D_2O - heavy water moderated and cooled reactor and FBR - fast breeder reactor. These data indicate that while the overall costs of reactor power have been greatly reduced, the fuel costs still account for 30 to 60 per cent of the total power cost. Further that in the future these charges will still account for 20 to 30 per cent of the overall charges.

In general a fuel cycle consists of three major steps: (1) initial production of the fuel material, (2) fabrication of the fuel elements, and (3) reprocessing of the irradiated fuel elements, which includes the refabrication of fuel elements. Of these steps, the third is the most expensive, since

Table 2. Present and future costs and charges for various 300 MWE (megawatt electrical) plants

	PWR	BWR	OMR	SGR	GCR	D_2O	FBR
				Present			
Total capital costs (10^6\$)	73.4	78.9	66.0	90.9	114	108	76.5
Power costs (mils/KWH)							
Capital charges	5.05	5.26	4.39	6.05	7.60	7.08	5.10
Fuel cycle*	3.38	3.47	5.72	7.68	3.35	4.22	7.10
Operation and maintenance	0.59	0.61	1.09	0.70	0.61	0.93	0.79
Nuclear ins.	0.26	0.27	0.25	0.29	0.33	0.30	0.26
Total	9.28	9.61	11.45	14.72	11.89	12.50	13.25
				Future			
Total capital costs (10^6)	64.0	64.5	53.2	67.1	69.5	88.6	65.0
Power costs (mils/KWH)							
Capital charges	4.40	4.31	3.53	4.47	4.63	5.80	4.43
Fuel cycle*	2.56	2.29	1.83	2.00	2.62	1.21	1.99
Operation and maintenance	0.59	0.61	1.09	0.70	0.49	0.91	0.79
Nuclear ins.	0.25	0.24	0.22	0.25	0.24	0.28	0.25
Total	7.80	7.45	6.67	7.42	7.98	8.20	7.46

*Fuel cycle assumptions: reprocessing = \$15,300/day, A.E.C. schedule for UF_6 cost, shipping cost (irradiated fuel) = \$12.45/kg, conversion of uranyl nitrate solution to UF_6 = \$5.60/kg, conversion of plutonyl nitrate solution to Pu metal = \$1.50/gm, Pu buyback (credit) = \$12/gm.

it requires remote handling operations and includes the interest charges associated with maintaining the required fuel inventories. Therefore, the largest individual reduction in the fuel charges can be made in the development of rapid, efficient and relatively inexpensive techniques for reprocessing irradiated fuel systems. Of primary interest in this area is the development of a suitable pyrometallurgical reprocessing technique.

Before going further a definition of the term pyrometallurgical technique should be given. For the purpose of definition in this work, it is assumed that any process that (1) does not use aqueous solutions, (2) retains the metal in a metallic form, (3) operates at high (over 200°C) temperatures, and (4) may or may not utilize low (50 microns or less) pressures at these temperatures, is considered pyrometallurgical.

Since pyrometallurgical processes operate at elevated temperatures, the kinetics of the reactions are generally rapid. As yet, however, the pyrometallurgical processes have not shown the ability to perform as efficiently as the comparable aqueous techniques, with respect to total decontamination of irradiated uranium. Decontamination factors (DCF = initial concentration/final concentration) for pyrometallurgical systems approach 10^3, while aqueous systems often obtain values of 10^6. The primary advantages of the pyrometallurgical systems are that fuels can be reprocessed immediately following removal of the fuels from the reactor, and it is possible to retain the fuel itself in a metallic state, obviating the necessity for a conversion step back to the metal. It has been estimated that reduction of the "cooling time", i.e., the time that a fuel element is permitted to stand following removal from a reactor, to allow for partial decay of the radioactive fission products, from 120 days to 30 days, would result in a decrease of 50 per cent in the total reprocessing charges (4). The need for a cooling period is almost completely avoided in a pyrometallurgical process, since no radiation damage to the reagents occurs, as in the case of aqueous systems. Further, the heat generated by the decay of the fission products can easily be dissipated. Moreover, since conversions of various radioactive chemical compounds to metals may cost as much as $1000/kg, the potential advantages to be gained from the use of a pyrometallurgical process are quite large in an economic sense.

The problem of reprocessing irradiated fuels has been under investigation for a number of years (5), (6), (7). However, the main effort has been toward the development of aqueous techniques, probably because of the existence of known methods for handling aqueous systems. In recent years an increased effort has been made in the development of pyrometallurgical processes by a number of laboratories (8), (9), (10). These efforts are being culminated by the design and construction of a pyrometallurgical reprocessing plant to be operated in conjunction with EBR II at Arco, Idaho (11).

While the work performed in this area has been fairly extensive and detailed, the processes developed, in general, depend upon (1) relative solubilities of the materials and fission products in various solvents, (2) marked differences in the physical properties of certain chemical compounds (12), and (3) gross non-selective chemical reactions (13). Two notable exceptions to this generalization exist. They are the work of Gibson (14) and the LMFR (Liquid Metal Fueled Reactor) reprocessing system (15). The work of Gibson is the first reported in the area of selective oxidation-reduction cycles using halides and the studies by the LMFR group at the Brookhaven National Laboratories are an extension of this work using only a selective oxidation step. While complete descriptions of these processes are given in the references, it should be mentioned that both of these investigations clearly indicated the potential value of selective oxidation-reduction cycles in the reprocessing of nuclear fuels using fused salts.

This thesis is a further extension of the selective oxidation-reduction cycle and is designed to extend the work of Chiotti and Shoemaker (16) in the reprocessing and separation of thorium and uranium-233. Specifically, this work covers the final separation and purification of the impure uranium residue as obtained from the magnesium extraction of thorium from the contained uranium-233 as generally outlined by Chiotti and Voigt (17). This residue contains as impurities thorium, protactinium-233, other isotopes and some of the fission products of uranium-233. The process that has been investigated consists of (1) dissolution of the impure uranium-233 in molten zinc, (2) oxidation of the uranium-zinc intermetallic compound to uranium trichloride by zinc chloride carried as a solute in a potassium chloride-lithium chloride eutectic fused salt, (3) distillation of volatile fission product and heavy isotope chlorides, and (4) reduction of the uranium trichloride by magnesium in a zinc-magnesium alloy. The final precipitation of the uranium and the distillation of the residual zinc and magnesium have not been included, since this area of investigation has been examined in detail by the Argonne National Laboratory (18).

This work was not intended to develop a complete fuel recycle system but was primarily designed to evaluate the possible application of a selective oxidation-reduction cycle to the reprocessing of irradiated nuclear fuels. Nor was there any attempt to evaluate the behavior of all the fission products during the process. In general, representative elements from the various atomic groups found in the fission product spectrum were used to indicate the probable behavior of the entire group. In addition to the selective oxidation-reduction experiments, considerable effort was expended in the development of additional process steps such as, the dissolution of uranium and zirconium in molten zinc or fused salts containing zinc chloride, the distillation of the chlorides of uranium, thorium and zirconium, the separation of impurities from magnesium-thorium eutectic alloys, and other problems such as development of container materials, etc. Further, while no experimental work involving plutonium has been performed, the probable behavior of this element has been evaluated from thermodynamic data for plutonium compounds and investigations performed elsewhere.

The work described herein outlines a pyrometallurgical reprocessing system for the thorium-uranium-233 fuel cycle and presents pertinent experimental data to indicate the probable efficiency of such a process. In addition, possible applications to other fuel cycles are discussed, and those areas in which additional work is needed are described. The immediate application of the proposed process to various scrap recoveries associated with the nuclear energy field is suggested and outlined.

II. CHEMICAL AND NUCLEAR PROBLEMS ASSOCIATED WITH THE THORIUM-URANIUM-233 FUEL CYCLE

In this section the two major problem areas in the reprocessing of thorium from the thorium-uranium-233 fuel cycle will be discussed. The first of these general problems is concerned with the generation and build-up of those isotopes and thorium, protactinium, uranium and the trans-uranium elements that are formed either by side nuclear reactions, or as intermediate steps in the fuel cycle. The second is the question of the production of the fission products created in the fissioning of the uranium-233 and the uranium-235 nuclei.

A. Heavy Isotopic Build-up

The build-up of what may be called "heavy" isotopes in the thorium-uranium-233 fuel cycle affects both the safety requirements for the handling of uranium-233 and the overall economics of any reprocessing system for irradiated thorium. Figure 1 presents the nuclear reactions that occur during the irradiation of thorium by thermal neutrons (19), (20). In addition, the thermal neutron cross-sections, half-lives and modes of decay are given where appropriate. The initial material is thorium-232, this being the only isotope of thorium occuring in nature other than daughters of other radioactive elements. While the thorium-232 is being

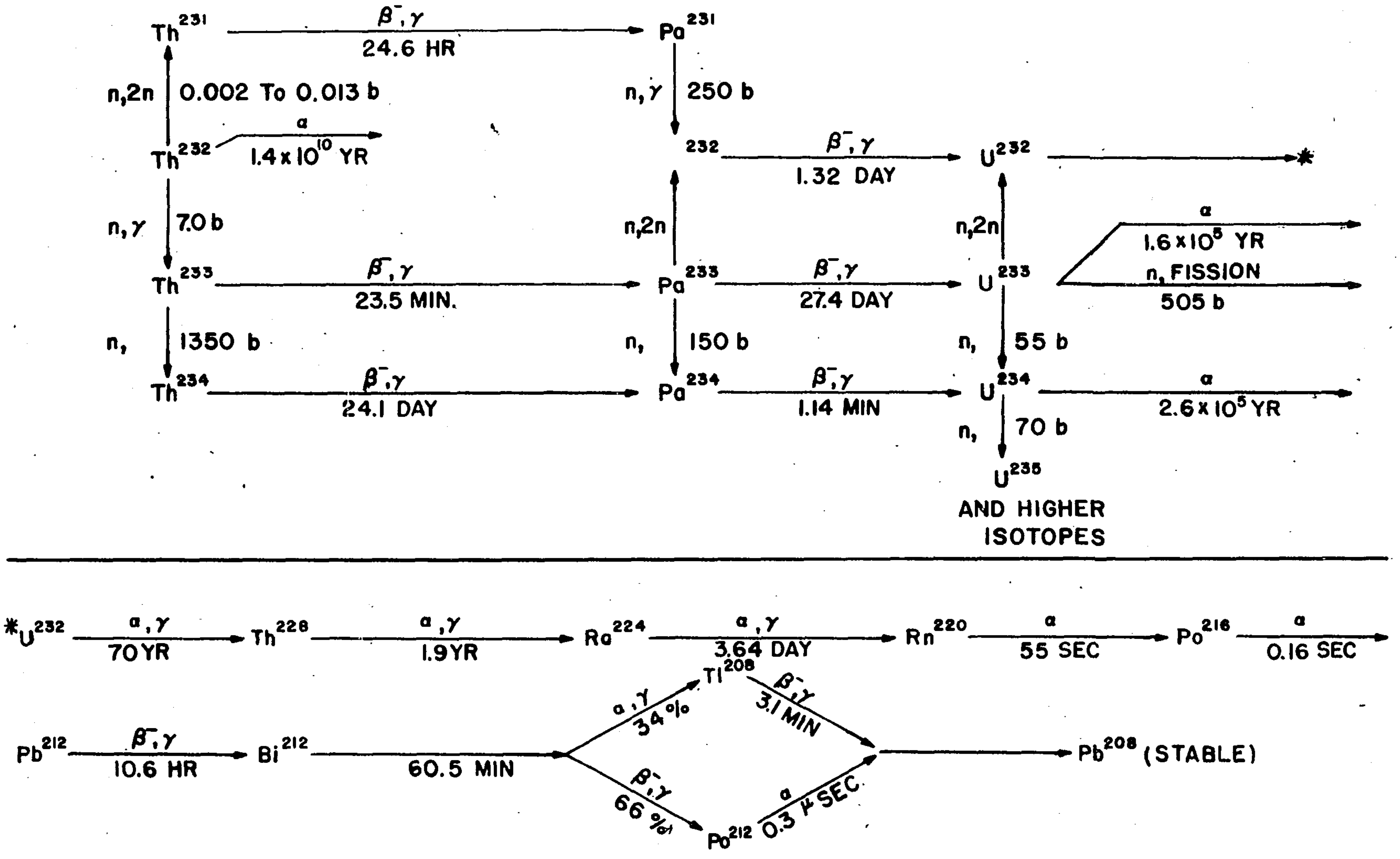


Figure 1. The thorium-uranium-233 fuel cycle (19)

irradiated, thorium-231 and thorium-233 are produced and these isotopes then either decay or capture neutrons and are transmuted. Of primary interest is the set of reactions that lead to the production of the fissionable isotope uranium-233. However, the side reactions that give rise to the formation of thorium-228 and uranium-234 are very important in the overall consideration of radiation safety and neutron economy.

The position of protactinium-233 as the daughter of the thorium-233 decay and the parent of uranium-233 makes its chemical and nuclear behavior very critical relative to any reprocessing scheme. As can be seen from Figure 1, the half-life of protactinium-233 is sufficiently long and its cross-section high enough that side nuclear reactions will occur if it is left in a neutron flux for an appreciable period of time. The primary hazard associated with uranium-232 is its alpha decay daughter, thorium-228. This isotope has a half-life of 1.9 years and emits an alpha particle and an energetic gamma ray upon decaying. These emissions are sufficiently dangerous to preclude the handling of uranium containing the 232 and 234 isotopes by any technique other than by remote and shielded operations. Other sources of uranium-234 are the n, 2n reactions with thorium-232 and uranium-233.

Due to the nature of its decay and the half-lives involved, the problems that develop from the formation and decay of uranium-232 are very unusual. This is caused by the fact that any uranium-232 present will be processed with the uranium-233, while the thorium-228 is separated. Unless certain time limits upon the reprocessing cycle are met, both fractions, the thorium and the uranium, will be so highly active as to require remote refabrication because of the activity of either uranium-232 or thorium-228. In general, these time limits are as follows: (1) to eliminate remote refabrication of the thorium, the irradiated material should be reprocessed within 30 days and not later than 60 days after removal from the reactor (19), (2) the "cooling" time has no effect upon the uranium-232 content, but any separated uranium containing uranium-232 should be fabricated within two weeks after separation to avoid the necessity of remote fabrication. Further, it should be noted that regardless of the processing system, any uranium-233 produced must be handled in glove-box facilities because of its alpha activity.

Beside the n,2n reaction that protactinium-233 takes part in, there is the n,gamma reaction which gives protactinium-234 and finally uranium-234. While uranium-234 is in itself not dangerous, neither is it fissionable with thermal neutrons. However, it does have an appreciable thermal neutron capture cross-section, and after an n,gamma reaction gives uranium-235. Uranium-235 is the fissionable isotope found in natural uranium. Even though uranium-235 is fissionable, the generation of this isotope has required the capture of two neutrons, rather than only the one required to produce uranium-233. Thus, the formation of appreciable amounts of uranium-235 in the thorium fuel cycle will act to reduce the overall neutron economy of the process.

A basic consideration in any processing scheme is the exact composition of material that is to be handled. In the case of the heavy isotopes, it is possible to calculate the exact concentration of any one isotope using the data in Figure 1, assuming various reactor conditions and solving the appropriate differential equations. Calculations of this nature have been made by the authors Gresky and Arnold (20) and Taraba (21). The equations and their derivations are given in the references. Figures 2, 3 and 4 show the effect of time of irradiation and neutron flux level upon the isotopic concentrations. The actual concentrations that may be encountered are, of course, largely dependent upon the nature of the reactor and its operating criteria, i.e., fuel recycle times, flux level, etc. If it is attempted to limit the formation of undesirable isotopes and fission products, relative to the uranium-233 and protactinium-233 generated, the data indicate that high flux levels for short times, i.e., 10^{15} nv for 60 days, are needed.

The curve in Figure 5 shows that the residual protactinium-233 content requires a decay period of at least six months to

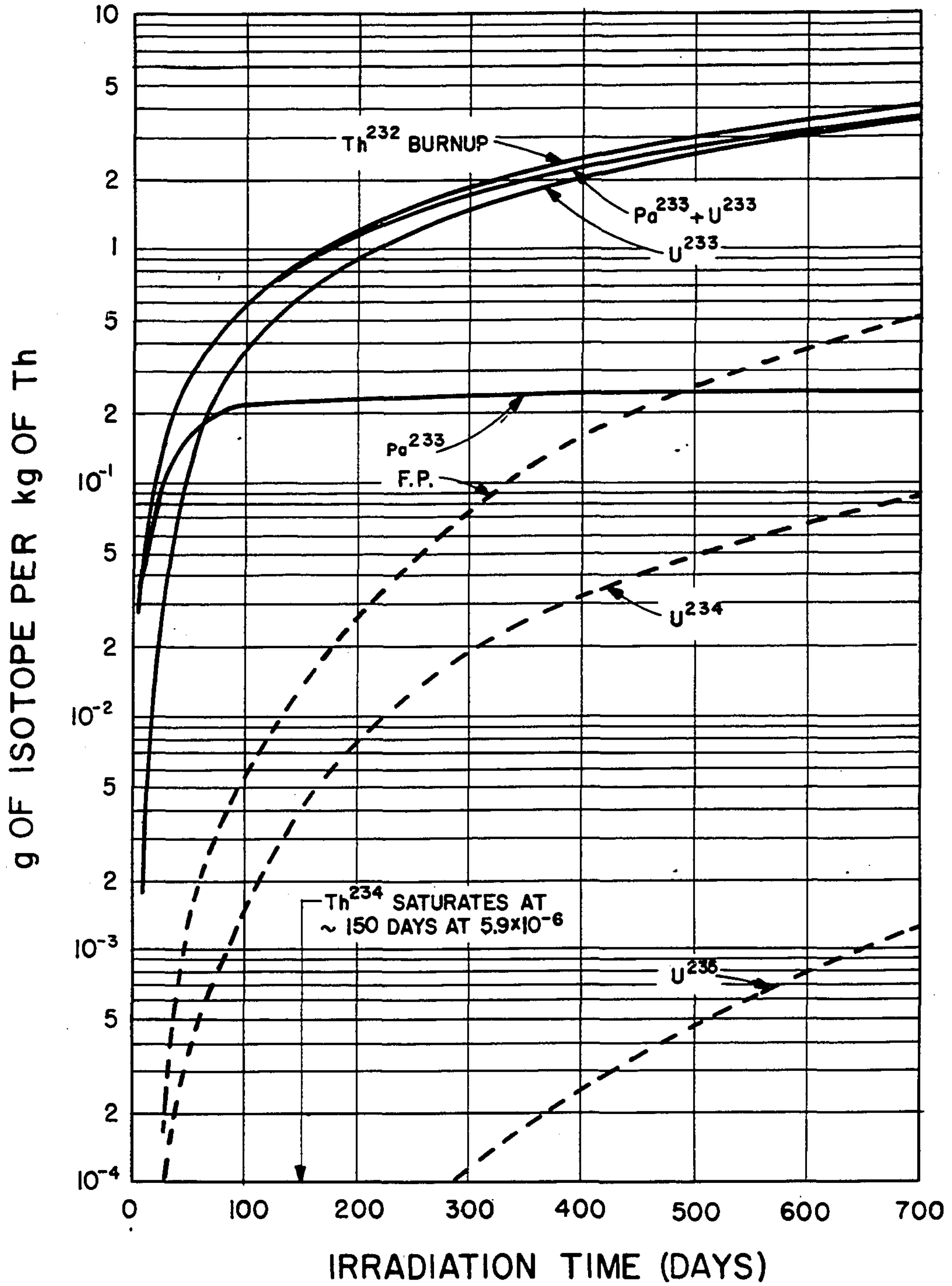


Figure 2. Products produced by neutron irradiation of thorium-232 at a flux of 10^{13} neutrons/cm^2/sec (20)

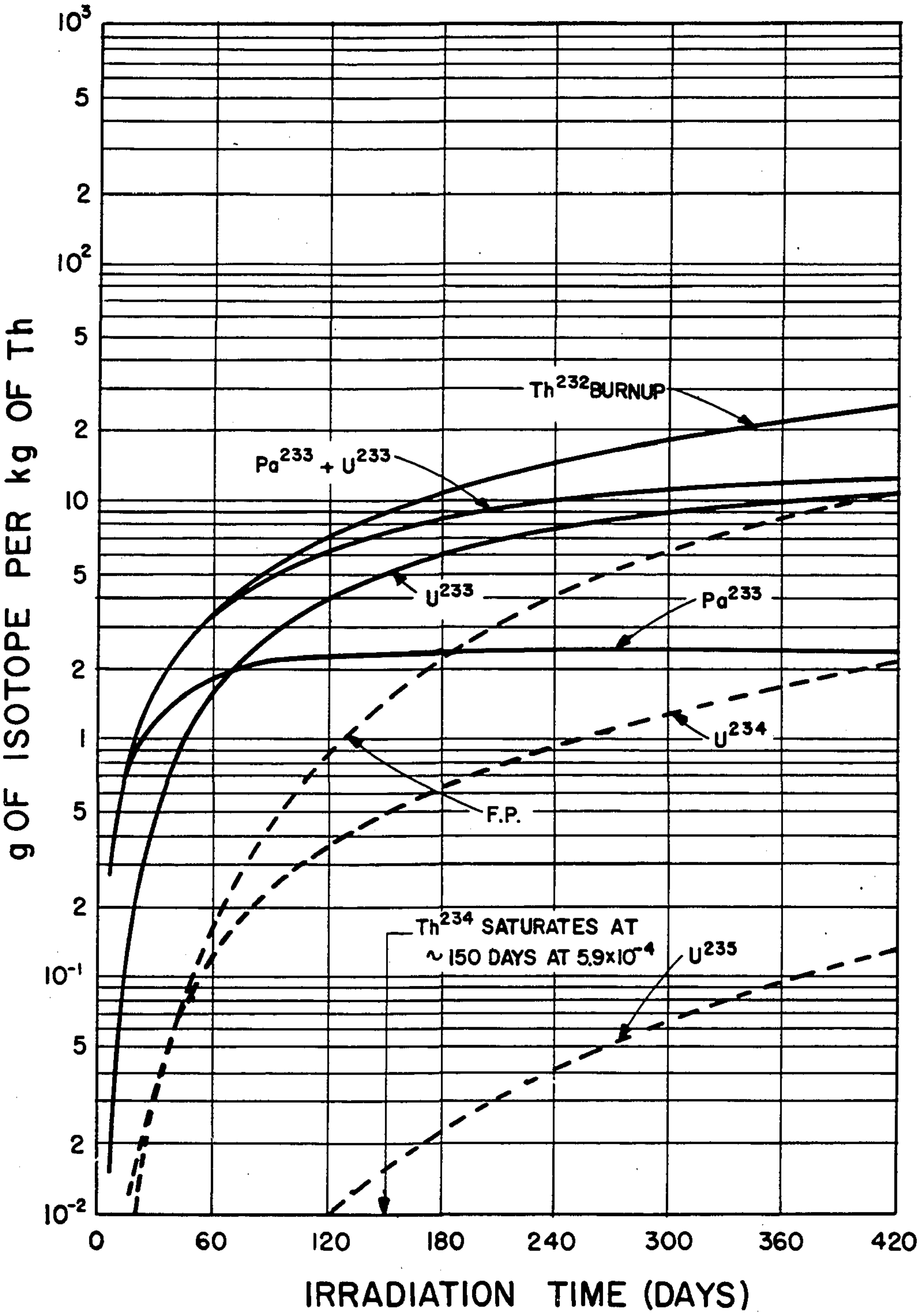


Figure 3. Products produced by neutron irradiation of thorium-232 at a flux of 10^{14} neutrons/cm^2/sec (20)

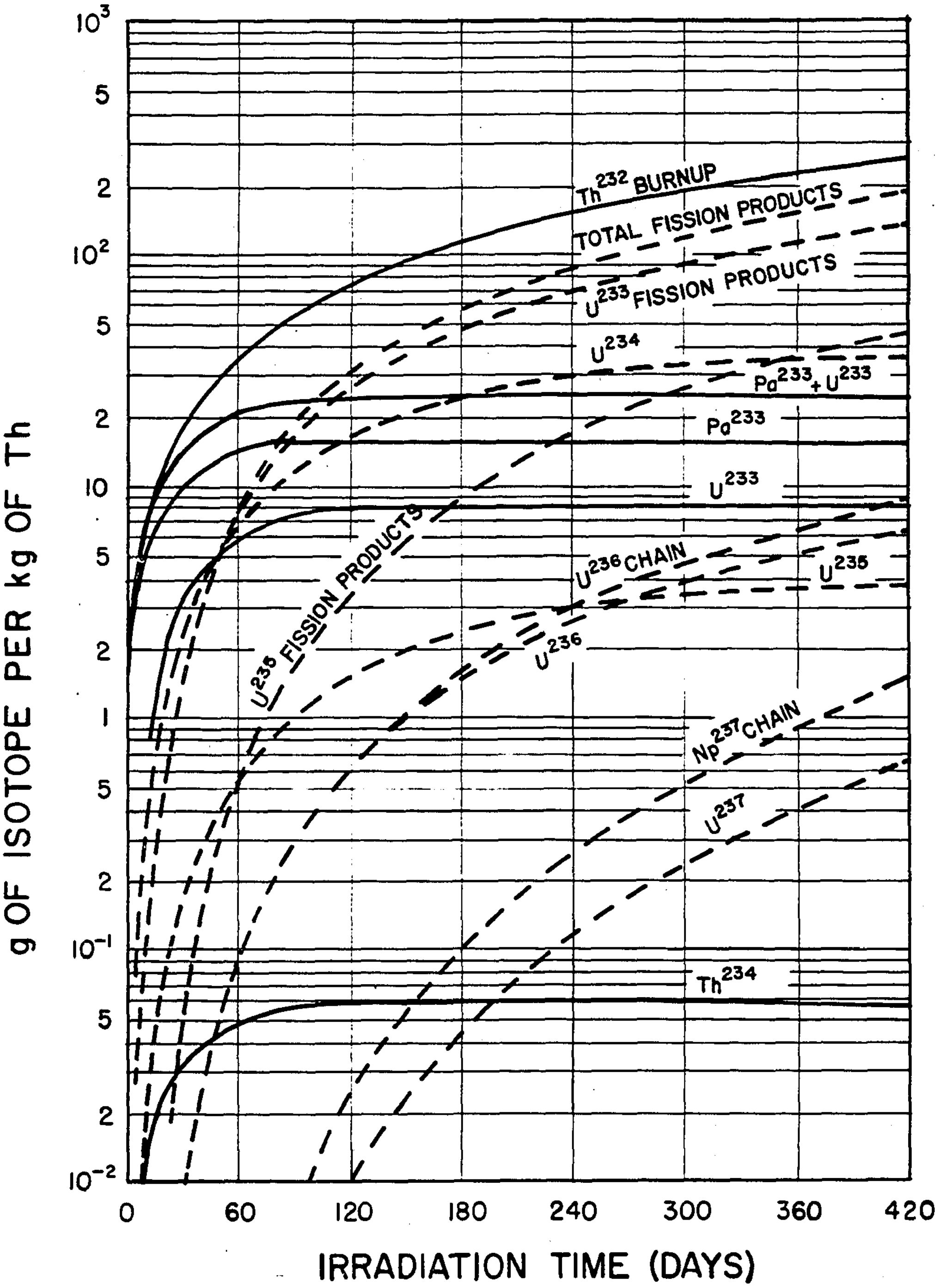


Figure 4. Products produced by neutron irradiation of thorium-232 at a flux of 10^{15} neutrons/cm^2/sec (20)

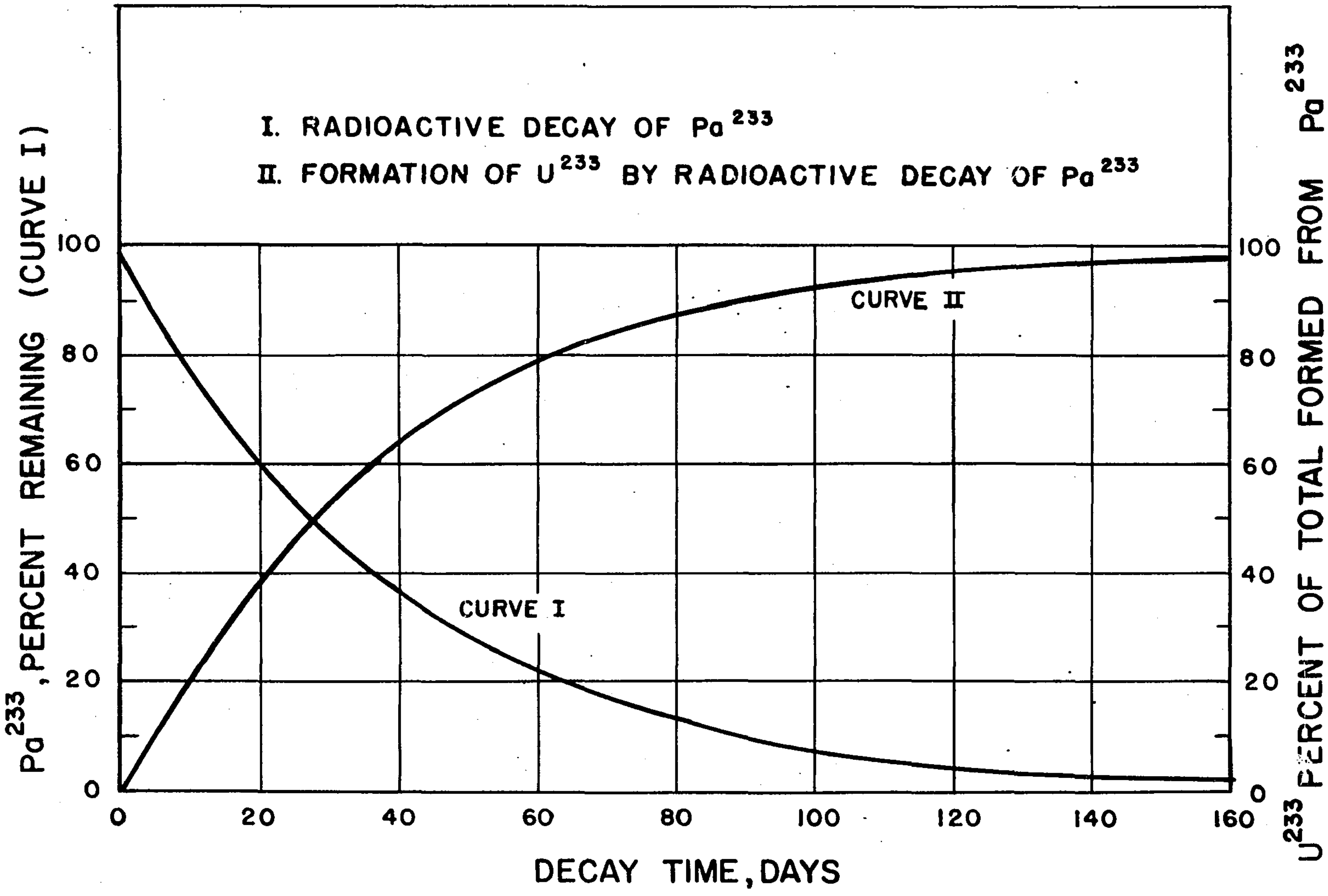


Figure 5. Per cent protactinium-233 remaining; or uranium-233, per cent of total formed as a function of time (19)

go below 2 per cent of its initial level. This fact serves to demonstrate the desirability of having a separation of uranium-233 from protactinium-233 in any reprocessing operation, due to the formation of heavy isotopes in the protactinium-233 if it is returned to a reactor, and because of the interest charges levied against fissionable material when held in fuel inventories.

B. Fission Product Build-up

The second major problem is that of fission product contamination. The fission products will be generated by the fissioning of both uranium-233 and uranium-235. As with the heavy isotopes, the problem is dual in nature. The intense radioactivity of these products requires their removal prior to unshielded handling of the thorium and uranium, and many of these have large enough thermal neutron cross-sections that they are considered reactor poisons and cannot be returned to the core.

The solid curve in Figure 6 (22) plots the per cent fission yield versus mass number of the fission product for the thermal neutron fission of uranium-233. The dotted curve presents the same data for the fission of uranium-235. Little difference between the curves can be observed. A plot of this nature does not indicate the actual elements that will be present after a period of irradiation and cooling. In order to evaluate the exact composition of the fission products,

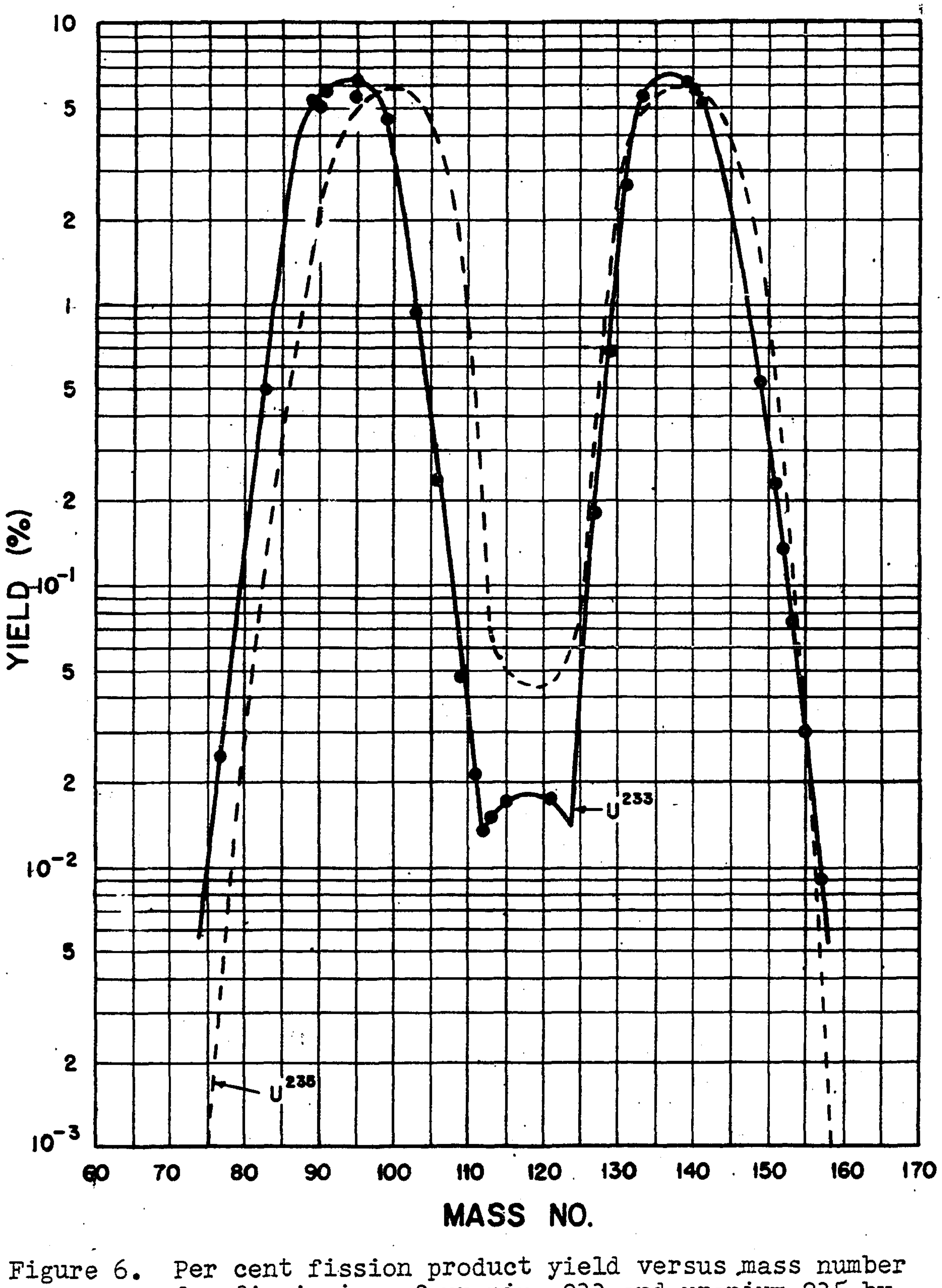


Figure 6. Per cent fission product yield versus mass number for fissioning of uranium-233 and uranium-235 by thermal neutrons (22)

additional data on the decay schemes of the various fission products must be consulted (23). Examination of these data indicates that the elements that may be expected to exist as fission products of uranium-233 extend from gallium, element 31, to dysprosium, element 66, in the periodic chart of the elements. These 35 elements may be considered as a number of groups whose gross chemical and/or physical properties are similar. For the purpose of this work, these groups are identified and catalogued as follows: (1) volatiles (bromine, iodine, krypton and xenon); (2) alkaline and alkaline earths (rubidium, strontium, cesium and barium); (3) lanthinides and rare earths (yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium and dysprosium); (4) noble and high melting (zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium and silver); (5) low melting (gallium, germanium, arsenic, selenium, cadmium, indium, tin, antimony and tellurium).

Of these five groups, the noble and high melting elements generally provide the most difficulty in separation by aqueous techniques. This is not the case in the removal of the volatiles where, in general, simple dissolution of the fuel is sufficient to effect the separation of the volatile fission products. The other three classifications of fission products are easily and completely removed by the standard aqueous techniques of solvent extraction, ion exchange, etc. Thus, to realize a significant improvement in reprocessing techniques, emphasis should be directed toward the removal of the noble and high melting elements that cannot be separated easily by aqueous processing.

In conclusion then, it may be said that any reprocessing operation for irradiated thorium should have the following characteristics: (1) be able to reprocess the material shortly after removal from the reactor, (2) permit rapid refabrication of the thorium and uranium into blanket and fuel elements, (3) remove the heavy isotopes and fission products generated during the irradiation, and (4) if possible provide a separation of protactinium-233 from uranium-233, and retain the protactinium-233 as a separate fraction. Pyrometallurgical reprocessing techniques are inherently able to satisfy the first two requirements; however, the ability of these techniques to perform the last two operations has yet to be demonstrated. On the other hand, while aqueous systems can perform good separations, they cannot be used without long cooling times and require conversions back to the metallic state.

III. DESCRIPTION OF THE PROCESS UNDER DEVELOPMENT

The complete process under development for the decontamination of irradiated uranium and thorium consists of a number of operations. In detail, starting with unalloyed thorium, these operations or separations may be outlined as follows: (1) dissolution of the thorium in magnesium to form the Mg-38w/oTh eutectic alloy; (2) an equilibration of the Mg-Th alloy with a fused salt bearing $MgCl_2$; (3) equilibration of the Mg-Th with either molten uranium, or an eutectic alloy of either U-5.2w/oCr or U-11w/oFe (these first three steps may, in fact, be consolidated into a single separation operation); (4) dissolution of the resulting uranium-rich phase in molten zinc; (5) selective oxidation of the uranium dissolved in the zinc to UCl_3 by $ZnCl_2$ carried in a solvent of KCl-LiCl eutectic; (6) distillation of any volatile chlorides away from the UCl_3; (7) selective reduction of the UCl_3 by magnesium carried in a Zn-Mg alloy; and (8) distillation of the residual zinc and magnesium, followed by consolidation of the purified uranium product. The emphasis of this work has been directed toward the evaluation of the feasibility of steps 2 to 7, while previous work (16), (24) has examined steps 1 and 3 in detail. Work at ANL has been done in the area of step 8, and no attempt has been made to repeat or verify that work.

A. Selective Oxidation-Reduction Separations

The thermodynamic bases for the selective oxidation and reduction cycles are found in the tables of the free energy of formation of various chlorides (25), (26) and of the zinc compounds of uranium (27), thorium (28) and zirconium (27). In Table 3, the values for $\Delta F°$ per chlorine atom for selected chlorides are given as a function of temperature. Figure 7 presents the same data in a graphical manner. Similar data for the zinc-metal compounds are presented in Table 4. Using the data given, it is possible to evaluate the change in standard free energy for equations of the following nature:

(1) $2M + x\ ZnCl_2 \rightarrow 2M\ Cl_x + x\ Zn$

(2) $2M\ Zn_y + x\ ZnCl_2 \rightarrow 2M\ Cl_x + (2y + x)\ Zn$

(3) $2M\ Cl_x + x\ Mg \rightarrow x\ MgCl_2 + 2M$

(4) $2M\ Cl_x + x\ Mg + 2y\ Zn \rightarrow x\ MgCl_2 + 2M\ Zn_y$

The $\Delta F°$'s for these reactions that can be calculated from the data given in Tables 3 and 4 clearly indicate that for materials in their standard states, $ZnCl_2$ should oxidize uranium, thorium and zirconium to their chlorides. Further, the data indicate that the rare earth, alkaline and alkaline earth fission products should also be chlorinated. However, those fission products that are contained in the second transition, low melting, and noble groups will not be so oxidized. These latter fission products are then expected to concentrate in the zinc phase upon the oxidation of the uranium.

Table 3. Standard free energy of formation of certain chlorides per chlorine atom at 500, 600, 700 and 800°C

	-ΔF°(Kcal/Cl atom)			
	500°C (773°K)	600°C (873°K)	700°C (973°K)	800°C (1073°K)
$MoCl_2$	10.35	8.80	7.55	6.34
$NbCl_5$	12.59	12.29	11.58	10.87
$BiCl_2$	13.12	13.43	13.57	13.21
$PbCl_2$	29.19	26.45	25.21	24.03
$CdCl_2$	30.07	29.75	28.37	28.08
$CrCl_2$	35.48	34.07	32.68	31.31
$ZnCl_2$	37.89	37.66	34.51	34.34
$ZrCl_4$	45.80	45.24	44.72	44.14
$ZrCl_3$	55.82	53.97	53.23	52.14
UCl_3	57.10	55.05	53.91	52.59
$ThCl_4$	57.40	55.70	54.03	53.85
$ZrCl_2$	59.29	57.49	55.92	54.40
$(PuCl_3)$	(59.5)	(58.0)	(57.0)	(55.5)
$MgCl_2$	60.82	58.41	57.69	56.57
$ThCl_3$	62.71	60.91	59.27	57.65
YCl_3	65.09	63.47	62.03	61.36
$PaCl_3$	67.20	65.09	63.44	61.82
$CeCl_3$	68.88	67.12	65.39	62.50

Table 4. Standard free energy of formation of the zinc compounds of uranium, thorium and zirconium at 500, 600, 700 and 800°C

Zinc compound	$-\Delta F°$ (Kcal/mole)			
	500°C	600°C	700°C	800°C
U_2Zn_{17}	54.0	46.0	38.1	28.9
Th_2Zn_{17}	85.8	79.9	73.5	65.5
$ZrZn_{14}$	33.9	--	--	--
$ZrZn_6$	31.0	26.8	21.3	16.4

Reactions 3 and 4 illustrate the reduction of the chlorides to either zinc-metal compounds or to the metal itself by magnesium or a magnesium-zinc alloy. The data indicate that both uranium and zirconium will be reduced from the chlorides by magnesium. In addition, the slightly positive $\Delta F°$'s of reaction calculated for the reduction of the chlorides of yttrium and cerium indicate that in the presence of excess zinc and magnesium these reactions may be pushed to the right due to the formation of either zinc or magnesium compounds.

In general, the reactions discussed above are for systems that have an excess of $ZnCl_2$ or magnesium. If we consider an equilibrium reaction of the following type, which would occur on the addition of controlled amounts of a reducible chloride,

$$(5) \quad MCl_3 + NZn_x \rightleftharpoons NCl_3 + MZn_x$$

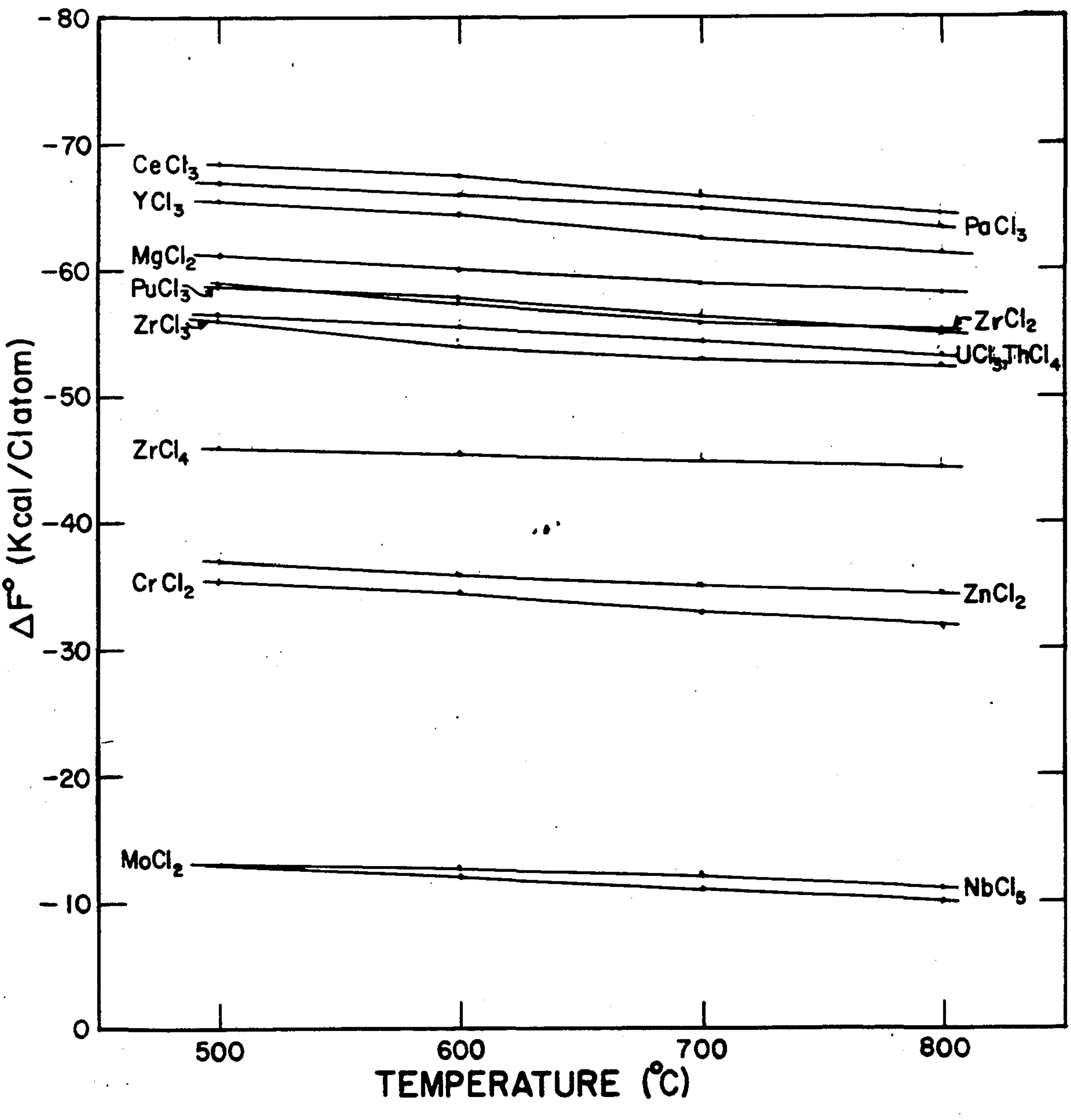


Figure 7. Standard free energy of formation of certain chlorides per chlorine atom as a function of temperature (29)

in which M and N are fission products or uranium, the possibility of better separations may be increased by the selective chlorination of one or another of the constituents. Table 5 contains the ΔF°'s for the following reactions, as functions of temperature.

(6a) $11\ Zn + U_2Zn_{17} + 2\ ZrCl_3 \rightleftharpoons 2\ ZrZn_{14} + 2\ UCl_3$

(6b) $U_2Zn_{17} + 2\ ZrCl_3 \rightleftharpoons 2\ ZrZn_6 + 2\ UCl_2 + 5\ Zn$

(7a) $2\ ZrCl_3 + Th_2Zn_{17} + 11\ Zn \rightleftharpoons 2\ ThCl_3 + 2\ ZrZn_{14}$

(7b) $2\ ZrCl_3 + Th_2Zn_{17} \rightleftharpoons 2\ ThCl_3 + 2\ ZrZn_6 + 5\ Zn$

(8) $2\ ThCl_3 + U_2Zn_{17} \rightleftharpoons 2\ UCl_3 + Th_2Zn_{17}$

Table 5. Change in standard free energy in reactions 6a, 6b, 7a, 7b and 8 at 500, 600, 700 and 800°C

	ΔF° (Kcal)			
Reaction	500°C	600°C	700°C	800°C
6a	-21.48	--	--	--
6b	-15.68	-14.08	-8.58	-6.60
7a	-23.34	--	--	--
7b	-17.54	-15.34	-5.34	-0.36
8	+ 1.86	+ 1.26	-3.24	-6.24

Examination of these data indicates that both UCl_3 and $ThCl_3$ should displace zirconium from $ZrCl_3$ at all temperatures considered. However, it is seen that at temperatures below

700°C, $ThCl_3$ may displace UCl_3, or that a co-oxidation of both uranium and thorium contained in liquid zinc is possible.

Three complications exist in the straightforward analysis of these thermodynamic data. They are: (1) the undetermined nature of the oxidation state of some of the elements under the actual experimental conditions, (2) the lack of information as to the phase diagram of the metal and salt system or systems under consideration, and (3) the fact that all of the previous data are for materials in their standard states. This last factor is probably the most critical and has the largest effect on the theoretical analysis of the system. In general, the $ZnCl_2$ and $MgCl_2$ are carried as solutes in a eutectic mixture of KCl-LiCl and the various elements may or may not dissolve ideally in zinc or zinc-magnesium solutions. As a consequence, the actual separations that will be observed experimentally may have little relation to those predicted by the thermodynamic data on the basis of unit activities.

The oxidation states assigned to uranium, thorium and zirconium are based upon predictions of the thermodynamic data.

The basic ideas behind the selective oxidation-reduction separations have been discussed in some detail above. The separations obtained are dependent upon the equilibrium between the metal chlorides and metal-zinc compounds as in reaction 8. Numerous reactions of this general nature can be written, and the change in the free energy associated with such reactions may be evaluated with appropriate free energy data. Assuming the plus 3 oxidation state for both uranium and thorium in the system under consideration, it is then possible to define certain relationships between uranium and thorium concentrations from reaction 8.

Starting with: $\Delta F° = -RT\ln K$

where:

$$K = \frac{a_{UCl_3}}{a_{ThCl_3}}\left(\frac{a_{Th}}{a_U}\right)_{Zn}$$

it is possible to obtain the following:

$$\frac{-\Delta F°}{2.303RT} = \log_{10}\frac{N_{UCl_3}}{N_{ThCl_3}}\left(\frac{N_{Th}}{N_U}\right)_{Zn}\cdot\frac{\gamma_{UCl_3}}{\gamma_{ThCl_3}}\left(\frac{\gamma_{Th}}{\gamma_U}\right)_{Zn} = \log K_n K_\gamma$$

Where $(N_U)_s$ refers to the molar concentration of uranium in the salt phase and γ_{UCl_3} indicates the activity coefficient of UCl_3 in the salt. Similar nomenclature holds for thorium and for the zinc phase.

If the assumption is made that the solutions (both the zinc and salt) are dilute, then the term K_γ may be assumed to be a constant. From which we obtain:

$$K_n = C' \text{ (a constant)}$$

The term K_n relates the molar concentrations of the solutes in the two phases and may be considered as either an equilibrium constant or a separation coefficient. The term $(N_{Th}/N_U)_{Zn}$ is the ratio of the solubility limits, if the solution is saturated with respect to the metal compounds.

The term separation coefficient will be used in later references to the term K_n. It can be seen that if K_n does not have any molar concentrations raised to powers, then weight percentages or concentrations may be used interchangeably with molar concentrations. This relationship only holds for those cases in which the two constituents have the same oxidation state.

The list of equations and defined K_n's given below contain those separations which were studied in this work. The subscripts s and Zn refer to molar concentrations in the salt and zinc phases respectively.

(9) $U(Zn) + 3/2\ ZnCl_2 \rightleftharpoons UCl_3 + 3/2\ Zn$

$$K_n = (N_U)_s / \left[(N_U)_{Zn}\ (N_{Zn})_s{}^{3/2}\right]$$

(10) $ThCl_3 + U(Zn) \rightleftharpoons UCl_3 + Th(Zn)$

$$K_n = \left[(N_U)_s\ (N_{Th})_{Zn}\right] / \left[(N_U)_{Zn}\ (N_{Th})_s\right]$$

(11) $UCl_3 + Ce(Zn) \rightleftharpoons CeCl_3 + U(Zn)$

$$K_n = \left[(N_{Ce})_s\ (N_U)_{Zn}\right] / \left[(N_{Ce})_{Zn}\ (N_U)_s\right]$$

(12) $Ce(Zn) + 3/2\ ZnCl_2 \rightleftharpoons CeCl_3 + 3/2\ Zn$

$$K_n = (N_{Ce})_s / \left[(N_{Ce})_{Zn}\ (N_{Zn})_s{}^{3/2}\right]$$

(13) $ZrCl_3 + U(Zn) \rightleftharpoons UCl_3 + Zr(Zn)$

$$K_n = \left[(N_U)_s\ (N_{Zr})_{Zn}\right] / \left[(N_U)_{Zn}\ (N_{Zr})_s\right]$$

(14) $3/4\ ZrCl_4 + U(Zn) \rightleftharpoons UCl_3 + 3/4\ Zr(Zn)$

$$K_n = \left[(N_U)_s / (N_U)_{Zn}\right] / \left[(N_{Zr})_s / (N_{Zr})_{Zn}\right]^{3/4}$$

(15) $3/2\ ZnCl_2 + Th(Zn) \rightleftharpoons ThCl_3 + 3/2\ Zn$

$$K_n = (N_{Th})_s / \left[(N_{Th})_{Zn}\ (N_{Zn})_s{}^{3/2}\right]$$

(16) $3/2\ ZnCl_2 + Zr(Zn) \rightleftharpoons ZrCl_3 + 3/2\ Zn$

$$K_n = (N_{Zr})_s / \left[(N_{Zr})_{Zn}\ (N_{Zn})_s^{3/2}\right]$$

(17) $2\ ZnCl_2 + Zr(Zn) \rightleftharpoons ZrCl_4 + 2\ Zn$

$$K_n = (N_{Zr})_s / \left[(N_{Zr})_{Zn}\ (N_{Zn})_s^{2}\right]$$

(18) $PaCl_3 + U(Zn) \rightleftharpoons UCl_3 + Pa(Zn)$

$$K_n = \left[(N_U)_s\ (N_{Pa})_{Zn}\right] / \left[(N_U)_{Zn}\ (N_{Pa})_s\right]$$

(19) $YCl_3 + U(Zn) \rightleftharpoons UCl_3 + Y(Zn)$

$$K_n = \left[(N_U)_s\ (N_Y)_{Zn}\right] / \left[(N_U)_{Zn}\ (N_Y)_s\right]$$

(20) $ZnCl_2 + Cr(Zn) \rightleftharpoons CrCl_2 + Zn$

$$K_n = (N_{Cr})_s / \left[(N_{Cr})_{Zn}\ (N_{Zn})_s\right]$$

There are certain components whose oxidation states under our operating conditions are unknown. If, after appropriate experimentation using M_1 and M_2, one takes the values of $(N_{M_1})_s/(N_{M_1})_{Zn}$ and $(N_{M_2})_s/(N_{M_2})_{Zn}$ and plots them on a log versus log scale, the value of the relative oxidation states of M_1 and M_2 may be determined by examination of the slope of the resulting line. This fact may be confirmed by considering the following:

$3\ ZnCl_2 + 2\ U(Zn) \rightleftharpoons 2\ UCl_3 + 3\ Zn$

$$-\frac{\Delta F°}{2.303RT\log K} = \log \frac{(N_{UCl_3})^2}{(N_{U_{Zn}})^2}\ \frac{1}{(N_{ZnCl_2})^3}$$

from which a log versus log plot will give:

$$3/2 \log N_{ZnCl_2} + C = \log \frac{N_{UCl_3}}{(N_U)_{Zn}}$$

The slope of a line relating the molar concentrations of uranium and zinc is then seen to be 3/2, i.e., the ratio of their oxidation states.

In the foregoing development, the molar concentration of the elements under consideration in the zinc phase formed an integral part of the evaluation of K_n. In those situations where the solubility limit of a component has been exceeded, the value used to represent the concentration in the zinc is the solubility limit. A table of solubility limits to be used in this work has been compiled from a number of sources (10), (27), (28), and is given in Table 6. These values will be used where appropriate to evaluate both K_d's and K_n's.

Table 6. Solubility limits of various elements in zinc and zinc-magnesium solutions (10), (27), (28) in w/o

	500°C	650°C	700°C
	Pure zinc		
Chromium	1.2	(2.4)	(3.0)
Iron	0.20	1.75	3.85
Yttrium	0.013	--	1.44
Zirconium	0.70	2.92	4.28
Niobium	0.0728	0.120	0.163
Molybdenum	0.0122	0.0222	0.0224
Cerium	0.012	0.27	0.82
Thorium	0.022	0.510	0.99
Uranium	0.033	0.67	1.48
	Zinc - 6 w/o magnesium		
Uranium	0.025	0.52	1.10
	Zinc - 46.5 w/o magnesium		
Uranium	0.060	0.125	0.153

B. Distillation Separations

While the selective oxidation-reduction cycle is the primary separation technique proposed in this work, another major separation operation that has been investigated is the distillation of volatile chlorides from one another. Distillation operations on both chlorides and flourides and the elements themselves have been investigated as a possible decontamination process (9), (12), (13). A theoretical basis for chloride volatility separations can be found in tables of the vapor pressures of selected chlorides (29).

Examination of these data indicates that UCl_3 has a relatively low vapor pressure compared to the tetravolent chlorides of zirconium, thorium and elements in the second transition group. Thusly, it is expected that, with appropriate process controls, as to temperature and pressure, it would be possible to preferentially distill out the chlorides of zirconium, thorium and the second transition group, other than yttrium, from a mixture of fused chlorides containing UCl_3.

IV. EXPERIMENTAL APPARATUS AND PROCEDURES

In this section, the equipment and procedures used throughout the work will be discussed. Based upon the weight of charge and volume of material used, a general distinction can be made concerning the experimental work in the study. Micro-scale work is classed as that using less than five grams of oxidizable material in an experiment containing less than 50 grams of total material. These experiments were carried out in sealed tantalum cans. However, those experiments in which more than 1000 grams of total material was used are considered macro-scale. On the macro-scale, besides the selective separation studies, exploratory experiments were performed to investigate the rates of dissolution of zirconium and uranium in liquid zinc, as were a few tests on the corrosion of structural materials by liquid zinc. Data concerning these experiments are presented in the Appendix. On both a micro- and macro-scale level, preliminary tests were made on the separation of zirconium and thorium from uranium by distillation of the volatile chlorides.

A. Micro-scale Experimentation

As has been previously mentioned, the micro-scale work is sub-divided into two general classes. These various systems are schematically presented in Figures 8 and 9. Figure 8 is a drawing of the sealed tantalum can system used to equilibrate

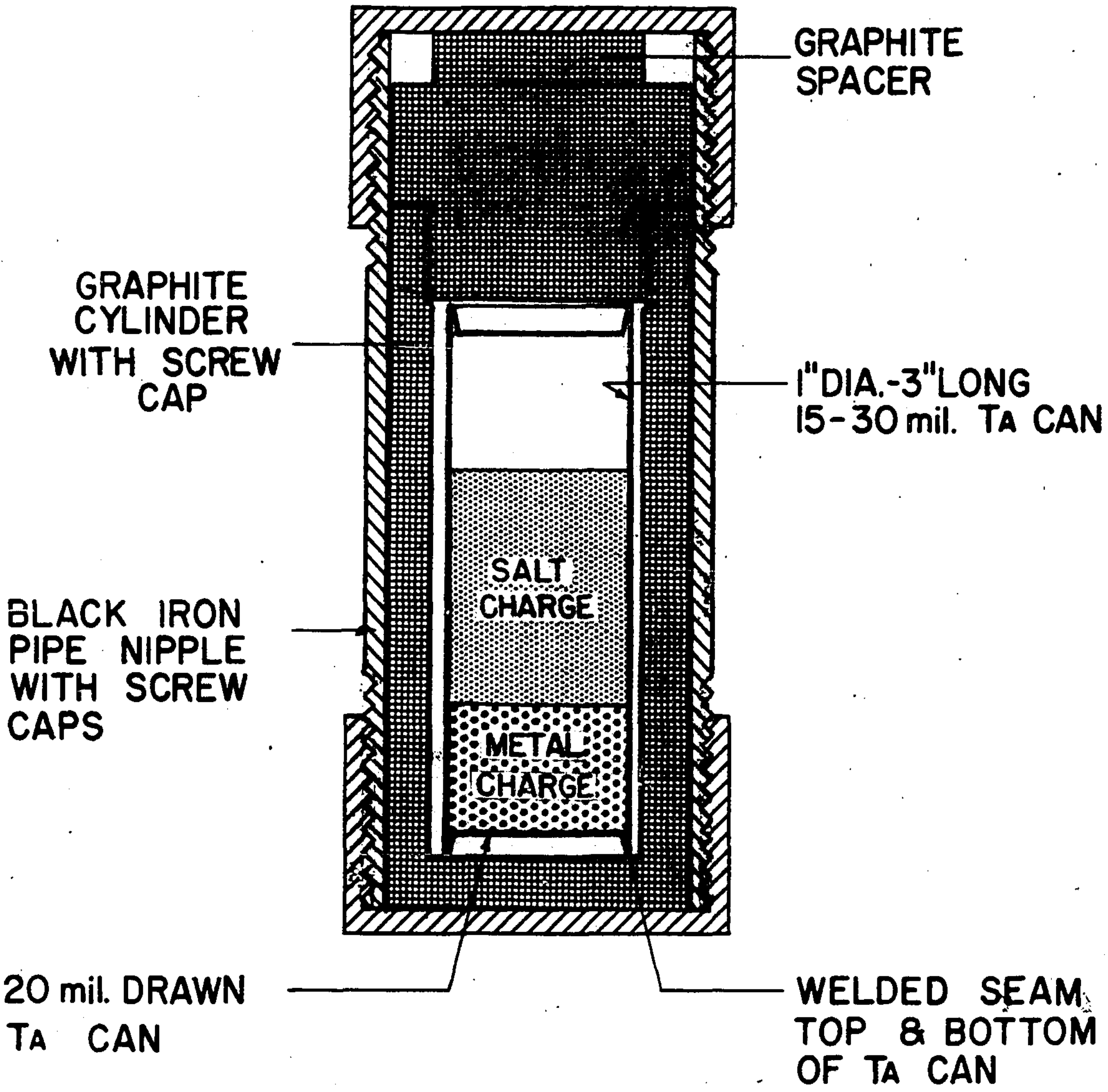


Figure 8. Sealed tantalum can system for micro-scale equilibration at elevated temperatures (16)

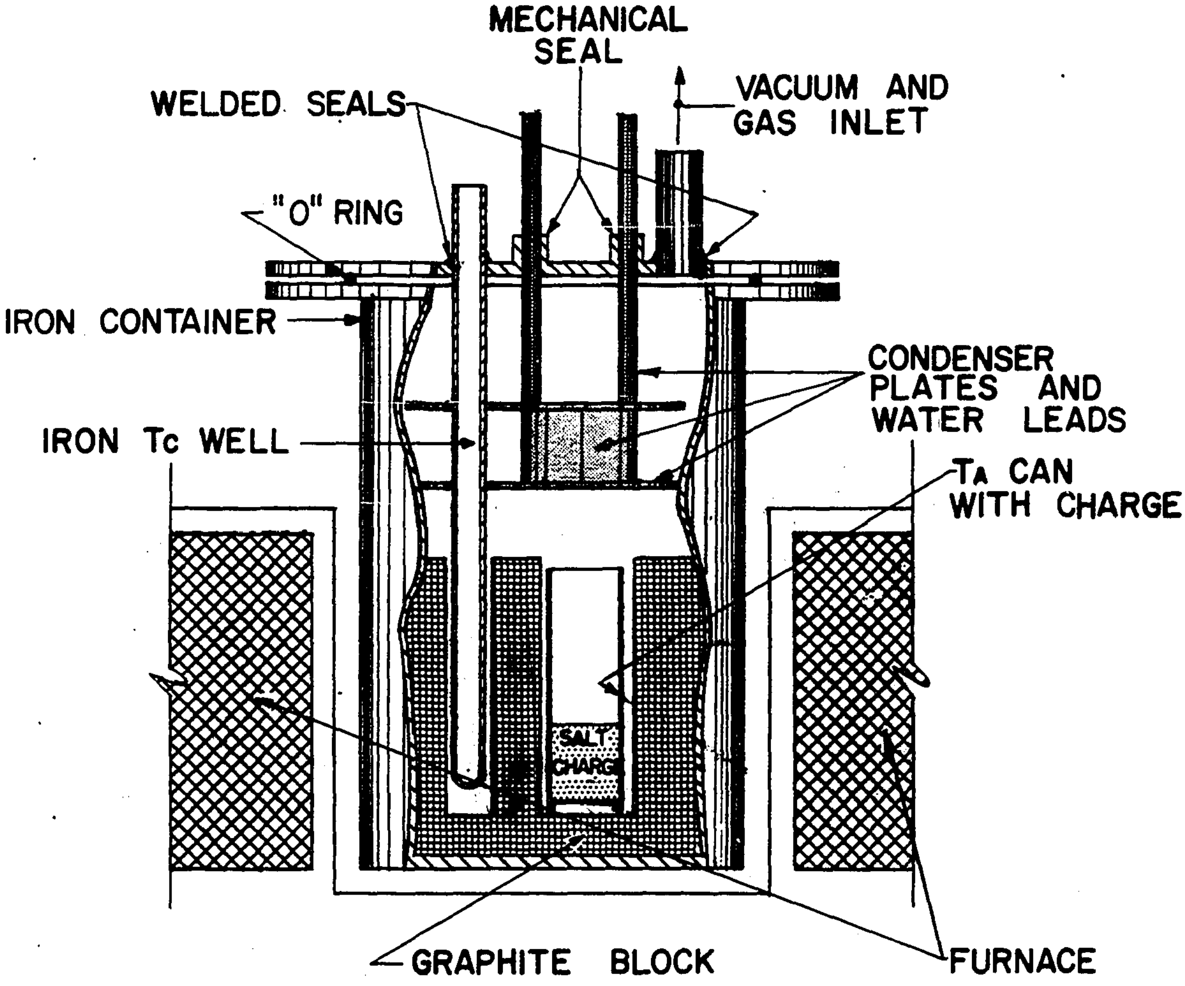


Figure 9. Micro-scale distillation apparatus

mixtures of fused salts and liquid metals. The apparatus consists of: (1) an inner can of tantalum 1 inch in diameter by 3 inches high with a wall thickness of 15 or 30 mils, both ends being sealed by drawn tantalum caps welded to the can; (2) a graphite container to hold any leakages, since the liquid metals used in the experimentation are in general corrosive to steel; and (3) an outer iron casing to protect the graphite from air oxidation at elevated temperatures. Graphite spacers were added between the top of the graphite and the iron casing to prevent movement of the inner container during agitation. The entire assembly was placed in a suitable furnace alternately rotated 180° to provide mixing of the separate phases. The initial rotation speed used provided inversion of the melt four times a minute, but this speed proved not to be rapid enough to break up the surface films that appeared to be formed. For this reason, a second apparatus with a cyclic speed of 60 cpm or 120 inversions a minute was constructed and used for the remainder of the work. This increase in number of rotations tended to increase the observed distribution coefficients, but a large degree of scatter, possibly due to impurities in the system, was still observed.

The general experimental procedure used is as follows: First the various components of the experiment were prepared, i.e., the salts purified and metallic constituents cleaned and weighed. Then the samples were loaded in the tantalum can, with one end sealed, placed in a welding dry box, a vacuum applied and inert gas allowed to fill the enclosure. The open end of the can would then be sealed by welding on a drawn tantalum cap 20 mils thick. The can was next placed in the graphite and enclosed in the iron container, and the entire assembly placed in a furnace and the equilibration performed. In general, the experiment was finished by a quench of cold air on the iron casing to retain the equilibrium conditions. Following removal, the can would be opened, the phases sampled and then analyzed. This type of operation proved to be very effective in the determination of distribution coefficients of radioactive elements and high melting constituents. In general, no experimental difficulties were experienced if high quality tantalum was used, and if a good welding procedure was employed.

Distillation studies on a micro-scale were performed in the equipment illustrated in Figure 9. The apparatus consists of an iron container approximately 3 inches in diameter and 6 inches high and a cover. Attached to the cover was an iron thermocouple well and a combination vacuum and gas inlet line. Also on the cover were "Cenco" seals for attaching a condenser and its water leads. The sample being studied was placed in a tantalum can which was inserted in a machined graphite block. A hole was provided in the block to permit insertion of the thermocouple well. A chromel-alumel thermocouple was used to measure the temperature. Using this apparatus in conjunction with a mechanical vacuum pump, it was possible to maintain a vacuum of 10 microns at temperatures up to 700°C.

The experimental procedure used was: (1) equilibration of a fused salt and liquid metal charge in the sealed can apparatus, Figure 8, (2) physical separation of the resulting salt and metal phases, (3) insertion of the salt into the distillation apparatus, and (4) performing the distillation operation. Prior to the distillation, the initial salt would be weighed; and following the operation, the residue weight and condensate weight would be evaluated by difference measurements, the initial weight of the condenser being known.

B. Macro-scale Experimentation

The macro-scale experiments have been generally limited to work involving up to 50 grams of oxidizable materials, such as uranium, thorium, zirconium, etc., and one kilogram each of fused salt and zinc. The container for the reaction vessel is shown in Figure 10 and consists of a four inch diameter mild steel tube closed at the lower end and with a flange on the top. The external surface was covered with 1/16 inch type 304 stainless steel to prevent air oxidation at elevated temperatures. Inside the external container or "pot" an inner liner of mild steel served to hold any spilled materials, preventing

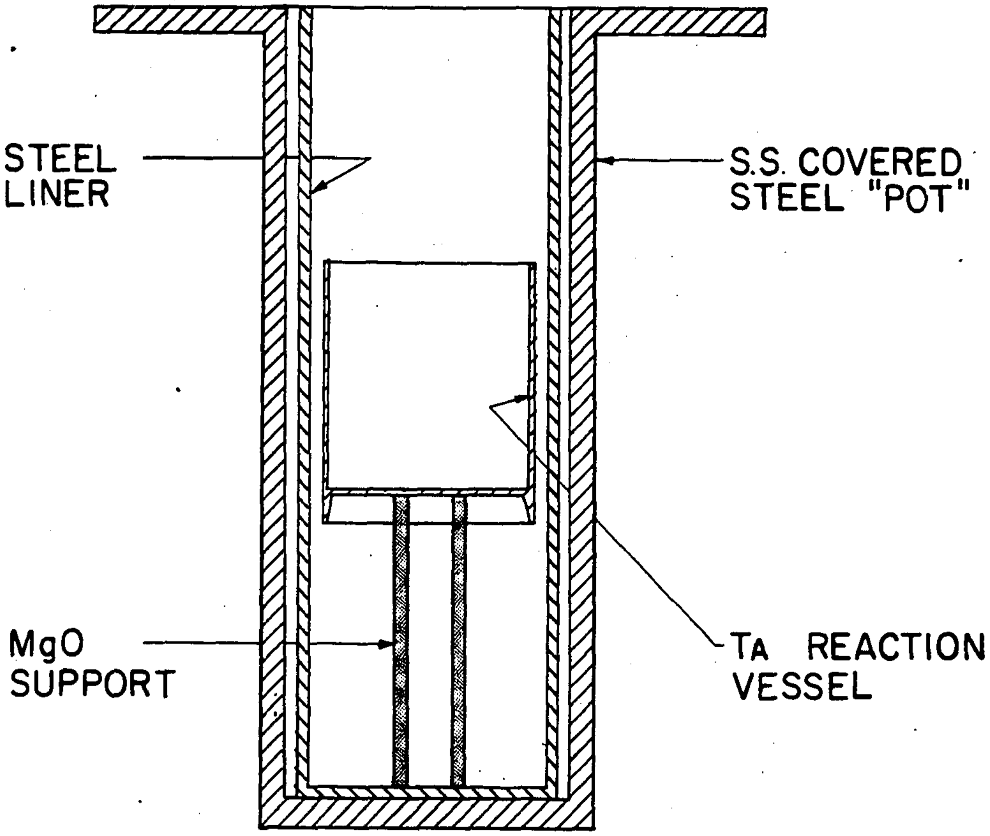


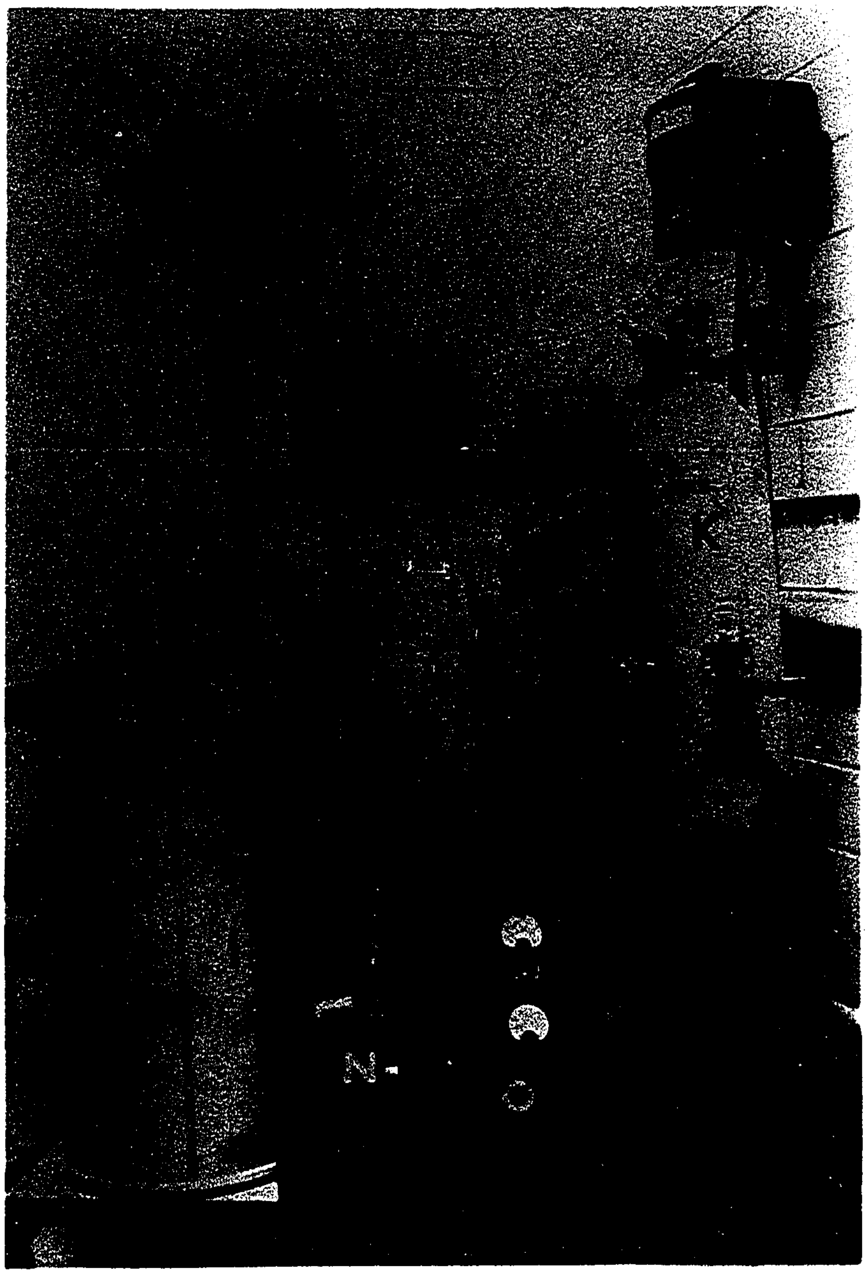
Figure 10. Reaction vessel container

loss or burn-through of the pot. Support for the tantalum reaction vessel was provided by a MgO support. The tantalum vessels used in this apparatus were nominally three inches in diameter and eight inches high, made of 30 mil tantalum sheet. The sheet was rolled to form a cylinder, a stove pipe seam made along the long axis and then welded. A spun tantalum bottom was heli-arced to one end of the can. The manufacture of these vessels proved to be one of the more critical operations in preparing these experiments, and care was taken that they were properly constructed.

Covers for the "pot" were equipped with appropriate ports for temperature measurement, sampling and addition operations, vacuum and gas inlet, stirring and, in later work, visual observation of the melt. All entrances to all covers were supplied with "Cenco" seals to permit evacuation of the system. In addition, all covers were so fabricated that they might be interchanged on the pots as desired and would match the auxiliary equipment. In addition, the apparatus consisted of the following: (1) argon gas source, (2) gas purification train consisting of uranium turnings maintained at 600°C, (3) mechanical vacuum pump and filter, (4) temperature indicating and controlling devices, and (5) an electrical stirrer. The entire apparatus was mounted as a unit on a movable cart and could be placed where appropriate utility services were available, see Figure 11.

Figure 11. Pictorial view of the macro-scale apparatus

A. Furnace
B. "Pot"
C. Selective separation head
D. Sample entry port
E. Thermocouple
F. Stirrer rod
G. Stirrer motor
H. Potentiometer
I. Vacuum gauge
J. Furnace controller
K. Argon gas tank
L. Gas purification train
M. Filter
N. Vacuum pump
O. Meters
P. Furnace variac
Q. HCl gas tank


K
N

The experimental procedure used in the selective separation studies is as follows. The metallic components were cleaned and weighed and sometimes arc-melted together, if the elements were amenable to arc-melting. The inside of the container was cleaned, as was the reaction vessel, and the charge of 800 to 1000 grams of dried KCl-LiCl eutectic and approximately an equal amount of zinc added to the vessel. The arc-melted or individual constituents were attached, by tantalum wire, to the tantalum stirrer. The system was then sealed and heated. At a temperature of 200-300°C, after several alternate flushes of argon and evacuations, the system was filled with argon to prevent excessive volatilization of either the zinc or the salts. When a temperature of 700°C was reached, the stirrer and component metals were inserted in the melt of zinc and salt and rotated at approximately 150 rpm for several hours to dissolve the constituents. Limited tests indicated that such a treatment was sufficient to affect the complete dissolution of the oxidizable elements. After this treatment, the temperature of the system was adjusted to the experimental temperature, which was either 500 or 700°C.

Stirring was continued until the equilibrium temperature had been reached. Prior to the addition of any $ZnCl_2$, samples were withdrawn from both the zinc and salt phases by siphoning with a hand bulb into pyrex glass tubing. In general, the melts were permitted to stand for 15 minutes prior to withdrawal of any samples to permit particulate material to settle. These initial samples were taken to indicate the approximate impurity content in the salt and the success of dissolution of the oxidizable materials in the zinc. Subsequently, additions of $ZnCl_2$ were made, the melts stirred for periods of time ranging from 30 minutes at 700° to 3-3/4 hours at 500°C, and samples taken from the salt phase. In this manner, it was possible to follow the incremental transfer of the oxidizable elements to the salt. Knowing the initial weights of materials used and the amount of $ZnCl_2$ added, it was then possible to add an appropriate amount of $ZnCl_2$ sufficient to raise the zinc concentration to 2-5 per cent in the salt phase. When this point had been reached, an additional sample of the zinc phase would be taken to indicate the residual level of the oxidizable elements. This would complete the oxidizing sequence of the experiment.

In a similar manner, magnesium was added to the melt to reduce the chlorinated elements. Excesses of magnesium relative to the moles of $ZnCl_2$ were added, with appropriate sampling as the magnesium was being added. The addition of an excess of magnesium would complete the reduction phase of the experiment.

C. Salt Purification

In the operations described previously, fused chloride salts were used as solvents or oxidizing agents. The removal of moisture or oxides from these materials is a very important step that has required considerable effort and care. A number of references for the purification of salts are available (31), (32), but in essence the procedure suggested is as follows: (1) heat below the melting point under a reduced pressure to remove water, (2) melt with HCl passing through the mixture, (3) filter to remove undissolved foreign material, (4) electrolize the salt to remove impurities such as iron, etc., and (5) remove dissolved HCl by reducing the pressure of the system. Steps 3 and 4 are primarily designed to remove small amounts of those materials which may interfere with or confuse very precise emf measurements. Because of the rather large size of the experiments being performed in this work, it was felt that the impurity levels present would not affect the results obtained. For this reason, these two steps were not included in the purification operation. The purification operation used in this work consisted of steps 1, 2 and 5. In general the salts so purified appeared clear, although some impurities apparently were retained, because it was observed that oxidizable elements were transferred to the salt phase before $ZnCl_2$ had been added to the experiment, see Figures 12, 15, 18, 22, etc.

D. Analytical Procedures

The analyses performed in this work were done by the Analytical and Radio-chemical Groups of the Ames Laboratory. A brief summary of some of the analytical techniques used is given below.

1. Non-radioactive analyses

Methods used in the analysis of lithium chloride-potassium chloride salt mixtures and zinc metal:

a. Thorium   When present in large amounts in the salt phase, the thorium was determined directly on aliquots of the sample by precipitation of thorium oxalate using methyl oxalate as the precipitant. The oxalate was then ignited to the oxide and weighed.

When present in small amounts in either the salt or zinc phases, the thorium was determined spectrophotometrically using thorin after separation from uranium, zirconium and zinc by passing a chloride solution of the sample through a Dowex-1 anion exchange column.

b. Uranium   Large amounts of uranium were determined by passing a chloride solution of the sample through a lead reductor, collecting the effluent in iron(III) chloride and titrating the iron(II) formed with standard cerium(IV) sulfate.

Small amounts of uranium were determined spectrophotometrically by measuring the absorbance of the uranium-thiocyanate complex.

c. Zirconium   A spectrophotometric method was used for the determination of zirconium. The absorbance of the zirconium Alizarin Red S complex was measured.

d. Cerium   The method used for the determination of large amounts of cerium involves the oxidation of cerium(III) to cerium(IV) using potassium peroxydisulfate with a small amount of silver ion present, followed by the reduction of cerium(IV) to cerium(III) with a measured excess of standard iron(II) sulfate and titration of the excess iron(II) with standard cerium(IV) sulfate solution.

e. Magnesium Magnesium was determined by titration with standard ethylenediaminetetraacetic acid (EDTA) at pH 10. An extraction with tri-*n*-octylphosphine oxide is used to remove thorium, zirconium, uranium and chromium before the titration. Sodium cyanide is added to prevent interference in the titration by zinc.

f. Zinc A polarographic method was used for the determination of zinc. The supporting electrolyte was a mixture of acetic acid and ammonium acetate and the maximum suppressor was methyl red. No separations are necessary for these particular samples, but the uranium must be oxidized to uranium(IV) before the polarogram is run.

g. Chromium The chromium was determined using a spectrophotometric method which consisted of measuring the absorbance of the chromium-diphenylcarbazide complex.

2. Radioactive analyses

a. Zirconium The zirconium tracer used was 63.3 day zirconium-95 which was produced by neutron irradiation of zirconium. The zirconium was analyzed by dissolution and chemical separation from the other activities present in the sample. A brief description of the procedure used follows: (1) Remove uranium and thorium daughter products and rare earth activity by a rare earth fluoride scavenge. Thorium and some magnesium, if present, precipitate also. (2) Precipitate barium fluozirconate to separate the zirconium from the bulk of the sample. (3) Precipitate zirconium mandelate to separate from any contaminating activity or salt remaining. Ignite to the oxide at 800°C. (4) Filter the sample on a filter disc, weigh and mount for counting. The samples were counted using a G.M. tube and model 186 Nuclear-Chicago scaler. The zirconium activity in a sample was determined as the difference observed in counting using a 20 mg/cm^2 aluminum absorber and a 100 mg/cm^2 aluminum absorber. This method was necessary to prevent contribution of β and γ activity by the 35 day niobium-95 daughter.

<u>b. Protactinium</u> The protactinium tracer used was the 27.4 day protactinium-233 daughter of 23.5 minute thorium-233 which was produced by neutron irradiation of thorium. The protactinium was analyzed by dissolution and direct counting of either evaporated samples or aliquots of the sample. The samples were counted on a model 1820 Nuclear-Chicago γ spectrometer at 310 kev. The specific activity of the protactinium in the thorium was approximately 5 x 10^7 d/m/g. This value was high enough to make any contribution by uranium

for thorium daughter products negligible.

<u>c. Cerium</u> The cerium tracers used were 32 day cerium-141 and 290 day cerium-144. The cerium-141 was obtained by neutron irradiation of cerium. The cerium-144 was obtained in solution, mixed with cerium salt, made anhydrous as the chloride and reduced with calcium. The cerium-141 was analyzed by dissolution and counting of aliquots using a model 1820 Nuclear-Chicago γ spectrometer at 145 kev. Contribution at this energy by uranium daughter products was considered negligible. The cerium-144 was analyzed by separation as the fluoride, uranium and thorium daughter products removed by zirconium iodate scavenges, and weighing and counting as the oxalate. The samples were counted on a model 186 Nuclear-Chicago decade scaler with a G.M. tube using a 20 mg/cm^2 aluminum absorber to absorb cerium-144 β's and count the praseodymium-144 β of 2.98 mev. Some cerium-144 analyses were made by solution counting of its 134 kev γ, but only when no other activities were present, since the specific activity was somewhat lower than for the irradiated cerium.

<u>d. Yttrium</u> The yttrium tracer used was 64.8 hour yttrium-90 produced by neutron irradiation of yttrium. This activity was determined by precipitation as the fluoride, removal of uranium and thorium daughter products by zirconium iodate scavenges, and precipitating and weighing as the oxalate. Samples were counted on a model 186 Nuclear-Chicago decade

scaler with a G.M. tube. The 1.7 mev β of the yttrium-90 was counted.

e. Chromium The chromium tracer used was 27.8 day chromium-51 produced by neutron irradiation of chromium. The samples were analyzed by dissolution and counting on a model 1820 Nuclear-Chicago γ spectrometer at 320 kev. The specific activity of the chromium was approximately 5×10^8 d/m/g in chromium. Contribution of uranium daughter product activity was negligible.

V. EXPERIMENTAL RESULTS

In this section the various experimental results will be presented. The results are separated into five general groups which are: (1) Mg-38w/oTh/$MgCl_2$ distributions, (2) Mg-38w/o Th/U-5.2w/oCr distributions, (3) micro-scale selective separations, (4) macro-scale selective separations, and (5) distillation separations, both micro- and macro-scale. The work under micro-scale selective separations is further sub-divided into three areas, which are, excess $ZnCl_2$, insufficient magnesium, and excess magnesium. In all three sub-sections, the data are tabulated by the individual elements whose behavior were investigated. All K_d's presented are calculated from the weight percentages of the components of interest.

A. Distribution of Cerium, Yttrium and Protactinium between Mg-38w/oTh Eutectic and KCl-LiCl Eutectic Containing $MgCl_2$

The primary purpose of this work was to evaluate the distribution of cerium, yttrium and protactinium between a fused salt, nominally 85w/oKCl-LiCl - 15w/o$MgCl_2$, and the Mg-38w/oTh eutectic. No attempt was made to produce anhydrous $MgCl_2$, but the salts were prepared by the equilibration of an 80w/oKCl-LiCl eutectic - 20w/o$ZnCl_2$ fused salt with some Zn-47w/oMg eutectic. The magnesium acted to reduce the zinc chloride, leaving $MgCl_2$ in the salt. Further, this operation acted to remove residual dissolved gases and combined water, producing a salt of high purity. In some of the work, small amounts of zinc were present in the metal phase, since the initial salt used was 80w/oKCl-LiCl eutectic - 20w/o$ZnCl_2$, not a $MgCl_2$ bearing salt.

1. Cerium

In a series of 11 experiments, the effect of $MgCl_2$ concentration, relative weights of the phases and the temperature of equilibration upon the distribution of cerium between a $MgCl_2$ bearing salt and the Mg-38w/oTh eutectic was evaluated. The $MgCl_2$ was carried in a KCl-LiCl eutectic solvent salt. The results of these experiments are summarized in Table 7.

The following conclusions may be drawn from these data: (1) the K_d and amount of cerium recovered in the salt phase are increased by the use of a higher concentration of $MgCl_2$ in the salt, (2) a lower operating temperature favors a higher K_d and larger per cent removed from the metal, and (3) the K_d is only slightly affected by changes in R (weight salt/weight metal).

The effect of zinc in the Mg-38w/oTh alloy was checked by a group of four experiments using a 20w/o$ZnCl_2$ and the Mg-38w/oTh eutectic. The zinc being displaced by the available magnesium, giving an alloy of approximately 10 w/o zinc. The data from these experiments are presented in Table 8.

Table 7. Comparison of per cent cerium recovered, K_d's and R's for various fused salt versus Mg-Th eutectic equilibrations*

Salt and temperature	Exp.	% Ce recovered in salt phase	K_d conc.in salt / conc.in metal	R wt.salt / wt.metal
5 w/o $MgCl_2$ 700°C	20	69.2	0.485	4.66
	21	78.4	0.748	4.85
	22	54.4	0.251	4.77
	23	83.4	1.05	4.79
			Ave. 0.633	
15 w/o $MgCl_2$ 700°C	24	87.7	2.56	2.85
	25	89.1	2.47	3.29
			Ave. 2.51	
15 w/o $MgCl_2$ 800°C	26	87.0	2.03	3.27
	27	84.5	1.21	4.53
			Ave. 1.62	
15 w/o $MgCl_2$ 800°C	13	76.3	2.14	1.51
	14	52.6	1.72	0.646
	15	63.3	2.30	0.751
			Ave. 2.05	

*Additional experimental details are given in Table 73, Appendix F.

These K_d's are somewhat higher than those obtained using Mg-38w/oTh free of zinc, indicating that the presence of small amounts of zinc in the Mg-Th phase has no deleterious effect on the distribution coefficient. The K_d's being slightly increased from 2.05 to 2.71.

Table 8. Per cent cerium recovered, K_d's and R's for the equilibration of 85w/oKCl-LiCl eutectic, 15w/oMgCl$_2$ salt and 90w/oMgTh eutectic - 10w/oZn, equilibrated at 800°C*

Exp.	% Ce recovered in salt phase	K_d $\frac{\text{conc. in salt}}{\text{conc. in metal}}$	R $\frac{\text{wt. salt}}{\text{wt. metal}}$
9	44.4	3.00	0.267
10	64.0	3.01	0.592
11	49.7	2.56	0.384
12	60.6	2.28	0.674
		Ave. 2.71	

*Additional experimental details are given in Table 73, Appendix F.

2. Yttrium

The distribution of yttrium between a 15w/oMgCl$_2$ salt and the Mg-38w/oTh eutectic was investigated in a series of three experiments. The results of these experiments are presented in Table 9. Apparently nearly 90 per cent of the yttrium is extracted from the Mg-Th by a single equilibration. The K_d's for yttrium are higher than those obtained for cerium, indicating a stronger interaction of cerium with the Mg-Th than yttrium with the Mg-Th alloy. The average K_d in this case is 7.51.

Table 9. Per cent yttrium recovered, K_d's and R's for the equilibration of 85w/oKCl-LiCl eutectic, 15w/o$MgCl_2$ salt and Mg-38w/oTh eutectic, with small amounts of zinc, equilibrated at 600°C*

Exp.	% Y recovered in salt phase	K_d conc. in salt / conc. in metal	R wt. salt / wt. metal
13	89.2	8.68	0.953
14	90.8	7.07	1.402
15	87.8	6.79	1.054
		Ave. 7.51	

*Additional experimental details are given in Table 74, Appendix F.

3. Protactinium

The behavior of protactinium contained in a Mg-38w/oTh eutectic when contacted with KCl-LiCl eutectic - 15w/o$MgCl_2$ salt has been examined in two experiments. Different salts were used in each experiment. In one a KCl-LiCl eutectic containing 20w/o$ZnCl_2$ was used, while in the other experiment KCl-LiCl eutectic - 15w/o$MgCl_2$ prepared as previously described was used. In either case, the final salt composition was the same. However, in one case, zinc is transferred to the Mg-Th phase. The effect of the work is, then, to see if the presence of minor amounts (10 per cent) of zinc in the metal phase adversely affects the distribution of protactinium.

The data are given in Table 10. While more protactinium was transferred to the salt with the $ZnCl_2$ salt, it is not felt that the variation in the protactinium recovery is significant although the relative K_d's do vary by a factor of five. It is noted that neither salt will remove appreciable amounts of the contained protactinium. It should also be noted that the activity levels in the two experiments are quite different.

Table 10. Analyses and equilibrium distributions of protactinium between Mg-38w/oTh eutectic and 85w/oKCl-LiCl eutectic - 15w/o$MgCl_2$ fused salt, equilibrated at 700°C*

Exp.	Final phase	Weight (calc. gms)	Pa-233 act. x 10^{-5} (cpm/gm)	% Pa recov. in phase	K_d $\frac{\text{act. salt}}{\text{act. metal}}$
--	Salt	15.58	0.018	1.02	1.05×10^{-2}
	Metal	10.31	1.73	98.98	
12	Salt	15.68	12.00	0.3	0.2×10^{-2}
	Metal	11.87	5980.00	99.7	

*Additional experimental details are given in Table 70, Appendix F.

B. Distribution of Protactinium and Cerium between the Mg-38w/oTh and U-5.2w/oCr Eutectics

1. Protactinium

A considerable amount of work has been done on the distribution of protactinium between the Mg-38w/oTh and U-5.2w/oCr eutectics by previous investigators (33). Using a similar apparatus, the results previously obtained were duplicated in this work. It was observed that up to 99.87 per cent of any protactinium present could be extracted from a parent phase of Mg-Th alloy by either molten uranium or U-5.2w/oCr alloy. The K_d obtained for protactinium under these conditions was 7.94×10^{-3}.

2. Cerium

A sequence of three experiments was performed to evaluate the distribution of cerium between the Mg-38w/oTh and U-5.2w/o Cr eutectics. In these experiments, Mg-Th and U-Cr eutectic samples were equilibrated at 1000°C for one hour followed by a 15 minute stand in a vertical position at 1000°C and an air blast quench. It is apparent from the data in Table 11 that the cerium is almost quantitatively retained in the Mg-Th phase. The overall cerium material balances are generally good, and it is felt that the data show virtually complete separation of the cerium from the uranium. A small portion of the overall activity was observed at the interface of the two phases, and is recorded in Table 11 as interface.

Table 11. Analyses and equilibrium distributions of cerium between Mg-38w/oTh and U-5.2w/oCr eutectics, equilibrated at 1000°C for 1 hour*

Exp.	Final phase	Weight (calc. gms)	Ce-144 concentration (mg/gm)	Ce-144 recovered (%)	K_d $\frac{\text{act. Mg-Th}}{\text{act. U-Cr}}$
36	Mg-Th	27.17	4.88	99.2	578
	U-Cr	58.51	8.44×10^{-3}	0.4	
	Interface	1.58	0.39	0.4	
37	Mg-Th	29.11	4.94	97.8	3690
	U-Cr	62.66	1.34×10^{-3}	0.1	
	Interface	3.68	0.87	2.1	
38	Mg-Th	32.23	6.26	99.1	3039
	U-Cr	70.56	2.06×10^{-3}	0.1	
	Interface	1.26	1.4	0.8	

*Additional experimental details are given in Table 73, Appendix F.

C. Micro-scale Selective Separations

The micro-scale experimentations were performed in the sealed tantalum can apparatus. This area of the study is subdivided into three general classifications. These separate classifications result from the nature of the experimental work. The technique employed is as follows: (1) the various components of the experiment, i.e., the oxidizable constituents, the $ZnCl_2$ bearing salt and the zinc metal were prepared and weighed; (2) depending upon the weight of the salt and oxidizable materials, an amount of magnesium was weighed out and added to the charge; this amount of magnesium determined whether the mixture contained an excess of magnesium, an insufficiency of magnesium or an excess of $ZnCl_2$ relative to the oxidizable elements; and (3) the materials were sealed in the tantalum can and the experiment performed. The three groupings of the selective separations are, then: (1) excess $ZnCl_2$, (2) excess magnesium, and (3) insufficient magnesium, all relative to the oxidizable materials. Further, under each of these classifications, the separation of each element from uranium is considered individually.

1. Excess $ZnCl_2$ separations

a. Yttrium-uranium In Table 12, data for the equilibration of yttrium and uranium samples between a zinc phase and a salt phase containing an excess of $ZnCl_2$ are presented. Experiments 7 and 9 give very high K_d's for both

Table 12. Analyses and equilibrium distributions of yttrium and uranium between a zinc phase and a LiCl-KCl eutectic - $ZnCl_2$ fused salt, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phases			% of component recovered in final phases		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$	
			%Zn (calc.)	%U	%Y	%U	%Y	U	Y
7	Salt	16.50	8.0	3.92	0.575	99.89	99.98	980	5750
	Metal	18.85	-	0.004	0.0001	0.11	0.02		
8	Salt	16.70	6.8	7.33	1.35	99.68	93.04	407	104
	Metal	21.50	-	0.018	0.0786	0.32	6.96		
9	Salt	17.70	7.1	6.49	0.874	99.90	99.97	1081	4370
	Metal	20.68	-	0.006	0.0002	0.1	0.03		

*Additional experimental details are given in Table 74, Appendix F.

yttrium and uranium, while in the eighth the distributions are not as clean-cut. These data indicate essentially complete oxidation of both yttrium and uranium by an excess of $ZnCl_2$.

b. Chromium-uranium Both radioactive and non-radioactive samples of chromium were used to evaluate the transfer of chromium by excess $ZnCl_2$. The data from the first non-radioactive study are given in Table 13, as a function of equilibration time. No particular dependence on time is noted in the behavior of the K_d's or the K_n. In Table 14, the experimental results are summarized for the four experiments using radioactive chromium, while in Table 15 the results of two experiments using non-radioactive material are presented. The solubility data, as previously presented, were used to calculate the K_d's and the K_n when that limit had been exceeded in the experiment. Comparable results for these quantities were obtained when either non-radioactive or radioactive chromium was used.

c. Cerium-uranium The distribution of cerium and uranium between a zinc phase and KCl-LiCl eutectic containing $ZnCl_2$ was determined in two experiments. Data from these experiments are presented in Table 16. The percentages of recovered material in the salt phases and the K_d's demonstrate that both cerium and uranium are quantitatively transferred to the salt phase by an excess of $ZnCl_2$.

d. Molybdenum-uranium In the sealed tantalum can

Table 13. Analyses and equilibrium distributions of uranium and chromium between a zinc metal phase and a LiCl-KCl eutectic - $ZnCl_2$ fused salt, equilibrated at 650°C*

Exp.	Equil. time (hrs.)	Final phase	Weight (calc. gms)	Composition of final phases			% of component recovered in final phases		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$		K_n** (Cr,Zn)
				%Zn (calc.)	%U	%Cr	%U	%Cr	U	Cr	
1	0.5	Salt	18.3	5.40	10.45	0.040	98.8	14.7	317	0.172	3.2×10^{-2}
		Metal	20.7	-	0.093	0.232	1.2	85.3			
2	1.0	Salt	20.0	6.2	8.72	0.045	99.3	19.5	265	0.246	3.96×10^{-2}
		Metal	20.3	-	0.076	0.183	0.7	80.5			
3	1.5	Salt	20.0	5.8	9.68	0.044	98.4	15.4	293	0.210	3.61×10^{-2}
		Metal	22.95	-	0.140	0.210	1.6	84.6			
SP-4	2.0	Salt	30.66	7.6	5.07	0.068	99.6	34.0	154	0.349	4.59×10^{-2}
		Metal	20.54	-	0.08	0.195	0.4	66.0			

*Additional experimental details are given in Table 72, Appendix F.

**See equation 20, page 30c.

Table 14. Analyses and equilibrium distributions of uranium and radioactive chromium between a zinc metal phase and a fused salt phase containing excess $ZnCl_2$ at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phases			% of material recovered in final phases		K_d conc. salt / conc. metal		K_n** (Cr, Zn)
			%Zn (calc.)	%U	%Cr	%U	%Cr	U	Cr	
1	Salt	15.68	7.2	5.07	0.2364	99.1	26.4	154	0.99	13.7×10^{-2}
	Metal	12.95	-	0.0650	0.7972	0.9	73.6			
2	Salt	17.53	7.8	4.75	0.1496	98.8	15.65	144	0.623	8.02×10^{-2}
	Metal	13.58	-	0.0967	1.0390	1.2	84.35			
3	Salt	18.24	8.2	3.37	0.1213	67.4	11.32	102	0.505	6.10×10^{-2}
	Metal	25.09	-	1.19	0.6902	32.6	88.68			
4	Salt	18.54	6.8	6.41	0.0914	98.6	19.35	194	0.381	5.6×10^{-2}
	Metal	19.40	-	0.0968	0.3650	1.4	80.65			

*Additional experimental details are given in Table 72, Appendix F.

**See equation 20, page 30c.

Table 15. Analyses and equilibrium distributions of uranium and chromium between a zinc metal phase and LiCl-KCl eutectic - $ZnCl_2$ fused salt, equilibrated at 500°C for 1/2 hour*

Exp.	Final phase	Weight (calc. gms)	Composition of final phases			% of material recovered in final phases		K_d conc. salt / conc. metal		K_n** (Cr, Zn)
			%Zn (calc.)	%U	%Cr	%U	%Cr	U	Cr	
4	Salt	18.55	4.7	12.45	0.079	97.34	13.68	519	0.329	$7x10^{-2}$
	Metal	17.90	-	0.35	0.518	2.66	86.32			
5	Salt	17.50	6.5	8.0	0.123	92.31	16.85	242	0.512	$7.9x10^{-2}$
	Metal	16.65	-	0.7	0.636	7.69	83.15			

*Additional experimental data are given in Table 72, Appendix F.

**See equation 20, page 30c.

Table 16. Analyses, equilibrium distributions and recoveries of uranium and cerium between a zinc metal phase and KCl-LiCl eutectic - $ZnCl_2$ fused salt, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phases			% of material recovered in final phases		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$	
			%Zn (calc.)	%U	Ce (cpm/gm x10^{-3})	%U	%Ce	U	Ce
2	Salt	14.51	8.4	2.60	24.91	99.6	99.6	236	207
	Metal	13.21	-	0.011	0.12	0.4	0.4		
4	Salt	13.64	9.0	1.03	30.56	99.3	100.0	147	15,280
	Metal	15.52	-	0.007	0.002	0.7	0.0		

*Additional experimental details are given in Table 73, Appendix F.

using non-radioactive samples of molybdenum and uranium between a zinc phase and a salt phase, with an excess of $ZnCl_2$, was determined as a function of time. The data resulting from these experiments are given in Table 17. No molybdenum was observed in the salt, while virtually all the uranium is found therein. The K_d for the molybdenum is extremely low. It is constant, because the solubility limit of molybdenum had been exceeded in all cases.

<u>e. Zirconium-uranium</u> The distributions of uranium and zirconium were evaluated using both radioactive and non-radioactive samples of zirconium. Table 18 gives the data for the non-radioactive material, while Table 19 presents similar data for the radioactive samples. The data from the experiments using radioactive zirconium are not as consistant as the others. This is due to the fact that these experiments did not have large excesses of $ZnCl_2$ present, but attempted to oxidize only the uranium. The attempt was only partially successful in experiment 8. The three experiments show that, as the amount of zirconium transferred to the salt is increased the residual uranium in the metal decreases. Further work in this area will be presented in the macro-scale selective separation section.

<u>f. Protactinium</u> A set of four samples of uranium and eight of U-5.2w/oCr, all containing protactinium-233, were equilibrated with zinc and 80w/oKCl-LiCl eutectic - 20w/o$ZnCl_2$

Table 17. Analyses and equilibrium distributions of uranium and molybdenum between a zinc metal phase and KCl-LiCl - $ZnCl_2$ fused salt, equilibrated at 650°C*

Exp.	Equil. time (hrs.)	Final phase	Weight (calc. gms)	Composition of final phase			% recovered final phase		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$	
				%Zn (calc.)	%U	%Mo	%U	%Mo	U	Mo
1	0.5	Salt	22.47	6.6	7.62	2 ppm or less	99.8	0	231	< 0.0164
		Metal	19.93	-	0.033	0.21	0.2	100		
2	1.0	Salt	22.62	6.7	7.51	2 ppm or less	99.5	0	228	< 0.0164
		Metal	20.38	-	0.051	0.28	0.5	100		
3	1.5	Salt	22.40	7.4	5.43	2 ppm or less	99.5	0	164	< 0.0164
		Metal	21.15	-	0.059	0.12	0.5	100		
SP-2	2.0	Salt	32.75	6.8	7.30	2 ppm or less	95.2	0	22.1	< 0.0164
		Metal	21.05	-	0.57	0.57	4.8	100		

*Additional experimental details are given in Table 75, Appendix F.

Table 18. Analyses and equilibrium distributions of uranium and zirconium between a zinc metal phase and KCl-LiCl eutectic - $ZnCl_2$ fused salt, equilibrated at 650°C*

Exp.	Equil. time (hrs.)	Final phase	Weight (calc. gms)	Composition of final phase			% recovered in final phase		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$	
				%Zn (calc.)	%U	%Zr	%U	%Zr	U	Zr
Zr-2	1.0	Salt	23.81	6.6	7.34	0.35	99.8	96.6	432	25.0
		Metal	21.39	-	0.017	0.014	0.2	3.4		
Zr-3	1.5	Salt	23.85	7.0	6.13	0.265	99.9	96.4	557	24.1
		Metal	20.20	-	0.011	0.011	0.1	3.6		
SP-3	2.0	Salt	23.66	7.8	4.30	0.048	94.9	90.4	13.0	8.0
		Metal	20.74	-	0.271	0.006	5.1	9.6		

*Additional experimental details are given in Table 71, Appendix F.

Table 19. Analyses and distribution of uranium and radioactive zirconium between a zinc metal phase and KCl-LiCl eutectic - $ZnCl_2$ fused salt, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phase			% recovered in final phase		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$	
			%Zn (calc.)	%U	%Zr	%U	%Zr	U	Zr
Zr-8	Salt	10.79	1.4	19.1	0.25	94.3	22.2	579	1.04
	Metal	21.93	-	0.36	0.43	5.7	77.8		
Zr-10	Salt	13.13	3.4	14.1	0.590	95.2	90.8	428	14.7
	Metal	22.36	-	0.43	0.04	4.8	9.2		
Zr-11	Salt	13.62	3.2	14.8	0.466	96.3	98.8	449	116
	Metal	22.16	-	0.36	0.004	3.7	1.2		

*Additional experimental details are given in Table 71, Appendix F.

at 700°C for one hour. The experimental procedures have been described previously. Table 20 presents the significant data obtained by radiochemical analyses for protactinium-233. The term per cent protactinium-233 in the salt phase refers to the amount of activity found in the salt relative to the entire amount of activity observed in both phases. It can be seen that virtually all of the protactinium is found in the salt. As an average, 98 per cent of the protactinium is so recovered. The average protactinium K_d for the uranium samples is 230 and 145 for the U-Cr samples.

g. Iron Two experiments were performed to evaluate the extraction of iron from a zinc phase by a KCl-LiCl eutectic -20 w/o $ZnCl_2$ salt. The data are presented in Table 21. Iron was used for two reasons: (1) uranium and iron form a eutectic that melts at a lower temperature than the uranium-chromium eutectic, and (2) iron, because of its position in the periodic series of the elements, may be used as a substitute for ruthenium, in the evaluation of the chemical behavior of ruthenium. In experiments 3 and 4, it is demonstrated that iron will not be extracted by excess $ZnCl_2$ from zinc. The K_d's presented are based upon the solubility limit of iron in zinc at this temperature.

h. Niobium Three experiments, the results of which are presented in Table 22, were performed to evaluate the degree of transfer of niobium from a zinc solution to a fused

Table 20. Tabulation of radiochemical analyses for protactinium-233 in samples taken from the equilibration of uranium and uranium-chromium samples, which contained protactinium-233 with zinc and 80w/oLiCl-KCl eutectic - 20w/o$ZnCl_2$ fused salt, equilibrated 1 hour at 700°C

Sample	Phase	Final weight (gms)	Pa-233 activity x 10^{-4} (300 gamma Kev) (counts/min/gm)	K_d act. salt / act. Zn	% Pa-233 recovered in salt phase
U-2	Salt	20.26	4.59		
	Zn	28.69	0.081	56.4	97.7
U-3	Salt	19.91	5.47		
	Zn	29.79	0.139	39.4	96.4
U-4	Salt	21.53	28.0		
	Zn	30.12	0.044	645	99.8
U-6	Salt	19.95	12.8		
	Zn	31.70	0.056	277	99.3
U Cr-1	Salt	11.70	20.9		
	Zn	32.85	0.21	101.4	97.5
U Cr-2	Salt	16.95	95.7		
	Zn	30.45	0.198	484	99.7
U Cr-3	Salt	17.80	20.2		
	Zn	29.95	0.296	68.4	97.1
U Cr-4	Salt	16.25	11.3		
	Zn	31.15	0.142	79.7	97.7
U Cr-5	Salt	19.16	4.94		
	Zn	31.04	0.138	35.8	95.8
U Cr-6	Salt	20.98	13.4		
	Zn	29.97	0.0748	179	99.3
U Cr-7	Salt	20.01	14.7		
	Zn	31.34	0.183	80.4	97.9
U Cr-8	Salt	17.95	21.5		
	Zn	30.60	0.176	122	98.6

Table 21. Analyses and equilibrium distributions of iron between a zinc metal phase and a fused salt phase containing excess $ZnCl_2$ at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phase		%Fe recovered in final phase	K_d $\frac{\text{conc.salt}}{\text{conc.metal}}$ Fe
			%Fe	%Zn (calc.)		
F-3	Salt	14.89	<2 ppm	9.97	0.0	2×10^{-3}
	Metal	23.38	11.91	--	100.0	
F-4	Salt	16.53	0.0164	9.66	0.002	0.164
	Metal	22.35	13.50	--	99.998	

*Additional experimental details are given in Table 66, Appendix F.

Table 22. Analyses and equilibrium distributions of niobium between a zinc metal phase and a fused salt phase containing excess $ZnCl_2$ at 500°C*

Exp.	Final phase	Weight (calc. gms)	% Nb	% Nb recovered	K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$
N-4	Salt	13.14	<25 ppm	0.009	0.035
	Metal	24.22	12.45	99.991	
N-5	Salt	10.85	<25 ppm	0.009	0.035
	Metal	23.15	13.04	99.991	
Blank	Salt	14.39	<25 ppm	--	--
	Metal	17.26	0.20	--	

*Additional experimental details are given in Figure 67, Appendix F.

salt by excess $ZnCl_2$. The data indicate the absence of any tendency for niobium to be oxidized by $ZnCl_2$. The experiment labeled Blank was included to help evaluate the possible interference of tantalum, from the container, with the determination of the niobium levels. Based upon these data, it is felt that the niobium concentration in the salt is certainly below 15 ppm, and is, in fact, beyond the limits of analytical detection. The K_d's for niobium are based upon the solubility limit of niobium in zinc at this temperature.

2. Excess magnesium separations

In this group of experiments, dilute solutions of magnesium were not used, but the concentration of magnesium normally ran about 47w/o. For this reason, distributions observed herein may not represent the best possible extractions and should not be too closely compared with data obtained under grossly different conditions.

a. Yttrium-uranium distributions The data in Table 23 show the effect of equilibration with excess magnesium upon the distributions of uranium and yttrium. The uranium did not entirely dissolve due to the low solubility of uranium in zinc-magnesium alloys in the range of 50w/o zinc. Since the Zn-Mg alloy used in this work was the 47w/o magnesium eutectic, the uranium did not dissolve and the data for uranium are not complete. The overall yield of the uranium was assumed to be 100 per cent, and the per cent of uranium

Table 23. Analyses and equilibrium distributions for yttrium and uranium between a Zn-Mg alloy phase and a KCl-LiCl eutectic - $MgCl_2$ salt phase, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phases			% of component recovered in final phases		K_d conc. salt / conc. metal	
			%Mg (calc.)	%U	%Y	%U	%Y	Y	U
10	Salt	15.60	3.8	0.080	0.539	1.09	31.4	0.431	1.33
	Metal	14.74	43.0	---	1.247	---	68.6		
11	Salt	12.40	3.8	0.063	0.333	0.74	20.4	0.339	1.05
	Metal	16.41	45.0	---	0.982	---	79.6		
12	Salt	15.16	3.8	0.048	0.609	0.63	26.4	0.338	0.80
	Metal	14.38	42.0	---	1.80	---	73.6		

*Additional experimental details are given in Table 74, Appendix F.

recovered was calculated on that basis. The data for uranium indicate that one per cent or less of the uranium is retained in the salt phase. The K_d's for uranium were calculated from the known solubility limit of uranium. These data also indicate that under these conditions some 25 per cent of the yttrium present will be retained in the salt phase.

b. Cerium-uranium distributions The results of three experiments having large excesses of magnesium present are listed in Table 24. The uranium yields in these experiments are unusually low, averaging less than 5 per cent. This is due to the sample preparation technique used by the radiochemist. The samples were etched in nitric acid to remove a blackish material on the surface of the sample. Undoubtedly this blackish material was precipitated metallic uranium. The K_d for the cerium is 0.0324, and an average of 95.6 per cent of the cerium is transferred to the metal phase. The K_d's for uranium are comparable to those obtained from the previous section.

c. Protactinium distribution Investigations into the reduction of $PaCl_3$ by excess magnesium produced the data given in Table 25. In addition, several of the experiments used calcium as the reductant rather than magnesium. The experimental procedure used in this work was: (1) heat to 700°C rotating vigorously, (2) slow cool to 500° still rotating, (3) hold at 500° for 1/2 hour while rotating, (4) still at

Table 24. Analyses and equilibrium distributions of uranium and cerium between LiCl-KCl eutectic - $ZnCl_2$ fused salt and Zn-Mg alloy at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phase			% of component recovered in final phase		K_d $\frac{\text{conc. salt}}{\text{conc. metal}}$	
			%Mg (calc.)	%U	Ce(cpm/gm $x10^{-3}$)	%U	%Ce	Ce	U
6	Salt	11.40	3.4	0.035	1.821	0.36	4.6	0.0326	0.58
	Metal	7.39	38.0	---	55.83	---	95.4		
7	Salt	13.05	3.7	0.038	1.06	0.30	3.1	0.0268	0.63
	Metal	10.11	33.0	---	39.48	---	96.9		
8	Salt	13.42	2.7	0.083	2.81	0.57	8.8	0.0606	1.38
	Metal	8.32	40.0	---	46.36	---	91.2		
5	Salt	15.72	3.8	0.015	0.427	0.67	1.2	0.0082	0.25
	Metal	8.01	32.0	---	52.17	---	98.8		

*Additional experimental details are given in Table 73, Appendix F.

Table 25. Distribution of protactinium-233 between liquid zinc-rich alloy containing calcium or magnesium or both and a fused salt consisting primarily of KCl-LiCl eutectic, equilibrated at 500°C*

Exp.	Pa-233 activity x10^{-3} (300 Kev gamma) (counts/min/gm) Zinc-rich phase	Salt phase	K_d act. metal / act. salt	% Pa-233 activity in metal	Calculated residual Mg or Ca content in zinc-rich phase
Pa-1	156	0.13	1200	100	2.92% Mg
Pa-2	140	0.028	5000	100	3.53% Mg
Pa-3	124	0.5	248	100	3.54% Mg
Ca-1	53.1	0.27	197	100	2.72% Ca
Ca-2	46.0	0.212	207	100	2.68% Ca
Ca-3	122	0.034	3590	100	3.18% Ca
Ca-4	134	0.064	2098	100	2.66% Ca
MC-1	72.3	0.106	682	100	4.29% Mg
MC-2	30	0.28	109	100	3.025% Mg
MC-3	139	0.00	infinity	100	3.29% Mg
MC-4	151	0.00	infinity	100	3.175% Mg
M-1	54.2	0.071	764	100	3.095% Mg
M-2	50	0.211	237	100	3.295% Mg
M-3	124	0.112	1108	100	2.535% Mg
M-4	75	0.136	552	100	2.66% Mg

*Additional experimental details are given in Table 69, Appendix F.

500°, hold in a vertical position, and (5) rapidly cool the sample with an air blast.

The following conclusions may be drawn from these data: (1) little protactinium is found in the salt phases (in the opinion of the radiochemist, the values of activity in the salt are so low as to be considered meaningless), (2) the K_d's are apparently independent of residual calcium or magnesium content, and (3) both magnesium and calcium will reduce $PaCl_3$ with equal efficiency.

3. Insufficient magnesium

a. Yttrium-uranium separations The data presented in Table 26 are from a series of equilibrations between a $ZnCl_2$ bearing salt and a zinc metal phase. In these experiments, some magnesium had been added to reduce the amount of available $ZnCl_2$. In all cases, the amount of $ZnCl_2$ available was insufficient to oxidize both the yttrium and the uranium, based on a plus 3 oxidation state for both elements. As can be seen from the data, the yttrium appears to precede the uranium into the fused salt, but both elements are being oxidized simultaneously. The experiments are presented in the order of increasing availability of $ZnCl_2$. The average separation coefficient (K_n) for this case is 1.171.

b. Cerium-uranium separations Data for five experiments in which the amount of magnesium added was insufficient to reduce chlorides of the contained cerium and

Table 26. Analyses and equilibrium distributions of yttrium and uranium between a zinc phase and LiCl-KCl eutectic - $MgCl_2$ fused salt, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phases		% of initial component recovered in final phases		K_n** (U, Y)
			%U	%Y	%U	%Y	
1	Salt	11.0	0.25	0.186	2.5	9.8	0.530
	Metal	22.90	4.75	0.822	97.5	90.2	
2	Salt	11.35	1.09	0.553	16.6	39.7	0.775
	Metal	21.24	2.93	0.448	83.4	60.3	
3	Salt	12.10	1.17	0.242	12.1	32.3	1.91
	Metal	25.40	4.06	0.242	87.9	67.7	
4	Salt	14.50	1.03	0.432	16.3	72.7	0.941
	Metal	20.69	3.72	0.114	83.7	27.3	
5	Salt	12.50	3.38	1.21	58.5	76.2	1.10
	Metal	25.77	1.17	0.184	41.5	23.8	
6	Salt	16.00	5.01	1.12	70.7	98.4	1.77
	Metal	24.42	1.36	0.0155	29.3	1.6	

*Additional experimental details are given in Table 74, Appendix F.

**See equation 19, page 30c.

uranium are given in Table 27. These experiments are tabulated in the order of increasing magnesium. Apparently, the cerium is largely unaffected, while the uranium is preferentially reduced. The data strongly indicate that separation of cerium and uranium is possible, if the available $ZnCl_2$ or magnesium is closely controlled. The average K_n for this separation from these data is 14.09.

c. Zirconium-uranium separations   In Table 28, the results of three experiments in the selective separation of zirconium and uranium are given. The largest portion of the contained zirconium has been removed from the salt phase in all cases. However, a portion of the uranium has also been reduced in each case. This indicates a possibility that a uranium-zirconium separation can be made by this technique. The average K_n of 1829 for plus 3 zirconium gives further support to that idea.

d. Protactinium, thorium and uranium separations Table 29 presents the data for equilibrations of KCl-LiCl eutectic with very small (less than 0.012 gms of $ZnCl_2$) additions of a 20w/o$ZnCl_2$ salt and liquid zinc at 500°C. In general, an increasing amount of $ZnCl_2$ caused an increased transfer of protactinium to the salt phase. However, the amounts of protactinium transferred do not indicate that it is possible to preferentially oxidize the protactinium and not the uranium. The amount of uranium transferred, while only

Table 27. Analyses and equilibrium distributions of uranium and cerium in equilibrations between LiCl-KCl eutectic - $MgCl_2$ and Zn-Mg alloy at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phase		% of recovered material in final phase		K_n** (Ce, U)
			%U	%Ce	%U	%Ce	
16	Salt	13.32	4.406	1.724	32.3	99.9	9.70
	Metal	18.29	6.714	0.00134	67.7	0.1	
17	Salt	14.71	3.762	1.782	33.2	99.9	8.19
	Metal	13.35	8.335	0.00191	66.8	0.1	
18	Salt	11.73	2.804	1.651	16.05	99.8	9.09
	Metal	17.85	9.633	0.00214	83.95	0.2	
19	Salt	74.33	0.1216	1.30	0.88	84.55	29.4
	Metal	18.81	10.46	0.181	99.12	15.45	

*Additional experimental details are given in Table 73, Appendix F.

**See equation 12, page 30b.

Table 28. Analyses and equilibrium distributions of uranium and zirconium in equilibrations between a KCl-LiCl eutectic - $MgCl_2$ salt and Zn-Mg alloy at 500°C*

Exp.	Final phase	Weight (calc. gms)	Composition of final phase %U	Composition of final phase %Zr	% of recovered material in final phase %U	% of recovered material in final phase %Zr	K_n** (U, Zr^{+3})
5	Salt	13.43	3.4	0.011	85	2.7	2240
	Metal	10.65	0.75	0.575	15	97.3	
6	Salt	13.96	2.7	0.007	71.4	0.8	2810
	Metal	10.72	1.4	1.38	28.6	99.2	
7	Salt	14.87	1.8	0.030	60.9	3.3	437
	Metal	10.74	1.6	1.46	39.1	96.7	

*Additional experimental details are given in Table 71, Appendix F.

**See equation 13, page 30b.

Table 29. Analyses and equilibrium distributions of uranium and protactinium in fused salt and liquid zinc phases, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Analytical results for final phases %U	Analytical results for final phases Pa(cpm/gmx10^{-6})	Recovered in final phase %U	Recovered in final phase %Pa	K_n** (U,Pa)
30	Salt	7.52	0.12	3.23	0.8	1.8	133
	Metal	16.17	6.53	119	99.2	98.2	
31	Salt	6.92	0.11	5.85	0.7	5.5	24.2
	Metal	16.40	6.47	42.5	99.3	94.5	
32	Salt	6.83	0.084	5.24	0.6	4.7	21.5
	Metal	16.42	6.24	44.3	99.4	95.3	
33	Salt	8.11	0.12	20.6	0.9	8.2	20.4
	Metal	16.23	6.67	116	99.1	91.8	

*Additional experimental details are given in Table 70, Appendix F.

**See equation 18, page 30c.

one per cent or less of the total uranium available, is probably 10^6 times the amount of protactinium so transferred. In contradiction to the observed facts is the distribution coefficient of 22.1 which indicates that uranium should precede the protactinium and be separated from it. A complicating factor is probably the relative masses of the two elements.

In ten additional experiments, in which the additions of $ZnCl_2$ were much larger, the separation of these elements was studied. The data in Table 30 illustrate the gradual but coincident transfer of uranium, protactinium and thorium from the metal phase to the salt as a function of increasing $ZnCl_2$ availability. The experiments listed in Table 30 are presented in the order of increasing $ZnCl_2$ availability, and the transfer of the constituents can be readily observed. It may then be concluded that it is impossible to effect a separation of these constituents in a single equilibration. Assuming a plus 3 oxidation state for all components, the appropriate K_n's vary from 4.1 to 107 for uranium-protactinium, and from 0.606 to 32.5 for uranium-thorium, with averages of the closest grouping of figures of 19.51 and 1.49, respectively.

Table 30. Analyses and equilibrium distributions of uranium, thorium and protactinium in fused salt and Zn-Mg phases, equilibrated at 500°C*

Exp.	Final phase	Weight (calc. gms)	Analytical results for final phases			Recovered in final phases			K_n**	
			%U	Pa(cpm/gm x10^{-6})	%Th	%U	%Pa	%Th	U, Pa	U, Th
14	Salt	13.18	0.14	14.2	0.154	1.6	9.4	11.6	30.2	0.606
	Metal	17.86	6.33	101	0.864	98.4	90.6	89.4		
4	Salt	17.89	0.84	8.8	0.0963	26.5	12.3	16.2	11.8	5.82
	Metal	27.48	1.52	40.8	0.326	73.5	87.7	83.8		
5	Salt	17.41	4.71	33.2	0.0969	96.3	90.0	35.1	9.6	32.5
	Metal	26.12	0.121	2.22	0.120	3.7	9.1	64.9		
6	Salt	17.49	6.96	93.8	0.695	98.6	96.7	74.0	4.1	6.69
	Metal	30.36	0.056	1.84	0.141	1.4	3.3	26.0		
15	Salt	14.21	5.20	60.1	1.44	96.0	55.0	98.0	107	2.41
	Metal	17.06	0.18	40.9	0.0242	4.0	45.0	2.0		
9	Salt	17.13	7.58	43.0	3.40	99.6	98.0	98.8	52.0	1.49
	Metal	25.81	0.02	5.90	0.0278	0.4	2.0	1.2		
8	Salt	15.96	7.72	145	3.04	99.9	97.6	99.2	16.5	1.09
	Metal	26.04	0.007	2.17	0.0142	0.1	2.4	0.8		
10	Salt	17.15	9.34	246	2.987	99.1	99.5	98.7	9.82	2.08
	Metal	25.30	0.058	0.855	0.0283	0.9	0.5	1.3		
11	Salt	17.74	8.40	290	4.35	99.7	90.1	99.3	15.4	0.948
	Metal	25.30	0.014	17.5	0.0162	0.3	9.9	0.7		
7	Salt	18.34	5.86	219	2.58	99.4	94.1	97.9	9.8	1.52
	Metal	23.04	0.03	11.0	0.0447	0.6	5.9	2.1		

*Additional experimental details are given in Table 70, Appendix F.

**See equations 12 and 18, pages 30b and 30c.

D. Macro-scale Selective Separations

The experimental procedure used in this work has been described previously. Three groups of elements were used to evaluate the possibility of selective separations by the addition of controlled amounts of either $ZnCl_2$ or magnesium. These groups are: (1) uranium, thorium and zirconium; (2) zirconium and chromium; and (3) cerium, uranium and zirconium.

The elements to be studied were split into these groups, because of the difficulty in analyzing a single sample for all the various components. Also, while there is considerable interest in the behavior of yttrium, it was not included due to the lack of analytical procedures for low yttrium concentrations. All three sets of elements were used in both oxidation and reduction sequences, at both 500 and 700°C.

In addition to the selective separation experiments, three experiments using only one oxidizable element were performed. The purpose of these experiments was to obtain clear evidence as to the correct oxidation state of the various constituents. The three elements investigated were cerium, thorium and zirconium. While the cerium and thorium experiments were done at 700°C, the zirconium test was run at 500°C to lessen, as much as possible, the amount of distillation of $ZrCl_4$ from the melt. Samples with the notation (M) indicate zinc metal samples.

1. Single component experiments

a. Cerium The experiment numbered as the "1600" series used only cerium as the oxidizable material. Tables 31 and 32 give the pertinent experimental details and results. Using these data, it is possible to make appropriate computations concerning the transfer of the cerium from one phase to another. These calculations include corrections for sampling losses and permit the evaluation of a material balance on both the cerium and the $ZnCl_2$. Figures 12, 13 and 14 present the results of these calculations for the oxidation and reduction sequences of the experiment and the overall molar balance of cerium versus $ZnCl_2$ reacted. In Figure 14, the oxidation state of cerium is clearly indicated as plus 3.

Table 31. Experimental details of the cerium-zinc selective separation experiments at 700°C, "1600" series

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Weight cerium = 6.9138 gms = 0.0493 moles

Weight zinc = 1124 gms = 17.22 moles

Weight salt (KCl-LiCl eutectic) = 987 gms

moles KCl = 7.41 moles moles LiCl = 10.29 moles

Temperature = 698-700°C

Equilibration periods = 1-1/2 hrs. during oxidation
1/2 hr. during reduction

Table 32. Experimental results of the "1600" series experiment, cerium at 700°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% Ce	% Zn	Sample wt.gms
1600(M)	0	-	0.433	-	21.45
1601	0	-	0.0395	0.0041	13.53
1602	3.51	-	0.262	0.0047	12.45
1603(M)	3.51	-	0.256	-	18.01
1604	7.60	-	0.551	0.0055	14.21
1605(M)	7.60	-	0.024	-	23.65
1606	12.30	-	0.600	0.2005	13.34
1607(M)	12.30	-		-	13.38
1608	15.54	-	0.614	0.354	12.16
1609(M)	15.54	-		-	20.62
1610	-	0.73	0.618	0.155	15.15
1611(M)	-	0.73		-	19.94
1612	-	1.52	0.479	0.0076	14.37
1613(M)	-	1.52	0.084	-	9.97
1614	-	2.35	0.178	0.0053	13.45
1615(M)	-	2.35	0.303	-	17.46
1616	-	3.18	0.070	0.0092	12.07
1617(M)	-	3.18	0.4665	-	14.55

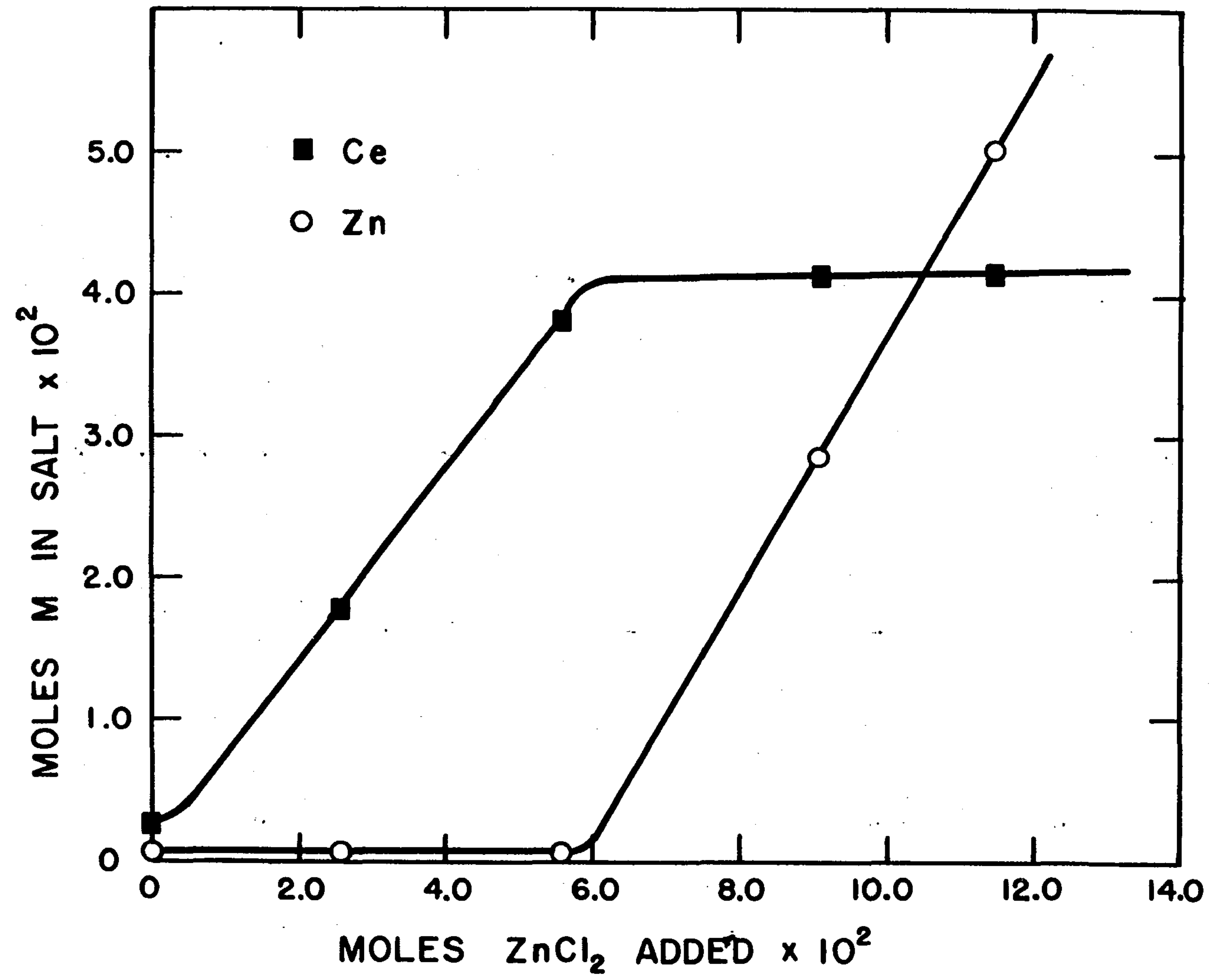

Figure 12. Transfer of cerium from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (cerium, zinc) in salt versus moles $ZnCl_2$ added at 700°C

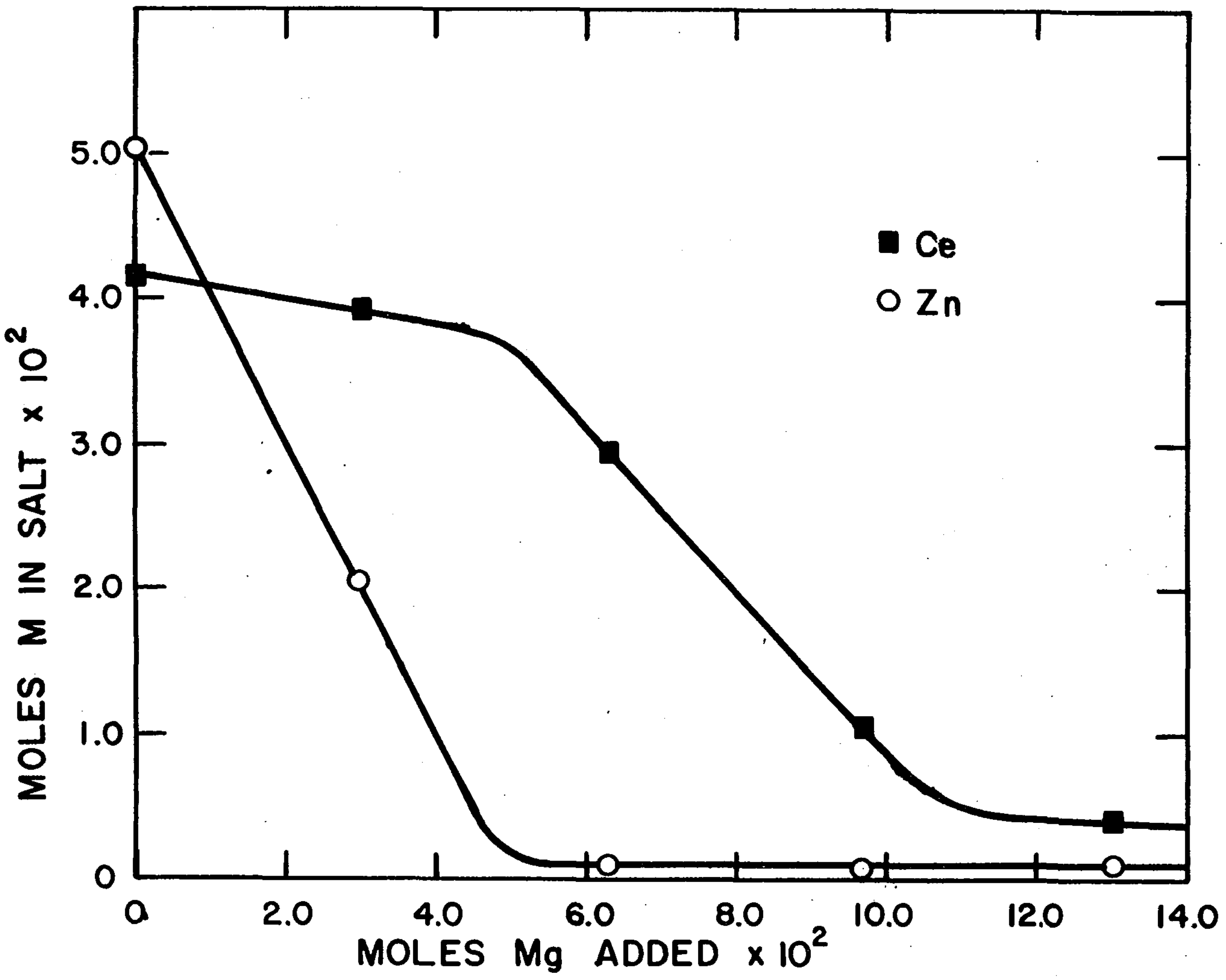

Figure 13. Transfer of cerium from KCl-LiCl eutectic to zinc-rich phase by reduction with magnesium, moles M (cerium, zinc) in salt versus moles magnesium added at 700°C

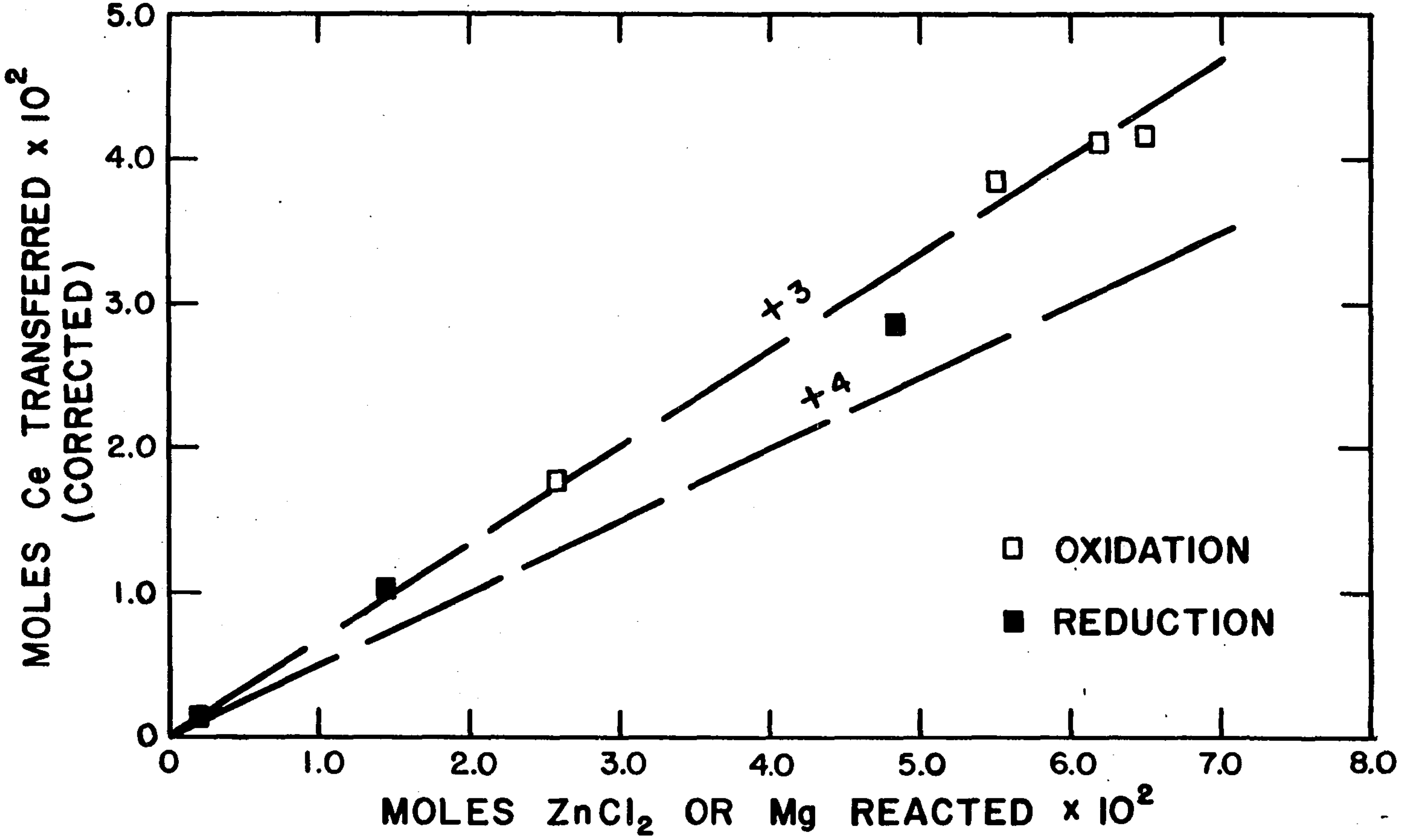

Figure 14. Transfer of cerium between a KCl-LiCl eutectic and zinc-rich phase by oxidation or reduction with $ZnCl_2$ or magnesium, moles cerium transferred versus moles $ZnCl_2$ or magnesium reacted at 700°C

b. Thorium In the "1700" series tests, only thorium was present to be oxidized. The details and results of the experiment are given in Tables 33 and 34; while in Figures 15, 16 and 17, the results of the appropriate computations are graphically presented. For thorium, a plus 3 oxidation state is indicated in Figure 17. This fact confirms the predictions of the thermodynamic data. There was a possibility that excess $ZnCl_2$ might actually cause the further oxidation of plus 3 thorium to a plus 4 state. This situation was not experimentally observed. One data point on Table 34 is apparently in error. It is assumed that this was caused by entrapped zinc.

Table 33. Experimental details of the thorium-zinc selective separation experiment at 700°C, "1700" series

Weight thorium = 6.8817 gms = 0.0296 moles

Weight zinc = 887 gms = 13.59 moles

Weight salt (KCl-LiCl eutectic) = 951 gms

moles KCl = 7.14 moles moles LiCl = 9.89 moles

Temperature = 699°C

Equilibration period = 1 hour during entire exp.

Table 34. Experimental results for the "1700" series experiment, thorium at 700°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% Th	% Zn	Sample wt.gms
1700	0	-	0.0406	0.0034	16.00
1701(M)	0	-	0.58	-	14.03
1702	2.96	-	0.355	0.0150	11.80
1703(M)	2.96	-	0.31	-	15.84
1704	5.84	-	0.650	0.0135	13.98
1705(M)	5.84	-	0.0222	-	22.50
1706	7.14	-	0.645	0.108	13.49
1707(M)	7.14	-	0.0029	-	13.59
1708	8.61	-	0.675	0.21	13.56
1709(M)	8.61	-	0.0023	-	19.22
1710	-	0.42	0.675	0.089	15.27
1711(M)	-	0.42	0.0031	-	9.40
1712	-	0.86	0.40	0.070	11.52
1713(M)	-	0.86	0.225	-	21.16
1714	-	1.65	0.0034	0.012	14.63
1715(M)	-	1.65	0.28	-	16.27
1716	-	2.50	0.0037	0.0082	13.35
1717(M)	-	2.50	0.285	-	16.63

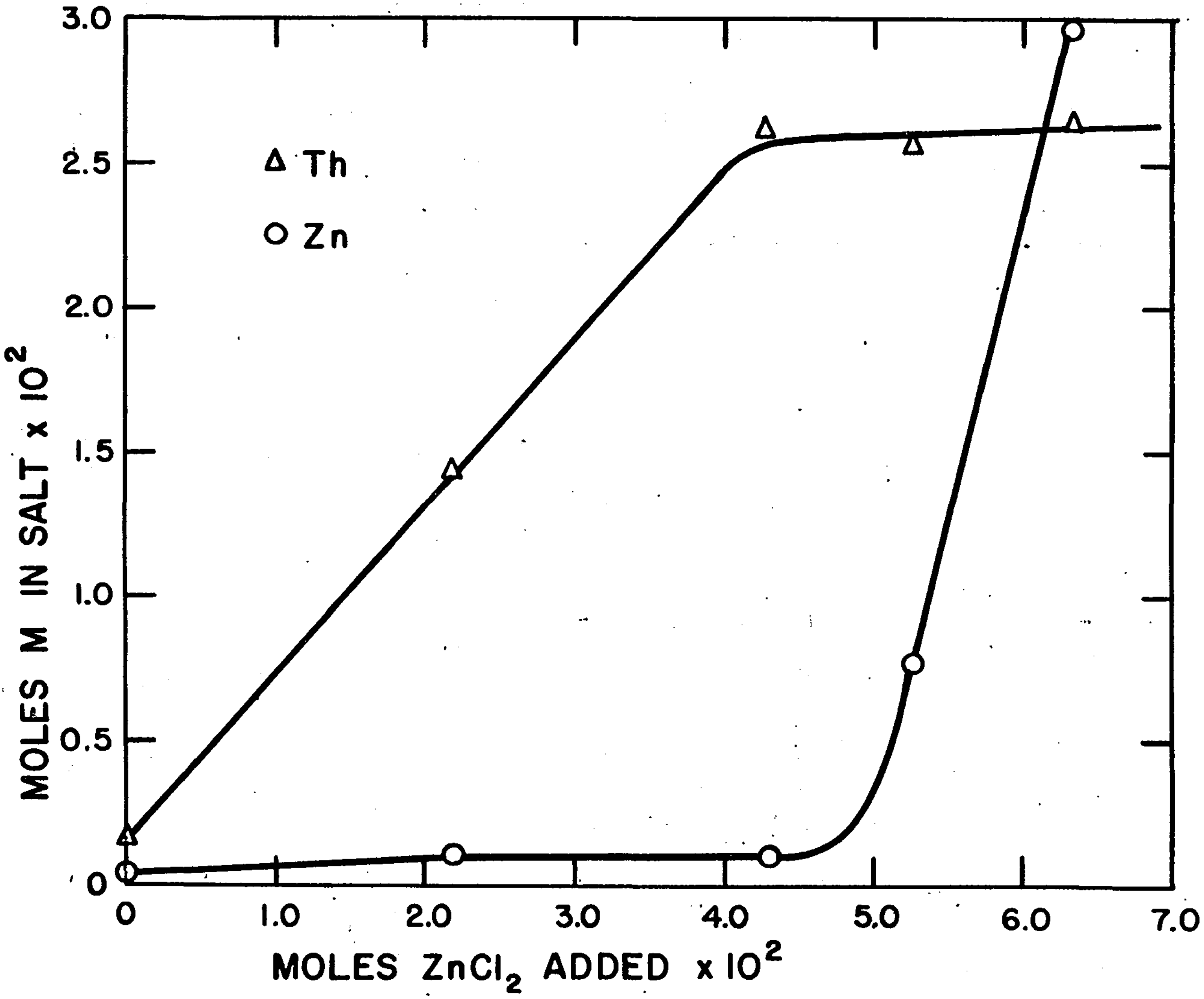

Figure 15. Transfer of thorium from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (thorium, zinc) in salt versus moles $ZnCl_2$ added at 700°C

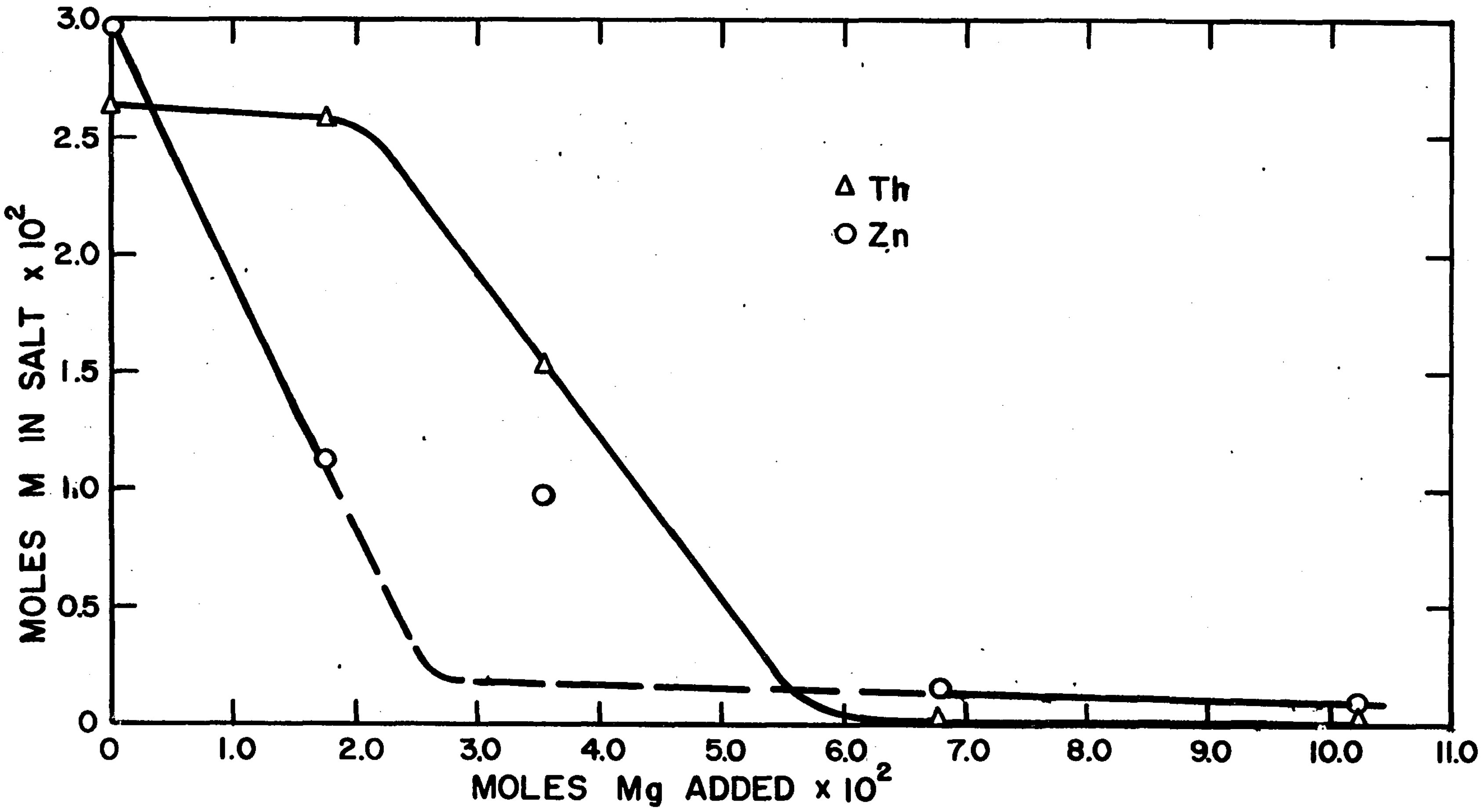

Figure 16. Transfer of thorium from KCl-LiCl eutectic to zinc-rich phase by reduction with magnesium, moles M (thorium, zinc) in salt versus moles magnesium added at 700°C

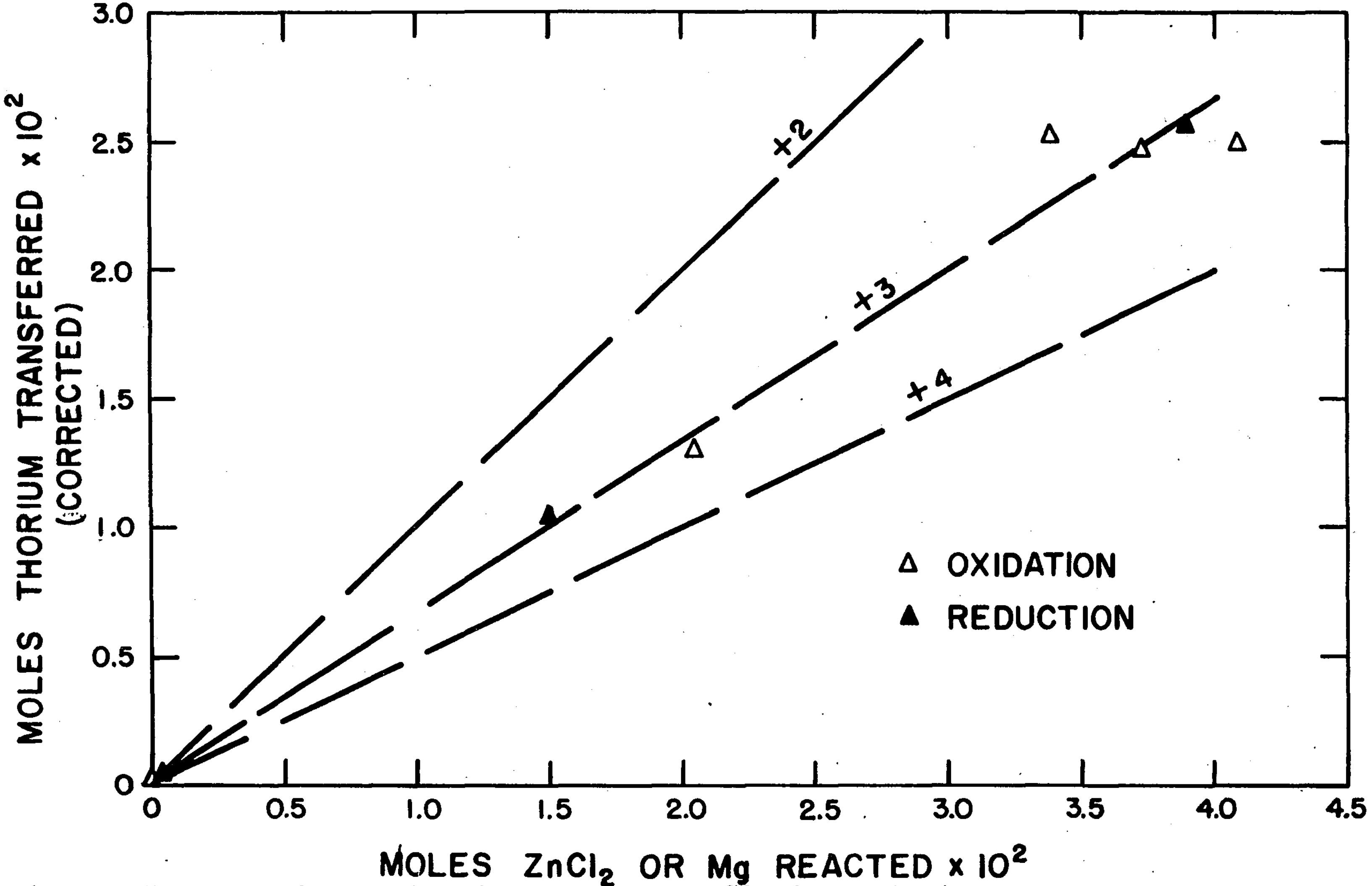

Figure 17. Transfer of thorium between a KCl-LiCl eutectic and zinc-rich phase by oxidation or reduction with $ZnCl_2$ or magnesium, moles thorium transferred versus moles $ZnCl_2$ or magnesium reacted at 700°C

c. Zirconium Considerable doubt as to the actual oxidation state of zirconium has been raised. There is not available in the literature any clear-cut definition of the behavior of zirconium in fused salts in contact with a strong reducing medium such as zinc. Preliminary thermodynamic calculations indicated that under these conditions plus 3 zirconium should be expected. However, these figures had considerable possible error in them and did not include any allowances for complexing reactions. The "2000" series work used only zirconium, and the experiment was done at 500°C, to reduce distillation losses of $ZrCl_4$. The details and results of the experiment are given in Tables 35 and 36, with these data plotted in Figures 18, 19 and 20.

Table 35. Experimental details of the zirconium-zinc selective separation experiment at 500°C, "2000" series

Weight zirconium = 8.8999 gms = 0.0977 moles

Weight zinc = 1026 gms = 15.70 moles

Weight salt (KCl-LiCl eutectic) = 463 gms

moles KCl = 3.48 moles moles LiCl = 4.83 moles

Temperature range = 494-499°C

Equilibration periods = 3-1/2 hrs. during oxidation
1 hr. during reduction

Table 36. Experimental results of the "2000" series experiment, zirconium at 500°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% Zn	% Zr	Sample wt.gms
2000(M)	0	-	-	0.8585 (700°C)	23.66
2001(M)	0	-	-	0.3247	21.38
2002	0	-	0.0685	0.0073	16.44
2003(M)	2.73	-	-	-	-
2004	2.73	-	0.244	0.0424	10.11
2005(M)	5.11	-	-	0.4320	24.00
2006	5.11	-	0.405	0.1088	12.72
2007(M)	8.61	-	-	0.3485	22.35
2008	8.61	-	0.630	0.2210	17.07
2009(M)	11.89	-	-	0.6695	23.62
2010	11.89	-	0.801	0.3415	13.86
2011(M)	15.63	-	-	0.8890	20.53
2012	15.63	-	0.985	0.5285	6.86
2013(M)	19.00	-	-	-	-
2014	19.00	-	1.13	0.769	15.76
2015(M)	22.78	-	-	0.4935	24.06
2016	22.78	-	1.27	0.9430	15.84
2017(M)	-	0.87	-	0.4750	13.47
2018	-	0.87	1.0	0.6790	15.01
2019(M)	-	1.70	-	0.6590	21.15
2020	-	1.70	0.7325	0.3705	14.80
2021(M)	-	2.50	-	0.8125	19.69
2022	-	2.50	0.3805	0.3705	16.82
2023(M)	-	3.37	-	0.6410	17.94
2024	-	3.37	0.0155	0.0034	5.57
2025(M)	-	4.27	-	0.8070	19.20
2026	-	4.27	0.0136	0.0038	14.17

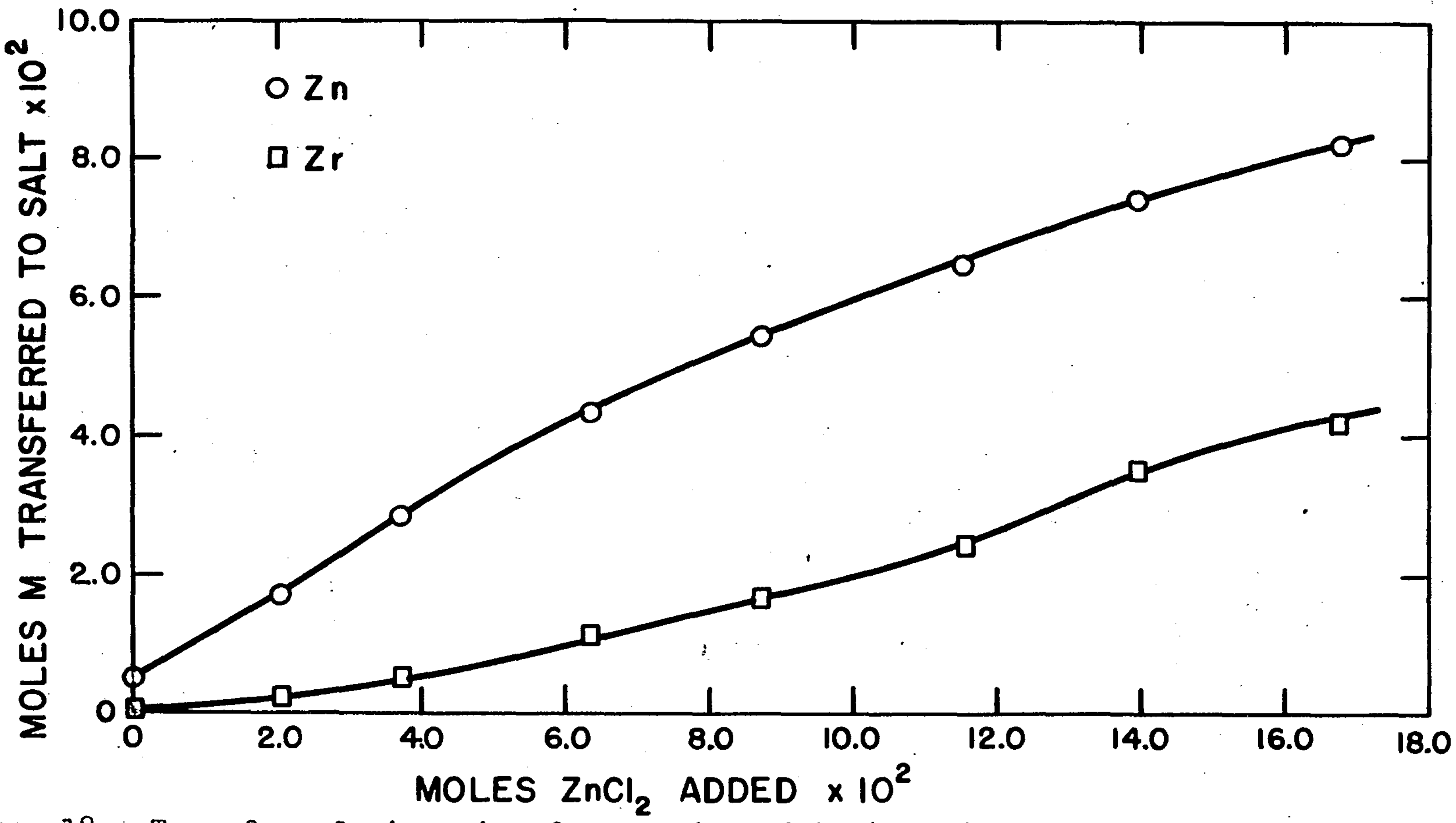

Figure 18. Transfer of zirconium from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (zirconium, zinc) in salt versus moles $ZnCl_2$ added at 500°C

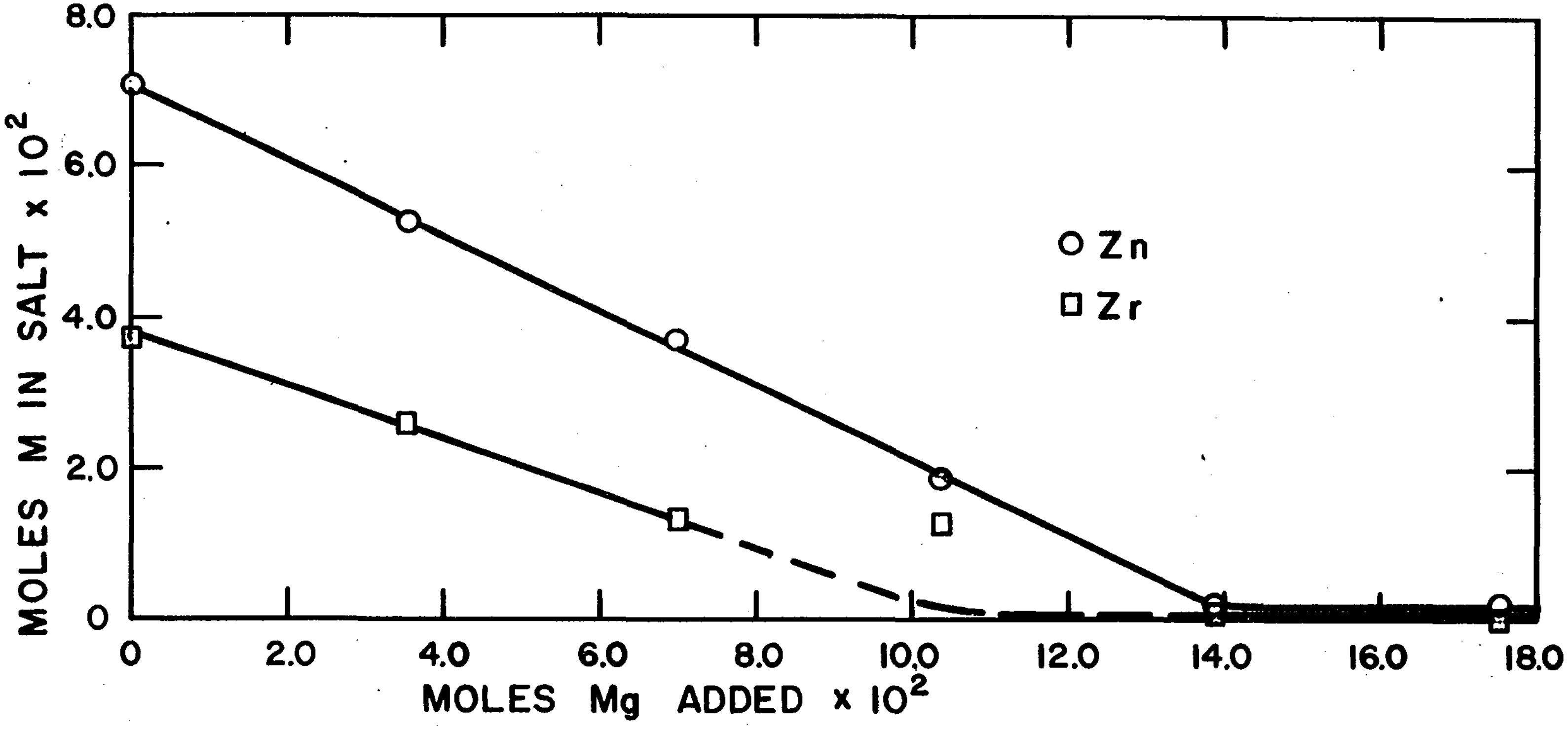

Figure 19. Transfer of zirconium from KCl-LiCl eutectic to zinc-rich phase by reduction with magnesium, moles M (zirconium, zinc) in salt versus moles magnesium added at 500°C

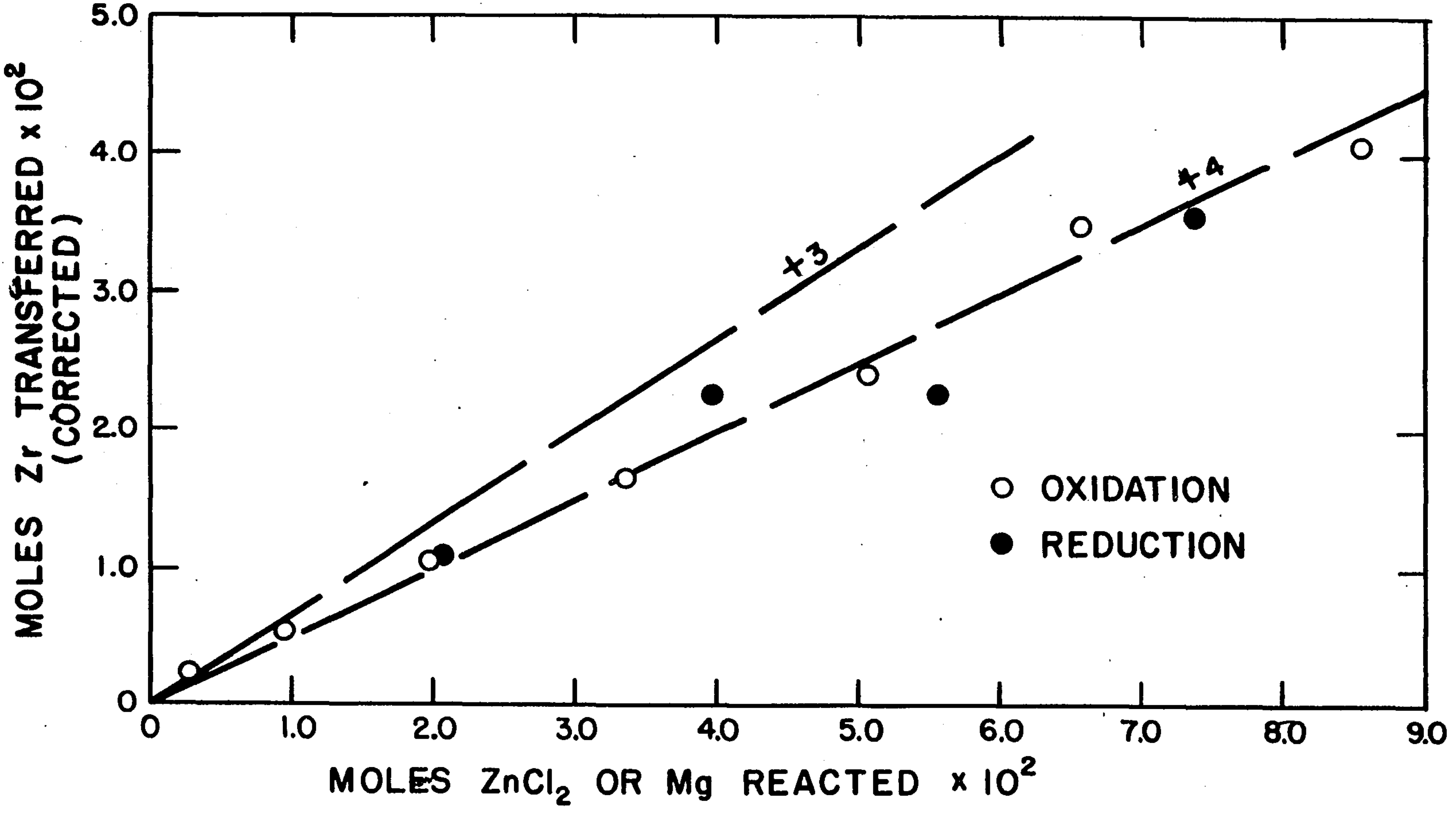

Figure 20. Transfer of zirconium between a KCl-LiCl eutectic and zinc-rich phase by oxidation or reduction with $ZnCl_2$ or magnesium, moles zirconium transferred versus moles $ZnCl_2$ or magnesium reacted at 500°C

For zirconium at 500°C, these plots indicate an oxidation state of plus 4. It should be noted that no distillation of $ZrCl_4$ was observed and that the concentration of zirconium in the zinc phase was at all times in excess of the solubility limit. If distillation of $ZnCl_4$ did occur, this would tend to lower the observed oxidation state from plus 4 to plus 3.

Figure 21 gives a log log plot of $(N_{Zr})_s/(N_{Zr})_{Zn}$ versus $(N_{Zn})_s$. Drawn on the data are lines of slope 1.5 and 2.0. It can be seen that the lower points could be represented by a line of slope 1.5, indicating plus 3 zirconium; while the later points are best represented by a line of slope 2.0. This indicates that there may be an equilibrium between two oxidation states of zirconium, and that both species are present to an appreciable extent. To allow this, on the basis of Figure 20 in which the oxidation state was indicated to be plus 4, some distillation must have occured. Left off of this plot were three data points from the reduction sequence. In two of them, the concentrations were so low as to make the points very suspect; the remaining point was discarded on the basis of Figure 19. The single point for zirconium that lies off the main curve for the zirconium data is that point which was discarded.

2. Uranium, thorium and zirconium separations

The several experiments involving the separation of uranium, thorium and zirconium are listed as the "300", "500",

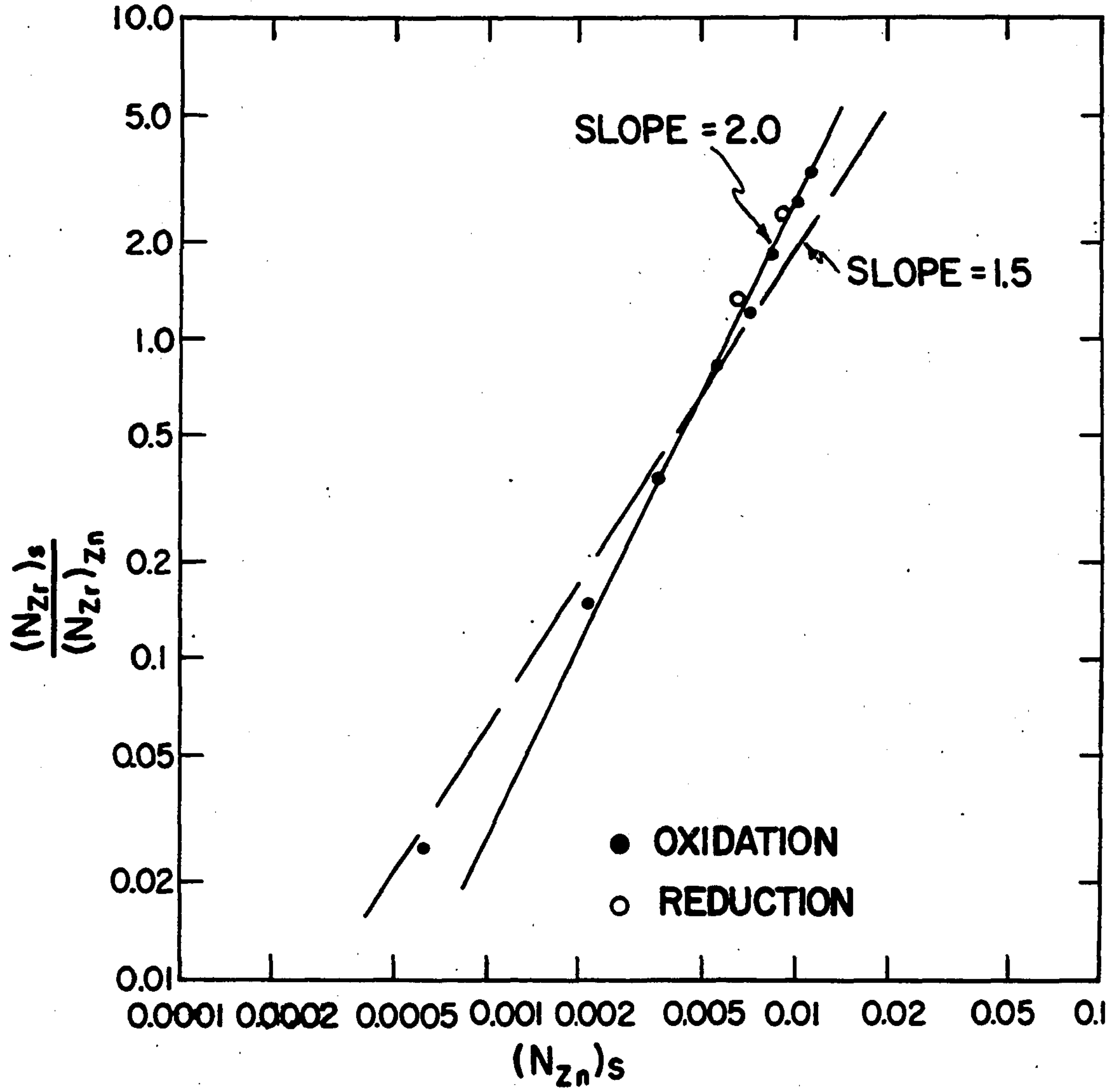

Figure 21. A log log plot of the ratio of molar concentrations of zirconium in KCl-LiCl eutectic and a zinc-rich phase versus molar concentration of zinc in KCl-LiCl eutectic at 500°C

"1000" and "1800" series experiments. The "300" and "1800" experiments were done at 700°C, while the other two were run at 500°. Only the reduction sequence of the "500" series was used due to non-equilibrium conditions existing in the melts during the oxidation sequences. In the "1000" series, the salt resulting from the oxidation sequence was used to investigate the possibility of selective distillation of the various chlorides on a macro scale. Therefore, only the oxidation sequence of that test is available.

Table 37 contains the experimental details of the "300" series experiment. The pertinent experimental data are presented in Table 38. Figures 22 and 23 present the data in a graphical manner for the oxidation and reduction sequences.

Table 37. Experimental details of the "300" series selective separation experiment

---

Weight uranium - 35.6616 gms = 0.1498 moles

Weight thorium - 23.3705 gms = 0.1009 moles

Weight zirconium - 9.7172 gms = 0.1066 moles

Weight salt (LiCl-KCl eutectic) - 805 gms (estimated at start)

moles KCl = 6.05 moles LiCl $\doteq$ 8.36

Weight zinc - 1624 gms = 24.85 moles

Temperature - from 692°C to 714°C

Table 38. Experimental results for the "300" series experiment, uranium, thorium and zirconium at 700°C

Sample	Gms $ZnCl_2$ added	Gms Mg added	% U	% Th	% Zr	% Zn	Sample wt. gms
351	0	-	0.0082	0.02	0.001	0.0022	10.34
352(M)	7.39	-	0.115	0.15	0.001	-	6.08
353	13.90	-	1.90	-	0.0034	-	3.63
354	21.13	-	2.68	0.427	0.0075	-	4.15
355	29.37	-	3.405	0.7835	0.0106	-	2.41
358	34.20	-	-	1.03	0.0063	-	5.90
360	40.59	-	3.81	1.45	0.0108	-	5.35
361	47.08	-	4.05	1.605	0.0194	0.038	7.09
362	55.08	-	4.49	2.075	0.0468	0.196	7.35
363	60.38	-	4.085	2.335	0.0542	0.167	8.49
365	65.66	-	4.26	2.365	0.0562	-	5.42
366	72.11	-	-	2.495	0.15	-	6.04
367	77.32	-	4.25	2.54	0.35	-	5.09
368	82.75	-	-	2.60	0.42	1.10	5.71
372	88.56	-	-	2.635	0.755	1.27	5.59
373	95.92	-	-	-	1.015	1.68	5.72
374	105.80	-	4.245	2.635	1.08	1.96	5.79
376	105.80	0	4.185	2.70	0.97	1.68	7.59
378	-	1.0	4.225	-	0.795	1.225	4.96
379	-	3.01	-	2.67	0.47	0.79	4.94
380	-	5.04	4.25	2.70	0.335	-	7.07
381	-	7.02	4.22	2.07	0.0218	-	3.99
382	-	9.02	3.875	0.93	0.0137	-	4.00
383	-	11.03	2.93	0.443	0.008	-	7.08
385	-	13.03	1.555	-	0.0028	-	6.18
386	-	15.02	0.0168	0.02	-	-	5.68
387	-	17.04	0.0038	-	0.0005	-	4.87
388	-	19.02	0.0028	-	-	-	4.55

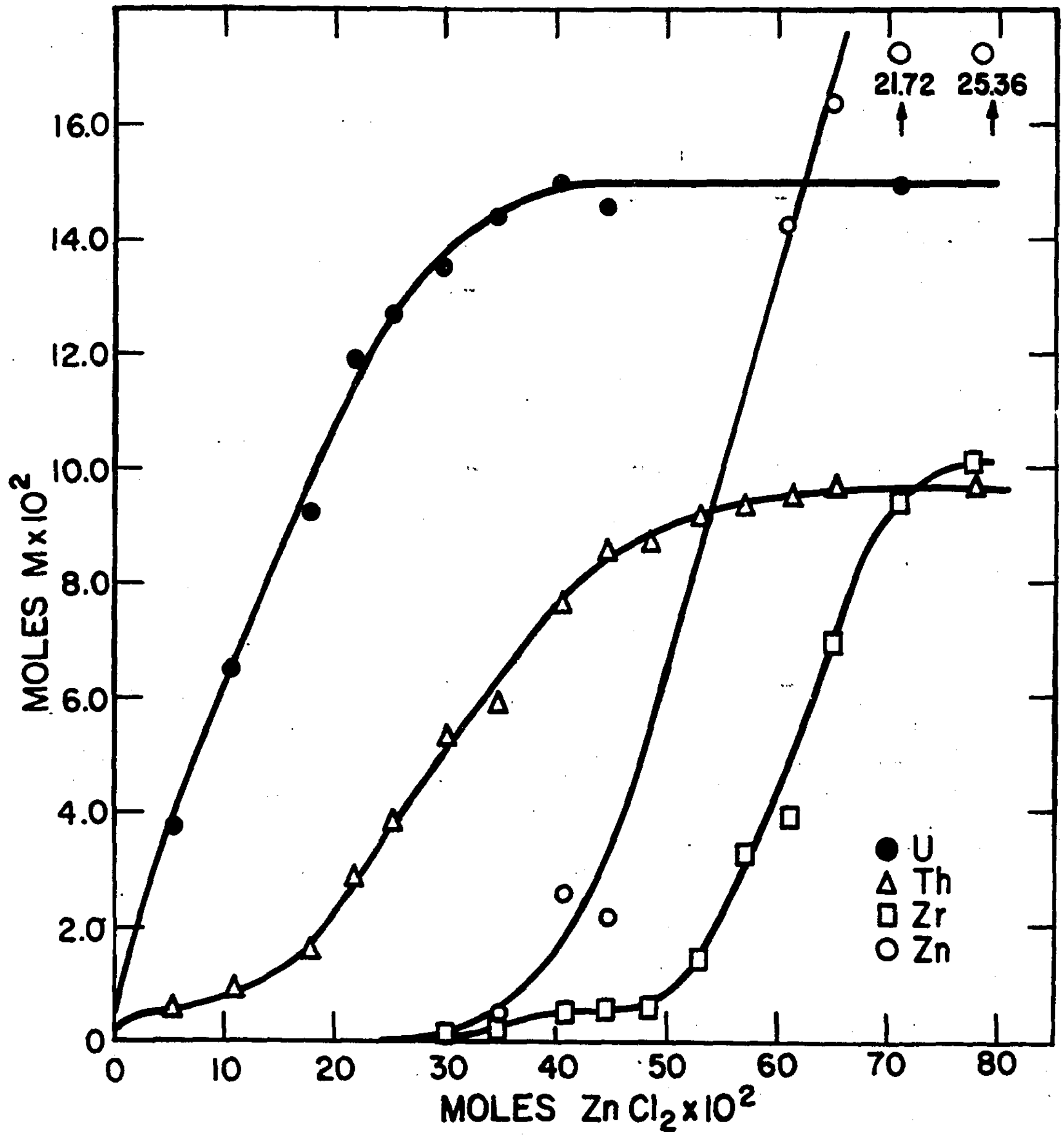

Figure 22. Transfer of solutes (uranium, thorium, zirconium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (uranium, thorium, zirconium) in salt versus moles $ZnCl_2$ added at 700°C

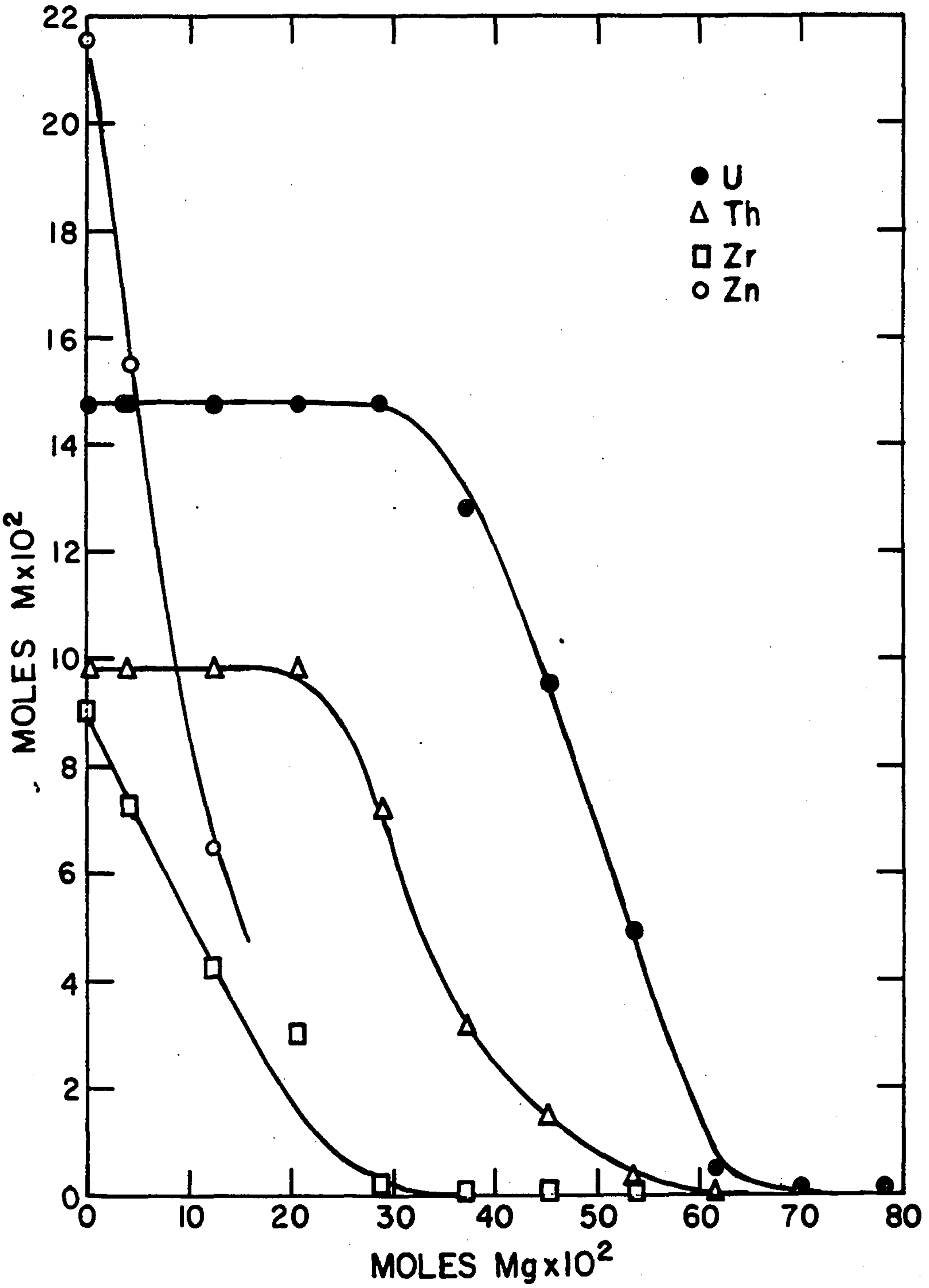

Figure 23. Transfer of solutes (uranium, thorium, zirconium) from KCl-LiCl eutectic to zinc-rich phase by reduction with magnesium, moles M (uranium, thorium, zirconium) in salt versus moles magnesium added at 700°C

Several conclusions concerning the experiment may be drawn from Figures 22 and 23: (1) the order of oxidation is uranium, thorium and zirconium, while this order is reversed, zirconium, thorium and uranium, during the reduction cycle; (2) excess $ZnCl_2$ is required to chlorinate zirconium (as seen in "2000"); (3) a good separation between uranium and zirconium or thorium and zirconium is possible; and (4) a clean-cut separation of uranium and thorium does not seem possible in a single equilibration. None of these conclusions are at variance with thermodynamical predictions, although somewhat better separations were hoped for from the thermodynamic calculations.

In Table 39, the analytical results for samples taken from the zinc phase are given. Of most significance are samples 375 and 377, which indicate the lowest concentration levels which can be reached upon the addition of excess $ZnCl_2$. These concentrations represent approximately 0.4, 4.3 and 10.3 per cent of the total uranium, thorium and zirconium, respectively. The low residual content for uranium indicates that process losses for the uranium will probably be quite small.

In the "1800" series, uranium and thorium were used as the oxidants at 700°C. The previous work using these elements at 700° was not completely satisfactory due to the complications added by the presence of zirconium. The experimental

Table 39. Analytical results for uranium, thorium and zirconium in samples taken from the zinc phase of the "300" series experiment

Sample	% U	% Th	% Zr
350	1.1165	0.40	0.685
357	0.510	0.42	0.655
364	0.0305	0.0490	0.555
361	0.0215	0.0330	0.275
375	0.0157	0.0600	0.0815
377	0.0079	0.0600	0.0520
384	0.35	0.38	0.23
389	0.88	0.33	0.37

details and results are given in Tables 40 and 41. The data are plotted in Figures 24, 25 and 26. Figures 24 and 25 again show that, while a partial separation of uranium and thorium is feasible, there exists a certain degree of co-transfer of the elements. Figure 26 shows the transfer of uranium and thorium as a function of $ZnCl_2$ reacted. It is indicated that both uranium and thorium are in the plus 3 oxidation state, although what might be a shift toward plus 4 is observed. This shift could be caused by thorium being oxidized to plus 4. However, behavior of this nature was not observed when thorium was the only element being studied, see

Figure 17. In Figure 27 a log log plot of $(N_U)_s/(N_U)_{Zn}$ versus $(N_{Th})_s/(N_{Th})_{Zn}$ shows a slope of 1.0, indicating that both uranium and thorium are present in the same oxidation state, although a line of slope 3/4 can also be drawn to represent the data. A slope of 3/4 would indicate plus 4 for thorium and plus 3 for uranium.

Table 40. Experimental details of the uranium-thorium selective separation experiment at 700°C, "1800" series

---

Weight uranium = 10.8887 gms = 0.0466 moles

Weight thorium = 10.3037 gms = 0.0444 moles

Weight zinc = 1059 gms = 16.21 moles

Weight salt (KCl-LiCl eutectic) = 995 gms

moles KCl = 7.46 moles moles LiCl = 10.38 moles

Temperature range = 696-704°C

Equilibration periods = 1-3/4 - 5-3/4 hrs. during oxidation
1 hr. during reduction

Table 41. Experimental results of the "1800" series experiment, uranium and thorium at 700°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% U	% Th	% Zn	Sample wt.gms
1800(M)	0	-	0.61	0.8555	-	20.67
1801	0	-	0.02	0.0138	-	14.42
1802	3.01	-	0.35	0.0445	0.011	11.88
1803	4.99	-	0.54	0.0797	0.0145	14.29
1804	7.06	-	0.72	0.135	0.017	13.93
1805	12.54	-	0.955	0.43	0.0125	10.47
1806	16.01	-	1.03	0.685	-	13.87
1807	20.47	-	1.07	0.835	0.145	12.06
1808(M)	20.47	-	-	0.0024	-	14.29
1809	-	0.82	1.025	0.70	-	14.48
1810	-	1.72	0.88	0.35	-	14.90
1811	-	2.59	0.545	0.0716	-	14.99
1812	-	3.42	0.01	0.0125	0.0023	13.96

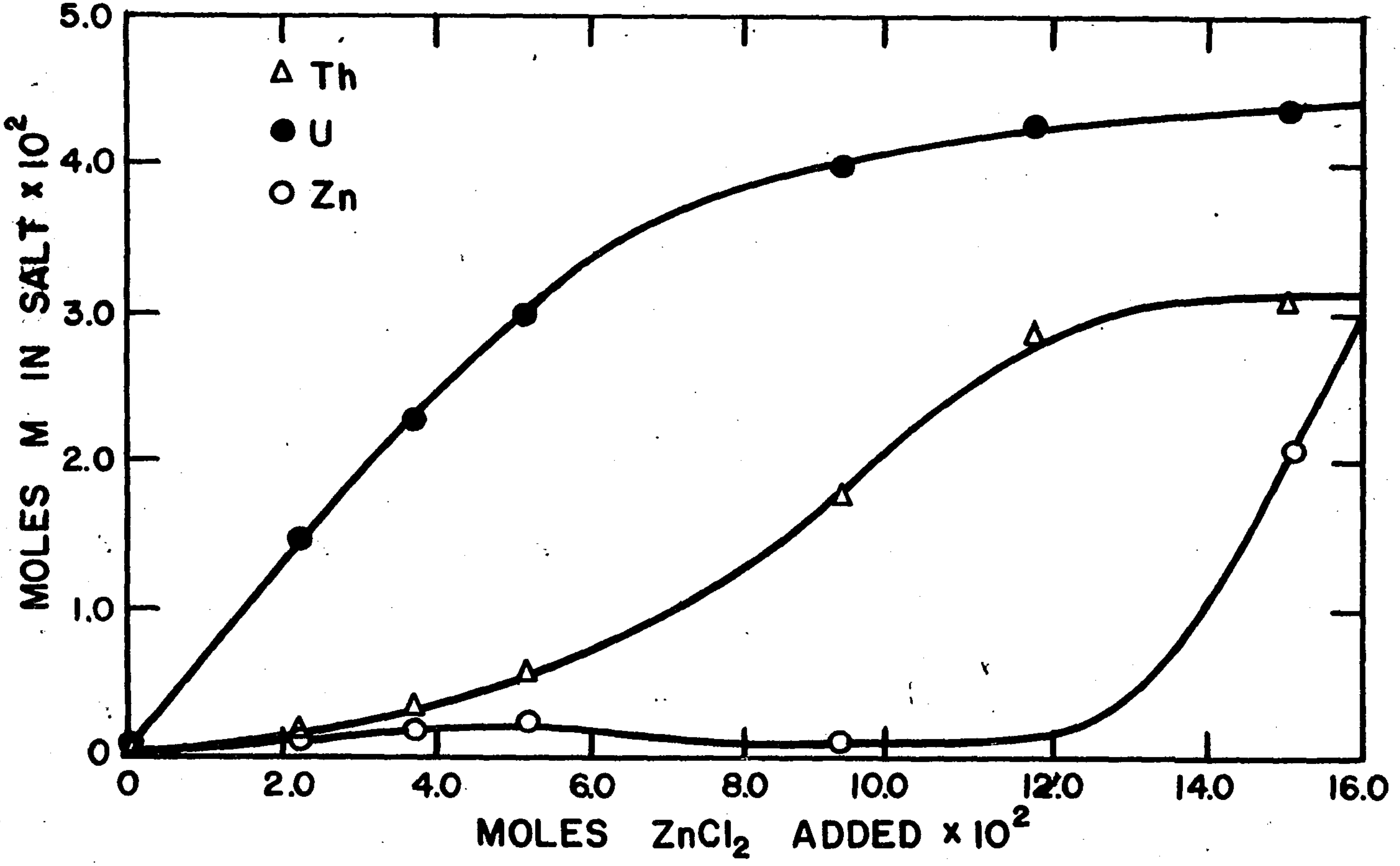

Figure 24. Transfer of solutes (uranium, thorium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (uranium, thorium) in salt versus moles $ZnCl_2$ added at 700°C

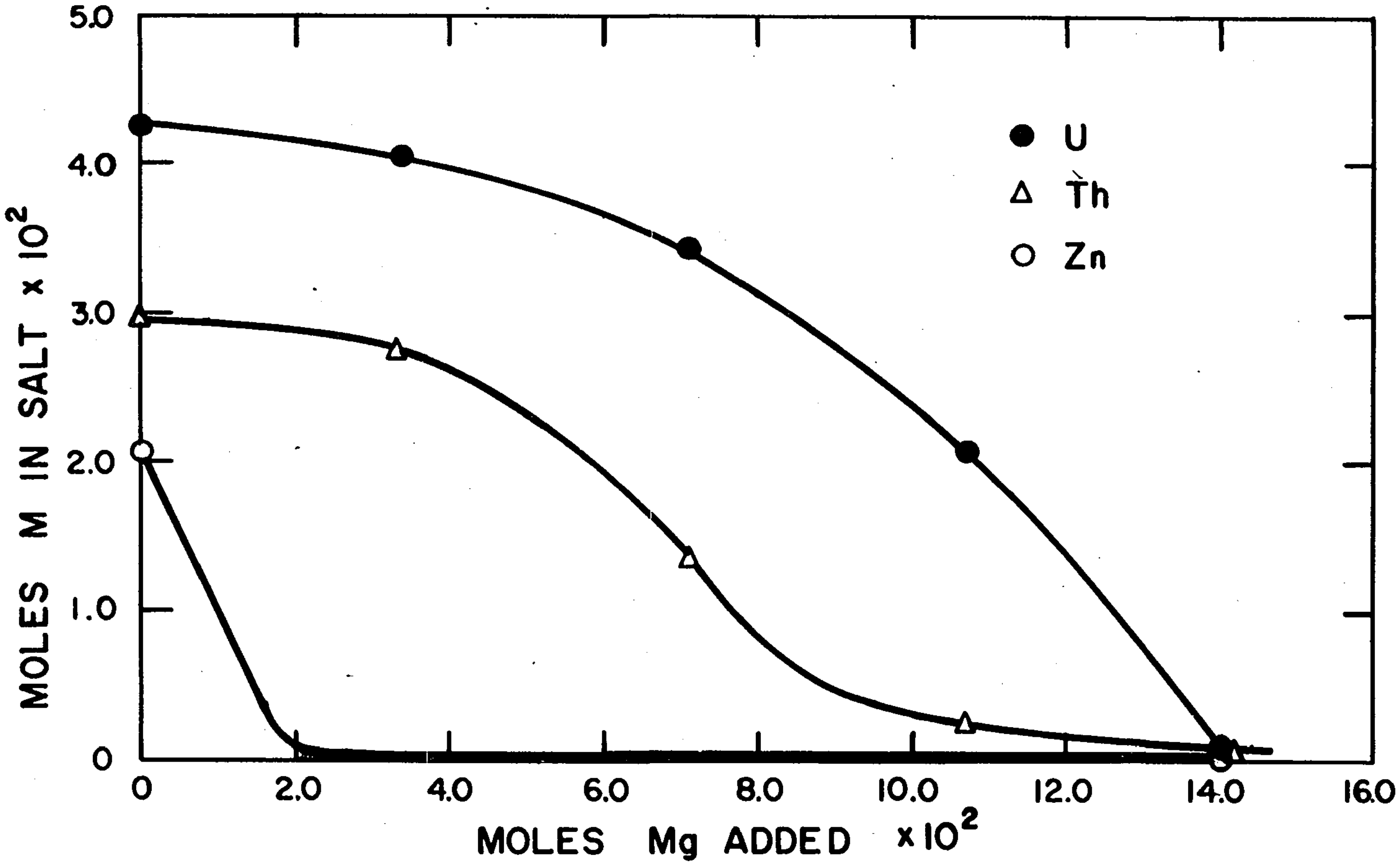

Figure 25. Transfer of solutes (uranium, thorium) from KCl-LiCl eutectic to zinc-rich phase by reduction with magnesium, moles M (uranium, thorium) in salt versus moles magnesium added at 700°C

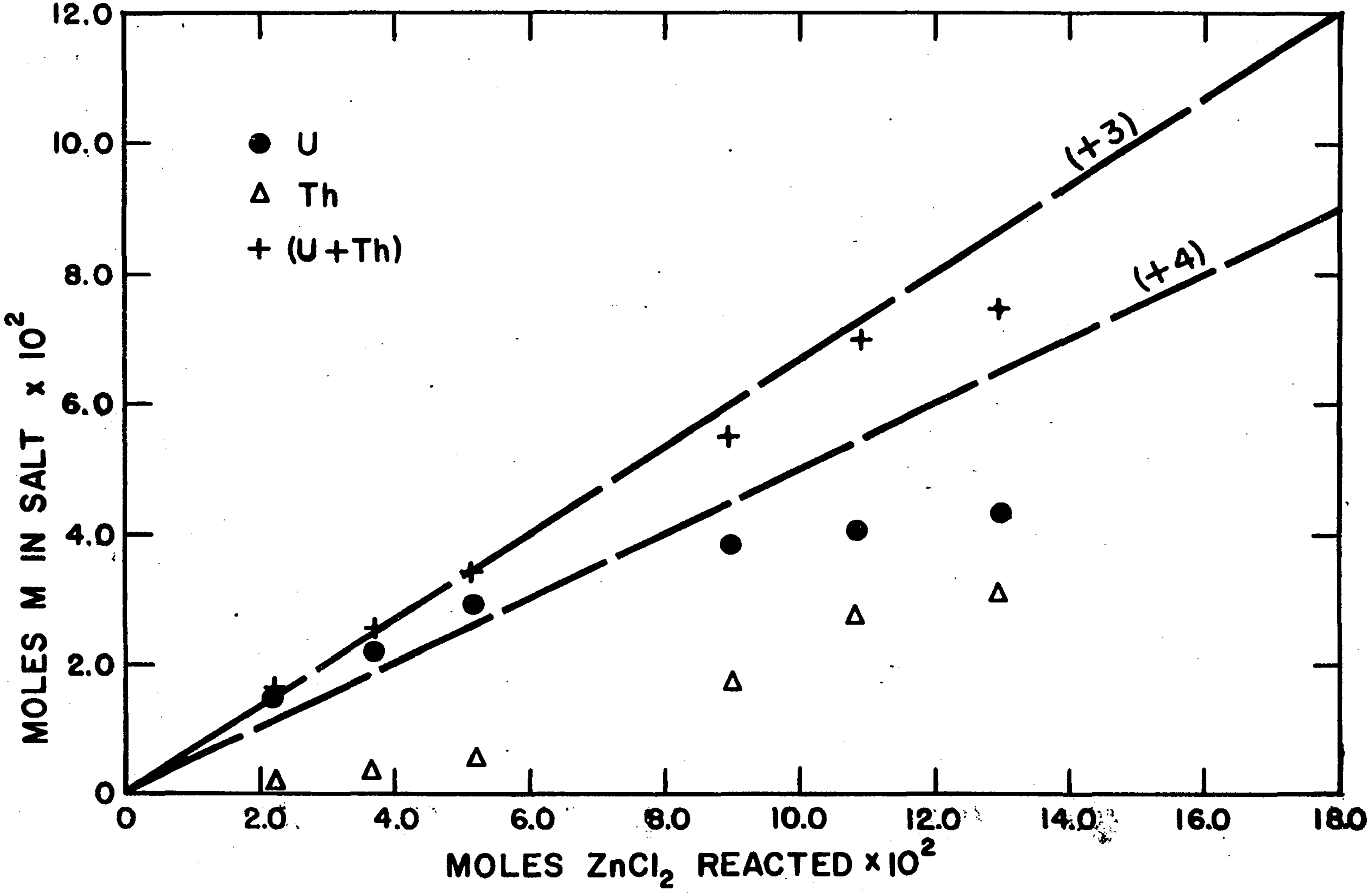

Figure 26. Transfer of uranium and thorium to a KCl-LiCl eutectic from a zinc-rich phase by oxidation with $ZnCl_2$, moles M (uranium, thorium) in salt versus moles $ZnCl_2$ reacted at 700°C

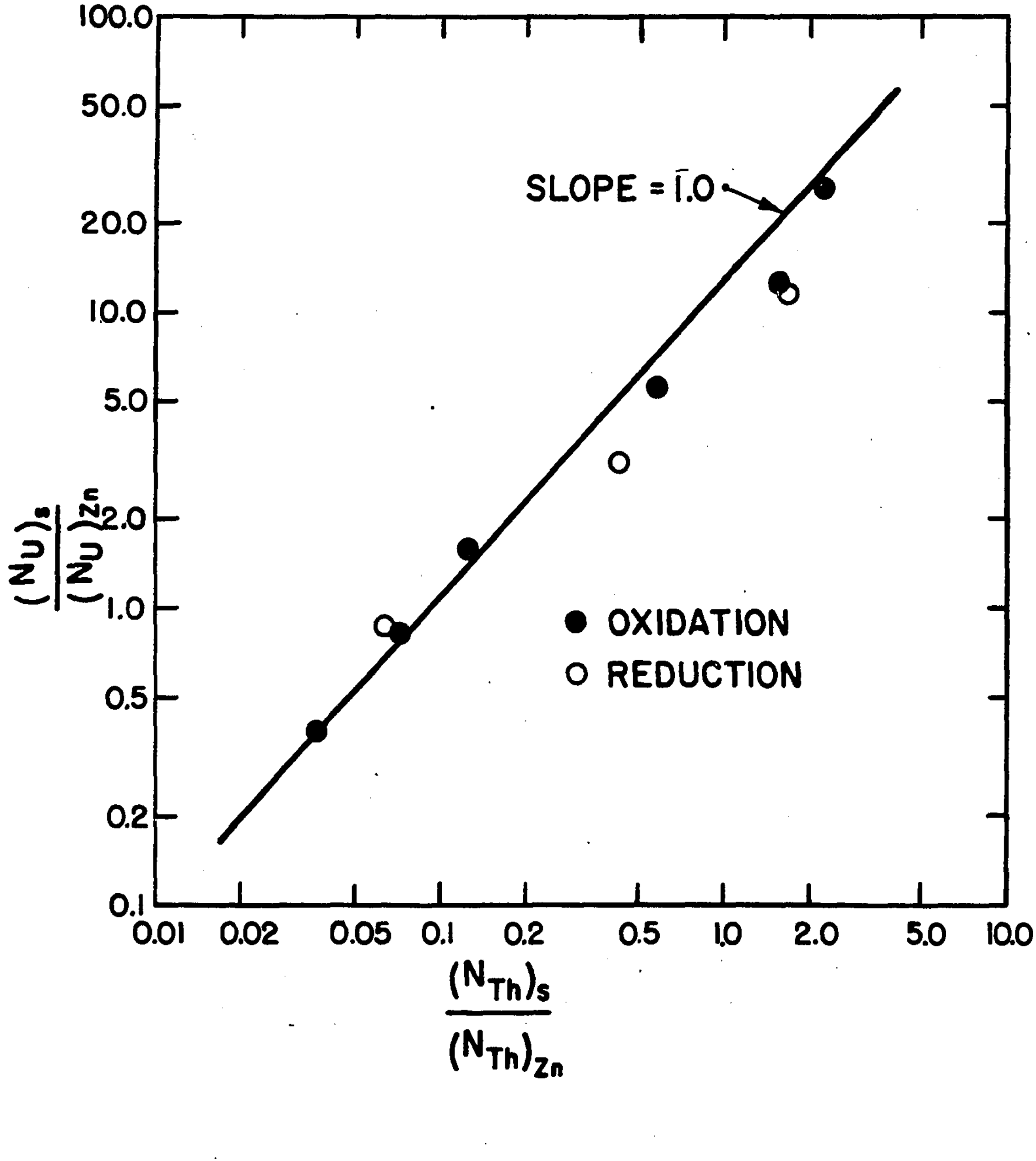

Figure 27. A log log plot of the ratio of molar concentrations of uranium in KCl-LiCl eutectic and a zinc-rich phase versus ratio of molar concentration of thorium in KCl-LiCl eutectic and a zinc-rich phase at 700°C

Table 42 tabulates the experimental details of the "1000" series experiment which was concerned with the oxidation of uranium, thorium and zirconium at 500°C. The data from this experiment are listed in Table 43 and presented graphically in Figure 28. The reduction of the same constituents was performed in a similar experiment, the "500" series, also at 500°C. The details and data for this experiment are presented in Tables 44 and 45, with Figure 29 giving the data as a series of curves.

Comparison of Figures 22 and 23 or 24 and 25 with 28 and 29 illustrates the fact that a better separation of uranium from thorium is possible at 700°C than at 500°C. This fact agrees very well with the predictions made by the thermodynamic calculations.

The data given in Table 46 indicate that the residual concentrations of the oxidizable constituents in the zinc phase can be reduced to very low levels. The uranium remaining in the zinc represents, as an average, 0.71 per cent of the total uranium in the various experiments. For thorium, the value of 0.53 per cent and for zirconium, values of 22.8 per cent at 700°C and 2.24 and 7.67 per cent at 500°C were obtained. These values compare with values of 0.4, 4.3 and 10.3 per cent obtained for uranium, thorium and zirconium in a similar experiment at 700°C. These data again indicate that process losses of uranium and thorium will

Table 42. Experimental details of the "1000" series selective separation experiment, oxidation sequence only

---

Weight uranium = 35.5700 gms = 0.1494 moles

Weight thorium = 24.1162 gms = 0.1039 moles

Weight zirconium = 10.1429 gms = 0.1112 moles

Weight salt (KCl-LiCl eutectic) = 636 gms

moles KCl = 4.77 moles   moles LiCl = 6.60 moles

Weight zinc = 1504 = 23.03 moles

Temperature range = 488-516°C

Equilibration period = 3-3/4 hrs. during the oxidation cycle

Table 43. Experimental results for the "1000" series experiment, uranium, thorium and zirconium at 500°C, oxidation sequence only

Sample no.	Gms $ZnCl_2$ added	% U	% Th	% Zr	% Zn	Sample wt.gms
1000(M)	0	2.95	1.84	1.75	-	20.01
1001	0	0.02	0.0215	0.0006	0.0	17.03
1002	9.18	0.73	0.55	-	-	16.63
1003	17.40	1.53	1.145	0.07	0.121	14.72
1004	27.32	2.705	1.915	-	-	16.31
1005	36.95	3.455	2.37	0.092	0.155	16.39
1006	47.17	3.935	2.715	0.333	0.325	15.90

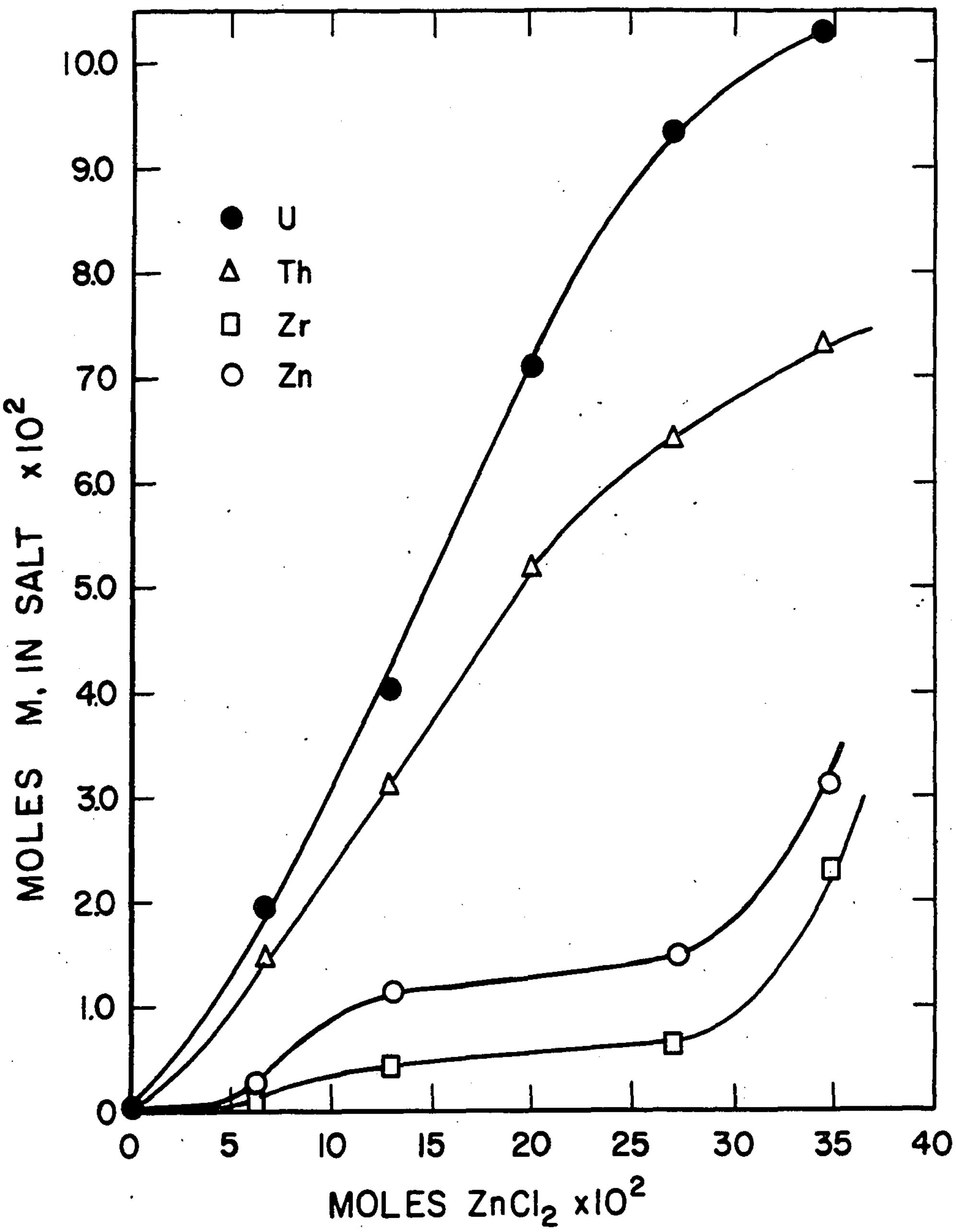

Figure 28. Transfer of solutes (uranium, thorium, zirconium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (uranium, thorium, zirconium) in salt versus moles $ZnCl_2$ added at 700°C

Table 44. Experimental details of the "500" series selective separation experiment, reduction sequence only

Weight uranium = 34.8940 gms = 0.1467 moles

Weight thorium = 24.5144 gms = 0.1057 moles

Weight zirconium = 10.6119 gms - 0.1151 moles

Weight salt (KCl-LiCl eutectic) = 900 gms (calculated)

moles KCl = 6.76 moles moles LiCl = 9.34 moles

Weight zinc = 910 gms (calculated) = 13.91 moles

Temperature range = 480-525°C

Equilibration period = 1 hr. during reduction cycle

Table 45. Experimental results for the "500" series experiment, uranium, thorium and zirconium at 500°C, reduction sequence only

Sample no.	Gms Mg added	% U	% Th	% Zr	% Zn	Sample wt.gms
516	0	3.22	2.34	1.23	2.09	8.50
517(M)	0	0.0405	0.022	0.0871	-	12.85
518	2.10	3.43	2.39	1.04	1.555	11.08
519	4.60	-	-	0.687	0.77	9.51
520	7.10	-	-	0.154	0.37	8.14
521	9.31	3.19	2.17	0.0279	0.009	7.30
522	11.62	2.44	1.365	-	-	7.84
524	13.26	1.83	0.34	-	-	5.99
526	15.62	0.745	-	-	-	11.16
527	17.32	0.0051	0.0192	0.0068	0.01	8.89
528	19.68	0.0062	0.0187	0.0063	-	7.45
529	19.68	2.62	1.235	1.45	-	13.79

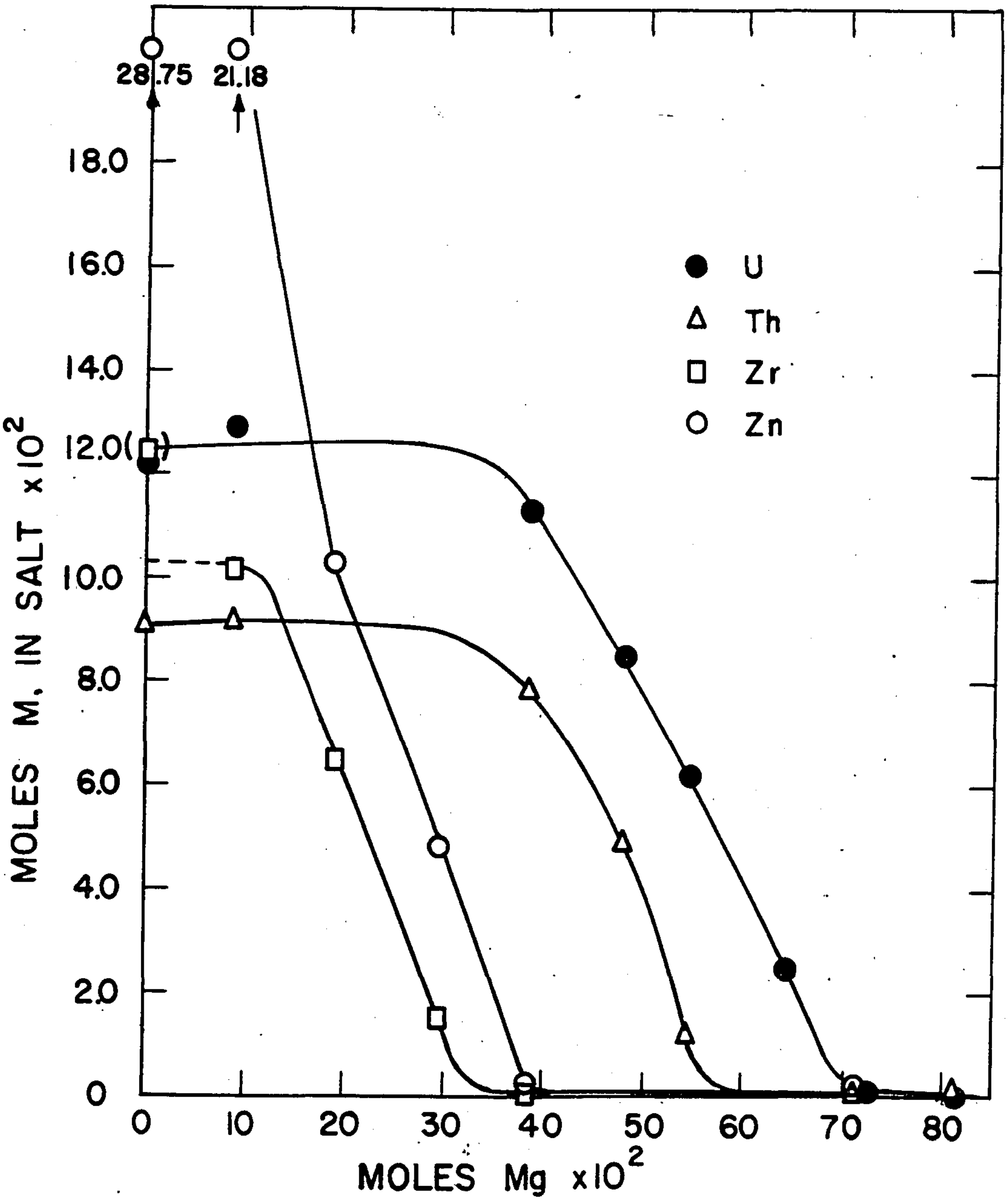

Figure 29. Transfer of solutes (uranium, thorium, zirconium) from a KCl-LiCl eutectic to a zinc-rich phase by reduction with magnesium, moles M (uranium, thorium, zirconium) in salt versus moles magnesium added at 500°C

Table 46. Data and results for samples of the zinc phases from experiments "400, 500 and 1000", after the addition of an excess of $ZnCl_2$

Sample no.	Temp. (°C)	% Excess $ZnCl_2$	w/o U	w/o Th	w/o Zr
413	700	26.6	0.0229	0.0110	0.236
1014	500	36.4	0.01	0.006	0.016
517	500	24.0	0.041	0.022	0.087

probably be very low in this step of the process. Further, the effect of adding excess $ZnCl_2$ is illustrated by the fact that the residual amounts of uranium and thorium are cut in half in sample 1014 versus sample 517, for 36.4 versus 24.0 per cent excess $ZnCl_2$. The residual concentrations of uranium and thorium agree fairly well with the concentrations observed in the metal phases of some of the micro-scale experiments; for examples, see Tables 12, 16, 17, 18 and 30. The presence of a large excess of zinc, approximately 6 to 9 per cent, in the latter cases apparently does not result in much further reduction of the uranium and thorium concentrations. This observation is not in agreement with the behavior predicted by thermodynamic considerations. It is possible that the assumptions made in such predictions are not valid at very low concentrations in the zinc. The behavior of zirconium cannot be compared in a similar manner because of the different experimental conditions used.

3. Zirconium and chromium separations

The next series of experiments utilized zirconium and chromium as the oxidizable materials at 700 and 500°C. Tables 47 and 48, with Figures 30 and 31, present the data for the experiment at 700°C; while Tables 49 and 50 with Figures 32 and 33 present similar data for work at 500°C. These two sets of experiments are listed as the "600" and "700" series. Comparison of Figures 30 and 32 indicate that it is highly probable that non-equilibrium conditions existed during the initial portion of the oxidation sequence of the "700" series experiment.

Examination and comparison of these data show that an excess of $ZnCl_2$ is necessary to cause the transfer of either zirconium or chromium into a KCl-LiCl salt phase. Further, it is indicated that the oxidation state of zirconium under these conditions is plus 4. No coloration of the salt was observed, indicating the absence of $ZrCl_2$ which is black. A gradual transfer of chromium is observed upon the addition of $ZnCl_2$, while the zirconium concentration apparently levels off appreciably as distillation of $ZrCl_4$ occurs, see Section E.

In Figure 34, a log log plot of $(N_{Cr})_s/(N_{Cr})_{Zn}$ versus $(N_{Zn})_s$ is given, based on the data from the "600" series experiment. The slope of the best line through these data is seen to be 1.0, giving an oxidation state of plus 2 for chromium, if plus 2 is accepted for zinc.

Table 47. Experimental details of the "600" series selective separation experiment

---

Weight zirconium = 13.3059 gms = 0.1459 moles

Weight chromium = 11.4592 gms = 0.2135 moles

Weight salt (KCl-LiCl eutectic = 837 gms

moles KCl = 6.28 moles   moles LiCl = 8.68 moles

Weight zinc = 805 gms = 12.32 moles

Temperature range 687-700°C

Equilibration periods - 1/2 hr. during oxidation and reduction

Table 48. Experimental results for the "600" series experiment, zirconium and chromium at 700°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% Zr	% Cr	% Zn	Sample wt.gms
601	-	-	0.0004	0.0022	-	11.54
602(M)	-	-	1.415	1.20	-	15.14
603	8.67	-	0.117	0.0169	0.293	8.30
604	17.44	-	0.260	0.0307	0.436	10.97
605	24.21	-	0.419	0.0417	0.5735	5.99
606	31.03	-	0.596	0.0522	0.714	12.20
607	39.11	-	0.661	0.0671	0.90	11.82
608	45.68	-	-	0.0816	1.06	11.58
609	52.85	-	0.966	0.1004	1.311	8.21
610	66.23	-	-	0.1350	1.74	8.88
611	80.22	-	1.02	0.1768	2.305	8.77
612(M)	80.22	-	0.0859	1.04	-	26.92
613	-	3.28	0.883	0.1259	1.48	8.80
614	-	6.17	0.6225	0.0795	0.926	9.44
615	-	8.18	0.405	0.0501	0.5775	7.98
616	-	10.16	0.166	0.0275	-	8.70
617	-	12.15	0.0074	0.025	-	10.75
618	-	14.10	0.0036	0.0008	0.0121	11.68
619(M)	-	14.10	0.831	1.14	-	24.67

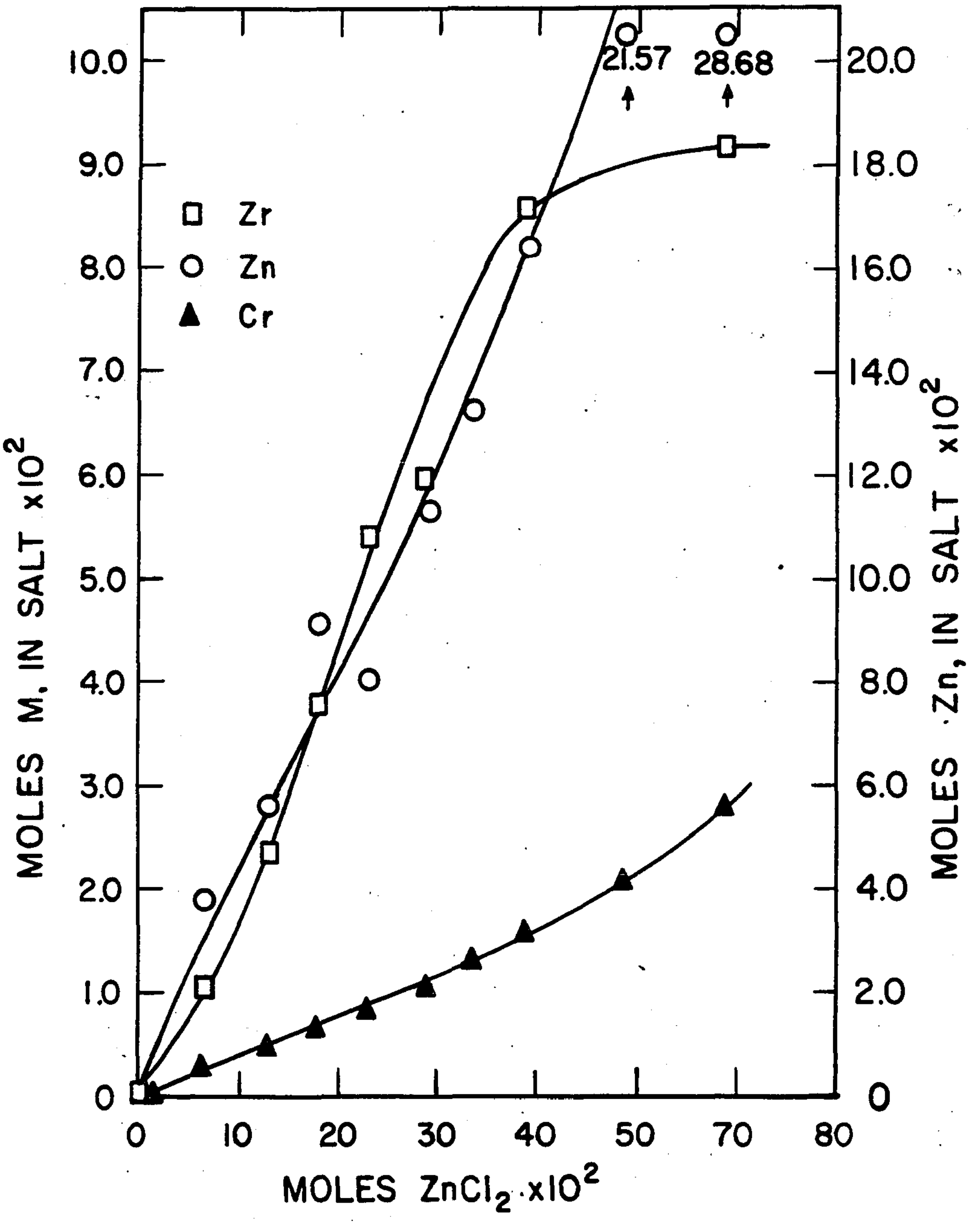

Figure 30. Transfer of solutes (zirconium, chromium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (zirconium, chromium) in salt versus moles $ZnCl_2$ added at 700°C

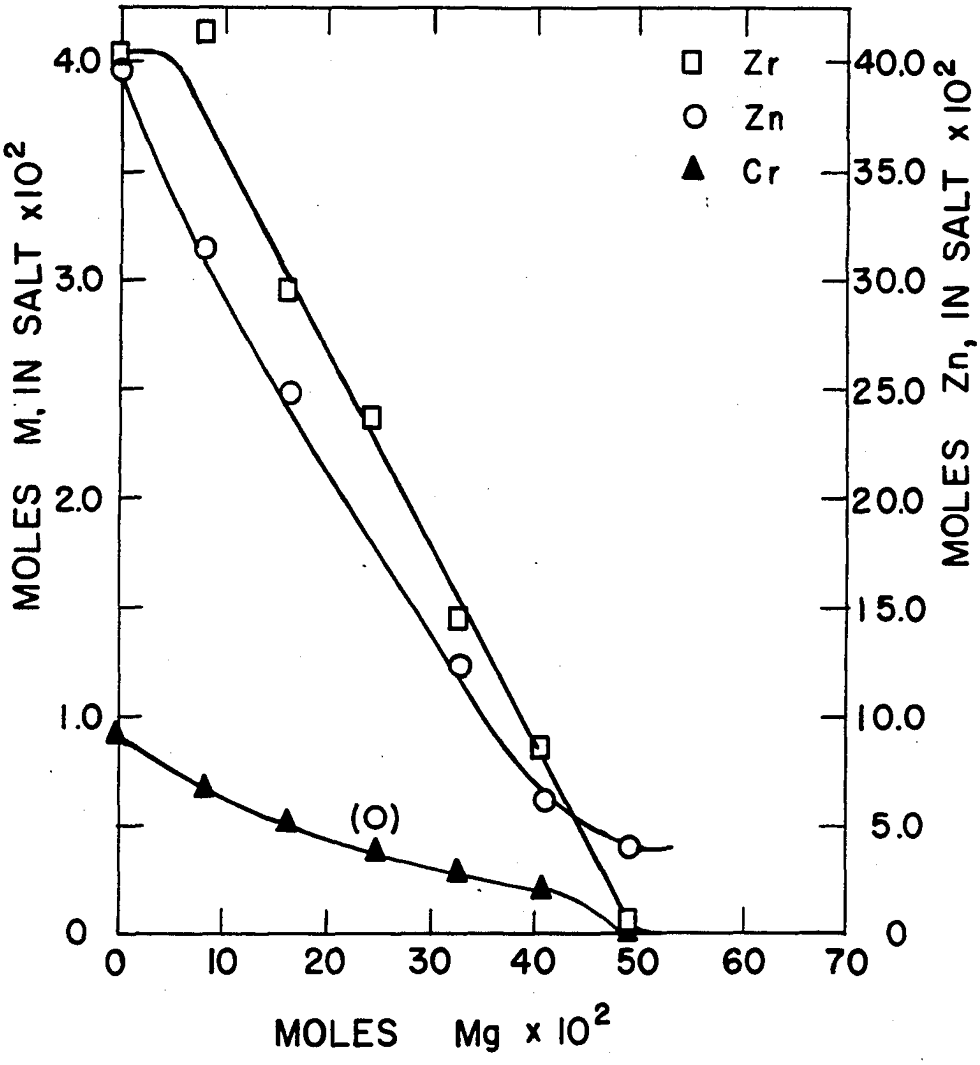

Figure 31. Transfer of solutes (zirconium, chromium) from a KCl-LiCl eutectic to a zinc-rich phase by reduction with magnesium, moles M (zirconium, chromium) in salt versus moles magnesium added at 700°C

Table 49. Experimental details of the "700" series selective separation experiment

Weight zirconium = 10.2825 gms = 0.2170 moles
Weight chromium = 11.1982 gms = 0.2148 moles
Weight zinc = 927 gms = 14.19 moles

Weight salt (KCl-LiCl eutectic) = 660 gms
moles KCl = 4.96 moles moles LiCl = 6.85 moles

Temperature range = 479-525°C

Equilibration periods = 2 hrs. during the oxidation cycle
1 hr. during the reduction cycle

Table 50. Experimental results for the "700" series experiment, zirconium and chromium at 500°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% Zr	% Cr	% Zn	Sample wt.gms
701	0	-	0.0005	0.0007	0.034	10.82
702(M)	0	-	0.1365	0.536	-	14.09
703	6.82	-	0.0085	0.0085	0.472	10.09
704	16.0	-	0.0385	0.0188	1.07	10.76
705	25.50	-	0.0832	0.040	1.565	7.75
706	32.24	-	0.329	0.0436	1.795	11.46
707	42.95	-	0.443	0.0466	2.055	11.79
708	55.01	-	0.550	0.0530	2.184	10.83
709	68.04	-	0.551	0.0679	3.325	12.95
710	78.88	-	0.572	0.0737	4.024	11.36
711(M)	78.88	-	0.0813	0.818	-	13.68
712	-	1.97	0.60	0.0558	3.40	10.63
713	-	3.94	0.438	0.0436	2.65	10.09
714	-	5.91	0.3655	0.0342	0.59	4.09
715	-	7.89	0.223	0.0251	1.37	10.92
716	-	9.87	0.131	0.0182	0.665	8.92
717	-	11.85	0.0063	0.001	0.439	10.03

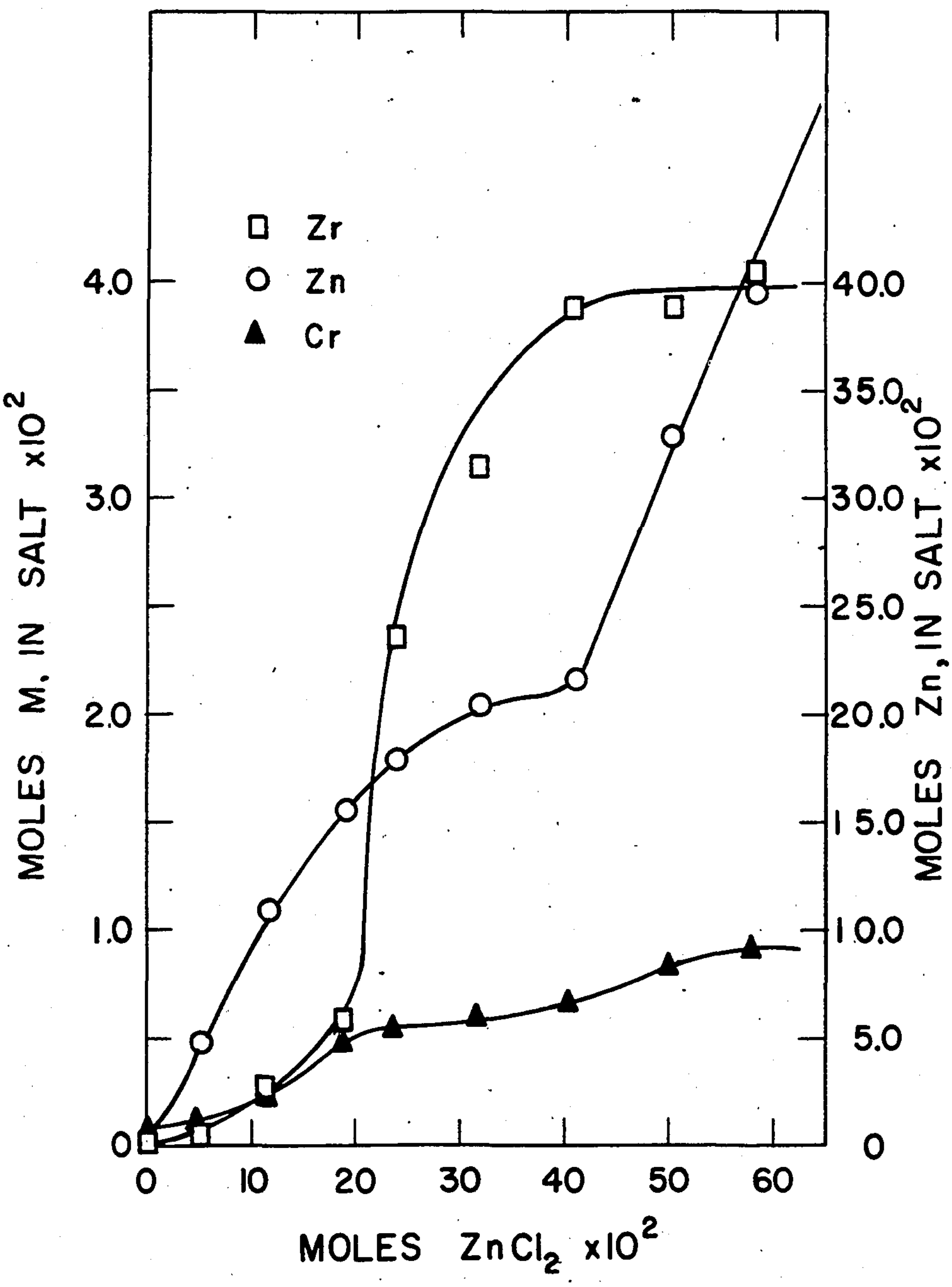

Figure 32. Transfer of solutes (zirconium, chromium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (zirconium, chromium) in salt versus moles $ZnCl_2$ added at 500°C

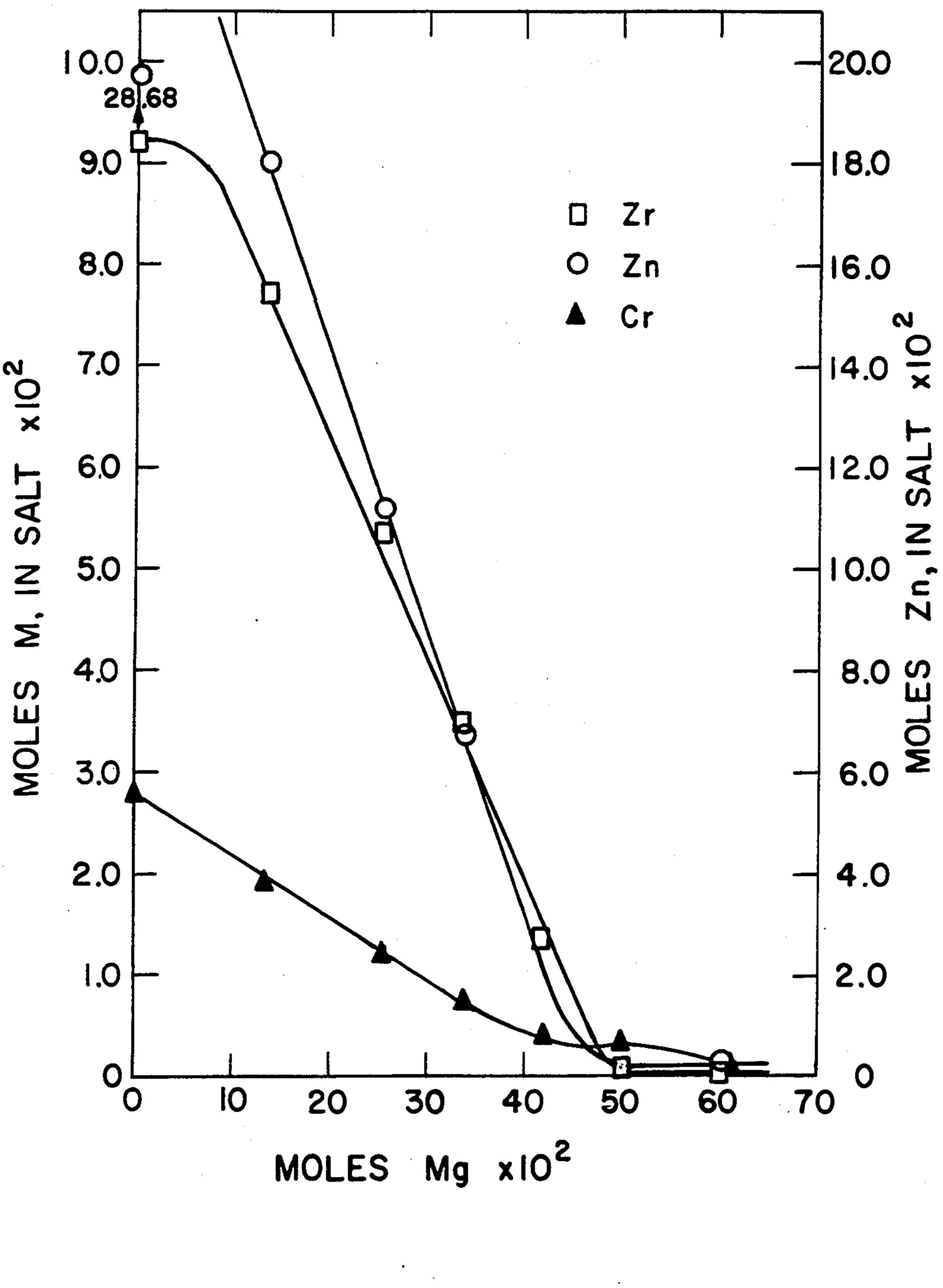

Figure 33. Transfer of solutes (zirconium, chromium) from a KCl-LiCl eutectic to a zinc-rich phase by reduction with magnesium, moles M (zirconium, chromium) in salt versus moles magnesium added at 500°C

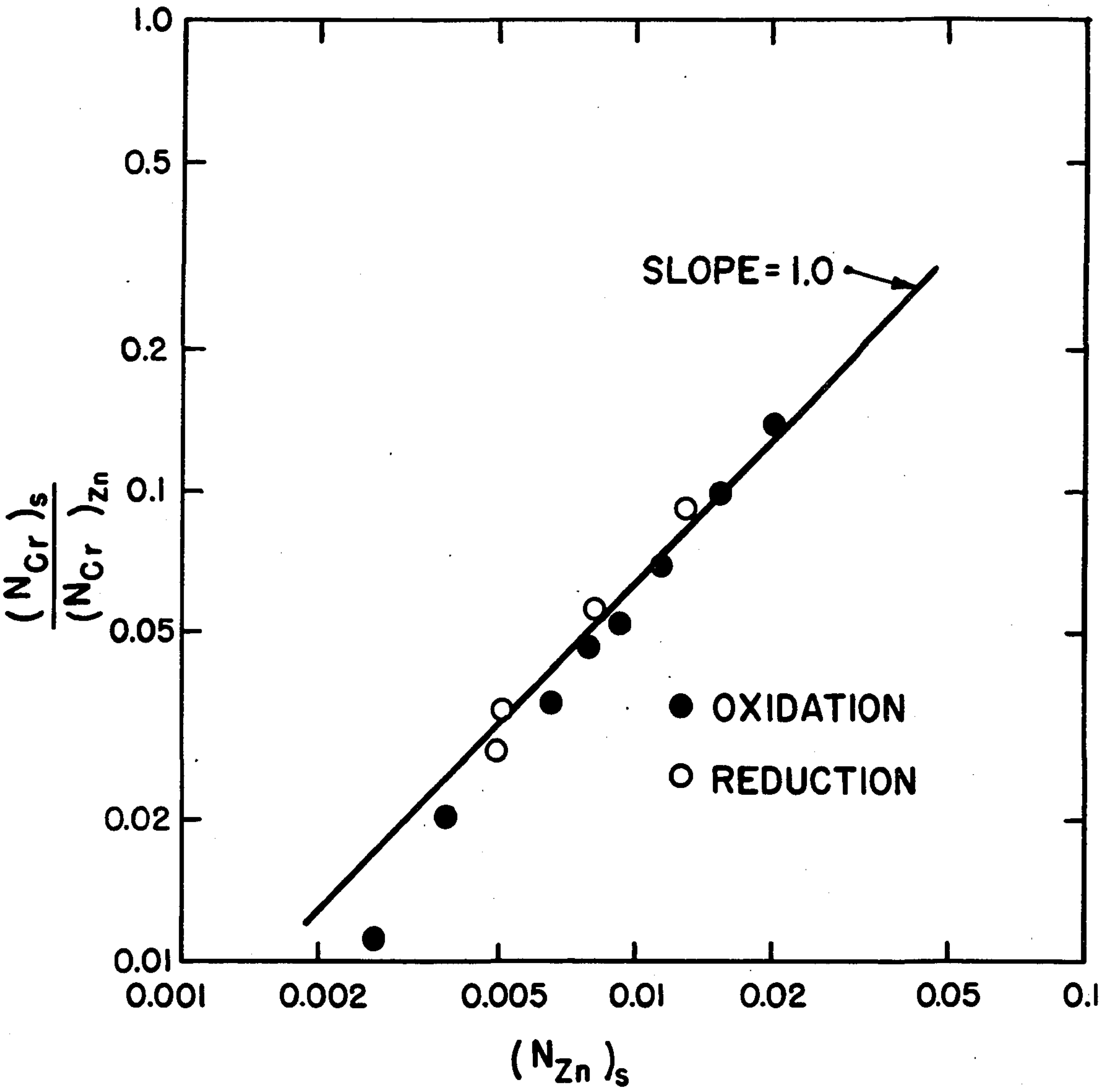

Figure 34. A log log plot of the ratio of molar concentrations of chromium in KCl-LiCl eutectic and a zinc-rich phase versus the molar concentration of zinc in the KCl-LiCl eutectic phase at 700°C

4. Cerium, uranium and zirconium separations

The "800" series test was done at 700°C and used cerium, uranium and zirconium as the elements to be studied. The experimental details and data are given in Tables 51 and 52. Figures 35 and 36 plot the data. A fair degree of separation between cerium and uranium is observed, and an excellent separation between uranium and zirconium. A slight plateau in the zinc data indicated the possibility of oxidation of plus 3 cerium to plus 4. This point was not observed in the experiment using only cerium.

A number of experiments on the separation of cerium and uranium were done at 500°C. Reliable results were difficult to obtain, due to non-equilibrium conditions

Table 51. Experimental details of the "800" series selective separation experiment

Weight cerium = 16.8197 gms = 0.1202 moles

Weight uranium = 35.4602 gms = 0.1490 moles

Weight zirconium = 10.7108 gms = 0.1174 moles

Weight salt (KCl-LiCl eutectic) = 844 gms

moles KCl = 6.34 moles   moles LiCl = 8.75 moles

Weight zinc = 722 gms = 11.04 moles

Temperature range = 678-718°C

Table 52. Experimental results for the "800" series experiment, cerium, uranium and zirconium at 700°C

Sample no.	Gms $ZnCl_2$ added	Gms Mg added	% Ce	% U	% Zr	% Zn	Sample wt.gms
801	0	0	0.072	0.0062	0.0009	0.0015	10.85
802(M)	0	0	-	0.925	1.70	-	13.09
803	6.52	-	0.616	0.0075	0.0008	-	12.99
804	12.02	-	1.0505	0.0150	0.001	0.0015	9.61
805	19.94	-	1.5575	0.285	0.001	0.0015	10.14
806	26.69	-	1.7055	0.975	0.0009	0.01	11.13
807	33.97	-	-	1.77	0.0009	0.01	10.89
808	44.33	-	-	3.055	0.0008	0.08	12.27
809	50.43	0	1.950	3.835	0.0035	0.08	11.29
810	54.86	-	-	4.17	0.0051	0.18	12.13
811	63.96	-	-	-	0.165	0.54	11.83
812	73.44	-	-	-	0.228	0.67	10.34
813	84.51	-	-	4.265	0.395	1.07	11.90
814	101.31	-	1.8665	4.215	0.494	1.86	9.89
815(M)	101.31	-	-	0.10	0.0902	-	13.09
816	-	1.81	-	-	0.404	1.42	10.48
817	-	3.63	-	-	0.2995	0.96	11.10
818	-	5.45	1.891	4.29	0.142	4.24	11.59
819	-	7.27	-	4.135	-	-	12.54
820	-	9.37	1.903	2.21	-	-	10.11
821	-	11.46	1.889	0.255	0.0009	-	11.56
822	-	13.56	1.042	0.0084	-	-	10.92
823	-	15.56	0.771	0.0095	-	-	10.81
824	-	19.58	0.024	0.0043	0.0008	0.011	12.87
825(M)	-	19.58	-	1.18	0.771	-	15.88

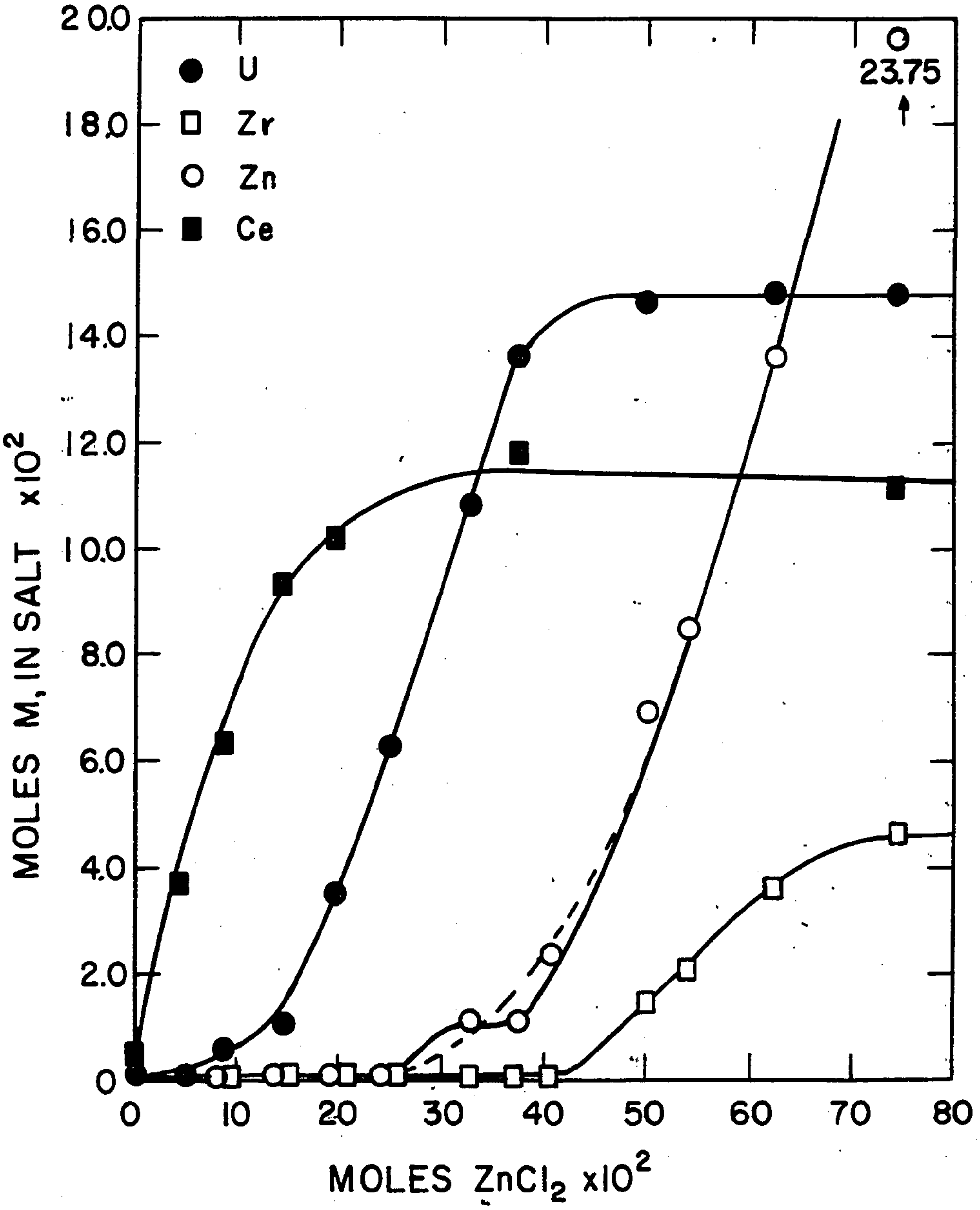

Figure 35. Transfer of solutes (cerium, uranium, zirconium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with $ZnCl_2$, moles M (cerium, uranium, zirconium) in salt versus moles $ZnCl_2$ added at 700°C

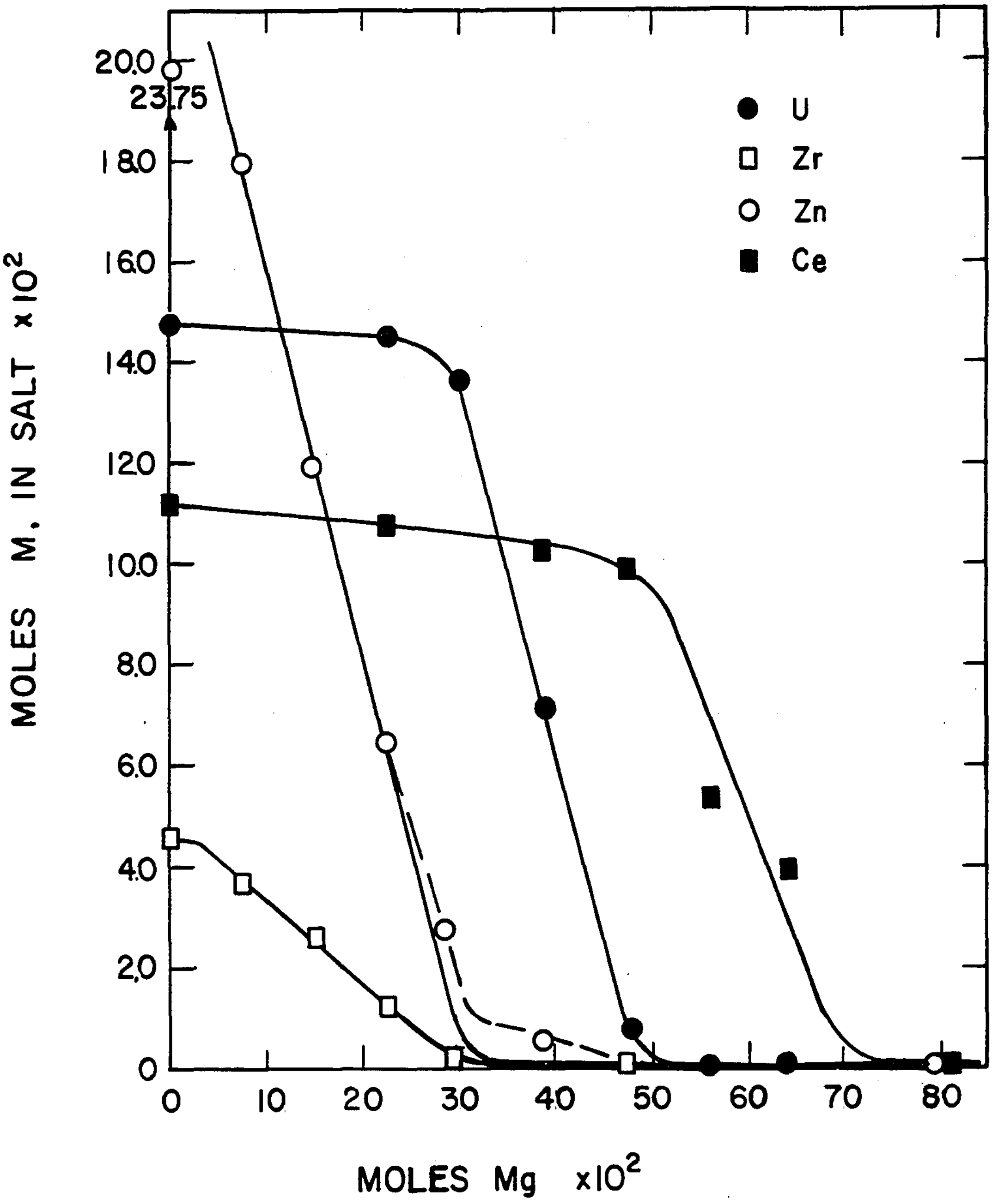

Figure 36. Transfer of solutes (cerium, uranium, zirconium) from a KCl-LiCl eutectic to a zinc-rich phase by reduction with magnesium, moles M (cerium, uranium, zirconium) in salt versus moles magnesium added at 700°C

existing in the melts.

In the "1500" series, reliable data for the selective oxidation of cerium and uranium were obtained from the reduction sequence of the test. The details and data of the experiment are presented in Tables 53 and 54. Figures 37 and 38 show the transfer of the constituents as a function of magnesium added, and of the magnesium reacted. The reason for the rise in zinc content at the end of the reduction sequence in Figure 37 is not known. The plus 3 oxidation state is clearly indicated for both cerium and uranium. A better separation between cerium and uranium is observed at this temperature than was the case at 700°C.

Table 53. Experimental details of the cerium-uranium selective separation experiments at 500°C, "1500" series

---

Weight cerium = 8.8774 gms = 0.0633 moles

Weight uranium = 24.4626 gms = 0.1029 moles

Weight zinc = 1210 gms = 18.52 moles

The above were prealloyed at 700°C; the resulting
weight after sectioning was 1041 gms.

Weight salt (KCl-LiCl eutectic) = 997 gms (at start)

moles KCl = 7.49 moles   moles LiCl = 10.38 moles

Temperature range = 497-506°C

Equilibration periods = 3 - 6 hrs. during oxidation
2-1/4 - 10 hrs. during reduction

Table 54. Experimental results for the "1500" series experiment, cerium and uranium at 500°C, reduction sequence only

Sample no.	Gms Mg added	% Ce	% U	% Zn	Sample wt.gms
1508	0	0.7375	2.30	0.859	14.27
1510	1.26	0.7355	2.265	0.487	14.65
1511	2.24	0.746	2.30	0.1565	16.33
1512	3.66	0.7435	1.465	0.0755	14.83
1513	4.52	0.7345	0.69	0.06	12.65
1514	5.42	0.6670	0.098	0.025	13.66
1515	6.32	0.231	0.09	0.072	15.67
1516	7.21		0.096	0.109	13.15

E. Distillation Separations

The general procedure used in these experiments has been discussed in some detail. The purpose of the work was twofold: (1) could zirconium, as $ZrCl_4$, be easily and completely removed from fused salt melts, and (2) during such an operation would any uranium present be carried over to the condensate. Similar information about the behavior of thorium was desired, but was not a primary goal of the experimentation. Since the objectives of the work were limited, no attempt to optimize the distillation rate was made, and care must be taken in

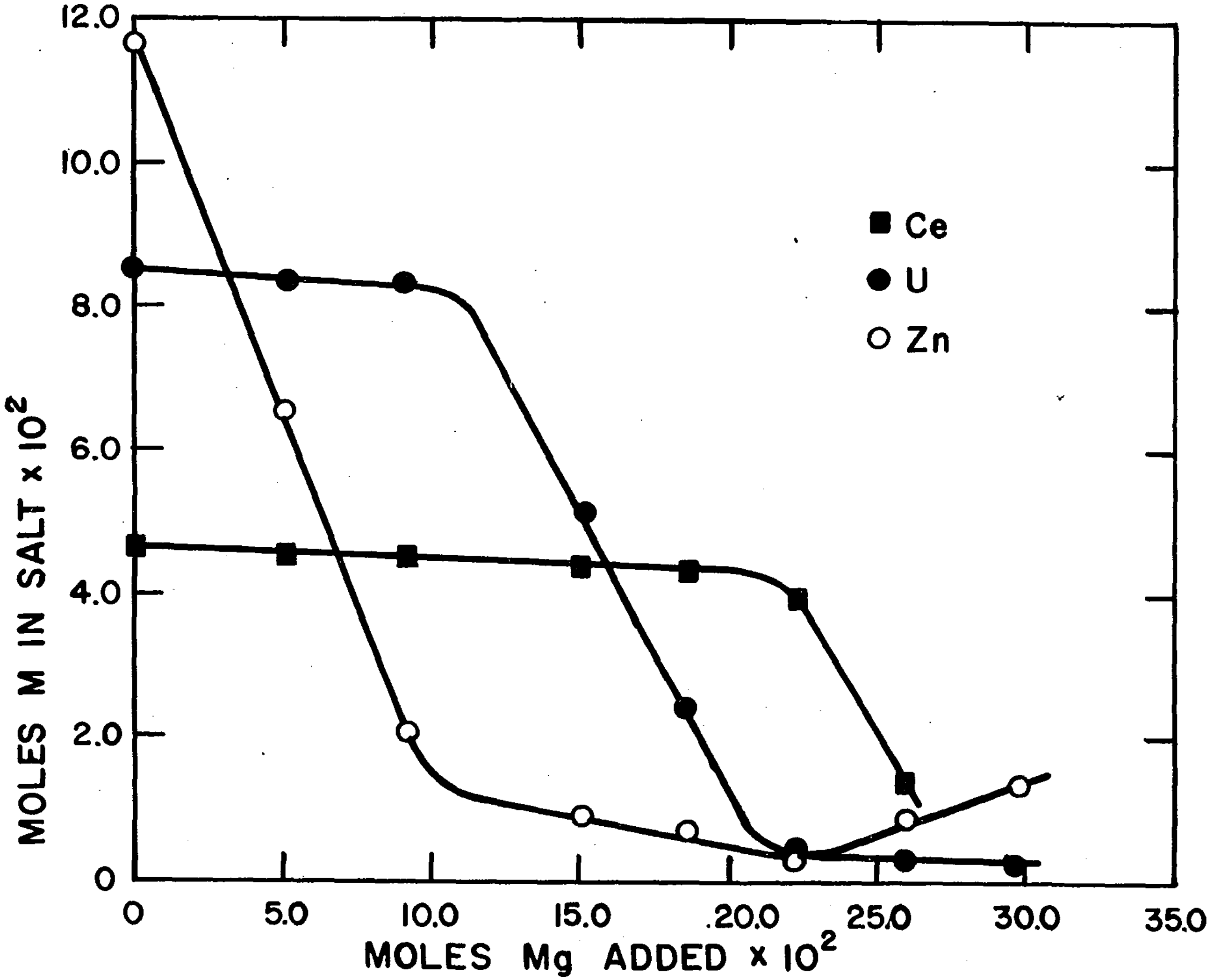

Figure 37. Transfer of solutes (cerium, uranium) from KCl-$LiCl$ eutectic to zinc-rich phase by reduction with magnesium, moles M (cerium, uranium, in salt versus moles magnesium added at 500°C

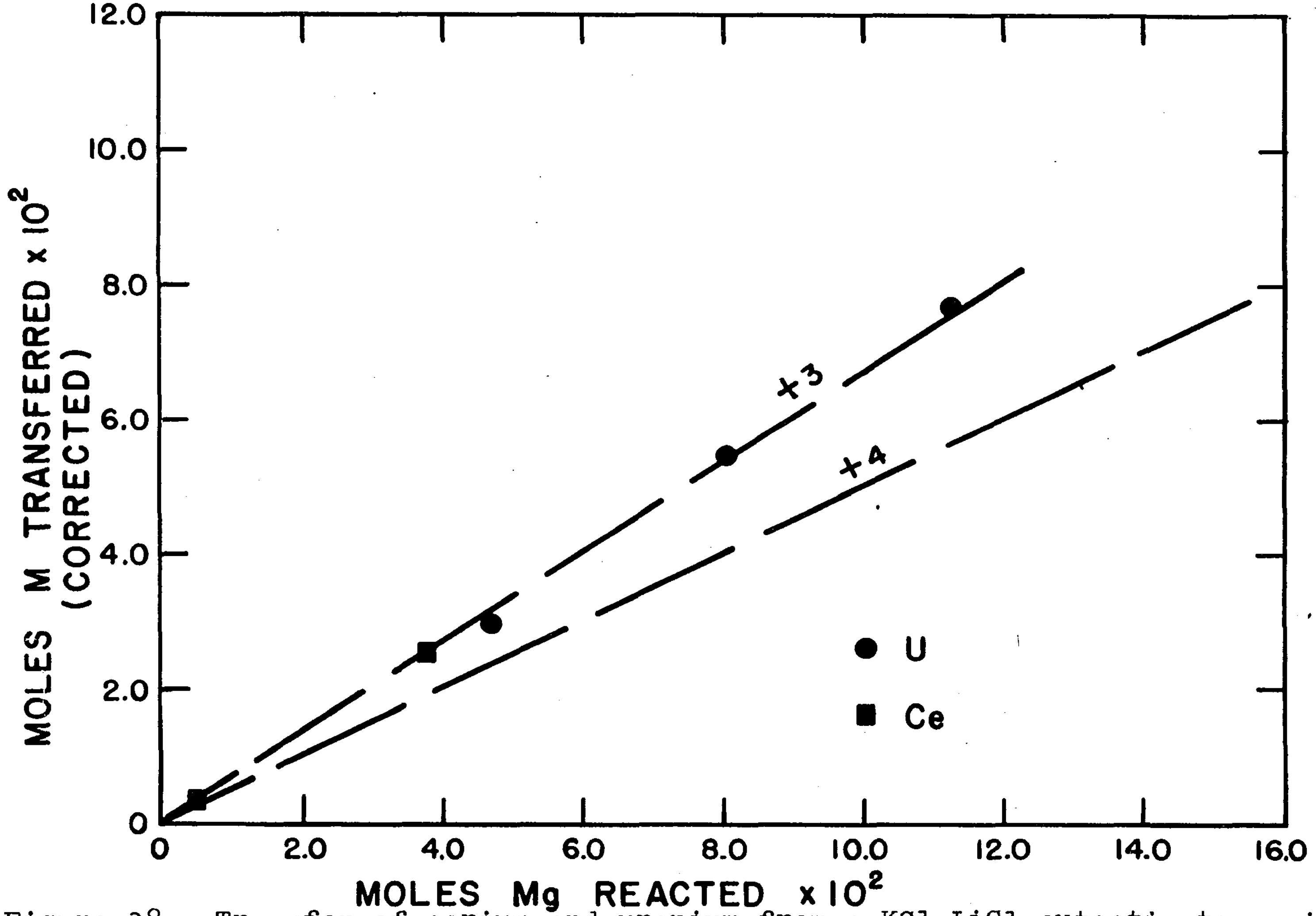

Figure 38. Transfer of cerium and uranium from a KCl-LiCl eutectic to a zinc-rich phase by reduction with magnesium, moles M (cerium, uranium) transferred versus moles magnesium reacted at 500°C

applying the results to situations other than those encountered experimentally.

1. Micro-scale distillations

The possibility of separating uranium and zirconium by distillation of the volatile $ZrCl_4$ was investigated in a series of 12 micro-scale experiments. In the first eight tests, samples of zirconium were equilibrated with zinc and KCl-LiCl eutectic containing an excess of $ZnCl_2$ relative to the available zirconium. The resulting salt, now containing $ZrCl_x$, $ZnCl_2$ and in some cases UCl_3, was then placed in the distillation apparatus, heated and a vacuum applied to the system. Samples were taken of the initial salt, distillate and residue. The chemical analyses of these samples then indicated the effectiveness of such a separation technique.

Table 55 summarizes the data from the eight experiments. The initial and final concentrations in the salt are given, as are the overall recovery and per cent of the material recovered in the distillate. The first four experiments did not have uranium present, while the last four did. The D.C.F. (decontamination factor) (% in initial / % in final) for zirconium ranges from 2.6 to infinity, with three experiments giving the latter value. The material recoveries for the zirconium are, in general, poor. The overall material balances, shown in Table 56, are very good. Data for experiments 11 and 12 are not available, since the condensate

Table 55. Treatment, analyses and recoveries in distillation experiments for zirconium-uranium separation*

Exp.	Vacuum treatment (<10μ)	Initial concentration in salt			Final concentration in residual salt			Overall recovery in distillation operation			Per cent recovered in the condensate		
		% U	% Zr	% Zn	% U	% Zr	% Zn	% U	% Zr	% Zn	% U	% Zr	% Zn
5	550°C-1 hr.	-	4.38	3.52	-	0.56	2.36	-	70.2	100	-	83.8	40.3
6	600°C-1 hr.	-	3.51	4.75	-	1.326	4.97	-	88.1	118	-	60.7	18.8
7	575°C-2 hrs.	-	4.41	4.98	-	0.410	2.35	-	72.0	97.3	-	89.4	59.9
8	550°C-2 hrs.	-	3.51	2.19	-	0.064	1.74	-	78.8	124.1	-	98.0	43.1
9	500°C-14 hrs.	5.14	2.42	6.65	5.45	0.0282	3.18	96.4	10.9	100.8	0.152	90.2	56.9
10	500-600°C -1 hr.	3.22	2.28	5.72	3.55	n.d.**	5.14	103.5	141.0	87.7	0.284	100.0	5.1
11	600°C-6 hrs.	3.98	2.35	4.61	3.38	n.d.	2.73	80.6	29.7	128.8	0.072	100.0	56.4
12	575°C-14 hrs.	2.91	1.84	5.42	4.09	n.d.	0.27	94.1	56.3	106.8	0.069	100.0	83.1

*Additional experimental details are given in Table 68, Appendix F.

**n.d. indicates none detected.

Table 56. Material balances for the distillation experiments

Exp.	Initial salt weight	Residue weight	Condensate weight	Total charge accounted for (%)
5	12.34	11.00	1.32	99.8
6	16.65	15.21	1.48	100.1
7	13.88	11.44	2.38	98.8
8	16.97	15.10	1.91	100.2
9	15.95	14.51	1.35	99.4
10	15.93	14.94	0.92	99.5
11	18.66	16.70	-	-
12	12.21	8.13	-	-

was not directly weighed in these two cases, due to the very high humidity present on the days on which those experiments were run, and the extremely hydroscopic nature of those samples.

The general conclusions that can be made about this work are: (1) essentially complete removal of the zirconium can be obtained by holding the melt at 600°C under a vacuum of less than 10 microns for a period of time greater than 1 hour, (2) less than 0.3 per cent of the uranium present will be carried over into the condensate under these conditions, (3) removal of a large amount of the zinc present, as $ZnCl_2$ or zinc metal vapor can be avoided by a short treatment time, and (4) apparently the removal of the zirconium is improved by the presence of UCl_3.

Analytical data for the last four experiments are given in Table 57. The initial mixtures of $ZnCl_2$ bearing salt, zinc and zirconium were heated to 700°C and equilibrated for three hours in a sealed tantalum can. Following this equilibration, the resulting salt and metal phases were separated and the salt phase saved for later experimentation. This salt is called "initial salt" in Table 57. Since a large excess of zirconium, relative to the available $ZnCl_2$, had been present initially, the zinc phase contained the major portion of the zirconium.

After weighing, the resulting salt samples were placed in the distillation apparatus and heated to 600°C for two hours under a vacuum of approximately 10 microns. The salt left after the distillation is referred to as the residue in Table 57, and the collected material, the condensate. In experiment 13, it was impossible to weigh the condensate due to the high humidity present that day.

It is apparent that the residual zirconium concentration can be reduced to low levels, approximately 100-200 ppm by a simple distillation treatment. Further, it is indicated by the summation of the concentrations in the condensate that either the potassium or lithium chlorides are also partially

Table 57. Results and analyses of micro-scale distillations of zirconium and zinc chlorides at 600°C for 2 hours under a vacuum of 10 microns*

Exp.	Phases	Weight gms	% Zr	% Zn	% Cl	mg Zr	mg Zn	D.C.F. w/o $\frac{\text{Zr initial}}{\text{Zr residue}}$
	Initial salt	4.02	6.76	0.971	-	252.0	39.0	
13	Residue	2.78	0.0146	0.140	-	0.406	3.89	453
	Condensate	-	9.90	3.50	57.47	-	-	
	Initial salt	8.04	6.50	0.979	-	522.0	78.6	
14	Residue	6.38	0.0072	0.453	-	0.459	28.9	903
	Condensate	1.84	29.47	4.24	57.76	543.0	77.9	
	Initial salt	4.35	6.81	1.288	-	296	56.0	
15	Residue	3.40	0.1568	1.160	-	5.33	39.4	43.4
	Condensate	1.06	24.28	4.30	56.68	257.5	45.5	
	Initial salt	2.91	6.12	1.281	-	178.1	37.3	
16	Residue	2.21	0.0297	0.097	-	0.656	2.14	206
	Condensate	0.82	19.05	4.73	57.48	156.2	38.8	

*Additional experimental details are given in Table 68, Appendix F.

distilled. The decontamination factors for the zirconium removal are quite good with one exception. In general, the material balances for the zinc and zirconium are good, indicating generally reliable data.

If the initial and final concentrations of zinc and zirconium in the salt phases are known, it is possible to evaluate the moles of zirconium transferred to the salt per mole zinc reacted. This calculation was made for the 12 micro-scale experiments using 9.64 per cent zinc in the initial salt for the first eight experiments, and 9.47 per cent for the last four. The results of this calculation were somewhat scattered but indicated an oxidation state of 3.64. If we assume that zirconium is transferred to the salt in a plus 3 state, we must accept the following reaction as the mode of oxidation to plus 4, when a vacuum is applied to the system.

$$ZrCl_3 + 1/2\ ZnCl_2 \rightleftharpoons \overline{ZrCl_4} + 1/2\ Zn$$

In the last four of the micro-scale distillations, the amount of zinc available for such a reaction is insufficient to account for the amount of zirconium removed. In the first eight experiments, the amount of zinc removed appears to be a function of the length of the distillation period. None of these facts in themselves clearly indicate the actual oxidation state of the zirconium, but they do seem to infer the presence of plus 4, or that there is present a mixture of plus 3 and plus 4 zirconium.

The initial concentrations of zirconium and zinc that were observed experimentally, and which are presented in Tables 55 and 57, are much different than those obtained in the micro-scale work, see Table 18. This fact is somewhat misleading. However, it must be remembered that the equilibration temperatures for the several sets of experiments are different, being 500°C for the micro-scale work and 700°C for the distillation studies. This fact alone will probably account for the observed variations in the concentration levels.

2. Macro-scale distillations

Two macro-scale distillation experiments were performed in an attempt to evaluate the possibility of a separation of both thorium and zirconium from uranium as volatile chlorides. In the first experiment a KCl-LiCl eutectic containing uranium, zirconium, thorium and zinc as chlorides was taken and heated to 590°C. A vacuum was applied and samples taken after certain periods of time had passed by siphoning from the residual melt. Prior to sample withdrawal, inert gas was bled into the system, and the sample withdrawn at atmospheric pressure. The analytical results from these samples are presented in Table 58. The initial salt weight was 376 grams. After a total of four hours at 590°C, the temperature was raised to 750°C and a vacuum applied for an additional four hours. Following this treatment, no sample was left, the entire mixture having been distilled.

Examination of the data in Table 58 shows that as zinc and thorium are removed the concentrations of the uranium and zirconium increase, indicating a net weight loss of the salt. This means that the zirconium content can be reduced to about 100 ppm, while the uranium level is unaffected. Thorium and zinc levels are reduced by about 48 and 91 per cent respectively under these conditions. It should be noted that the pressure was somewhat higher in this experiment than in the micro-scale experiments.

In previous work, it has been shown that thorium is present as $ThCl_3$. Since $ThCl_4$ is the most likely volatile

Table 58. Analytical results for the distillation of a mixture of uranium, thorium and zirconium chlorides

Sample	Time (mins)	Minimum pressure (microns)	Temp. (°C)	% U	% Th	% Zr	% Zn
Zr-Th-1	zero	1 atm	594	1.03	4.13	0.0098	-
Zr-Th-2	15	70	580	1.07	3.63	0.0095	6.60
Zr-Th-3	30	50	582	1.095	3.185	0.0094	5.89
Zr-Th-4	60	40	588	1.145	2.595	0.0101	4.55
Zr-Th-5	120	35	593	1.20	2.56	0.0129	2.69
Zr-Th-6	240	30	589	1.26	2.69	0.0126	0.715
Zr-Th-7	240 (additional to the above)	20	750	(no sample could be taken)			

compound of thorium to be distilled, an equilibrium of the following nature is required:

$$ThCl_3 + 1/2\ ZnCl_2 \rightleftharpoons ThCl_4 + 1/2\ Zn$$

Since the zinc content had been drastically reduced, it is possible that this reaction limited the amount of thorium that was removed.

In the second experiment, an arc-melted button, U-35.34 gms, Th-0.525 gms, Zr-10.68 gms, was dissolved in 684 gms of 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$. Samples were taken before and after the distillation operation. The data are presented in Table 59. Following the 12 hours at 650°C, the

Table 59. Analytical results for the distillation of a mixture of uranium, thorium and zirconium chlorides at 600° and 640°C

Sample	Treatment	Minimum pressure (microns)	% U	% Th	% Zr	% Zn
Zr-Th-7	nothing	--	5.235	0.0801	0.799	4.79
Zr-Th-9	6 hrs-600°C	25	5.87	0.0721	0.0220	0.655
Zr-Th-8	12 hrs-650°C (additional)	50	6.43	0.0436	0.0683	0.102

entire mixture was cooled and weighed. Only 96 grams of salt were observed, indicating that virtually all the salt was distilled. This indicates that 600°C should be considered the maximum operating temperature for distillation operations of this nature.

Examination of the initial concentration of zirconium indicates that a large portion of it has already distilled, assuming complete dissolution of the alloy button. The uranium is accounted for if a salt weight of 674 grams is accepted. On this basis, 5.39 grams of zirconium and 0.541 grams of thorium are calculated in the salt. These figures represent 103 and 50.5 per cent of the thorium and zirconium, respectively. After 6 hours at 600°C, assuming that only the chlorides of thorium, zirconium and zinc have been removed, the residual salt weight is calculated at 603 grams, assuming no uranium transferred. On this basis, some 1.35 per cent of the zirconium and 82.7 per cent of the thorium are left in the salt. As previously discussed, it is felt that temperatures above 600°C result in the distillation of a major portion of the melt. These data indicate and confirm the possibility of uranium and zirconium separation by distillation of the volatile $ZrCl_4$, and further, they suggest that some degree of separation between uranium and thorium is possible by these techniques.

VI. CONCLUSIONS AND RECOMMENDED ADDITIONAL STUDIES

A. Conclusions

In a previous section, a general outline of the process under development was presented. In this sub-section, a detailed discussion of the process will be presented, with the schematic outline or flow diagram in Figure 39 used as a general guide. Following this, the results and general conclusions as to the effectiveness of the process will be presented.

The initial separation of uranium from thorium and the fission products occurs when the metallic unalloyed thorium is dissolved in magnesium to produce the Mg-38w/oTh eutectic mixture. Since the solubility of uranium is quite low in this solution, the uranium can be collected as an immiscible liquid beneath the eutectic. The uranium bred in the pile may be consolidated as the metal or as an eutectic of either chromium or iron. In this work, only the behavior of the U-5.2w/oCr alloy has been studied. Based upon the phase diagrams involved and their thermodynamics, it is expected that those elements which have an appreciable solubility in, or form compounds with, magnesium will concentrate in the Mg-38w/oTh phase, while those whose solubilities in magnesium are low will concentrate in the U-5.2w/oCr phase. In general, by the groups of fission products previously listed, the alkaline, alkaline earth, rare earth, low melting and lanthinide groups

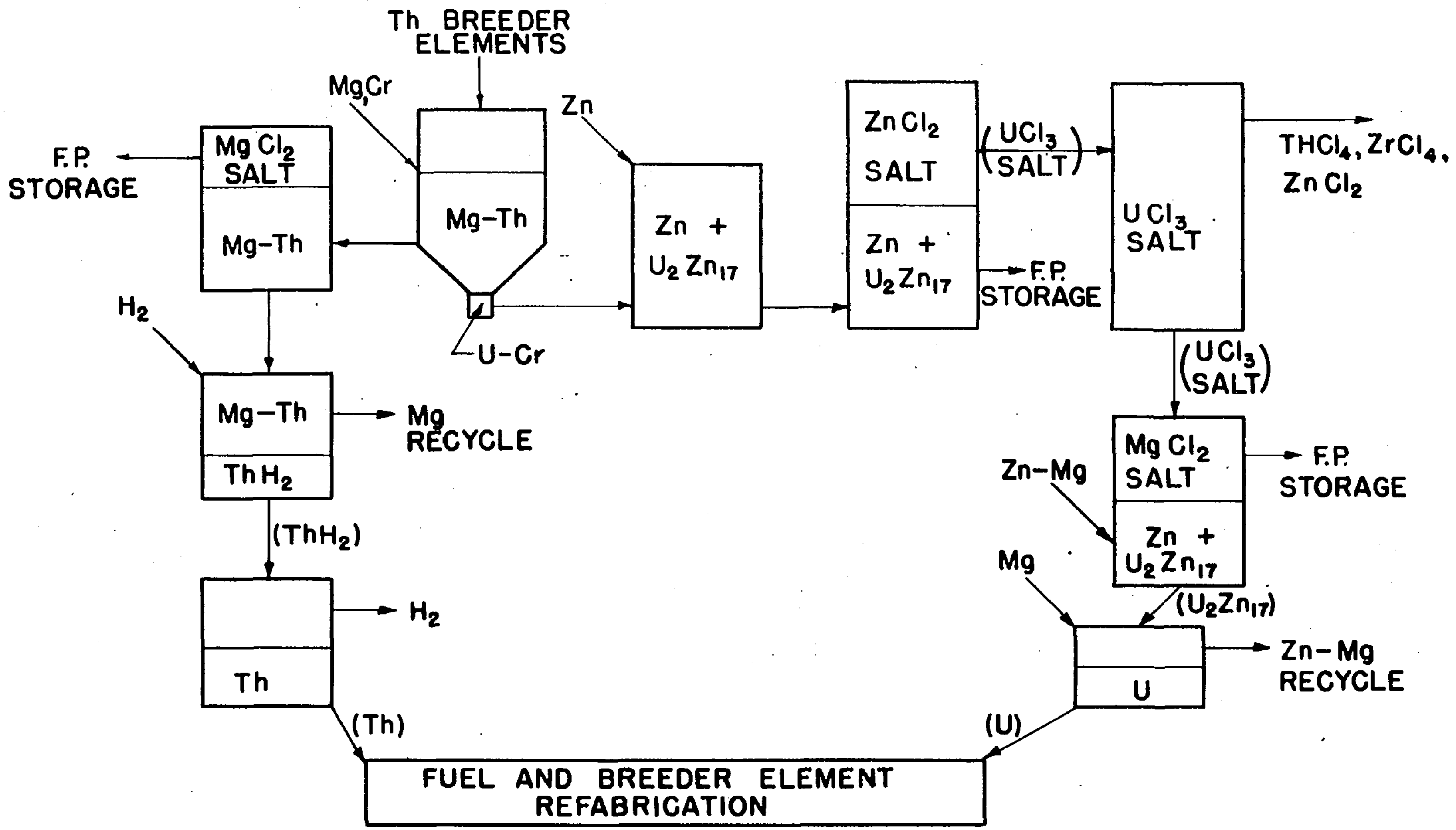

Figure 39. Proposed pyrometallurgical reprocessing system for the thorium-uranium-233 fuel cycle

will tend to segregate in the Mg-38w/oTh phase, while the noble and high melting groups are expected to move with the uranium. In addition, previous work has indicated that thorium is soluble to a limited degree in the uranium-rich phase (16). The volatile and low melting elements previously discussed will probably be distilled from the system during this operation or sequence of operations.

The two phases can probably be separated by siphoning or preferential freezing and decantation of the Mg-38w/oTh. The resulting U-5.2w/oCr can then be carried into the next operation. The Mg-38w/oTh phase is then equilibrated with a fused salt carrying $MgCl_2$. The thermodynamic data presented previously indicated the possibility of selective oxidation of the fission products in the alkaline, alkaline earth and rare earth groups from thorium and thorium melts. Multiple or even continuous equilibrations are possible in this step. Following separation of these phases, the Mg-38w/oTh can be reacted with H_2 to reduce the thorium content (24). The Mg solution can be recycled for further use while the ThH_2 is thermally decomposed and the thorium consolidated. The latter two steps should effectively remove any residual amounts of the low-melting fission products left with the thorium from the previous operations.

The uranium or U-5.2w/oCr phase collected in the Mg-Th/U or U-Cr separation is next taken to a dissolution operation.

The crude impure uranium-rich phase is placed in a liquid zinc solution and dissolved therein. Following dissolution of the uranium, the zinc phase is equilibrated with a salt phase containing $ZnCl_2$ that will act to oxidize the uranium to UCl_3. If an excess of $ZnCl_2$, relative to the uranium, is present any zirconium and thorium present will probably be oxidized also.

The resulting salt phase is then physically separated from the metal phase. It is expected that the noble, high-melting and residual low-melting fission products that accompanied the uranium during the Mg-Th/U or U-Cr separation will be left in the zinc phase, while any of the other fission products will be oxidized with the uranium. The salt is then placed under a partial vacuum, and the more volatile chlorides, $ThCl_4$, $ZrCl_4$ and $ZnCl_2$, are distilled away from the UCl_3.

The salt, now containing UCl_3, KCl and LiCl and the chlorides of those alkaline, alkaline earth and rare earth fission products carried along, is then equilibrated with a Zn-7 w/oMg alloy containing sufficient magnesium to reduce only the uranium present in the salt. The U_2Zn_{17} compound is formed, and the $MgCl_2$ salt is removed. The residual zinc-uranium alloy is then cooled to just above the melting point of zinc, to reduce the uranium content in the liquor, and the liquid phase is either decanted or siphoned off. A wash of magnesium is added to the U_2Zn_{17}. Excess magnesium acts to decompose the compound (30), leaving behind uranium metal.

The liquor is again removed, and the excess zinc and magnesium are distilled away while the uranium is consolidated. Following consolidation, the purified uranium can be sent to fuel element refabrication operations to permit reuse of the fuel.

Conclusions as to the effectiveness and potential value of the proposed process must be drawn from examination of the degree of separation indicated by both the micro- and macro-scale selective separation work and the distillation study. The critical data resulting from these studies are the appropriate distribution coefficients (K_d's), separation coefficients (K_n's) and decontamination factors (D.C.F.'s).

A table of K_d's from the micro-scale work is presented in Table 60. The K_d's are tabulated by solvent media and the elements being separated. All K_d's are defined by, conc. in light phase / conc. in heavy phase. For example, the K_d for cerium in the Mg-Th/$MgCl_2$ separation is 2.0. This means that the concentration of cerium in the $MgCl_2$ salt phase is twice that in the Mg-Th phase. All salts are primarily KCl-LiCl eutectic containing less than 25 w/o solute chloride. Both Mg-Th and U-Cr phases are the eutectic compositions of 42w/oTh and 5.2w/oCr.

Examination of these data indicate: (1) essentially complete separation of the alkaline, alkaline earth and rare earth fission products, including yttrium in the Mg-Th/U-Cr separation, (2) total separation of the noble, low melting

Table 60. Tabulation of distribution coefficients, K_d, evaluated from the micro-scale experiments

Equilibrated phases*	Element distributed	K_d w/o in light phase / w/o in heavy phase	R gms.light phase / gms.heavy phase	% Element extracted into light phase
Mg-38w/oTh/15w/oMgCl$_2$	Ce	2.51	3.07	88
"	Y	7.51	1.16	89
"	Pa	0.01 - 0.002	0.67	1.02 - 0.3
Mg-38w/oTh/U-5.2w/oCr	Pa	0.06 - 0.008	0.7	0.75 - 0.13
"	Ce	578 - 3690	0.67	99.7
Zn/14w/oZnCl$_2$	Y	104 - 5750	0.85	99.95
"	Cr	0.172 - 0.99	0.9	13.7 - 26.4
"	Ce	207 - 15,000	1.05	99.6 - 100.0
"	Mo	0.0164	1.10	0.0
"	Zr	14.7 - 25	1.10	90.4 - 96.6
"	Pa	35.8 - 645	0.67	95.8 - 99.8
"	Fe	0.164 - 0.002	0.65	0.002 - 0.000
"	Nb	0.035	0.58	0.001
"	U	100 - 1000	0.9 - 1.2	99.4 - 99.9
Zn-42w/oMg/15w/oMgCl$_2$	Y	0.338 - 0.431	1.0	20.4 - 31.4
"	U	0.25 - 1.38	1.0	0.3 - 1.1
"	Ce	0.06 - 0.008	1.0	1.2 - 8.8
Zr-3w/oMg/15w/oMgCl$_2$	Pa	zero - 0.09	1.0	zero - 0.01
Zn-3w/oCa/17w/oCaCl$_2$	Pa	zero - 0.09	1.0	zero - 0.01

*Primary constituent of all salt phases is KCl-LiCl eutectic.

and second transition group of fission products, except zirconium, upon the addition of an excess of $ZnCl_2$ to a fused salt over a zinc phase containing uranium and fission products, (3) the selective oxidation of uranium from contained zirconium by $ZnCl_2$ is possible, and (4) uranium is carried through the process almost quantitatively, with process losses of probably less than 2 per cent. Additionally, the selective oxidation of uranium from thorium or protactinium was not demonstrated. It is also evident that these elements will probably closely follow uranium. The addition of chromium or iron, as eutectic formers, does not appear to cause difficulties in the process, since these elements only appear to be oxidized to a limited degree by large excesses of $ZnCl_2$, if at all.

In Table 61, the separation coefficients that were evaluated from the micro- and macro-scale work are tabulated. The K_n's from the micro-scale experiments are listed within parentheses. In the table under the column headed "Separations" the components that are being separated are listed. The order of the elements under "Separations" defines the K_n. For example, the K_n for the U, Zn entry is $(N_U)_s/[(N_U)_{Zn}(N_{Zn})_s^{3/2}]$, and for Ce, U it is $[(N_{Ce})_s(N_U)_{Zn}]/[(N_{Ce})_{Zn}(N_U)_s]$, etc. Separation coefficients are given for both plus 3 and plus 4 zirconium. For either oxidation state, the values of K_n for the U, Zr separation indicate essentially complete partition of these

Table 61. Experimentally observed separation coefficients, K_n, from micro- and macro-scale experiments

Reaction (see pages 30b & c)	Separations	K_n 500°C	K_n 700°C
9	U, Zn	3.2×10^6	6.4×10^5
10	U, Th	0.97 (1.49)	7.69
11	Ce, U	15.0 (14.09)	10.8
12	Ce, Zn	$10^6 - 10^8$	--
13	U, Zr(+3)	680 (1829)	330
14	U, Zr(+4)	320	156
15	Th, Zn	1.3×10^6	2.7×10^5
16	Zr(+3), Zn	4,700	2,100 (1,421)
17	Zr(+4), Zn	46,900	25,100 (14,025)
18	U, Pa	(22.1)	--
19	U, Y	(1.17)	--
20	Cr, Zn	0.084 (0.0805)	(0.0384, 650°C) 0.0625

two elements. It is qualitatively observed that a K_n of 15 or more, for elements in the same oxidation state, denotes a high degree of selectivity in the oxidation-reduction reaction. These values of K_n were arrived at after examination of all the micro- and macro-scale work and are judged the most reliable numbers obtainable. The solubility limits listed in Table 6 were used throughout the work to evaluate both K_d's and K_n's. The absolute accuracy of these numbers is open to some question, especially the larger K_n's. Conservatively, the accuracy is estimated at ± 20 per cent for the larger K_n's, i.e., those over 100, and ± 5 per cent for the lower values. In the Ce, U, the U, Th and the Cr, Zn separations, the degree of correlation between the micro- and macro-scale work is gratifying. Similar agreement is not observed for the U, Zr separations.

It is interesting to observe that a good separation between uranium and protactinium is predicted, but was not observed. This was probably caused by the relative concentration levels used. The data generally indicate that better separations are possible at lower temperatures. A notable exception to this generalization is the U, Th separation. Of the elements studied, it appears that only thorium and yttrium cannot be readily separated from uranium by selective oxidation-reduction reactions. The K_n's presented have considerable value in predicting the probable degree of separation of two elements under varying of concentration relative to one another, and relative to the solvent media, i.e., the salt or zinc phases. However, it should be emphasized that these values are directly dependent upon the solubility limits of the various elements in zinc, and that these may be drastically altered by ternary or quaternary additions to the zinc phase. In this manner, the separation coefficients and the degree of partition may be changed somewhat.

A considerable amount of evidence as to the oxidation state of certain of the elements has been obtained and presented. This evidence shows that cerium, thorium and uranium are in the plus 3 oxidation state when carried in KCl-LiCl eutectic over liquid zinc. The further oxidation of plus 3 thorium to plus 4 by the action of excess $ZnCl_2$ was not observed. In addition, it was shown that chromium is in the plus 2 oxidation state in similar circumstances, if zinc is considered to be plus 2. The oxidation state of yttrium is indicated to be plus 3, by molar balances of certain of the micro-scale experiments.

A great deal of effort and consideration has gone into the evaluation of the oxidation state of zirconium under the above mentioned conditions. Every distillation, micro- and macro-scale experiment has been examined in minute detail in an attempt to answer this question. Due to the distillation of $ZrCl_4$ and possible partial distillation of $ZnCl_2$, attempts to obtain satisfactory and consistent molar balances have failed. Thermodynamic data predict plus 3, but these data have a considerable degree of permissible error and include no compensation for complexing reactions of either plus 3 or plus 4. In general, the molar balances on all the experiments indicate either an equilibrium between plus 3 and plus 4 or primarily plus 4. In a number of the macro-scale experiments, the data can be interpreted to predict either plus 3 or plus 4. However, based largely upon the "2000" series experiment and the molar balances, it is felt that zirconium when carried in KCl-LiCl eutectic in contact with liquid zinc most probably exists in both plus 3 and plus 4 simultaneously as an equilibrium mixture.

The D.C.F.'s obtained from the distillation study were presented in Table 57, and show that with proper process controls the residual zirconium concentration in a salt phase may be drastically reduced, without marked effect upon the uranium concentration.

A concluding summary is that, in general, the process appears to have a large degree of potential in performing a preliminary decontamination of thorium-bred uranium. It is estimated that the total fission product activity can be reduced by over 95 per cent with losses of uranium of less than 2 per cent. Separation of thorium and protactinium from uranium have not been clearly demonstrated, but there are indications that by either distillation or selective oxidation both of these elements may be eliminated.

B. Recommended Additional Studies

It is possible to suggest that a vast amount of additional work should be undertaken; and, in fact, the efficiency of the process urges one to do this. However, it is felt that due to the nature of the work done at the Ames Laboratory only certain limited studies be undertaken. These are: (1) extension of the work to lightly irradiated uranium, containing the full spectrum of the fission products, to check the separations of all the fission products at very low concentrations, (2) possible expansion of the studies to include other oxidants and reductants, (3) limited design of continuous or semi-continuous process equipment, (4) investigations to develop structural alloys to hold liquid zinc at elevated temperatures, and (5) development of rapid analytical techniques to give reliable data as to the concentrations of the various components in the fused salt. It is further suggested that a detailed study of the effect of ternary and quaternary elements upon the solubility limit of any one element in a solvent might prove to be a fruitful area for work of a theoretical nature.

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IX. APPENDICES

A. Predicted Plutonium Behavior in the Process

While development of a fuel reprocessing cycle for Th-U-233 is of considerable interest in future applications for thorium as a breeder material, there is now only one reactor under construction, or in an advanced planning stage, that makes use of thorium or ThO_2. This is due to a large degree to the present pricing schedules for Pu ($40/gm) and U-233 ($15/gm). In order that the scope and present applicability of the process could be widened, it was decided that an extensive literature search on the behavior of plutonium and plutonium compounds should be made.

The results of the search may be summarized as follows: (1) plutonium will reduce $ZnCl_2$ to zinc metal (34), (2) $PuCl_2$ is reduced by magnesium in zinc, (3) plutonium (as liquid metal) will not reduce $MgCl_2$ (35), (4) plutonium is highly soluble in magnesium, while uranium is not (36), and (5) the vapor pressure of $PuCl_3$ is $5 \times 10^{-3}\mu$ at 600°C, 0.3μ at 700° and 2μ at 750° (29). These facts indicate that plutonium will follow uranium through the process as now envisioned, and that a U/Pu separation is possible using a magnesium step following the final reduction of the chlorides.

B. Preferential Dissolution of Zirconium from Uranium in Molten Zinc

One of the most complex problems in fuel reprocessing is that of the removal of cladding from fuel elements prior to the decontamination of the fuel itself. The aqueous processes make use of strong acid or alkali solutions plus mechanical dejacketing techniques to remove the cladding. These highly corrosive solutions place very severe requirements upon the dissolution container and associated piping. In general, presently proposed pyrometallurgical operations involve mechanical de-cladding.

In the course of the studies concerning the dissolution of the impure uranium in either liquid zinc or a fused salt containing $ZnCl_2$, an anomoly in the corrosion rate or uranium in zinc was observed. At temperatures below 650°C, the observed dissolution rates were quite slow compared to those observed above 650°C. It was then hoped that this anomoly could be used to advantage in the selective dissolution of cladding from the interior fuel material.

To evaluate the dissolution rate of zirconium, samples, all thin rectangular plates 1/16 inch thick and having similar areas, were placed in molten zinc for controlled periods of time at known temperatures. Weight losses were determined by weighing before and after immersion. The true weight after immersion being determined by etching the sample free of adhering zinc with concentrated nitric acid, which does not readily attack the zirconium. Some 4283 gms of high purity zinc were placed in a tantalum container, and this was then placed in a stainless steel container or pot. The container had provisions for atmosphere and temperature control, insertion and removal of samples, and visual observation of the melt. Prior to use, the samples were etched clean in HNO_3 + 5% HF and stored so as to preserve their surfaces.

The data resulting from this work are given in Table 62. Considerable variation in the rate of dissolution is observed at temperatures above 600°C. The variations apparently result from the formation of an adherent, non-uniform film of Zn-Zr compound on the surface of the sample. The samples were held in the zinc on a tantalum rod in a stationary position, and the zinc was not stirred or mechanically agitated. While it is certain that motion of the zinc would cause an increased dissolution rate, it was not felt that such agitation could be duplicated in a commercial application or confirmatory experimentation due to the shape of the samples. The data indicate that the rate is increasing with temperature, but that no violent attack occurs up to 684°C. Throughout the entire experiment, the solubility of zirconium in zinc was not exceeded.

The samples of uranium were placed in the zinc to evaluate the relative rate of dissolution for uranium under similar

Table 62. Rates of dissolution of zirconium in molten zinc

Temp. (°C)	Rate of dissolution (gms/cm²/min) x 10^4							
	Time (mins)							
	15	30	60	90	120	180	420	1020
515	-	-	-	-	-	1.51	1.44	(diss)
595	-	-	7.36	-	7.15	(diss)	-	-
602-607	12.12	4.21-6.78	6.01-10.29	-	-	-	-	-
626-630	8.64	14.72	14.02	8.46	-	-	-	-
650	15.79	13.70	12.68	-	-	-	-	-
684	-	15.65	-	-	-	-	-	-

circumstances. At 684°C, a 14 gram sample of uranium in the shape of a thin square plate was dissolved in less than 15 minutes. This gives an approximate rate of 834 x 10^{-4} gms/cm^2/min. However, at 602°C, rates of 0.564 x 10^{-4} to 0.411 x 10^{-4} gms/cm^2/min were observed for times of 30 to 60 minutes. From these data then, it may be concluded that the selective dissolution of zirconium cladding from a uranium fuel element is feasible at temperatures below 600°C. Use of a procedure such as this would then obviate the need for mechanical dejacketing, etc.

In a similar manner, samples of zirconium and uranium were tested in a fused salt mixture of 75 w/o KCl-LiCl eutectic

-25 w/o $ZnCl_2$. A 25 w/o $ZnCl_2$ salt was used, rather than 20 w/o as had been used in previous experimentation, to allow for the decrease of $ZnCl_2$ content caused by the dissolution of either zirconium or uranium. The data from these experiments are presented in Tables 63 and 64.

Table 63. Rates of dissolution of zirconium in a 75 w/o KCl-LiCl eutectic

Temp. (°C)	Rate of dissolution (gms/cm^2/min) x 10^4		
	Time (mins)		
	5	15	30
520-532	-	21.4	15.98
610-612	81.8	40.1	37.2

Table 64. Rates of dissolution of uranium in a 75 w/o KCl-LiCl eutectic - 25 w/o $ZnCl_2$ fused salt

Temp. (°C)	Rate of dissolution (gms/cm^2/min) x 10^4				
	Time (mins)				
	5	10	15	20	30
513-520	-	-	48.1	38.7	-
610	(diss)	(diss)	-	-	(diss)

Examination of the data indicates that at both 520 and 610°C, uranium is more rapidly dissolved than is zirconium. This fact alone is sufficient to eliminate the use of a $ZnCl_2$ bearing salt to preferentially dissolve the cladding from a fuel element. The rate for uranium at 610°C indicated by dissolution in 5 minutes is $2,502 \times 10^{-4}$ $gm/cm^2/min$. It is further noted that, as in the zinc dissolution work, the rates drop off with time in solution and increase with temperature.

C. Containment of Liquid Zinc at Elevated Temperatures

A considerable effort in the development of a pyrometallurgical reprocessing system using liquid zinc has been expended by the Argonne National Laboratories (11). Recently (30) this work has been abandoned in favor of cadmium as the solvent, due to the corrosive nature of liquid zinc systems at elevated temperatures. In the process discussed in this work, zinc plays a large role. Work and a literature survey by the author had indicated that only refractory metals such as tantalum, tungstun or molybdenum or ceramic vessels would be satisfactory as containers for liquid zinc. However, these materials have limited service life and are either expensive or unwieldy to handle or fabricate. Thus, a satisfactory container material was of considerable interest.

Based upon thermodynamic and phase diagram considerations, it was suggested that an iron-silicon alloy might prove to be satisfactory for holding molten zinc. A series of limited tests indicated that a commercial iron known as Duriron, with a silicon content of approximately 14.5 per cent, is unaffected by zinc for up to 100 hours at 700°C. Further tests using grey iron, with approximately 2 per cent silicon, showed that that material is rapidly attacked by the zinc, and as a consequence is unsatisfactory at elevated temperatures. The Duriron samples used in this work were cut from a piece of scrap Duriron pipe. This pipe had been cast, and the internal and external surfaces showed a chill cast condition, while the interior of the samples indicated a slowly cooled structure.

A series of photomicrographs illustrating the behavior of both grey iron and Duriron in zinc have been prepared and are presented in Figures 40 through 46. Figure 40 presents the microstructure of grey iron in the as-cast condition. The dark, worm-shaped figures are graphite, and the lammelar structure of pearlite with a ferrite matrix is also present. Figure 41 is a photomicrograph of the surface of grey iron after being immersed in liquid zinc for 5 hours at 700°C. The interior of the sample shows the effect of annealing at 700°C with the pearlite being dissolved. The inner-most reaction layer shows the graphite flakes, what is probably an iron-zinc compound and an eutectoid reaction. The eutectoid is probably the gamma going to alpha and lambda that occurs at

623°C and 27.5 w/o zinc in the iron-zinc system. In the outer layer, a zinc matrix with compound particles is observed. Figure 42 shows the structure of Duriron near a chill-cast surface. The white material is ferrite with a complex Fe-Si-C precipitate. In Figure 43, we see the action of liquid zinc on the chill-cast Duriron. A thin reaction layer of zinc plus iron can be seen at the surface of the sample. The reaction layer is limited in thickness, and the interior of the sample shows the effect of annealing, with the dissolution of a majority of the precipitate. Apparently the corrosion has stopped in the interior of the sample. Those surfaces of the sample that were not chill-cast were completely free of any zinc attack. This sample was in zinc for 10 hours at 700°C. Since slow cooling or annealing apparently aided the corrosion resistance of the Duriron, a sample of Duriron was annealed for 20 hours at 1000°C and furnace cooled. The microstructure of this alloy is shown in Figure 44. The complex precipitate has coalesced and formed carbide plates or stringers, leaving the alpha solid solution of silicon and carbon. This material is highly resistant to the attack of liquid zinc and after 10 hours at 700°C in molten zinc, absolutely no attack was observed at any point on the sample.

An additional experiment using a sample of Duriron annealed at 950°C for 24 hours in vacuo was performed. This sample was immersed in molten zinc for 100 hours at 700°C.

Figure 45 presents a photomicrograph of a corner of the sample. No indication of attack is observed, although particles of a Fe-Zn compound can be seen in the adhering zinc phase.

It was further suggested that the action of Zn-Mg solutions might be markedly different from that of pure zinc, because of the tendency of the magnesium to reduce any oxide surface film that might act to inhibit zinc corrosion. To examine this possibility, a solution of Zn - 7 w/o Mg was prepared, and a Duriron sample immersed for 100 hours. This sample had previously been in zinc for 100 hours. Figure 46 is a photomicrograph of the sample surface. It is readily apparent that the surface has been attacked to some degree (approximately 0.03"). While this amount is not negligible, it is felt that it does not preclude the use of Duriron vessels for the containment of zinc and Zn-Mg solutions. However, this attack does present a problem in that the dissolved iron in the solution will act as a contaminant to the purified uranium present in the Zn-Mg solutions. Further, it should be noted that the effects of ternary and quaternary additions to liquid zinc or Zn-Mg alloys have not been checked. It is quite possible that additions such as uranium may have very adverse effects upon the resistance to corrosion by zinc of the Duriron.

Figure 40. Grey iron, 100X, etchant 5% HNO_3 in alcohol

Figure 41. Grey iron in zinc for 5 hours, 100X, etchant 5% HNO_3 in alcohol

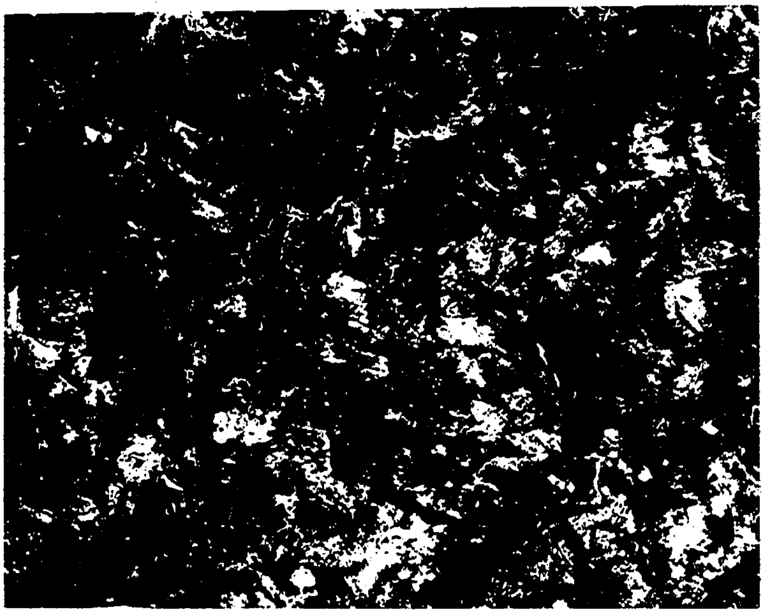
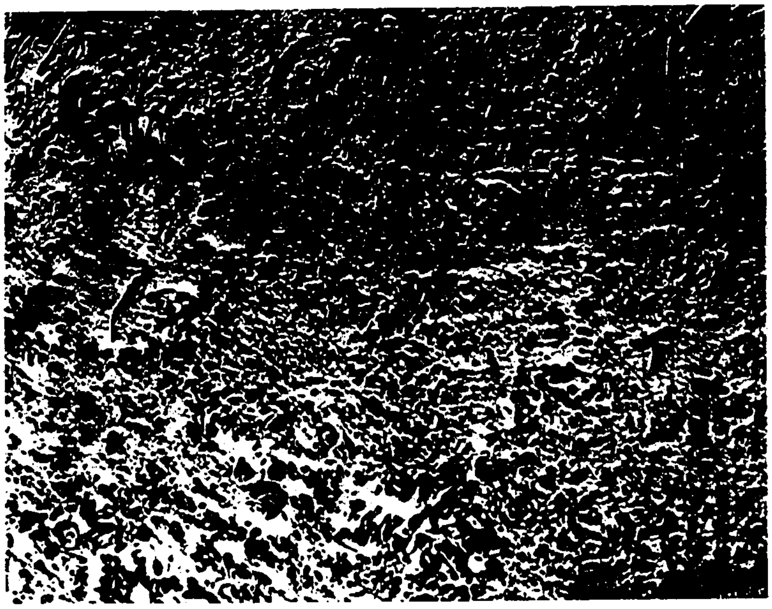


Figure 42. Duriron, as cast, 100X, etchant 10 ml HNO_3, 20 ml HF, 45 ml glycerol

Figure 43. Duriron, after 10 hours in zinc at 700°C, 100X, etchant 10 ml HNO_3, 20 ml HF, 45 ml glycerol



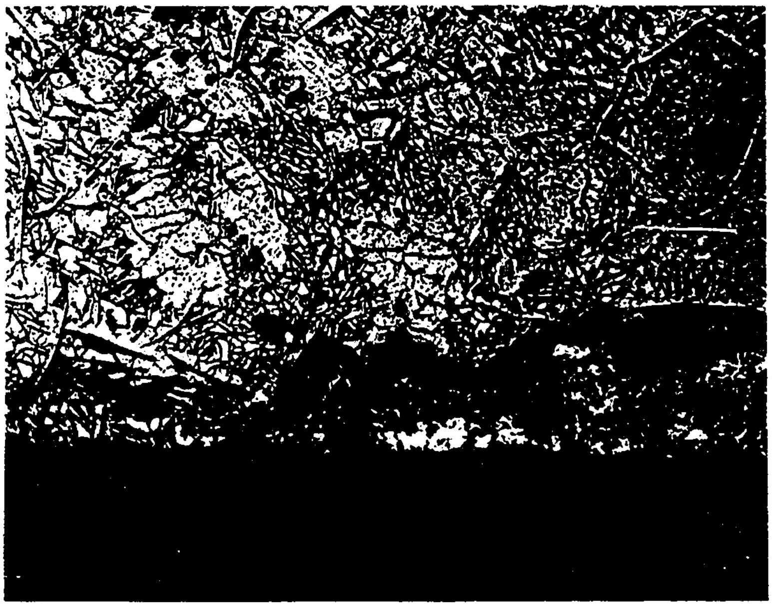


Figure 44. Duriron, annealed 20 hours at 1000°C, 100X, etchant 10 ml HNO_3, 20 ml HF, 45 ml glycerol

Figure 45. Annealed Duriron after 100 hours in zinc at 700°C, 100X, etchant 10 ml HNO_3, 20 ml HF, 45 ml glycerol

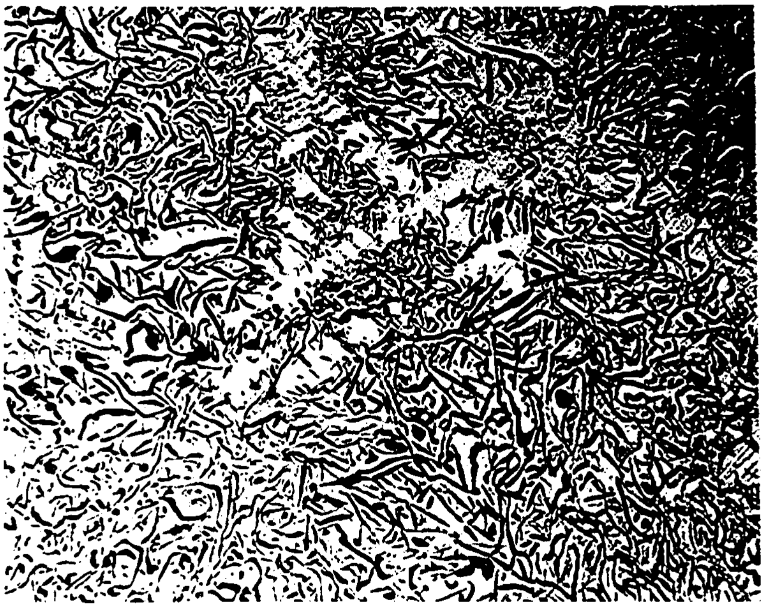


Figure 46. Annealed Duriron after 100 hours in zinc and 100 hours in Zn - 7 w/o Mg at 700°C, 100X, etchant 10 ml HNO_3, 20 ml HF, 45 ml glycerol

D. Additional Applications of the Process

While the number of possible variations in the process probably equals the number of various fuel element configurations, there are at least three specific additional applications of the process that are worthy of mention. The first is the possible application to plutonium bearing systems which has already been discussed. Additionally, the work under discussion might be applied to fuel systems containing oxides of uranium, plutonium or thorium, and to the recovery of enriched uranium scrap resulting from the fabrication of fuel elements.

1. Application to oxide bearing systems

The "melt refining process", as developed by the ANL, involves the formation of an oxide powder containing some of the uranium, plutonium, and a large portion of the fission products. These oxides are then reduced to metallic compounds by dissolution in Zn-Mg alloys (9). The insertion of such a step following or in conjunction with the cladding dissolution operation would seem to be a relatively straightforward procedure based upon ANL's experience. Inclusion of this technique would then permit the decontamination of the oxide fuels, whether they were present as compact pellets or dispersions in metallic matrices.

2. Application to the salvage of scrap materials

Under present operating procedures, any scrap materials generated in the fabrication of fuel elements are processed by standard aqueous techniques. Such operations are performed on a contractural basis, which costs about $1.00 per gram of enriched uranium. The primary scrap so handled consists of uranium and zirconium mixtures. As previously indicated, the U/Zr separation in the process under consideration is quite good and relatively straightforward. Thus, the potential financial incentives for the application of this work to scrap recoveries are very large.

E. Engineering Considerations for Commercial Application of the Process

A primary consideration in the application of the proposed process to commercial situations is the factor of system volume requirements. To evaluate these requirements, it is necessary to either estimate or measure a number of system criteria, such as densities and concentration levels. Based upon a 1 w/o uranium concentration in the initial thorium, and a 10 w/o uranium concentration in both the zinc and fused salt solutions and suitable assumptions as to the densities of the resultant solutions, a list of system volume requirements has been prepared. This list is presented in Table 65. No estimation for the volume required for a distillation operation has been made, since no specific design for a condenser system has been

Table 65. Container volume requirements for the fused salt extraction process

Process step	Volume*
Mg-Th/U separation	1000 cm^3/Kg Th
U-233 dissolution in Zn	1600 cm^3/Kg U
Oxidation of U to UCl_3	3400 cm^3/Kg U
Reduction of UCl_3	3100 cm^3/Kg U

*All volumes quoted include adequate excesses for clearance, and fused salt covers over the liquid metal phases.

made. However, the container volume for the salt would be the same as or less than that required for the oxidation of the U to UCl_3, i.e., 3400 cm^3/Kg U.

An additional factor in commercial operations is the time for the uranium to pass through the system. Taking one kilogram of crude, impure uranium, after the Mg-Th/U separation, the time required for dissolution, oxidation, distillation and reduction is estimated to be under six hours at 600°C. The time to retort the zinc and consolidate the uranium depends upon system volumes and equipment capacities. The overall time for operation of the process is estimated at less than 20 hours.

F. Initial Weights and Recoveries in the Micro-scale Experiments

In the following tables, the initial weights of the various components and the appropriate recoveries are listed for the various elements considered in the micro-scale work.

Table 66. Initial weight and recovery of iron used in micro-scale experiments

Exp.	Initial charge	Weight (gms)	% Fe recovered
3	Fe	2.80	100.1
	Salt 1*	14.89	
	Zn	20.58	
4	Fe	2.98	101
	Salt 1*	16.53	
	Zn	19.37	

*Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

Table 67. Initial weight and recovery of niobium used in micro-scale experiments

Exp.	Initial charge	Weight (gms)	% Nb recovered
4	Nb	2.94	103
	Salt 1*	13.14	
	Zn	21.28	
5	Nb	2.26	133
	Salt 1*	10.82	
	Zn	20.89	
Blank	Salt 1*	14.3854	-
	Zn	17.2574	

*Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

Table 68. Initial weights of components in micro-scale distillation experiments

Exp.	Zr	Zn	U	Salt 1*
5	0.8617	18.6234	--	17.8794
6	0.7778	18.7489	--	19.7169
7	0.8575	19.9607	--	16.4211
8	0.7399	23.5661	1.3573	19.0206
9	0.4621	17.0223	0.8993	17.8566
10	0.4192	12.7335	0.5762	18.0786
11	0.5419	16.2262	0.9109	21.3115
12	0.5080	16.8385	0.5514	18.3421
13	3.0481	22.6888	--	11.0471
14	3.2732	21.4511	--	12.2555
15	3.0753	21.4808	--	10.5307
16	3.3251	16.3613	--	11.0605

*Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

Table 69. Initial weights of components in micro-scale experiments using uranium and uranium - 5.2 w/o chromium containing protactinium

	Weight of initial components (gms)					
Exp.	Salt 1*	U	U-Cr	Zn	Ca	Mg
C-1	10.0	1.60	-	10.72	0.80	-
C-2	10.0	1.14	-	9.72	0.80	-
C-3	10.0	-	1.10	8.53	0.80	-
C-4	10.0	-	1.22	9.97	0.80	-
MC-1	10.0	1.97	-	10.62	0.10	0.59
MC-2	10.0	1.0	-	11.44	0.10	0.60
MC-3	10.0	-	1.33	12.04	0.11	0.62
MC-4	10.0	-	1.60	12.15	0.10	0.59
M-1	10.0	1.30	-	11.03	-	0.63
M-2	10.0	1.50	-	10.67	-	0.62
M-3	10.0	-	1.27	11.02	-	0.58
M-4	10.0	-	0.92	11.20	-	0.62

*Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

Table 70. Initial weights and recoveries of components in micro-scale experiments using thorium containing protactinium

Exp.	Weight of initial components (gms)								Recoveries	
	Salt 1*	Salt 2**	Salt 4***	Th#	U	Zn	Mg	Th	% U	% Th
1	-	-	11.1354	0.7217	1.4223	26.6703	-	-	71.6	-
2	-	-	12.5574	1.0978	1.6181	22.3529	-	-	71.9	-
3	12.4035	-	-	0.5339	1.5280	24.3977	0.4872	-	79.8	5.9
4	18.8624	-	-	1.4626	0.9678	23.4187	0.6480	-	58.6	7.3
5	17.7207	-	-	0.6046	1.1359	23.5656	0.4983	-	75.0	8.0
6	14.4995	-	-	0.7986	1.3726	27.5683	0.4323	-	89.9	16.8
7	17.7091	-	-	0.6192	1.1817	21.6728	0.1989	-	91.5	78.0
8	15.2227	-	-	0.5990	1.3855	24.5834	0.2084	-	89.1	81.6
9	15.9331	-	-	1.4236	1.3791	24.1092	0.0953	-	94.5	41.4
10	15.6040	-	-	1.1754	1.7540	23.9245	-	-	92.2	44.1
11	16.2660	-	-	1.1810	1.6214	30.9505	-	-	92.2	65.8
12	-	15.6794	-	0.9879	-	-	8.0665	2.8124	-	-
14	14.0311	-	-	0.9346	1.3846	14.3082	0.4918	-	83.0	18.7
15	14.5894	-	-	0.6948	0.9050	14.2190	0.3569	-	85.0	30.0
30	0.0300	-	7.4857	0.3627	1.1088	14.6996	-	-	95.4	-
31	0.0475	-	6.8719	0.3015	1.1354	14.9583	-	-	93.4	-
32	0.0406	-	6.7894	0.2581	1.1044	15.0550	-	-	93.6	-
33	0.0559	-	8.0549	0.3617	1.1813	14.6892	-	-	92.3	-

* Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

** Salt 2 = 85 w/o KCl-LiCl eutectic - 15 w/o $MgCl_2$.

*** Salt 4 = KCl-LiCl eutectic.

\# Indicates radioactive element.

Table 71. Initial weights and recoveries of components in micro-scale experiments using zirconium

Exp.	Weight of initial components (gms)						Recoveries	
	Salt 1*	Zr#	U	Zn	Mg	U-Zr	% U	% Zr
2	22.60	-	-	20.45	-	2.15	84.4	71
3	22.85	-	-	19.4	-	1.8	85.6	72.2
SP-3	22.6	-	-	19.9	-	1.9	87.4	24.4
5	13.8802	0.0779	0.5600	9.0427	0.4119	-	71.9	80.1
6	14.6094	0.1842	0.5952	8.9919	0.4453	-	88.5	80.8
7	15.5803	0.1786	0.4590	8.8067	0.4974	-	95.9	90.1
8	9.4709	0.1653	2.1477	20.9329	-	-	99.4	71.4
10	12.7453	0.1356	2.1178	21.4808	-	-	91.9	60.9
11	12.3158	0.0944	2.0741	21.3003	-	-	102.1	71.3

* Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

# Indicates radioactive element.

Table 72. Initial weights and recoveries of components in micro-scale experiments using chromium

Exp.	Weight of initial components (gms)						Recoveries	
	Salt 1*	Cr#	Cr	U	Zn	U-Cr	%U	%Cr
1	15.2326	0.1337	-	0.7758	12.4145	-	103.6	105
2	16.9309	0.1781	-	1.0135	12.9851	-	83.5	93.9
3	17.5380	0.2030	-	1.2346	24.3562	-	73.8	95.9
4	17.6754	0.0937	-	1.4784	18.6945	-	81.8	93.6
1	17.0	-	-	-	19.7	2.30	88.4	45.8
2	18.8	-	-	-	19.4	2.10	89.0	46.0
3	18.7	-	-	-	21.9	2.35	88.3	48.4
SP-4	29.6	-	-	-	19.7	1.90	82.7	61.0
4	18.25	-	-	-	15.35	2.85	86.9	84.9
5	17.35	-	-	-	14.80	2.00	80.3	127
6	14.8516	-	1.9414	-	19.8643	-	-	95.9
7	12.4751	-	2.0868	-	18.8873	-	-	95.8

* Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

# Indicates radioactive element.

Table 73. Initial weights and recoveries of components in micro-scale experiments using cerium

Exp.	Weight of initial components (gms)										Recoveries	
	Salt 1*	Ce#	U	Zn	Zn-47 w/oMg	Mg	Th	Salt 2**	Mg-42 w/oTh	Salt 3***	%U	%Ce
1	10.6918	0.3235	1.0932	10.9875	-	0.2042	-	-	-	-	81.9	-
2	13.8206	0.3725	0.5595	12.8321	-	0.1355	-	-	-	-	69.9	-
3	12.1913	0.4295	0.8357	12.9228	-	0.2336	-	-	-	-	84.2	-
4	13.1670	0.4229	0.3189	15.0892	-	0.1612	-	-	-	-	44.3	-
5	16.7389	0.4349	0.9653	-	5.5971	-	-	-	-	-	6.68	-
6	12.1753	0.4463	0.9644	-	5.2049	-	-	-	-	-	4.53	-
7	13.8868	0.4145	0.6636	-	7.2043	-	-	-	-	-	3.6	-
8	14.3030	0.3773	1.9326	-	5.1281	-	-	-	-	-	3.99	-
9	7.2691	0.3524	-	-	-	13.6100	11.8273	-	-	-	-	-
10	14.2730	0.5067	-	-	-	11.5089	11.1888	-	-	-	-	-
11	10.1700	0.2489	-	-	-	13.7920	10.4727	-	-	-	-	-
12	18.4570	0.4174	-	-	-	13.2872	11.1861	-	-	-	-	-
13	-	0.0984	-	-	-	5.8730	3.9473	14.8029	-	-	-	99.3
14	-	0.1860	-	-	-	8.0032	4.4789	7.9907	-	-	-	100.7
15	-	0.1470	-	-	-	6.0892	4.2303	7.6758	-	-	-	97.7
16	11.8010	0.1782	1.8605	17.4633	-	0.3123	-	-	-	-	97.6	127.9
17	14.4860	0.2304	1.7049	12.2247	-	0.4225	-	-	-	-	97.9	113.9
18	9.8806	0.1689	2.1722	17.0705	-	0.2935	-	-	-	-	94.4	114.1

* Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

\# Indicates radioactive element.

** Salt 2 = 85 w/o KCl-LiCl eutectic - 15 w/o $MgCl_2$.

*** Salt 3 = 95 w/o KCl-LiCl eutectic - 5 w/o $MgCl_2$.

Table 73. (Continued)

Exp.	Weight of initial components (gms)										Recoveries	
	Salt 1*	Ce#	U	Zn	Zn-47 w/oMg	Mg	Th	Salt 2**	Mg-42 w/oTh	Salt 3***	%U	%Ce
19	12.8460	0.2263	1.9502	17.7019	-	0.4110	-	-	-	-	101.7	95.7
20	-	0.1739	-	-	-	2.3711	1.8211	-	-	19.9530	-	170.2
21	-	0.2102	-	-	-	2.1011	1.5947	-	-	18.1121	-	91.7
22	-	0.1932	-	-	-	2.3399	1.6430	-	-	19.1895	-	114.5
23	-	0.1624	-	-	-	2.3407	1.7861	-	-	19.9651	-	95.2
24	-	0.1910	-	-	-	-	-	12.7266	3.9114	-	-	101.1
25	-	0.2067	-	-	-	-	-	18.1923	4.0150	-	-	98.1
26	-	0.1710	-	-	-	-	-	8.7887	3.0988	-	-	100.0
27	-	0.1838	-	-	-	-	-	10.8601	3.3251	-	-	101.7
				U-Cr		Mg-42w/oTh		MgCl$_2$	KCl-LiCl eutectic			
33		0.1745		-		4.1986		4.0062	5.9917			
34		0.1839		-		4.3751		3.9452	5.9406			
36		0.1707		60.0901		29.0022		-	-			78.6
37		0.1789		66.3444		28.9300		-	-			81.7
38		0.2573		71.8246		31.9703		-	-			78.3

Table 74. Initial weights and recoveries of components in micro-scale experiments using yttrium

Exp.	Weight of initial components (gms)								Recoveries	
	Salt 1*	Salt 2**	Y#	U	Zn	Zn-47w/oMg	Th	Mg	%Y	%U
1	10.9695	-	0.2099	1.3433	20.9958	-	-	0.3821	99.3	81.6
2	11.3365	-	0.1831	0.8638	19.8386	-	-	0.3675	87.8	86.7
3	12.0407	-	0.1130	1.3385	23.6150	-	-	0.3907	83.4	87.6
4	14.4029	-	0.1038	1.0506	19.1705	-	-	0.4671	86.2	87.5
5	12.3866	-	0.2288	0.7549	24.5866	-	-	0.3123	86.3	96.5
6	15.9403	-	0.2698	1.1766	22.6846	-	-	0.3543	67.4	96.2
7	16.1081	-	0.1189	0.6562	18.4642	-	-	-	79.1	98.1
8	16.1321	-	0.2703	1.1892	20.6122	-	-	-	89.9	103.1
9	17.2953	-	0.1903	1.1669	19.7179	-	-	-	81.4	98.3
10	16.6173	-	0.1851	1.1471	-	12.3791	-	-	141	-
11	13.2132	-	0.1880	1.0482	-	14.3588	-	-	107	-
12	16.1355	-	0.2462	1.1506	-	11.9981	-	-	141	-
13	-	9.0186	0.2829	-	-	-	3.8438	5.6667	92.8	-
14	-	14.9241	0.1904	-	-	-	4.4281	6.2104	99.3	-
15	-	10.6616	0.2428	-	-	-	3.6850	6.4427	73.8	-

* Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.

** Salt 2 = 85 w/o KCl-LiCl eutectic - 15 w/o $ZnCl_2$.

\# Indicates radioactive element.

Table 75. Initial weight and recovery of molybdenum used in micro-scale experiments

Exp.	Initial charge	Weights (gms)
1	U - 5 w/o Mo	2.1
	Salt 1*	21.3
	Zn	19.0
2	U - 5 w/o Mo	2.1
	Salt 1*	21.95
	Zn	19.45
3	U - 5 w/o Mo	1.4
	Salt 1*	21.65
	Zn	20.5
SP-2	U - 5 w/o Mo	3.0
	Salt 1*	31.0
	Zn	19.8

* Salt 1 = 80 w/o KCl-LiCl eutectic - 20 w/o $ZnCl_2$.