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TECHNOLOGY REVIEW REPORT
PYROCHEMICAL PROCESSING OF PLUTONIUM.

MELVIN S. COOPS
JAMES B. KNIGHTON
LAWRENCE J. MULLINS

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PYROCHEMICAL PROCESSING OF PLUTONIUM*

Melvin S. Coops
Lawrence Livermore National Laboratory, Livermore, CA 94550

James B. Knighton
Rockwell International, Rocky Flats Plant,
Golden, CO 80401

Lawrence J. Mullins
Los Alamos National Laboratory, Los Alamos, N.M. 87545

Non-aqueous processes are now in routine use for direct conversion of plutonium oxide to metal, molten salt extraction of americium, and purification of impure metals by electrorefining. These processes are carried out at elevated temperatures in either refractory metal crucibles or magnesium-oxide ceramics in batch-mode operation. Direct oxide reduction is performed in units up to 700 gram PuO_2 batch size with molten calcium metal as the reductant and calcium chloride as the reaction flux. Americium metal is removed from plutonium metal by salt extraction with molten magnesium chloride. Electrorefining is used to isolate impurities from molten plutonium by molten salt ion transport in a controlled potential oxidation-reduction cell. Such cells can purify five or more kilograms of impure metal per 5-day electrorefining cycle. The product metal obtained is typically >99.9% pure, starting from impure feeds. Metal scrap and crucible skulls are recovered by hydriding of the metallic residues and recovered either as impure metal or oxide feeds.

Introduction

The term "Pyrochemical Processing" is commonly applied to a family of chemical processes that utilize oxidation-reduction reactions to effect chemical separations at elevated temperatures. These reactions are carried out in the total absence of aqueous solvents, and are used to chemically isolate elements, or groups of elements, from impurities in the feed materials.

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Pyrochemical processes have significant advantages over aqueous processes for the purification of actinide metals for several reasons: the size of the equipment used to carry out the chemical processes is very compact, typically an order of magnitude smaller than that needed for aqueous methods; the chemical process can be designed to recycle many of the reagents used, thereby greatly minimizing waste disposal problems; nuclear criticality concerns are alleviated because non-moderating reagents can be used exclusively; pyrochemical processes can readily accept metallic feed stocks and produce high purity metallic products; and because pyrochemical processes require smaller facilities, generate less waste, and use less manpower, they are cheaper to operate. Like aqueous processes, pyrochemical systems utilize several different physical processes including liquid-liquid extraction, precipitation, filtration, evaporation and distillation. These are performed at elevated temperatures in either refractory metal or ceramic equipment. Molten metals and molten salts are used both as solvents and as immiscible extractants in various steps in the chemical purification sequence. Specialized process hardware has been constructed to meet the needs of these highly corrosive processes.

While pyrochemical processes have inherent advantages, they require sophisticated equipment and specialized operating conditions. One of the basic techniques used in pyroprocessing is liquid-liquid extraction between molten salts and molten metals. The process temperatures are typically 1100 K, and because both the process reagents and the refractory materials used to contain them are susceptible to air oxidation, process operations must be carried out in an inert atmosphere. As the actinide elements are inherently radioactive, work on actinide compounds is routinely carried out in tight process enclosures; pyroprocessing operations require that the atmosphere in contact with the process reagents be truly inert and also dry. Recirculating argon or helium atmospheres are used to meet this requirement. Where sealed reaction vessels are used, dry air enclosures are adequate.

In order to obtain maximum efficiency from pyroprocessing, very high purity reagents must be used. Obtaining satisfactory reagents has been a continuing problem but as the demand for high purity metals and salts rises, commercial sources become more available. At present it is necessary to dry all commercially obtained reagent salts prior to use.

The following pages will describe several examples of pyrochemical processing as applied to the recycle of plutonium, and will briefly review the fundamental chemistry of these processes. We shall review the conversion of plutonium oxide to plutonium metal by the direct oxide reduction process (DOR), the removal of americium from metallic plutonium by molten salt extraction (MSE), and the purification of metallic plutonium from dissolved impurities by the electro-refining technique (ER).

All actinide metals are pyrophoric and it is common practice to burn metallic scrap to oxide as a safety precaution. Plutonium is typically stored as PuO_2 and must be chemically reduced to metal prior to component manufacture. This has traditionally been done by precipitating $Pu_2(C_2O_4)_3$, $Pu(O_2)_2$, $Pu(OH)_3$, or PuF_3 from solution and converting it to PuF_4 for bomb reduction to metal. This method is now being replaced by direct reduction techniques.

Reduction of Plutonium Oxide to Metal

The first successful reduction of PuO_2 to metal with calcium was reported by Wade and Wolf(1) in 1968. Their process was carried out in two stages: an initial thermit reaction between PuO_2 and Ca, followed by a leaching step with $CaCl_2$ to dissolve the CaO reaction product and any unreacted Ca. The fluid flux permitted finely divided plutonium to coalesce into a pool of metal. Rotation of the inclined reaction vessel was used to promote slag dissolution and metal consolidation. The original process described by Wade has been significantly improved by workers at several DOE sites(2,3,4).

The DOR process presently used for production work utilizes a $CaCl_2$ (or $CaCl_2$-CaF_2) flux to both dissolve the CaO reaction product at the reaction site and to provide a fresh supply of Ca reductant to keep the reaction going. This process exploits the solubility of Ca and CaO in $CaCl_2$ while utilizing the insolubility of plutonium metal in the Ca-CaO-$CaCl_2$ reaction flux to permit metal consolidation. Vigorous stirring is used to keep the reactants in intimate contact so that the reaction is driven to completion. Workers at Los Alamos used the above process for ^{238}Pu metal production in 1975(4). That work led to a routine 700 gram scale oxide reduction process that has been in use since that time. Recent development work at LANL has increased the batch size to one kilogram of oxide feed. It appears that the ultimate limitation on DOR batch size will be from criticality safety constraints.

The use of this direct oxide reduction process is replacing fluoride reduction as it eliminates neutron exposure to operating personnel (alpha particles from plutonium decay have sufficient energy to eject neutrons from fluorine by the α,n reaction) and eliminates reduction residues which require subsequent recovery.

The reaction is carried out under an inert atmosphere in an open crucible at approximately 830°C. Figure 1 shows typical equipment used for direct oxide reduction. Vitrified magnesium oxide ceramic is commonly used as a container material, but tungsten and tantalum can also be used(3). If the latter are used, CaF_2 is added to lower the temperature needed to liquify the flux, thereby decreasing the corrosion of the crucible and subsequent contamination of the metal product. Intense stirring is required to keep all the reactants in contact as the very dense PuO_2 sinks and Ca metal floats in the melt. The reaction is exothermic and a temperature rise occurs after initiation. The overall chemical reaction is:

$$PuO_2 + 2Ca \rightarrow Pu + 2CaO$$
$$\Delta G = -44.27 \text{ KCal at } 1000 \text{ K}$$

The mechanism for the reaction is not fully understood at present but is believed to take place in several steps. Moseley et-al(3) found that β-Pu_2O_3 is formed as a solid residue when insufficient Ca is present to drive the reaction to completion.

Several of the possible reacting species and their free energy of formation are listed in the table below:

	ΔG @ 1000 K		
Compound	KCal/mole	KCal/gr-at oxygen	Ref
PuO_2	-210.130	-105.065	20
α-Pu_2O_3	-367.696	-122.565	20
β-Pu_2O_3	-343.942	-114.647	20
PuO	-113.057	-113.057	20
CaO	-127.200	-127.200	21

The reaction mechanism proposed by Moseley is:

Reaction	ΔG @ 1000 K
$2PuO_2 + Ca \rightarrow \beta Pu_2O_3 + CaO$	-50.882 KCal
$\beta Pu_2O_3 + 3Ca \rightarrow 2Pu + 3CaO$	-37.658 KCal

It is also feasible to assume the following mechanism:

$PuO_2 + Ca \rightarrow PuO + CaO$	-30.127 KCal
$PuO + PuO_2 \rightarrow \beta Pu_2O_3$	-20.755 KCal
$\beta Pu_2O_3 + Ca \rightarrow 2PuO + CaO$	- 9.372 KCal
$3PuO \rightarrow Pu + \beta Pu_2O_3$	- 4.771 KCal
$PuO + Ca \rightarrow Pu + CaO$	-14.143 KCal
$3PuO_2 + Pu \rightarrow 2\beta Pu_2O_3$	-57.497 KCal

An additional back reaction can occur between βPu_2O_3 *and* PuO_2 to form αPu_2O_3. Conditions leading to the formation of αPu_2O_3 are to be avoided as the reaction between a single atom of Ca and αPu_2O_3 is not thermodynamically favorable:

$$\alpha Pu_2O_3 + Ca \rightarrow 2PuO + CaO \qquad +14.382 \text{ KCal}$$

$$\alpha Pu_2O_3 + 2Ca \rightarrow Pu + PuO + CaO \qquad + 0.239 \text{ KCal}$$

$$\alpha Pu_2O_3 + 3Ca \rightarrow 2Pu + 3CaO \qquad -13.904 \text{ KCal}$$

Although the exact chemical mechanism for the direct oxide reduction reaction has not yet been fully characterized, it has been well established that the reaction goes to completion when excess calcium is present, sufficient $CaCl_2$ is available to dissolve the CaO produced, and adequate stirring is used. As calcium metal is soluble to about 1 wt% in $CaCl_2$ at 835°C, excess Ca insures that the reaction is driven to completion by mass-action effects.

The $CaCl_2$-rich end of the $CaO-CaCl_2$ and $CaO-CaCl_2-CaF_2$ phase diagrams have been worked out by Wenz et-al(6) and are shown in Figures 2 and 3. The phase diagrams indicate that CaO is soluble to 18.5 mole % in $CaCl_2$ at 835°C, but if the loading of CaO rises much above 14 mole % the increased viscosity of the melt retards consolidation of the droplets of plutonium into a single pool. The 700-gram PuO_2 reduction process at LANL(5) uses 50 mole % excess calcium reductant and a CaO loading in $CaCl_2$ of about 14 mole %, to give product yeilds in excess of 99.5%. After the melt is allowed to cool, an ingot of plutonium metal can be readily cleaved from the solidified flux. The salt phase contains negligible unreacted PuO_2. At present, both the $CaCl_2$-CaO salt residue and the excess calcium metal are discarded to waste. These materials are promising candidates for recycle; processes are presently being developed to recover these reagents for reuse.

Extraction of Americium With Molten Salt

All reactor-produced plutonium contains a mixture of several plutonium isotopes. The continuous decay of ^{241}Pu (14.8 year half-life) is the source of ^{241}Am. This isotope decays by alpha emission with the simultaneous emission of 60 kilovolt gamma rays in 80% abundance. In order to minimize personnel exposure, this element is removed from the metal prior to fabrication.

Early experimental work in electrorefining at Los Alamos by Mullins et-al(7) demonstrated that americium could be partitioned between molten plutonium and a molten NaCl-KCl salt containing Pu^{+3} ions, and Knighton et-al(8), working at ANL on molten salt separation processes for fuel reprocessing, demonstrated that americium could be extracted from Mg-Zn-Pu-Am alloys with immiscible molten magnesium chloride salts. Work was soon initiated by Long et-al(9) at Rocky Flats to study the extraction of americium from molten plutonium by contacting with molten NaCl-KCl salt containing a few percent of $MgCl_2$.

A production process has evolved from this original work, and is presently used for extracting americium from kilogram amounts of plutonium metal. This process is based upon equilibrium partitioning (by oxidation-reduction reactions) of americium and plutonium between the molten chloride salt and the molten plutonium phase. The chemistry of this process is indicated by the following reactions:

	ΔG @ 1000 K
$Pu + 3/2\ MgCl_2 \rightarrow PuCl_3 + 3/2\ Mg$	-2.4 KCal
$Am + PuCl_3 \rightarrow AmCl_3 + Pu$	-25.8 KCal
$Am + 3/2\ MgCl_2 \rightarrow AmCl_3 + 3/2\ Mg$	-28.2 KCal

The free energies of formation for the actinide compounds above are given by the following table:

Compound	ΔG @ 1000 K (KCal per gram-atom of chlorine)
$AmCl_3$	-67.0
$PuCl_3$	-58.4
$MgCl_2$	-57.6

The thermodynamic activity equilibrium constant (Ka) is expressed in terms of mole fraction (X) and activity coefficient (γ) by the following equation:

$$K_a = \frac{(X_{AmCl_3})(\gamma_{AmCl_3})(X_{Mg})^{3/2}(\gamma_{Mg})^{3/2}}{(X_{Am})(\gamma_{Am})(X_{MgCl_2})^{3/2}(\gamma_{MgCl_2})^{3/2}}$$

The term $\frac{X_{AmCl_3}}{X_{Am}}$ is defined as the distribition coefficient (D_{Am}) and is simply the ratio of the mole fraction of $AmCl_3$ in the salt to the atom fraction of Am in the metal.

The activity coefficients in the above equation may be determined by obtaining experimental data for D_{Am}, and relating K_a to the free energy change for the reaction using the equation $\Delta G_f = -RT \ln K$.

In laboratory work the following closely related, but not identical, relationship is used to determine the partition value between phases:

$$K_d = \frac{\text{conc. of } AmCl_3 \text{ in salt phase}}{\text{conc. of Am in metal phase}}$$

by convention, the above ratio is usually expressed in weight percent instead of mole fractions. For extraction work the term α is used for the extraction factor and is related to K_d in the following manner:

$$\alpha = (K_d)(\frac{s}{m})(F)(\beta)$$

where

α = extraction factor = $\frac{\text{Wt of solute in salt phase}}{\text{Wt of solute in metal phase}}$
K_d = distribution coefficient (as defined above)
s/m = salt to metal ratio by weight
F = fraction of equilibrium attained
β = effects of side reactions

For a multi-stage counter-current extraction operated in true equilibrium without side reactions, the partitioning of a solute into the metal phase (f_m) and the salt phase (f_s) is defined as follows:

$$f_m = \frac{(\alpha - 1)}{(\alpha^{n+1}) - 1} \qquad f_s = 1 - f_m$$

where n = number of counter-current stages.

For a cross-current extraction the equation is defined as follows:

$$f_m = \frac{1}{(1+\alpha)^n} \qquad f_s = 1 - f_m = \frac{(1+\alpha)^n - 1}{(1+\alpha)^n}$$

Both methods have been used at various times, but the counter-current method is the preferred technique as it minimizes salt use and plutonium losses.

Present production processes use two stage counter-current extraction to remove americium from molten plutonium with magnesium chloride based salts. Both 35 mole % NaCl - 35 mole % KCl - 30 mole % $MgCl_2$ and 50 mole % NaCl-26 mole % $CaCl_2$ - 24 mole % $MgCl_2$ are used for americium extraction. Figures 4 and 5 show the ternary phase diagrams for these salt systems(10). The above salt fluxes will extract 90% of the americium present when a salt-to-metal mass-ratio of 0.06 is used in a two stage counter-current extraction.

The NaCl-KCl eutectic is used when the pregnant extraction salt is to be processed by aqueous recovery (this is the salt currently used at Rocky Flats because calcium follows americium in the present aqueous recovery process). The NaCl-$CaCl_2$ system is used when the salt is processed by pyrochemical means to recover the americium and residual plutonium. When the pyrochemical recovery technique is used, the NaCl-$CaCl_2$-$MgCl_2$ salt is contacted with liquid calcium metal at approximately 850°C in a batch extractor. The calcium reduces $AmCl_3$, $PuCl_3$, and $MgCl_2$ to form a 50/50 mole % NaCl-$CaCl_2$ salt phase and a molten Am-Pu-Mg-Ca alloy which is immiscible in the above salt(10). After cooling, the metal phase is cleaved away from the salt phase and the salt phase is analyzed. Little, if any, Am or Pu remains in the salt phase and the salt residues can be discarded to waste. Metal recovery begins by evaporating magnesium and calcium from the residual metal button at about 800°C in vacuum. The americium can then be distilled away from the plutonium in a vacuum still operated at 1200°C, using yttria ceramic vessels to contain the molten metal fraction. The bottoms fraction contains the plutonium which is recycled back into the main plutonium stream.

Knighton(10) has calculated the values of K_d for both americium and plutonium in both of the salt diluents mentioned above for varying concentrations of magnesium chloride. These calculations were performed by using the chemical equilibrium values for Pu with 100% $MgCl_2$ and an empirical equation based on equilibrium values and measured K_d values for salts in the midrange and low end of the curves. The low end Pu data is from the work of Schweikhardt(11). Knighton's data is presented in graphic form for both of these salt systems in Figures 6 and 7.

Knighton has also constructed graphs for the relationship between salt-to-metal ratio for the extraction versus the concentration of magnesium chloride in the salt. The graphs for both the NaCl-KCl-$MgCl_2$ and NaCl-$CaCl_2$ $MgCl_2$ salt systems are shown in Figures 8 and 9. These graphs are for two stage counter-current systems with contour lines at 5% intervals from 80 to 99% americium removal efficiencies. Such graphs enable the operators to obtain almost any extraction constant required to lower the americium content to some acceptable personnel exposure value.

Figure 10 shows in graphic form the utility of molten salt extractions for americium removal in one, two, and three stage extractions for various salt-to-metal extraction feeds. This graph demonstrates the impressive power of molten salt extraction systems for purification of plutonium from americium and related rare earth elements.

Plutonium Electrorefining

The first publication related to plutonium electrochemistry dates back to Manhattan Project work at Los Alamos when Kolodney(12) reported making small amounts of metal by electrolysis. Leary et-al(13) published an article in the Geneva Proceedings in 1958 on the pyrochemical recovery of plutonium from metallic reactor fuels, and in 1960 Mullins et-al(14) reported a 300 gram scale electrorefining process for making high purity metal. Improvements continued, and in 1962 Mullins et-al(15) reported a production process (three kilogram scale) for routine production of >99.9% pure metal. Recent developments at Los Alamos have expanded the capacity of the electrorefining cells to about six kilograms per batch, with a cycle time of five days(16).

The principle of the electrorefining process is basically simple: plutonium is oxidized at a liquid metal anode containing impure metal feed and the resulting Pu^{+3} ions are transported through molten salt to a cathode where pure metal is produced. The transport salt is usually eutectic NaCl-KCl but $NaCl-CaCl_2$ can also be used. As liquid plutonium metal builds up on the cathode it drips off into an annular channel surrounding the anode cup where it coalesces into a pool of metal and is recovered after the cell is cooled. The entire chemical process is performed in a molten salt bath.

A schematic representation of an electrorefining cell is shown in Figure 11. The basic chemistry of the electrorefining technique is as follows:

ANODE REACTION: $Pu_{(\ell)}$ impure $\rightarrow Pu^{+3} + 3e^-$
CATHODE REACTION: $Pu^{+3} + 3e^- \rightarrow Pu_{(\ell)}$ pure

$PuCl_3$ must be added to the cell prior to operation to maintain a high concentration of Pu^{+3} ions in the salt phase. This $PuCl_3$ also acts as a salt-phase buffer to prevent dissolution of trace impurities in the metal feed by forcing the anode equilibrium to favor production (retention) of trace impurities as metals, instead of permitting oxidation of the impurities to ions. Metallic impurities in the feed fall into two classes, those more electropositive and those less electropositive than plutonium. Since the cell is operated at temperatures above the melting point of all the feed components, and both the liquid anode and salt are well mixed by a mechanical stirrer, chemical equlibrium is established between all impurities and the plutonium in the salt even before current is applied to the cell. Thus, impurities more electropositive than the liquid plutonium anode will be oxidized by Pu^{+3} and be taken up by the salt phase, while impurities in the electrolyte salt less electropositive than plutonium will be reduced by plutonium metal and be collected in the anode.

Those impurities less electropositive than plutonium that are already present in the molten anode will remain in the anode. The extent of these reactions will be determined by the reaction free energy and concentration for each of the impurities in the molten anode/electrolyte salt system. Americium can be used as an example of a very electropositive impurity:

$$\text{Am (metal)} + PuCl_3 \text{ (salt)} = AmCl_3 \text{ (salt)} + \text{Pu (metal)}$$

When current is passed through the cell, the concentration of impurities in the product obtained at the cathode will depend upon their concentration in the salt. If equilibrium conditions exist in the cell the following equation applies:

$$\frac{(Am)}{(Pu)} \text{ metal product } = \frac{1}{K} \frac{(AmCl_3)}{(PuCl_3)}$$

Where the parenthesis refer to the chemical activities of the reactants and K is the equilibrium constant for the previous equation. Similar considerations apply to the oxidation of less electropositive impurities from the anode when a current is passed through the cell. Thus, for the case of iron impurity in the anode, the reaction

$$3\ Fe + 2\ PuCl_3 = 2\ Pu + 3\ FeCl_2$$

favors the production of iron metal instead of ferrous ion since the free energy change for the reaction is +96 kilocalories (+96 KCal is equivalent to an equilibrium constant of 1×10^{-21} at 1000 K).

The composition of the salt electrolyte in the cell does not change during the electrorefining cycle so long as the driving potential of the cell is kept below the decomposition voltage of the electrolyte. The following table gives the decomposition potential of normal components of the electrolyte:

Chloride salt	Decomposition Potential at 800° C
$CaCl_2$	3.32
KCl	3.44
NaCl	3.24
$MgCl_2$	2.46
$PuCl_3$	2.40

Since the energy required to strip the electrons from plutonium metal at the anode is exactly matched by the energy returned at the cathode, the potential required by the process is only that required to overcome time invariant (I^2R) losses in the cell circuit, and time dependent resistance (electrode polarization).

Polarization of the anode occurs after most of the plutonium is transferred across the cell and impurities constitute a large percentage of the anode. The reason for this can be demonstrated by using the case of delta plutonium alloy feed. Delta alloy contains ∿ 1 wt % gallium. The normal operating temperature of the electrorefining cell is 750°C and at this temperature the delta alloy melts to form a liquid phase. The phase diagram for Pu-Ga is shown in Figure 12.

As electrorefining proceeds, plutonium is selectively removed from the anode and the composition of the anode becomes enriched in gallium. At approximately 18 mole percent gallium, the lower density eta phase Pu begins to form (at 750°C) and a mixture of solid eta phase and liquid is formed at the anode surface (eta phase floats on the liquid plutonium phase). The back-EMF of the cell will gradually increase as the eta phase is formed. Vigorous stirring will expose liquid plutonium and permit oxidation to proceed at the anode surface, but at 25 mole % gallium the anode will solidify. Continued operation of the cell will now oxidize gallium in the ratio of the composition of the solid anode.

To prevent the passage of impurities, the back-EMF of the cell is monitored at frequent intervals. The current to the electrodes is turned off, and the voltage of the cell is measured. When the back-EMF reaches a predetermined value, operation of the cell is terminated, and the cell is allowed to cool. The cathode product, which consists of very pure plutonium metal, is recovered from the solidified salt mass by breaking the ceramic vessel and brushing the ring free of adhering salt. The product ring typically amounts to about 85% of the original mass of the anode feed metal. The impurity level of the cathode product from electrorefining is usually below normal spectroscopic detectability levels if the cell is run at anode current densities of 0.60 amps per sq. cm. or less.

The level of purification that can be achieved from impurities by the electrorefining process is directly related to the free energy of formation of the chloride salt of each impurity present in the feed metal, as discussed above. Since both the lanthanide and actinide chlorides have very negative free energies of formation, the purification factors achievable for these elements by plutonium electrorefining is considerably lower than for most common impurities. For example, the typical purification factor obtained for americium is approximately 9, and the factor for neptunium is about 3. The decontamination from the lanthanides and americium is easily acomplished by the magnesium chloride based molten salt extraction described in the previous section. Neptunium is a relatively rare contaminant as it grows into plutonium as the daughter of americium-241 (453 year half-life alpha decay). Neptunium is separated with high efficiency in the initial chemistry used to isolate plutonium from irradiated uranium. If additional purification is necessary, neptunium can be extracted from plutonium by the "Salt Transport Method" in a compatible pyrochemical process.

The following table, excerpted from a Los Alamos production report, demonstrates typical feed and product purities achievable by the electrorefining method:

Comparison of Purities of Oxide Feed, DOR Metal, and
ER Metal Product, Run PMR 162*

Impurity levels reported as micrograms per gram of sample.

Element	Oxide-Feed	DOR Metal Product	ER Product
B	>150	>150	<1
Na	>233	10	6
Mg	>375	300	1
Al	500	500	<5
Si	283	1400	<5
K	>100	50	15
Ca	>750	100	<3
Ti	32	50	<5
Cr	317	360	<5
Mn	20	10	<1
Fe	>1500	>1500	<5
N	880	940	<5
Cu	24	7	<1
Y	>180	25	<25
Zr	>450	500	<100
Nb	85	60	<10
Mo	121	200	<3
Ta	>500	>500	<100
W	>500	>500	100
Pb	38	< 5	<5
Th	421	270	30
U	656	20	7
C	78	790	25
Am	655	795	219
Pu	82.23 (93.29% pure)	98.47%	99.96%

The anode residues must be chemically processed to recover the plutonium remaining in the residues. This may amount to about 10% of the feed mass if delta alloy is the feed metal. Either aqueous or pyrochemical processes may be used for anode recovery. One pyrochemical process used for recovery utilizes oxidation of the plutonium with zinc chloride to form plutonium chloride salt, followed by calcium reduction of the $PuCl_3$ contained in the salt phase to produce pure plutonium metal (the impurities follow the zinc metal obtained from the oxidation reaction and are discarded to waste). Impurities more stable than calcium chloride remain in the salt phase and are also

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*From LA-9154-MS

discarded to waste. This process, known as "Pyroredox" is still under development and is not yet available as a production method.

The electrolyte salt must be processed to recover the ionic plutonium orginally added to the cell. This can be done by aqueous chemistry, typically by dissolution in a dilute sodium hydroxide solution with recovery of the contained plutonium as $Pu(OH)_3$, or by pyrochemical techniques. The usual pyrochemical method is to contact the molten electrolyte salt with molten calcium, thereby reducing any $PuCl_3$ to plutonium metal which is immiscible in the salt phase. The extraction crucible is maintained above the melting point of the contained salts to permit any fine droplets of plutonium in the salt to coalesce with the pool of metal formed beneath the salt phase. If the original ER electrolyte salt was eutectic NaCl-KCl a third "black salt" phase will be formed between the stripped electrolyte salt and the solidified metal button. This dark-blue phase can contain 10 wt. % of the plutonium originally present in the electrolyte salt; plutonium in this phase can be recovered by an additional calcium extraction step(17).

Recent work by Coops et-al(18) has suggested that "black salt" is a dispersion of K_3PuCl_6 in a matrix of KCl and NaCl. K_3PuCl_6 is a highly insoluble complex salt that solidifies at 621°C from $PuCl_3$-KCl mixtures, and contains 42% plutonium by weight. This salt apparently can form during the extraction and trap droplets of plutonium metal in a viscous salt phase. K_3PuCl_6 also appears to be more thermodynamically stable than either $PuCl_3$ or NaCl; for this reason consideration is now being given to the utilization of either $CaCl_2$ or NaCl-$CaCl_2$ as the electrolyte salt for ER instead of NaCl-KCl.

The basic electrorefining process is now being used on a production scale for the purification of non-specification plutonium metal. The technology is sufficiently well developed to permit 24-hour unattended operation of the electrorefining cells, and the quality of the product metal is highly consistent. This technology is rapidly replacing aqueous chemistry for plutonium metal purification.

Metallic Scrap Recycle

The reaction between plutonium metal and hydrogen is exothermic and proceeds quite satisfactorily at room temperature in an atmosphere of pure hydrogen. The reaction is fully reversible and plutonium can be recovered by pumping off the hydrogen in a suitable vacuum system. Plutonium hydride that is formed below 250°C is granualar and friable; the particle size is very fine and the hydride does not adhere to the substrate surface. Above 250°C the product is a more adherent flaky scale. The rate of reaction, and hence the temperature of the reaction, is easily controlled by varying the hydrogen pressure in the reaction chamber. Since PuH_2 decomposes readily above

600°C, the rate of reaction tends to be self limiting at hydrogen pressures up to 10 torr. The hydriding technique is used to recover metallic plutonium residues clinging to the walls of ceramic crucibles, and can also be used to recover machining scrap if the feed is free of lubricants or oxides. Mulford and Sturdy(14) have found the heat of formation for the reaction

$$Pu + H_2 \rightarrow PuH_2$$

to be -37.4±1.2 KCal per mole, and observed the decomposition of PuH_2 between 400-800°C to follow the equation:

$$\log P_{mm} = (10.01 \pm 0.32) - (8165 \pm 263)/T$$

At 650°C the decomposition pressure of PuH_2 is 14.7 Torr.

The very chemically reactive plutonium hydride is usually decomposed in a vacuum-tight furnace capable of attaining a temperature of 700°C. Plutonium hydride that is decomposed under vacuum at temperatures below 400°C forms a very fine (<20μ) metallic powder; above 500°C the powder begins to sinter into a porous frit which melts at 640°C to form a consolidated metal ingot. This metal typically contains significant oxide slag but is suitable for feed to either molten salt extraction or electrorefining.

The advantage of hydride recovery is its ability to recover a large fraction of the scrap in metallic form. This method therefore has a major economic advantage over chemical recycle and subsequent reduction to metal. It is just beginning to be used as a production aid for metallic scrap recovery.

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List of Credits for Figures

Fig. 1	Los Alamos National Laboratory Report LA-9154-MS (1981)
Figs. 2-3	Journal of Chemical and Engineering Data Vol. 14, No. 2, April 1969.
Fig. 4	N. Jahrb. Min. B. Band 43, pp 251-294 (1920).
Fig. 5	Z. Anorg. Allgem. Chem. 279 pp 94-103 (1955).
Figs. 6-10	Rockwell International - Rocky Flats Plant Report RFP-2365 (1976).
Fig. 11	Los Alamos National Laboratory Report LA-9154-MS (1981).
Fig. 12	Plutonium Handbook - Vol I. (1967) Gordon and Breach, New York, N.Y.

Fig. 1 Stationary Extraction Furnace Assembly for Plutonium Reduction and Americium Extraction.

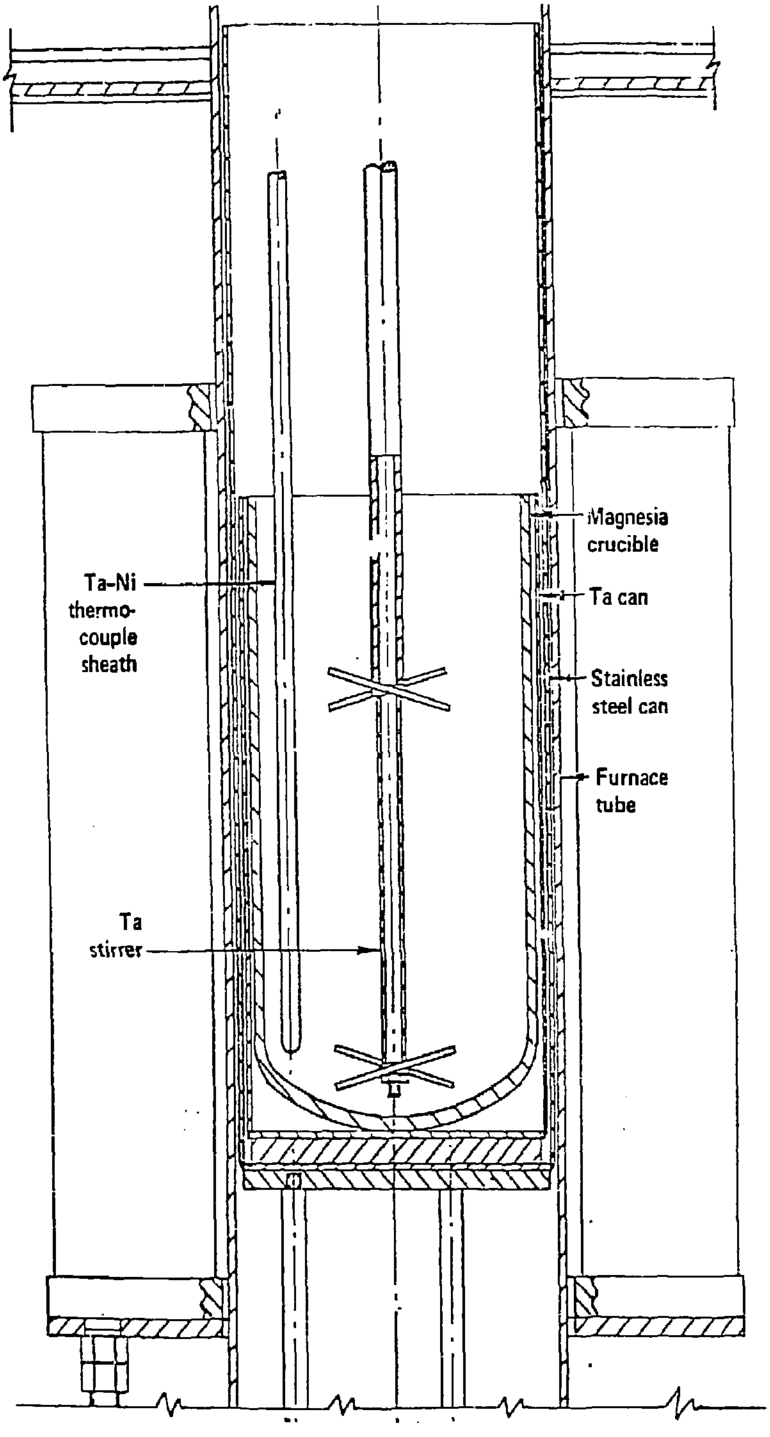


FIG. 1

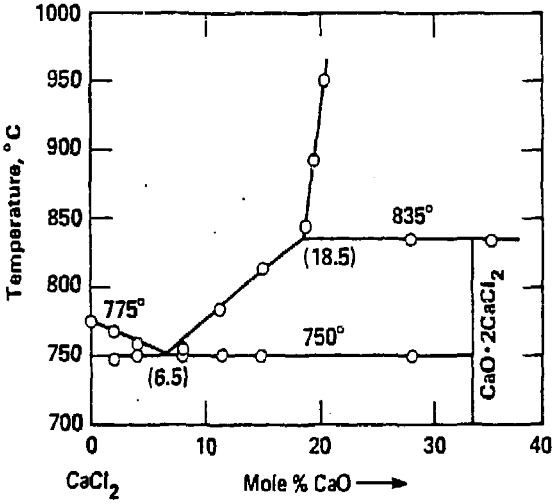


Fig. 2 Partial Binary Phase Diagram for the CaO-CaCl$_2$ System.

FIG. 2

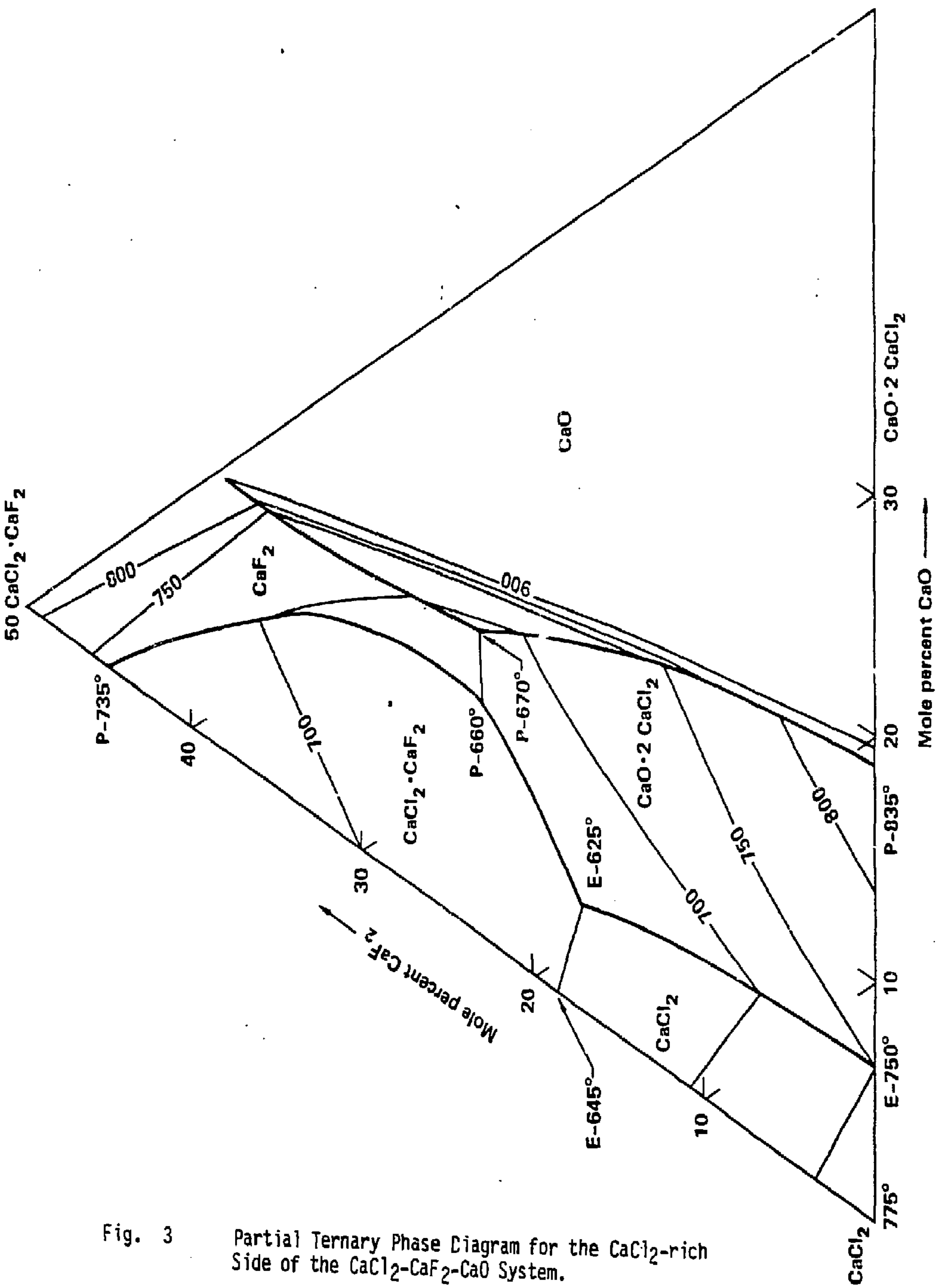


Fig. 3 Partial Ternary Phase Diagram for the $CaCl_2$-rich Side of the $CaCl_2$-CaF_2-CaO System.

FIG. 3

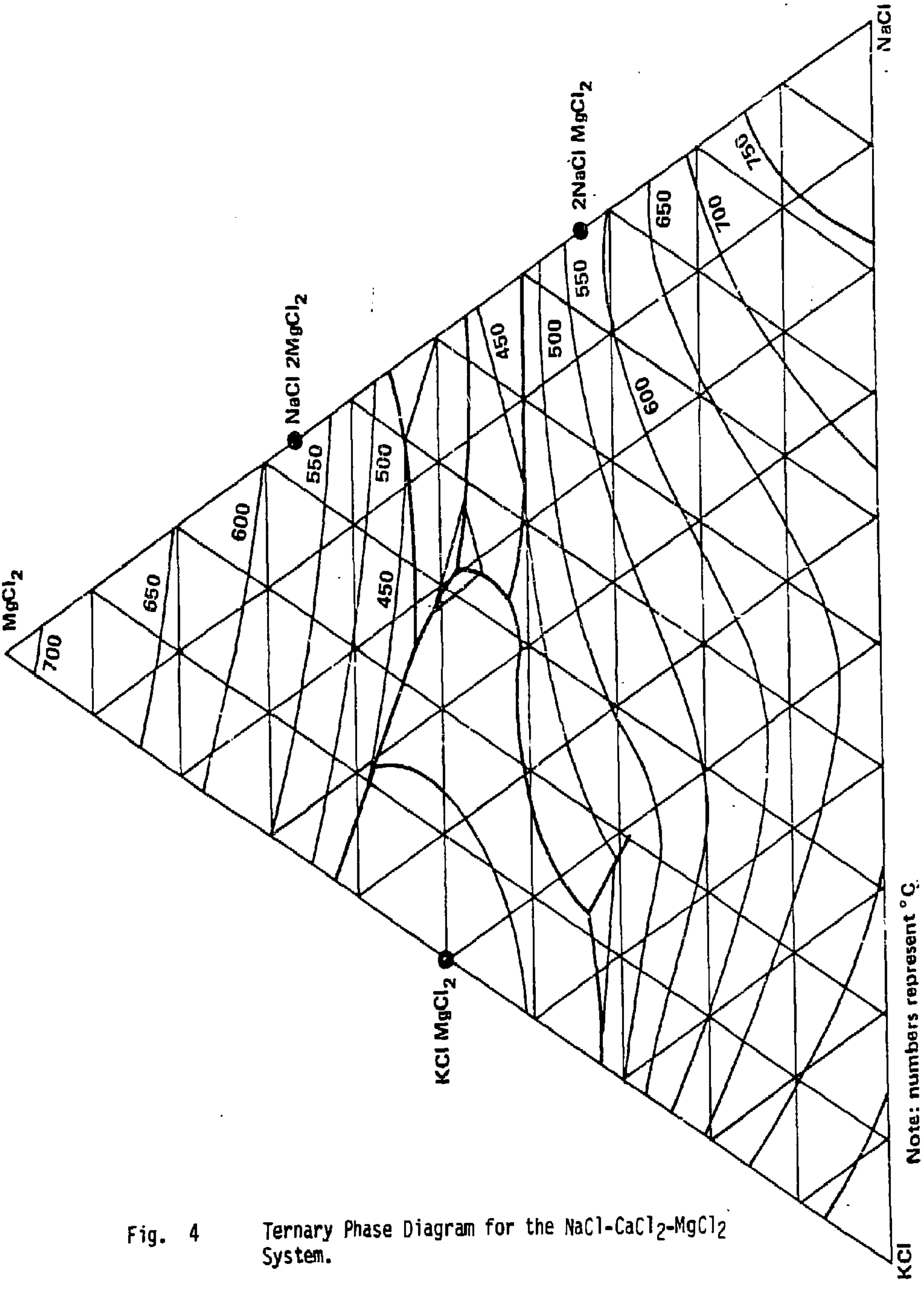
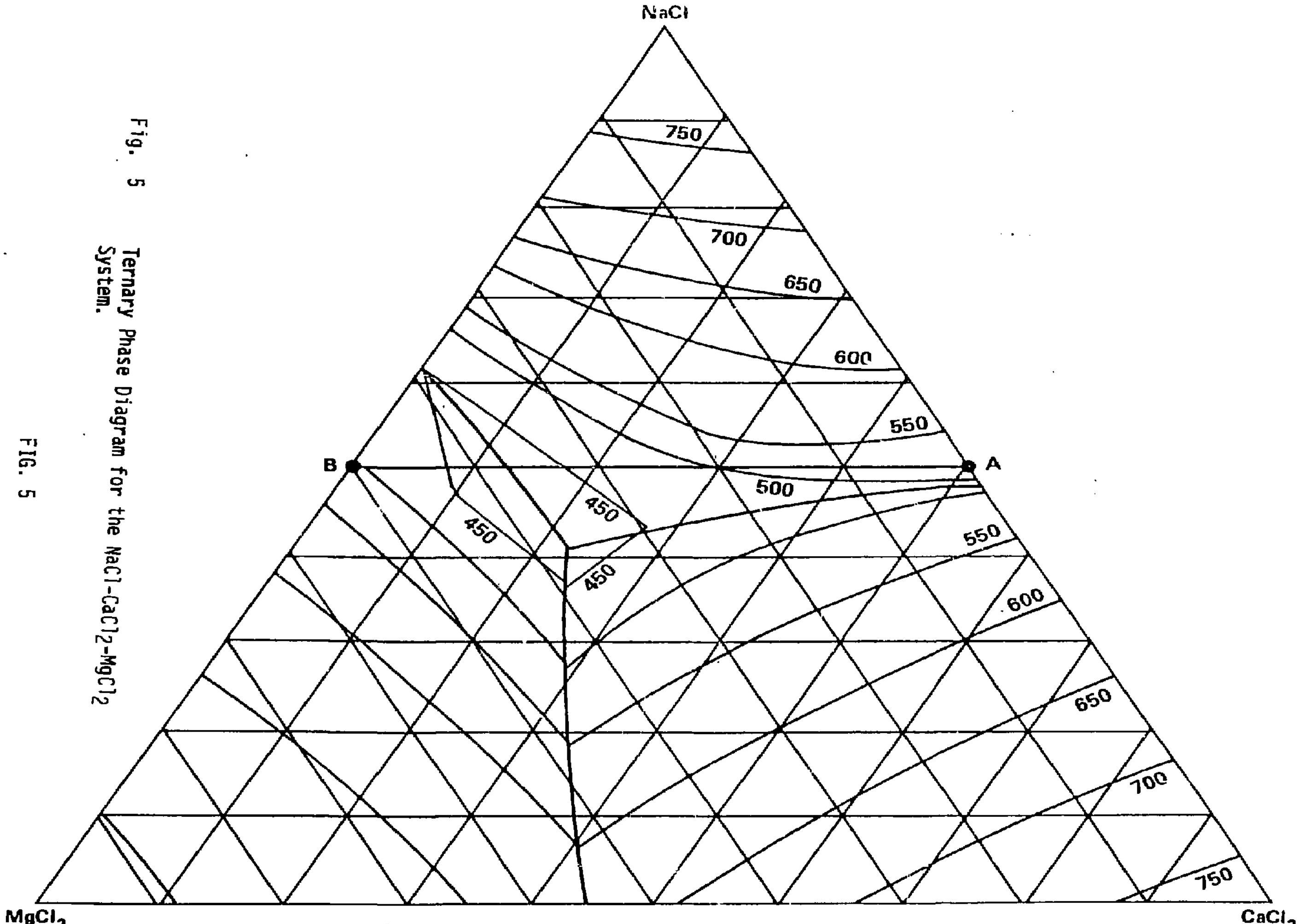


Fig. 4 Ternary Phase Diagram for the NaCl-CaCl$_2$-MgCl$_2$ System.

FIG. 4

Fig. 5 Ternary Phase Diagram for the NaCl-CaCl$_2$-MgCl$_2$ System.

FIG. 5



Note: numbers represent °C

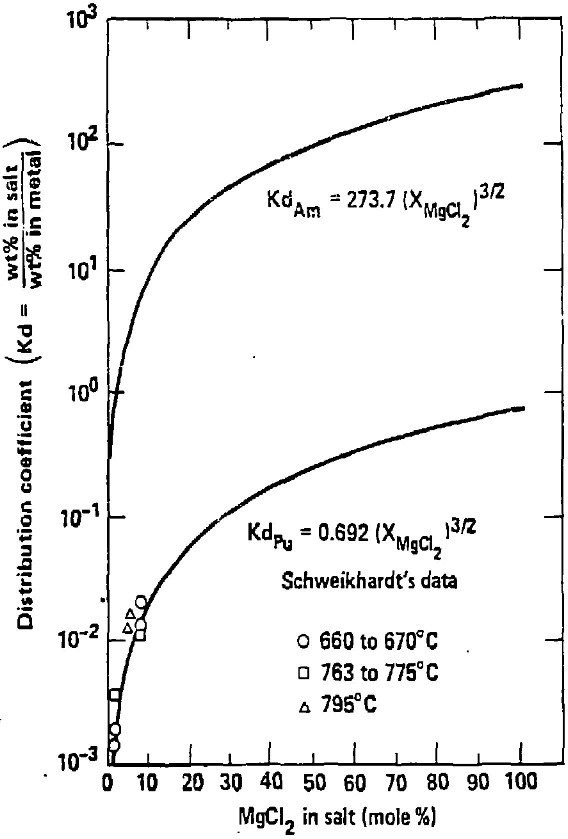


Fig. 6 Distribution Coefficients for Americium and Plutonium Extraction vs $MgCl_2$ Concentration in the $NaCl$-KCl-$MgCl_2$ Salt System.

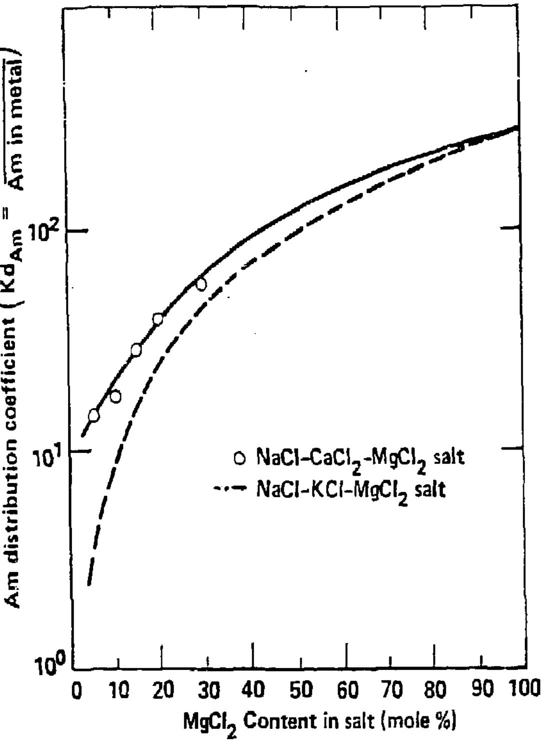


Fig. 7 Distribution Coefficient for Americium Extraction vs $MgCl_2$ Concentration in the NaCl-KCl-$MgCl_2$ and NaCl-$CaCl_2$-$MgCl_2$ Salt Systems.

FIG. 7

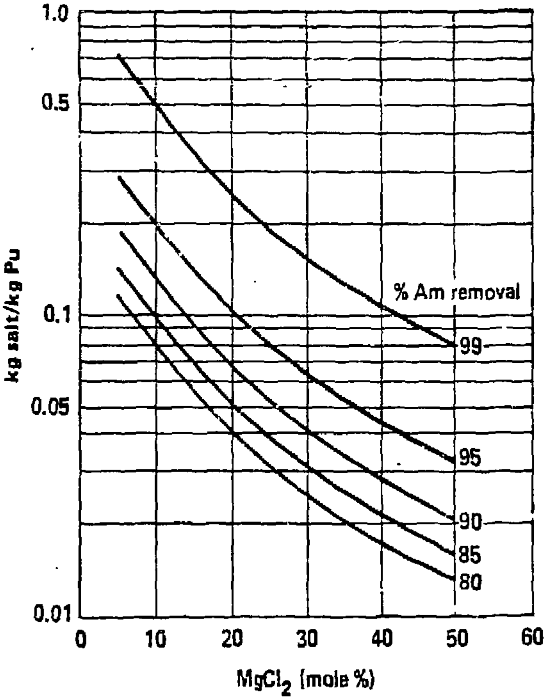


Fig. 8 Yield Curves for Salt-To-Pu Ratio vs Concentration of $MgCl_2$ for Extraction of Americium From $NaCl$-$CaCl_2$-$MgCl_2$ Salt Using 2-Stage Counter-Current Extraction

FIG. 8

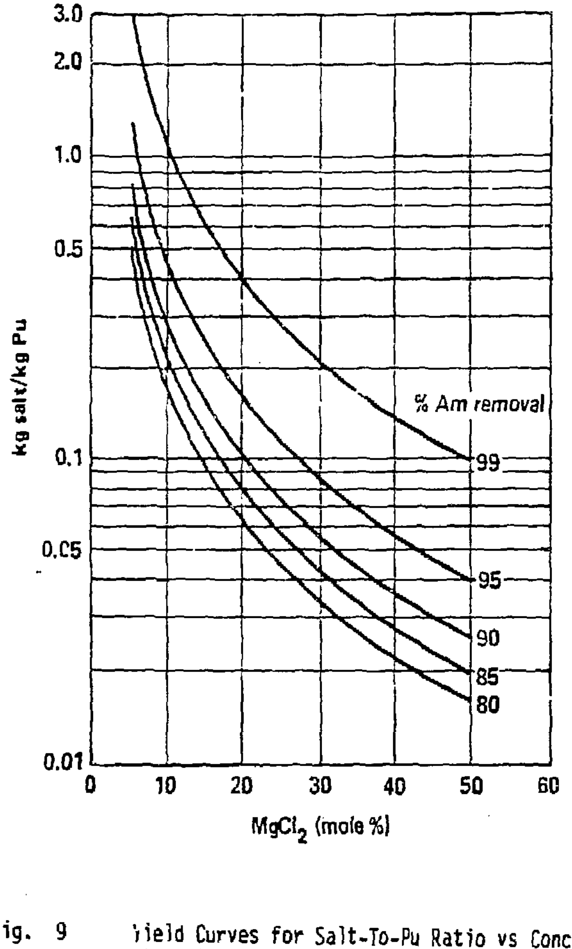


Fig. 9 Yield Curves for Salt-To-Pu Ratio vs Concentration of $MgCl_2$ for Extraction of Americium From $NaCl$-KCl-$MgCl_2$ Salt Using 2-Stage Counter-Current Extraction.

FIG. 9

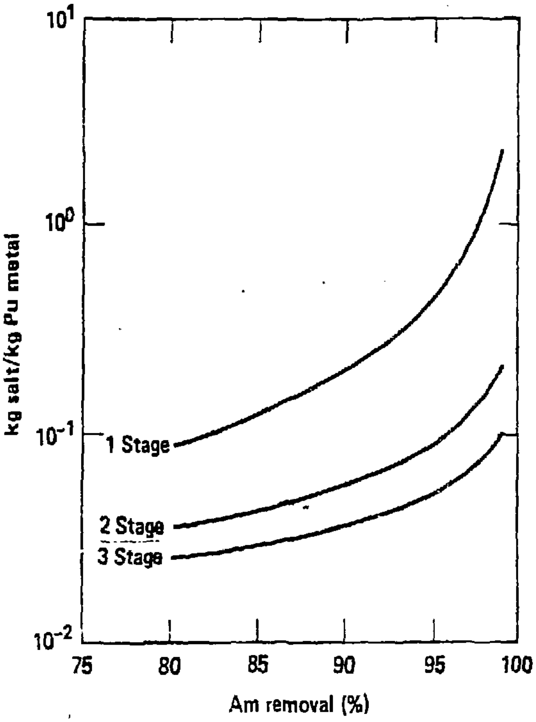


Fig. 10 Yield Contours for Americium Extraction vs s/m Ratio for 1, 2, and 3-Stage Counter-Current Extraction. Salt Composition: 30 $^m/o$ $MgCl_2$, 35 $^m/o$ NaCl, 35 $^m/o$ KCl.

FIG. 10

Fig. 11 Schematic of Electrorefining Cell Showing Major Features.

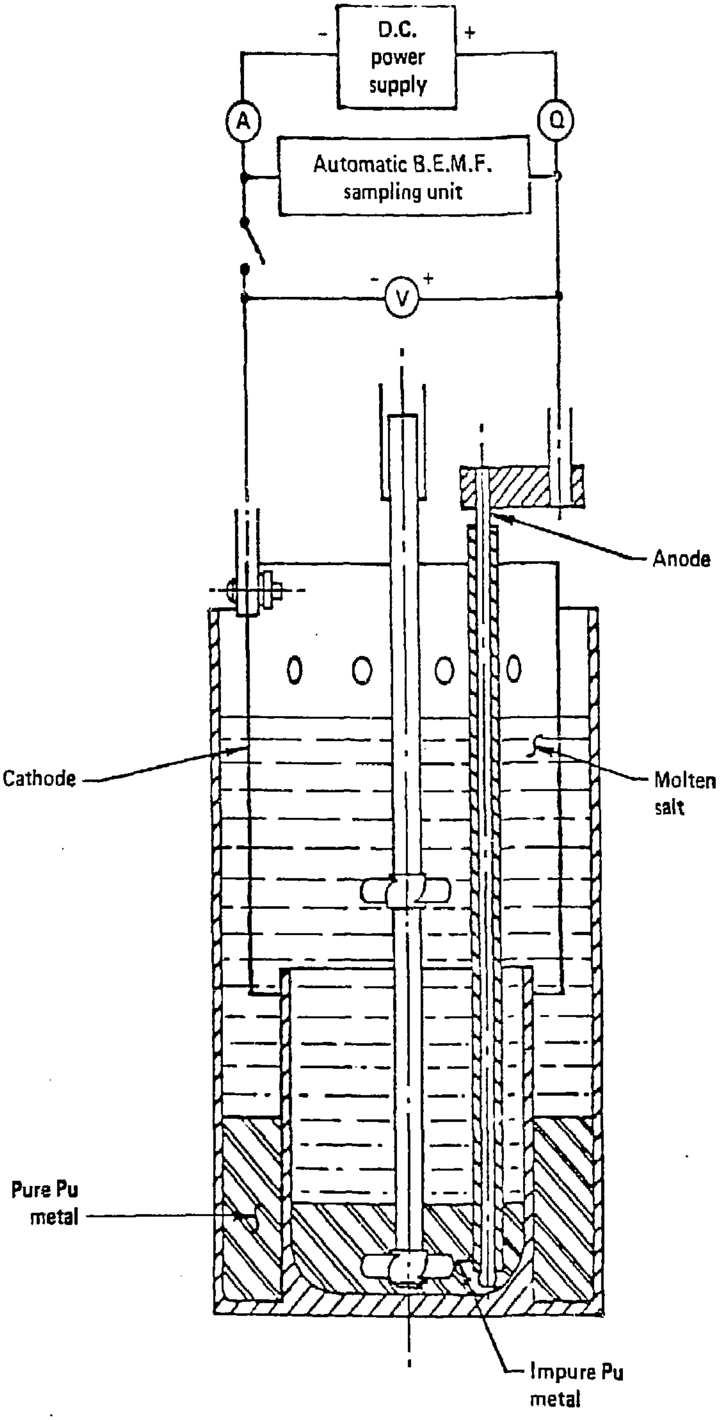


FIG. 11

Fig. 12 The Gallium-Plutonium Phase Diagram.

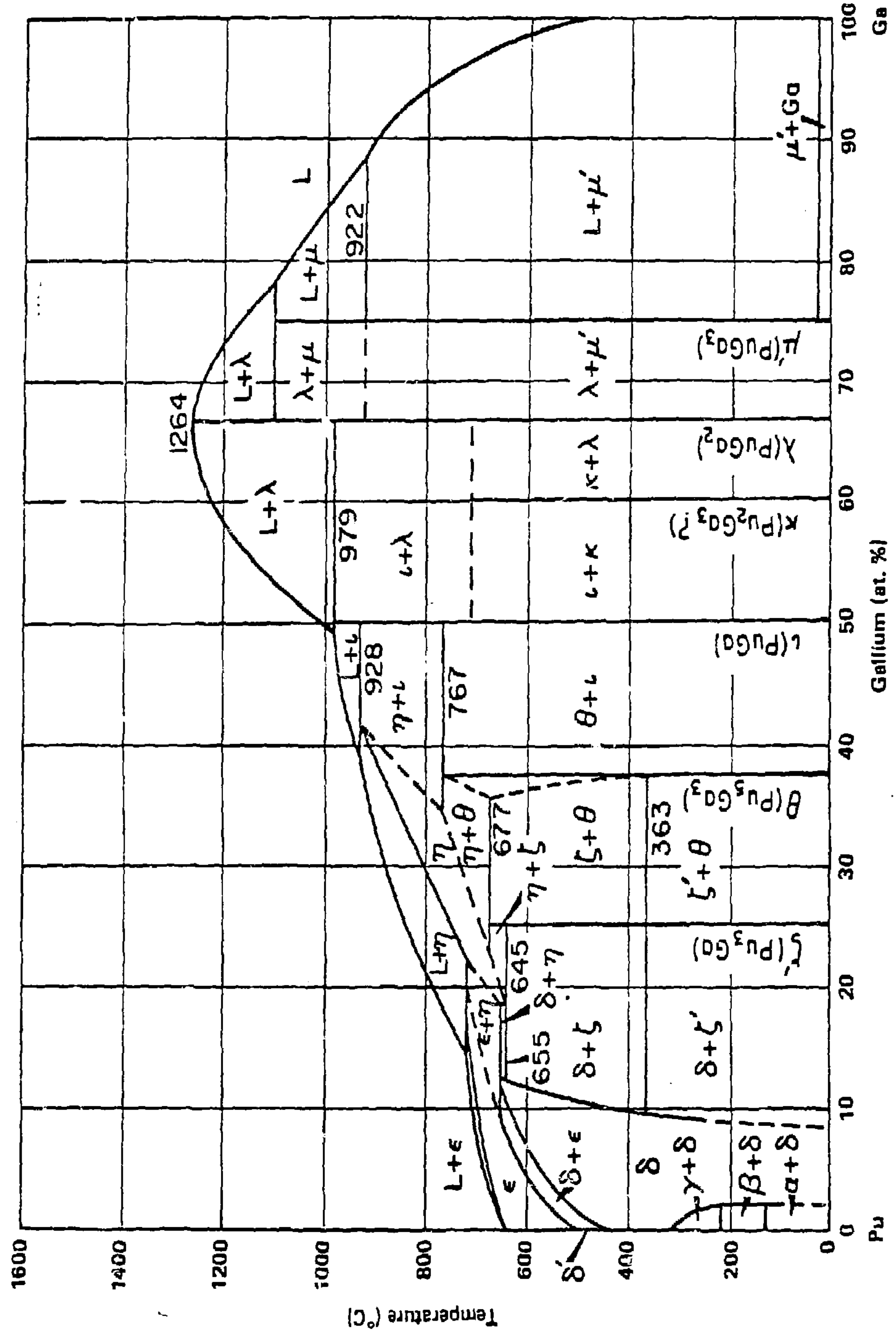


FIG. 12