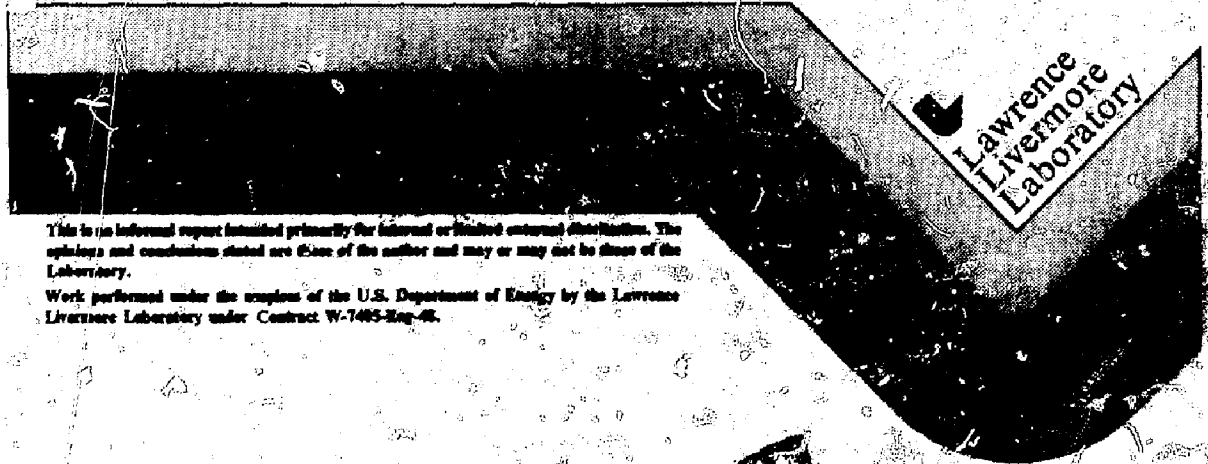# RECOVERY OF URANIUM-233 FROM A THORIUM BREEDING BLANKET BY PYROCHEMICAL TECHNIQUES

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DECEMBER 8, 1982

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Recovery of Uranium-233 From a Thorium
Breeding Blanket by Pyrochemical Techniques

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BY PYROCHEMICAL TECHNIQUES

Introduction

One of the options presently being considered for utilization of the
neutrons obtained from D-T fusion is absorption of slow neutrons (after
multiplication and moderation in a beryllium lattice) in a blanket of
fertile thorium metal. Since the fission cross-section of ^{232}Th is
negligibly low below the fission threshold of approximately 0.4 MeV, the
amount of fission products present in such a breeding blanket are a direct
function of the level of ^{233}U that is allowed to build up in the
blanket. If a simple, inexpensive uranium recovery process can be
achieved, the uranium concentration, and hence the level of fission in the
blanket, can be held to a very low value. Although the presence of even
small quantities of young fission products in the material to be processed
dictates that the processing must be performed by remote means, it is
possible to recover the uranium fraction without performing a specific
chemical separation to remove fission products first.

We have carefully evaluated several processes that might be suitable
for uranium recovery from thorium metal, and have chosen two that hold
great promise. Both are simple non-aqueous methods that can readily be
performed by remote means, and both require only a few simple process
steps.

Our first choice for uranium recovery is a process that exploits the
high solubility of thorium, and the low solubility of uranium, in molten
magnesium. Uranium metal is essentially insoluble in both pure magnesium
and magnesium-thorium alloys while thorium is quite soluble (see Figures
1,2,3, and 4). We propose to utilize thorium metal directly from the
blanket, which may contain from 0.5 to 1.5% uranium-233 plus a small
quantity of fission products, and dissolve it in a bath of molten
magnesium. The uranium contained in the original blanket will be
essentially insoluble in the melt at 950 K (677°C) and exist as
β-uranium metal. At 950 K the solubility of uranium in 33 wt% th-67 wt%
Mg alloy is 1.6 x 10^{-5} moles/mole solvent[1,2,3,4], or 0.032 wt% of
the thorium in the solvent. If we assume 0.94 wt% ^{233}U build-up in the

alloy, the uranium remaining dissolved in the solvent would be 3.4% of the initial uranium present. Essentially all of this ^{233}U can be recovered by scavenging the solvent alloy with an equal mass of ^{238}U, thereby diluting the isotopic purity to 50% ^{233}U. As safeguards regulations will probably require isotopic dilution prior to shipment of recovered ^{233}U anyhow, it is possible to protect the product in process by diluting the ^{233}U by a factor of five with ^{238}U at dissolution and eliminate the scavenging step after initial precipitation; this would lead to trace amounts of ^{239}Pu being formed during irradiation of the recovered thorium fraction.

The thorium is recovered from the magnesium alloy by simply distilling the volatile magnesium fraction away from the residual thorium and fission products. This distillation can be easily performed at 950 K under about one torr vacuum. The recovered magnesium will be used for dissolution of the next batch of blanket feed. The residual thorium and FP fraction can be refabricated into suitable metallic shapes for return to the breeder blanket assembly. Most of the fission products will remain in the thorium metal and decay away during the next irradiation sequence. After many blanket cycles the stable fission product concentrations may require removal, or alternatively, a replacement thorium blanket. The highly contaminated thorium blanket can simply be treated as fission product waste.

Our alternative method utilizes selective extraction of uranium from a molten thorium-uranium-copper-magnesium alloy into molten magnesium chloride salt at 1000 K. The feed (donor) alloy is formed by dissolving the thorium-uranium-FP blanket in a small amount of copper-magnesium diluent. The uranium can be extracted from this alloy as the chemical activity of uranium in copper-magnesium alloy is very high.

The uranium is then back extracted from the magnesium chloride molten salt by a small quantity of magnesium-zinc (acceptor) alloy. Uranium metal is recovered from the alloy by distilling off the volatile metal fraction (under vacuum). This process is a variant of the general family of molten salt extraction schemes known as "Salt Transport Processes". The basic utility of these processes was carefully studied by Argonne National Lab in the period 1965-1970, and the basic technology is fully understood and thoroughly documented[5,6]. Pilot-plant scale operations

of this type have been performed with radioactive feed stocks and perform
as predicted.

Magnesium Precipitation Process

For design purposes we shall assume that the concentration of
uranium-233 in the blanket thorium metal will be one percent by weight,
and the mass of thorium blanket that must be processed will be 600 tons
per year. Criticality considerations will limit ^{233}U batches to
approximately 10 kilograms each. In order to keep the operating
temperature of the process as low as practicable, the concentration of
magnesium must be maintained above 58% by weight; as a practical
compromise we have chosen to use 33% Th-67% Mg as a design alloy. The
solubility of uranium in this alloy is well documented[1-4].

The volume of Mg-33Th alloy needed to contain one ton of thorium is
1235 liters or 326 gallons; this can be contained in a cylindrical tank 48
inches in diameter by 48" tall (376 gallon capacity). The specific volume
of 10 kilograms of uranium metal is 0.524 liters in solid form; as a
finely divided powder a reasonable estimate would be 1.0 to 1.5 liters.
The separation of one liter of fine powder from 1200 liters of molten
alloy at 675°C is a formidable task.

We propose to circumvent this problem by utilizing the known property
of uranium to wet and adhere to the surface of either tungsten or tantalum
sheet to form a thin deposit of uranium metal on the substrate surface.
This thin deposit can be formed by suspending tungsten foil in the
thorium-magnesium alloy to collect uranium metal that will be precipitated
from the melt. The uranium can then be either oxidized to UO_2 or
hydrided to UH_3 to form a crystalline powder that can be mechanically
removed from the foil collector. If hydriding is chosen, it can be
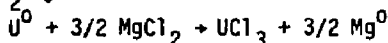converted back to metal by dehydriding under vacuum, and cast into ingot
metal.

An alternative recovery method that has been used in similiar
circumstances is centrifugal collection of the uranium powder by use of a
rotating bowl that is suspended in the liquid alloy. The bowl shape is
designed to pump liquid through the bowl during rotation, while collecting

In light of the above information, it appears practical at this time to propose that pyrochemical processing as a possible alternative method for uranium recovery from thorium blanket feeds. Estimates of the support facility capital costs to perform such a process are expected to be in the $100M range, based on FY'83 projections.
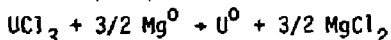
Salt Transport Alternative Process

Figure 5 shows a conceptual salt transport process for recovery of uranium from the thorium blanket. Because the reactor blanket is fission suppressed, the concentration of fission products is held to a very low level. The major objective of this flow sheet is to separate uranium from thorium; no special provisions have been made to remove fission products. However, because of the nature of the salt transport process, significant separation of uranium from FP-1 and FP-2* fission products will occur. Partial removal of FP-3 elements will also occur. The flow sheet shows a thorium metal blanket feed and either an oxide or uranium metal product.

In the salt transport process, a molten salt is circulated between a donor alloy and an acceptor alloy. At the donor, uranium is oxidized by $MgCl_2$ by the reaction:

$$U^0 + 3/2 \ MgCl_2 \rightarrow UCl_3 + 3/2 \ Mg^0$$

At the acceptor, uranium chloride is reduced by magnesium by the reaction:

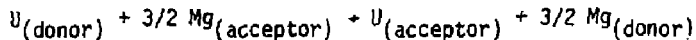$$UCl_3 + 3/2 \ Mg^0 \rightarrow U^0 + 3/2 \ MgCl_2$$

The acceptor reaction is the reverse of the donor reaction, i.e., the $MgCl_2$ consumed at the donor is regenerated at the acceptor. The $MgCl_2$ enters into the overall reaction, but is not consumed and may be reused indefinitely. The overall reaction is therefore uranium transfer from the donor to the acceptor, and the reverse transfer of magnesium needed to keep the chemical reaction balanced:

---

*FP-1 Fission products are the volatile elements at ⌐00°C.

FP-2 Elements are the refractory and noble metals.

FP-3 Elements are the rare-earth family of elements.

$$U_{(donor)} + 3/2\ Mg_{(acceptor)} \rightarrow U_{(acceptor)} + 3/2\ Mg_{(donor)}$$

For every mole of uranium transferred from the donor to the acceptor, there is the reverse transfer of 1.5 moles of magnesium from the acceptor to the donor. The driving force for this overall reaction is the difference between the uranium and magnesium activity in the donor and acceptor alloys.

Up to the present time no thorium based alloys have been identified as uranium donor alloys. The donor alloy must be liquid at the temperature needed to melt the transport salt, and should have the least possible magnesium content. Because of the very high melting point of thorium (1750^{0}C), pure thorium metal can not be used as a donor alloy. However, the addition of 8 wt% copper to the alloy causes a very dramatic decrease of melting point to 940^{0}C (Figure 6). Both thorium and copper form alloy systems with magnesium. The addition of small amounts of magnesium to the 92 wt% Th - 8 wt% Cu eutectic should further lower the melting point and form a uranium donor alloy. In the absence of experimental data, an alloy composition of 89 wt% Th, 8 wt% Cu, 3 wt% Mg is assumed as the uranium donor alloy. (It is interesting to note that regions of immiscibility exist in the three binary alloys Th-U, Cu-U, and Mg-U, which suggest that the uranium activity coefficient will be greater than unity in this proposed donor alloy.)

In the acceptor reaction uranium metal will be formed at the salt-metal interface; this uranium metal is taken up by the acceptor alloy. All zinc-magnesium alloys ranging from about 98 wt% Zn - 2 wt% Mg to about 95 wt% Mg - 5 wt% Zn are uranium acceptor alloys. The 80 wt% Mg - 20 wt% Zn alloy was selected as the uranium acceptor for the following reasons: (1) uranium metal is the equilibrium solid phase and no solvent metal is combined with uranium, (2) the alloy density is greater than the density of $MgCl_2$ (a density inversion is avoided), (3) the uranium solubility of 5×10^{-2} wt% at 800^{0}C is very low, (4) the bulk of the acceptor alloy can be easily

removed from the precipitated uranium, (5) the volume of the acceptor alloy is very small, and (6) the amount of volatile metals to be removed by distillation is held to an absolute minimum.

Magnesium chloride containing one percent thorium chloride is the preferred transport salt. 99% $MgCl_2$-1% $ThCl_4$ will give the largest value for the uranium distribution coefficient at the donor alloy, while minimizing build-up of magnesium in the donor as uranium is transported to the acceptor alloy phase. To drive the rate of uranium mass transfer between the donor and acceptor alloys, each salt-alloy system must be mixed, and the common salt phase circulated between the two alloys. Entrainment of metal in the salt must be avoided.

Although this process is not specifically designed for uranium-fission product separation, the very nature of the process will provide significant fission product decontamination of the recovered uranium fraction.

Transfer of uranium from the donor alloy to the acceptor alloy will be equilibrium limited. The following conditions are used to estimate the potential of the salt transport process to separate and recover uranium:

Donor -
    U Kd = 5 (estimated value)
    U solubility = 1 (all uranium is assumed to be in solution in the donor alloy)
Acceptor -
    U Kd = 2.5×10^{-1} (known for $MgCl_2$)
    U solubility = 5×10^{-2} wt% (known)
Transport Salt -
    99% $MgCl_2$-1% $ThCl_4$

The acceptor alloy salt equilibrium determines the equilibrium conditions at the donor.

The maximum uranium content in the transport salt in equilibrium with the acceptor is the product of the distribution coefficient and the uranium solubility in the acceptor.

    Maximum U in salt = Kd x solubility
                       = 1.25×10^{-2} wt% U

Shielded Containment Facility

We propose to use the existing argon-atmosphere Hot-Cell Facility at the EBR-II site at Idaho National Engineering Laboratory (HFEF-N)* as a prototype cell that would be suitable to contain all irradiated process materials and hardware needed to perform uranium recovery from irradiated blanket feedstock. This facility includes a 30 ft wide by 70 ft long fully-inert (argon) shielded cell with 15 master-slave operated work stations and viewing windows. The cell is shielded with 48 inches of high density concrete (220 lbs/cu ft) up to a height of 16 ft above the operating floor. The ceiling clearance within the cell is 25 ft, and the cell is constructed with a 10-foot-deep, readily accessible sub-cell below the normal operating floor (remotely removable floor plates). An air atmosphere support cell 30 ft x 20 ft adjoins the inert cell and is used to decontaminate process equipment prior to service or disposal.

According to Melvin Feldman, the engineer responsible for the design and construction of the existing facility, the entire operating facility could be duplicated today for $65M (1983 dollars)[8]. A basic facility layout is included in the appedix for engineering information.

A duplicate HFEF-N should provide adequate space to contain dissolver tanks, magnesium stills, electron beam consolidation furnaces, casting capabilities, and extrusion presses for refabrication of new breeder blanket targets. A cursory equipment layout indicates that the uranium recovery chemical equipment could be placed along one inner wall (7 work stations) and the refabrication equipment along the opposite wall (7 work stations). Such an arrangement should be able to process the proposed 600 tons of blanket feed per year. We can only guess at the cost of the fully outfitted facility, but $35M seems ample to cover the cost of the basic in-cell equipment, as much of the refabrication hardware is commercially available for industrial use. We have not identified the metallurgical process that would be needed to re-fabricate the recovered thorium to suitable metallic shapes.
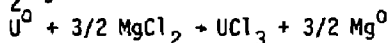
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*HOT FUELS EXAMINATION FACILITY - NORTH

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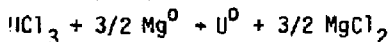
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The acceptor reaction is the reverse of the donor reaction, i.e., the $MgCl_2$ consumed at the donor is regenerated at the acceptor. The $MgCl_2$ enters into the overall reaction, but is not consumed and may be reused indefinitely. The overall reaction is therefore uranium transfer from the donor to the acceptor, and the reverse transfer of magnesium needed to keep the chemical reaction balanced:

---

*FP-1 Fission products are the volatile elements at 800^0C,

FP-2 Elements are the refractory and noble metals,

FP-3 Elements are the rare-earth family of elements.

Mass transfer will stop when the salt in equilibrium with the donor has a similar uranium content of 1.25×10^{-2} wt% U. The uranium content in the donor at equilibrium will therefore be:

$$\text{wt\% U in metal} = \frac{\text{wt\% U in Salt}}{\text{U Kd (donor)}} = \frac{1.25 \times 10^{-2}}{5} = 2.5 \times 10^{-3} \text{ wt\% U}$$

The uranium content of the thorium blanket is assumed to be about 0.9 wt%. The total uranium transferred out of the donor may therefore be approximated by:

$$\text{\% U transferred out of donor} = \frac{0.9 - .0025}{0.9} \times 100 = 99.5\%$$

Attainment of equilibrium conditions may take a considerable period of time as the transfer rate will decrease markedly as the uranium content of the donor is lowered. Uranium content of the transport salt will be 1.25×10^{-2} wt% U at equilibrium and the actual amount in the salt will be dependent up to the amount of molten $MgCl_2$ present in the system. This uranium in the salt does not represent a loss, just an in-process inventory.

The salt transport process is dependent upon the utilization of a uranium donor alloy. The proposed donor alloy uses copper and magnesium as alloying agents to obtain donor properties at $800^\circ C$. The magnesium may be removed from the depleted donor alloy by vacuum melting. Other processes for separation of copper and FP-4 elements from thorium would be required if thorium is to be recycled back to the breeder blanket. The economics of remote fabrcation of the thorium for recycle may dictate a once through cycle for thorium.

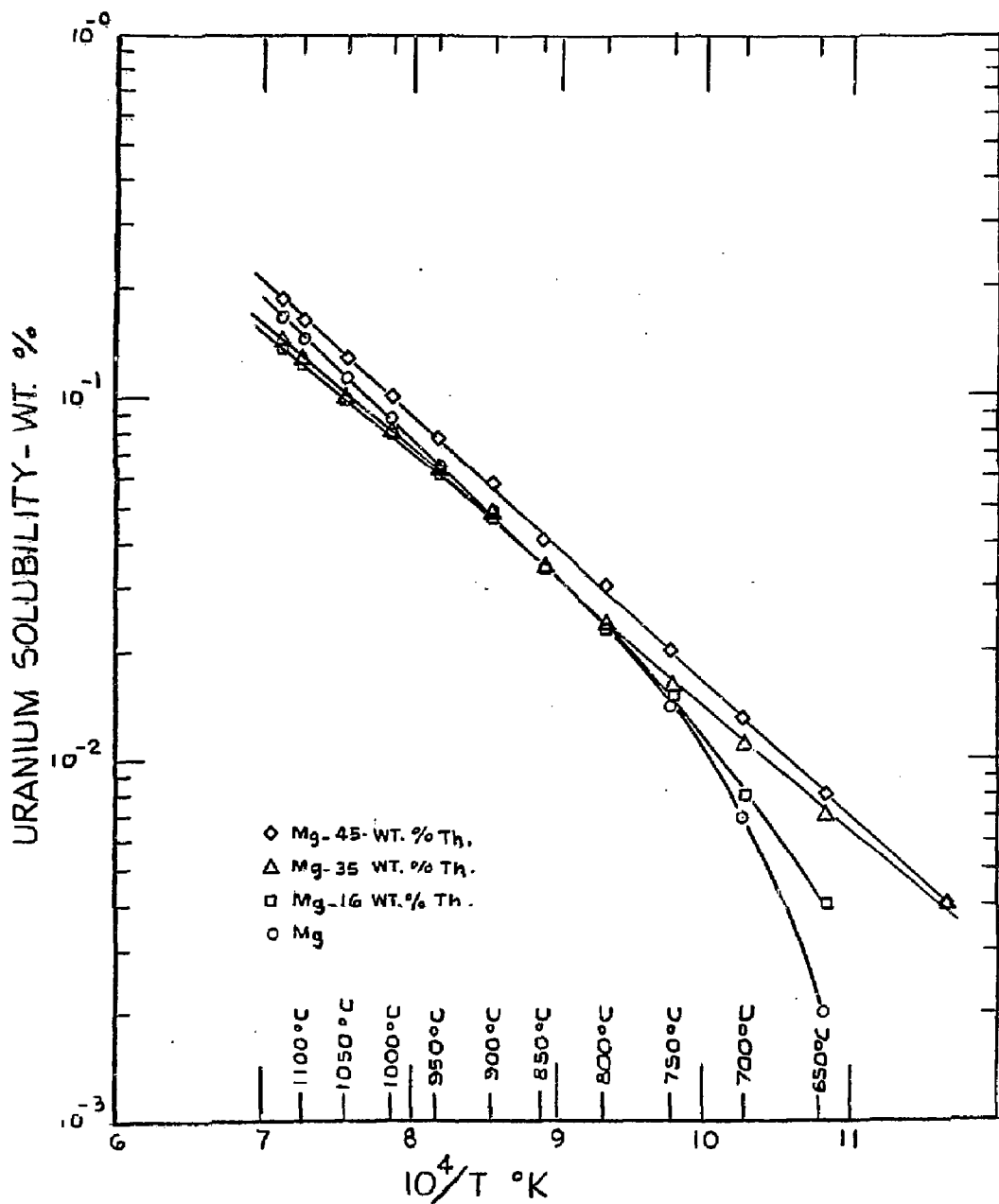Figure 7 shows a conceptual mode of operation for the salt transport process.

FIG. 2

DATA BY CHIOTTI AND VOIGT
IND. ENG CHEM,VOL. 50 PP. 137-140 (1958)

Solubility of Uranium in Pure Magesium and
Mg-33 wt% Th Between 600 and 850°C*

Temperature		U solubility (atom fraction) in indicated solvent	
(°C)	$10^4/T(°K)$	Mg	Mg-33 wt% Th
600	11.45	- -	7.1×10^{-6}
650	10.83	5.9×10^{-6}	1.3×10^{-5}
700	10.28	1.1×10^{-5}	- - -
750	9.78	1.68×10^{-5}	2.75×10^{-5}
800	9.32	2.73×10^{-5}	4.22×10^{-5}
800	9.32	2.38×10^{-5}	
850	8.90	4.04×10^{-5}	5.07×10^{-5}

Fig. 3

Fig. 1. Solubility of Uranium in Pure Magnesium and
Mg-Th Solutions between 600 and 850°C.
This study: ●, pure Mg; ▲, Mg-33 wt % Th.
Solid curves for pure Mg and Mg-35 wt % Th
from references 1 and 2.

Data from work by Fred J. Smith, October 6, 1982,
from Oak Ridge National Laboratory. Work
sponsored by Division of Chemical Sciences,
Office of Basic Energy Sciences, D.O.E.

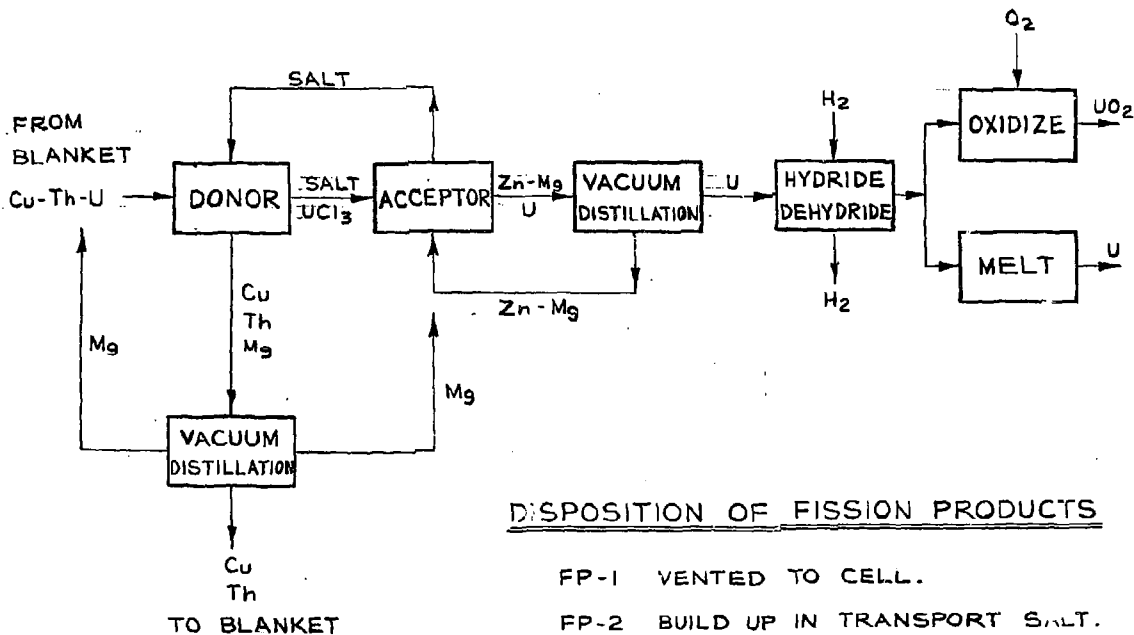# CONCEPTUAL SALT TRANSPORT FLOW SHEET
FOR PROCESSING THORIUM BLANKET

Fig. 5

DISPOSITION OF FISSION PRODUCTS

FP-1 VENTED TO CELL.

FP-2 BUILD UP IN TRANSPORT SALT.

FP-3 BUILD UP IN TRANSPORT SALT AND ACCEPTOR ALLOY.

FP-4 FOLLOW THORIUM, WILL FOLLOW COPPER IF THORIUM-COPPER SEPARATION IS MADE.

TEMPERATURE (K)

Th ←Th₂Cu

ThCu₂ →ThCu₃.₆ →ThCu₆

COPPER (wt %)

COPPER (at.%)

1273 K
1280 K
1153 K
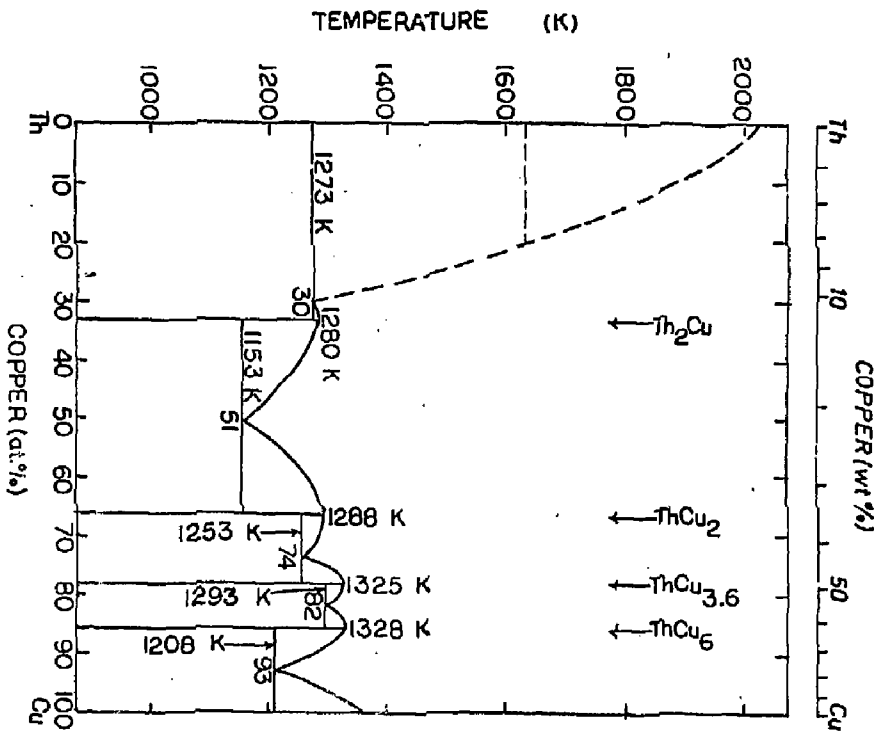1288 K
1253 K
1325 K
1293 K
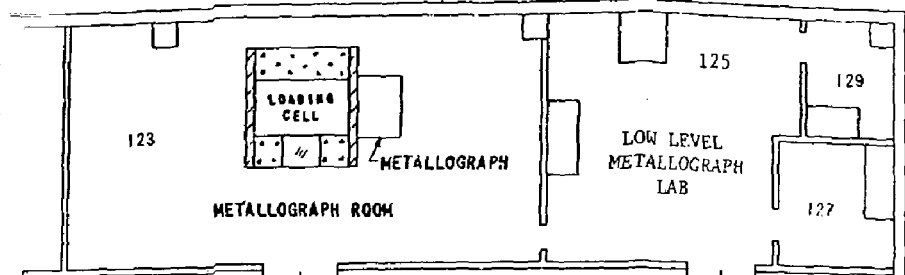1328 K
1208 K

FIG. 5.4. Phase diagram of the system thorium-copper.
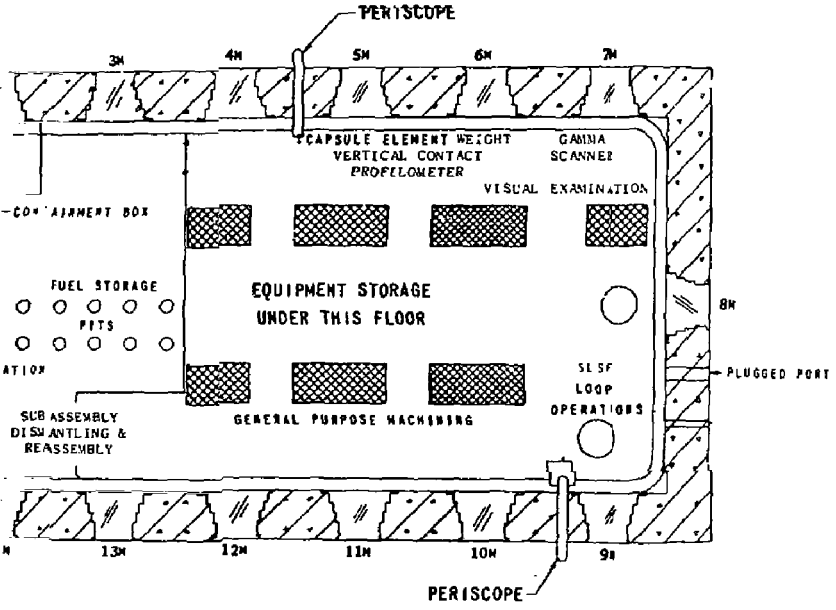
Fig. 6

FIG. 1-2   HFEF/N PICTORIAL

Facility floor plan. Labeled areas include:

- 128
- 130 — RADIATION SAFETY LAB.
- CLEAN METALLOGRAPH LAB
- 124
- 121 — PHOTO LAB
- 126
- UP / DOWN (stairs)
- HATCH TO CASK TUNNEL
- NORTH O
- SMALL EQUIPMENT TRANSFER PENETRATION
- SMALL EQUIPMENT TRANSFER PENETRATION
- PERSONNEL ACCESS DOOR
- 10 20 1N 2N
- HATCH TO CASK TUNNEL
- TRANSFER
- HATCH TO CASK TUNNEL
- CONTAINMEN
- SPRAY CHAMBER
- DECON CELL
- MAIN CELL
- FUEL S
- PIT
- HATCH TO TRANSFER TUNNEL
- HATCH TO TRANSFER TUNNEL
- INTERSTATION CART
- SUB ASSEMB DISMANTLIN REASSEMBL
- 6i 5i
- LOOP PIT
- STORAGE PITS
- TRUCK LOCK
- 40 30 15N 14N
- SMALL EQUIPMENT TRANSFER PENETRATION
- PEN 7.2009
- SOUTH OPERATIN
- ELEVATOR
- DUCT SPACE
- OPERATIONS OFFICE 114
- 112
- DUCT SPACE
- 110 MEN
- 104 CHANGE ROOM

123

LOADING CELL

METALLOGRAPH

METALLOGRAPH ROOM

125

LOW LEVEL METALLOGRAPH LAB

129

127

NORTH OPERATING CORRIDOR

TRANSFER

PERISCOPE

3M 4M 5M 6M 7M

CAPSULE ELEMENT WEIGHT
VERTICAL CONTACT
PROFILOMETER

GAMMA SCANNER

VISUAL EXAMINATION

CONTAINMENT BOX

FUEL STORAGE

PITS

EQUIPMENT STORAGE
UNDER THIS FLOOR

8M

SLSF LOOP OPERATIONS

PLUGGED PORT

ATION

SUB ASSEMBLY
DISMANTLING &
REASSEMBLY

GENERAL PURPOSE MACHINING

13M 12M 11M 10M 9M

PERISCOPE

OPERATING CORRIDOR

102

WOMEN

ROOM

ENTRY

CORRIDOR

DOWN UP

SECRETARY
AND FILES

103

OFFICE

107

OFFICE

109

OFFICE

111
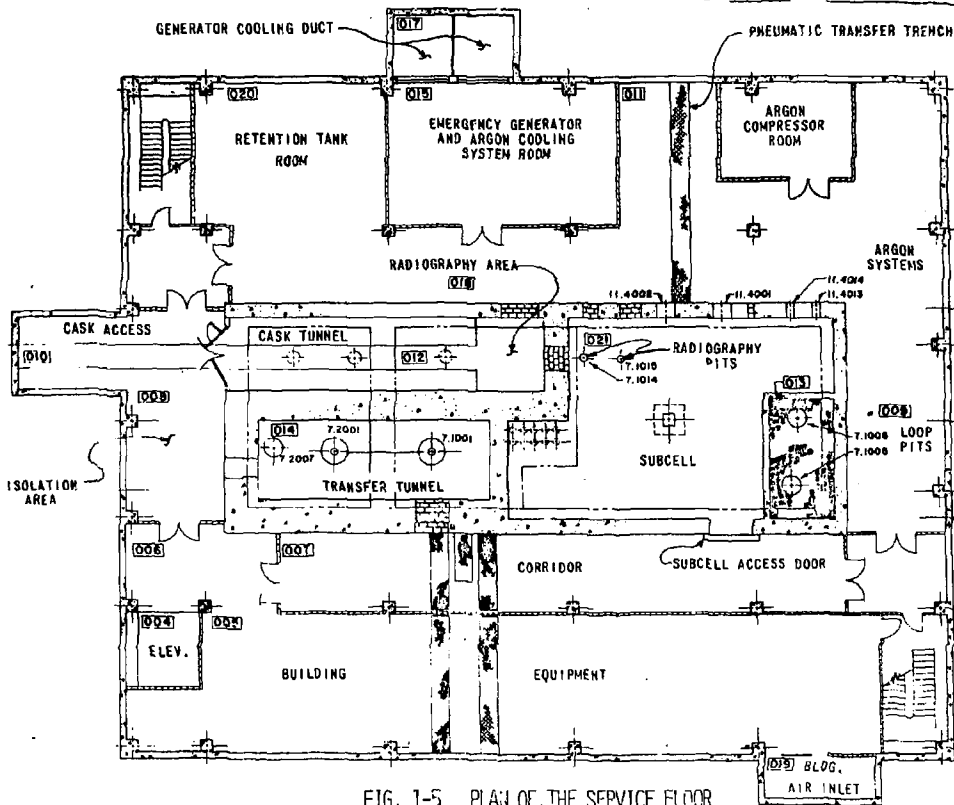
PLAN OF OPERATING FLOOR AND CELLS
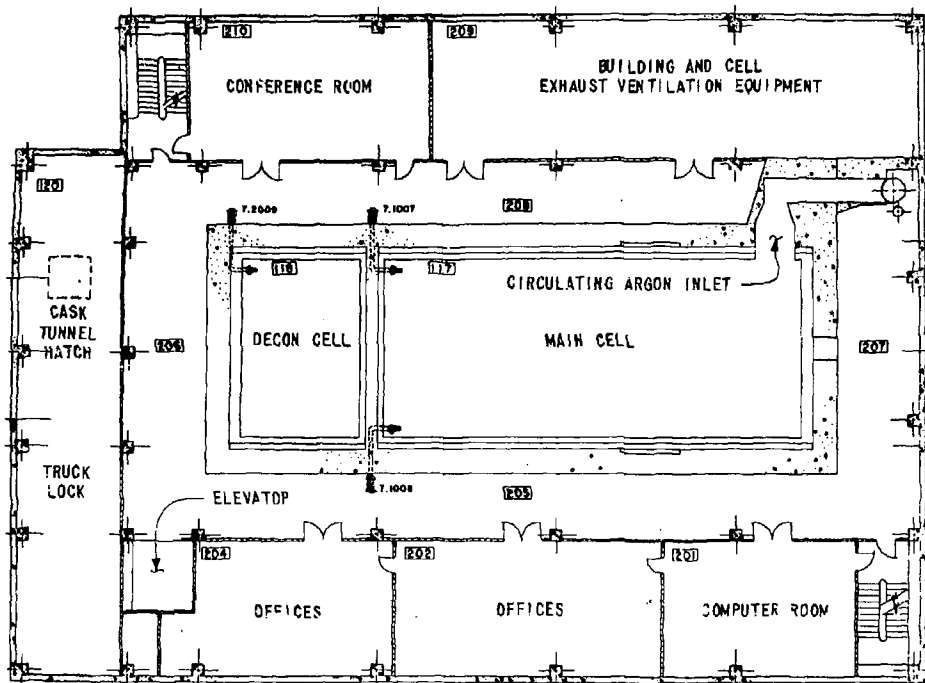
FIG. 1-5 PLAN OF THE SERVICE FLOOR
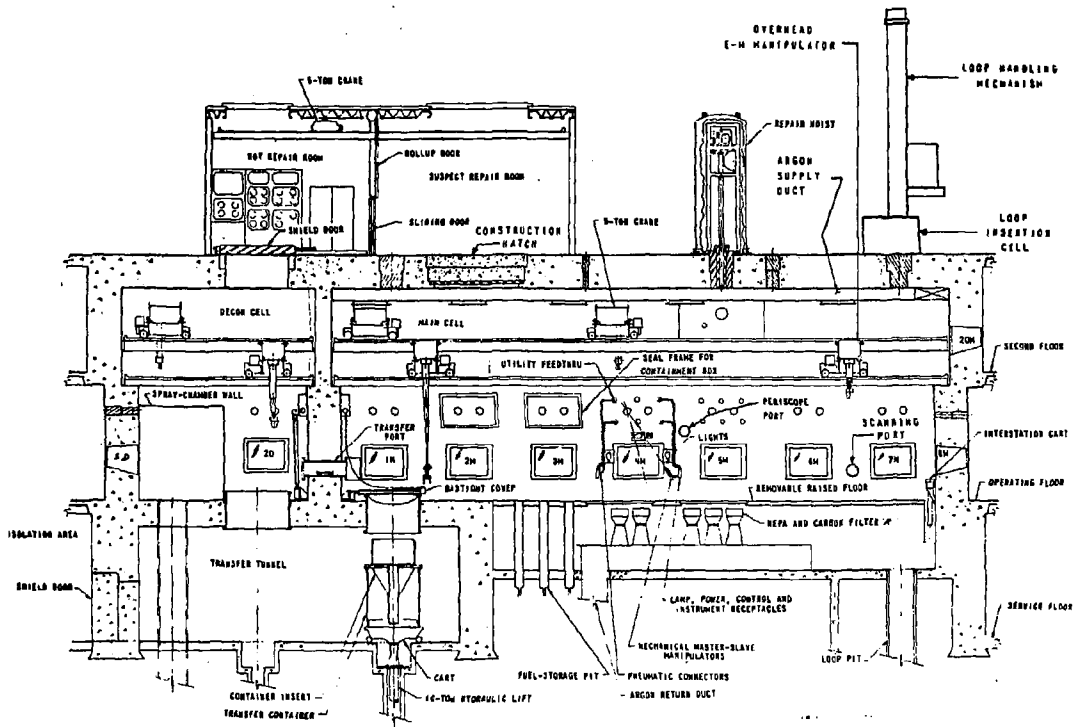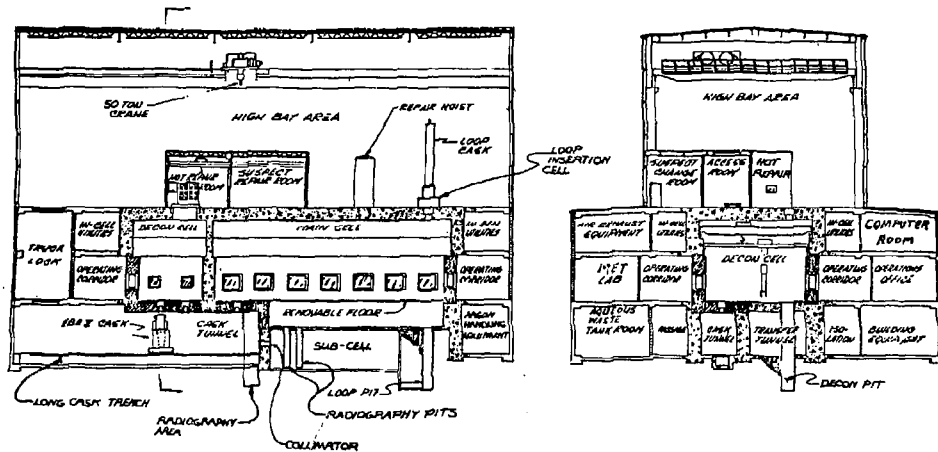
FIG. 1-6   PLAN OF THE SECOND FLOOR

FIG. 1-7   ELEVATION SECTION OF THE CELLS

FIG. 1-8   ELEVATION SECTIONS OF HFEF/N