ROUGH DRAFT

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# RECOVERY OF AMERICIUM AND CURIUM FROM NUCLEAR FUEL PROCESSING WASTE SOLUTIONS*

D. O. Campbell and S. R. Buxton

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MASTER

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# RECOVERY OF AMERICIUM AND CURIUM FROM NUCLEAR FUEL PROCESSING WASTE SOLUTIONS*

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One of the objections made to nuclear power is that it creates a long-term waste which poses a hazard to man for thousands — and even hundred of thousands — of years. The usual answer to this is to place the waste in a location and form such that it cannot get into the biosphere, but can anyone guarantee that?

Examination of the relative contributions of waste constituents shows that a preponderant part of the long-term hazard results from actinide elements which constitute only a tiny fraction of the waste. If these actinides could be removed and appropriately dealt with, then the bulk of the waste could be disposed of with less dependence on its permanent isolation. This concept is commonly referred to as "waste partitioning".

The first slide indicates the degree of removal of actinides I am talking about. The figures range from 99.99% — four 9's — for Pu, three 9's for U, Am, and Cm, on down to 95% for Np. If the actinide concentrations can be reduced by these factors the potential hazard after a few hundred years is about evenly divided between fission products and actinides.

The next slide (2) indicates the relative hazard of the waste plotted against an unusual scale, log time, from 10 to a million years. The ordinate relates to the hazard if the waste should somehow enter our environment, for example, drinking water, with no hold-up or retension. The upper curve shows the hazard of waste resulting from existing processing methods. The early part is controlled by the 30 year half-life of Cs and Sr, over a period of

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several hundred years. Then it flattens out when actinides become dominant, and subsequently drops very slowly.

If actinides are removed to the extent stated before, the hazard drops down along this lower curve. The difference doesn't look like too much on a log-log plot, but it amounts to a factor of a few hundred for the time beyond a few hundred years. Much is made of the fact that the hazard is reduced to something in the range of that of natural minerals — the upper line is the hazard from pitchblende, and the lower for a more or less typical Plateau uranium ore, so it is in a realm not totally foreign to our little world.

Now, I want to look at the relative contribution of the different elements to this hazard, from 1000 to a million years, this lower plateau — on the <u>next slide</u> (3). Over most of the time the fission product, Tc, is dominant. Then the various actinides follow — Pu, Am, and Cm drop off to some extent, and the very long-lived U and Np become relatively more important after very long times.

However, before we worry about any fission products we have to remove the actinides to reach these levels. Once again, I want to look at the actinide removals required — <u>next slide</u> (4). Now, part of this is done anyway in fuel processing. Economics requires the recovery of most of the U and Pu, typically somewhere around 99% of each. Neptunium has been recovered on a few occasions, to the extent of around 90%. Am and Cm are never recovered, and in fact cannot be recovered under the conditions of Purex extraction.

So, the problem in waste partitioning can be redefined in terms of the recovery in <u>addition</u> to that already achieved. It requires the recovery of an additional 99% of the Pu, 90% of the U, up to 95% of the Np, but the same 99.9% of the Am and Cm. There is reason to expect, or at least hope, that the present Purex process can be upgraded to meet the requirements for U and Np, and probably for Pu. However, some totally new approach is required for Am and Cm, and that is what I want to talk about today.

The next slide (5) represents the standard concept of waste partitioning. Following Purex as presently used there is a box called "exhaustive extraction" which accomplishes the required removal of U, Np, and Pu by some undefined means, but presumably solvent extraction. Then there is the removal of Am and Cm, and this black box is my subject.

Am and Cm exist in the trivalent state under conditions practical in reprocessing, and their chemistry is very similar to that of the rare earths which are present in relatively large amount as major fission products. Conceptual processes to recover Am and Cm, therefore, usually include two separate cycles; that is, this box becomes two boxes. The first is the recovery of Am, Cm, and any transcurium actinides, along with the lanthanides, but hopefully separated from all the rest of the fission products and bulk chemicals used in processing, like sodium nitrate, iron, and sulfate. The second cycle is the partition of Am, Cm, and possibly heavier actinides like Cf, from the fission product rare earths.

The first cycle, co-recovery of lanthanides and actinides, can, in principle, be accomplished by several methods including precipitation, solvent extraction, and ion exchange. Each has its own problems and limitations, as well as different interactions with the second cycle. I will not discuss solvent extraction which is under investigation elsewhere. My work has centered on two approaches, cation exchange and oxalate precipitation.

The next slide (6) shows the composition of a waste solution from Purex processing of LWR fuel, and this is the sort of waste we will be dealing with for the next few decades. It is about 2.5 to 3 M in $HNO_3$, and contains most of the elements from atomic number 32 to 66, many of them at a concentration of a few thousandths molar. Every chemical family is represented.

The composition could vary from this, down to perhaps half these concentrations, up to as much as ten times them for a waste concentrate if interim storage of liquid wastes is adopted. The relative amounts of the elements would be about the same, however. What we want to do is to recover this small amount of Am and Cm — some 300 g per MTU — such that less than 0.1% is left in all other process streams combined.

The first problem is that there is too much acid. For oxalate precipitation or ion exchange a much lower acid concentration is necessary, preferrably a few tenths molar. This can be accomplished by dilution with water or perhaps by evaporation or denitration. In tests of denitration, for example with sugar, substantial amounts of solids were formed if the acidity was reduced to the range of interest.

At best, solids may be a serious problem. If a solution like this, containing nitric acid at several molar concentration, is boiled for a few minutes or heated for a few days, there will be substantial solids formation. This happens more rapidly the lower the acidity and the higher the temperature, and it involves complex fission product interactions. A major constituent of the solids is a crystalline compound containing Zr and Mo in the ratio 1 to 2, but the compound has not been characterized. Unfortunately, this compound carries Pu. Conditions which lead to formation of this compound must be avoided, at least until Pu has been adequately removed from the waste.

The simplest way to reduce acidity without boiling or heating the solution is to dilute it. The trouble is that volumes become quite large, and that eventually translates into large evaporators. The next slide (7) shows a conceptual flowsheet for such a process, based on processing one metric ton of fuel. This is an ion exchange process which was tested with synthetic waste of the composition I just showed you, and Dowex 50 resin. Dilution to the range half to 1 M nitric acid permitted the rare earths and actinides to be loaded on the resin, and the resin requirement would be about 600 liters per metric ton of fuel.

There are some interferences. Certain Ru-species load very strongly and elute with the rare earth product. However, this was readily eliminated by complexing the solution, for example, with nitrite. Work with fully irradiated fuel indicates that similar complexing with radiolysis products will give the same result spontaneously. In fact, it probably cannot be avoided.

Zirconium also loads very strongly, but it is fairly difficult to elute, so only a small fraction of the zirconium ends up in the rare earth-actinide product. However, zirconium does occupy a substantial amount of resin, thereby increasing the size of the resin column.

One disadvantage of this approach is that solution volumes are quite large; some 20,000 liters/MTU goes to waste solidification in this case. This translates into large waste evaporators.

The advantage of the process is that the only chemical added to the system is nitric acid, aside from ion exchange resin. Since nitric acid can be recovered or recycled by evaporation and there is much experience with this, the process appears to be operable, although it might be awkward.

A promising alternative is based on oxalate precipitation for primary recovery of rare earths and actinides with an ion exchange polishing step. Oxalate forms soluble complexes with some impurity elements such as Zr and iron, thereby diminishing their interference with the process.

The next slide (8) shows a simplified summary of the process, along with the results of a hot run. This process was tested with synthetic waste and also with real waste on a scale of about 200 g of $UO_2$. These numbers are for a test using fuel from the Carolina Power and Light H. B. Robinson Reactor irradiated to 31,000 MWD/MTU and cooled 2 years. I am carrying out some fuel cycle studies with such fuel. It was carried through a process based on the projected flowsheet for the Allied-General Nuclear Services plant at Barnwell, SC, the AGNS plant.

The fuel was dissolved in nitric acid containing some gadolinium as a soluble poison, and then batch extracted with 30% TBP to remove about 99% of the U and Pu. The raffinate was evaporated to produce a waste concentrate, and presently AGNS proposes to temporarily store this waste concentrate until a decision is made about the final disposition of such wastes.

We added oxalic acid to the concentrate and diluted it to 1 M nitric acid 0.2 M oxalic acid. A series of solubility measurements were made as it was diluted over an additional factor of 2. With increasing dilution the solubility decreased faster than the volume increased, and the overall loss dropped from 0.4% to 0.2% of the Am and Cm.

The oxalate precipitate becomes the feed to an actinide-lanthanide partition step to recover purified Am and Cm, and I will get to that shortly. The oxalate can easily be converted to a dry oxide which could be stored. This would provide a convenient decoupling of the subsequent Am-Cm recovery from the processing prior to this step. The precipitate also carries most of the residual Pu, part of the Ba and Sr, and some 5 to 10% of the Zr. Everything else is in the supernate.

The supernate was then passed through a small column of Dowex 50 ion exchange resin which loaded nearly all the remaining Am, Cm, and rare earths, whether ionic or particulate. The column acts as a polishing filter as well as ion exchanger, so a quantitative solids recovery operation up here is not necessary.

Although most Pu precipitated with the oxalate, the Pu which did not precipitate also did not load on the ion exchange resin; it passed through into the raffinate. As a result the requirement for Pu recovery in the solvent extraction plant may be greatly reduced, and a separate Pu recovery step may not be required — that is, the "exhaustive extraction" step. In this test with batch extraction of about 99% of the Pu, we end up with about 0.01% of the Pu in the final waste — right at the specified limit. Americium and Cm are factors of 5 to 10 below their limit. This raffinate is suitable for waste solidification.

The next slide (9) shows a conceptual flowsheet based on this process. I don't want to get involved in all the details, but note that the ion exchange column is now much smaller — probably around 50 liters per MTU, compared to 600 liters before. This results because the quantity of rare earths to be loaded is very much smaller, and also because interferences such as Zr and iron are complexed and do not compete for resin sites. The ion exchange resin requirement is determined by distribution coefficient in this case, as opposed to loading capacity in the previous case.

A second significant advantage here is that the product — the oxalate precipitate — can be dissolved in a small volume of nitric acid; the oxalate can be destroyed chemically or radiolytically; and a much smaller volume of product results. This yields a far better feed for the partitioning process than the first flowsheet.

So, the oxalate precipitation-ion exchange process has been tested with full activity process solutions, and it appears to be very promising. This is the only process I know of which has been tested with representative LWR solutions.

I would like to turn now to actinide-lanthanide partitioning by ion exchange chromatography. Displacement development chromatography has been around for over 25 years in the rare earth industry, and Wheelwright used it in the 1960s to recover Am and Cm from waste solutions. More recently it has been used at Savannah River to recover several kgs of Cm. Our problem differs primarily in that process losses must be very much smaller than in the earlier work, and we want to minimize the addition of permanent solids.

We need to recover all the Am and Cm, and as little as possible of the rare earths. There are some complexing agents which elute Am and Cm before the fission product rare earths, and DTPA is a good one. DTPA is diethylenetriaminepentaacetic acid. The next slide (10) shows an idealized elution curve for a waste solution and DTPA elution. Note that Am and Cm elute first, with the very small amount of some heavy rare earths, and then Gd, Eu, and the lighter rare earths come off successively.

A major objection to this approach is that two new components, in addition to resin, are introduced into the system; and they may interfere with subsequent waste processing and solidification. One is the DTPA itself, associated with a cation such as sodium or ammonium, and the other is a metal barrier ion. In displacement development about half the resin is initially loaded with a metal such as Zn or Ni, and this metal elutes, along with DTPA, throughout the early part of the elution. The result is that there is a large volume of dilute solution of the barrier ion and DTPA which poses a problem of recovery and recycle; we dom't want all this material going to waste solidification.

We have done some work on the use of hydrogen ion for the barrier, or really a mixed barrier containing mostly hydrogen ion and some metal such as zinc. The next slide (11) shows an elution curve for an experiment using a synthetic waste mixture with erbium to represent the behavior of Am and Cm. Here, the barrier was mostly hydrogen ion with about 20% Zn and a little Ni.

The column effluent during the first part of the run is pure water. This is in marked contrast to the usual situation; with the barrier all zinc all this effluent would contain zinc and DTPA at a few hundredths molar concentration. The DTPA interacts with the hydrogen-form resin to form cations such as $H_6DTPA^+$ which load strongly and also serve as effective barrier ions. Nickel forms a similar cation, probably $H_4NiDTPA^+$, which is blue and can be seen on the column. So, the effluent is just water for quite a while, and this can be easily recycled or disposed of. Then about half way out to the actinide bands, there is a breakthrough of Ni and DTPA, and Zn follows the Ni. The DTPA concentration rises to about twice the eluent concentration as the cationic species is eluted.

Following this, the actinides elute, represented here by erbium, and then the fission product rare earths. The major advantage of the mixed barrier is that recycle and waste evaporation problems are greatly reduced. The disadvantage is that there may be some loss in resolution or separation efficiency in the first part of the elution, which is where we need good resolution. However, results indicate that if about 20% of the barrier is a metal like zinc, resolution is adequate for this purpose.

The next slide (12) shows another problem which is generally overlooked, but which is significant here because losses must be so low — hundredths of a percent. This is band tailing. This is an elution similar to the last, with the product concentrations plotted on a linear scale as they usually are. The bands are sharp and drop down to zero — or do they?

We used tracer holmium to represent the actinides, and also tracer praseodymium, out here, and measured these two bands down to concentrations not usually measured. The next slide (13) shows the same data plotted on a log scale. It is quite obvious that the bands flatten out down here, some 4 or 5 orders of magnitude below the peaks, and a low level tail extends indefinitely. This is really a quite general phenomenon; it just isn't usually observed because concentrations aren't measured over a wide-enough range.

The question is — does this tailing contribute an intolerable loss, which would be the range of a few hundredths of one percent? Or — how far out do we have to carry the elution before we can strip off the rest of the elements and send them to waste solidification? Fortunately, once you get out past this bend and integrated loss due to this tail is well under a tenth percent.

In practice, we would probably collect the peak region for a product and recycle both edges of the band — the sharp, leading edge which would also contain some barrier ion, and maybe quite a bit of the trailing edge which will include part of the fission product gadolinium and europium.

We have looked at flowsheets based on these experiments, and the next slide (14) shows the loading step, normalized for one tonne of fuel. The feed could be several thousand liters as shown here, if the ion exchange process I showed earlier is used to recover the trivalent fraction from the waste; or it could be a few hundred liters from the oxalate precipitation process. It would be loaded on about 250 liters of resin, washed, and eluted with DTPA through additional ion exchange columns.

The next slide (15) represents these as a 200-liter column — it would really be several separate columns in series. This process doesn't look too unreasonable, especially when compared to the alternatives. All volumes and flows are in the realm of experience. Product cuts are reasonably small — a hundred liters or so. There would be recycle of band edges, as mentioned before, but recycle is quite common with ion exchange processing. Most of the barrier ion, and hopefully, most of the DTPA, would be recycled. Recycle of barrier and DTPA, however, requires much more attention.

My conclusion, based on experimental work with both synthetic and real process solutions representative of full-level LWR processing, is that the goals of waste partitioning can almost certainly be accomplished, at least for the waste from the Purex process. Now, that is my opinion. There are people who will argue using data from work which was not designed to solve this problem. I really believe there are no basic or fundamental obstacles which preclude attaining these goals; the chemistry is there. The problems will be in engineering — handling recycle, coupling successive steps, the usual engineering problems of integrating a series of operation into a process.

# Goals for Actinide Recovery

(i.e. Recovery Required for LWR Fuel)

| Element | Recovery |
|---|---|
| U | 99.9 % |
| Np | 95 |
| Pu | 99.99 |
| Am | 99.9 |
| Cm | 99.9 |

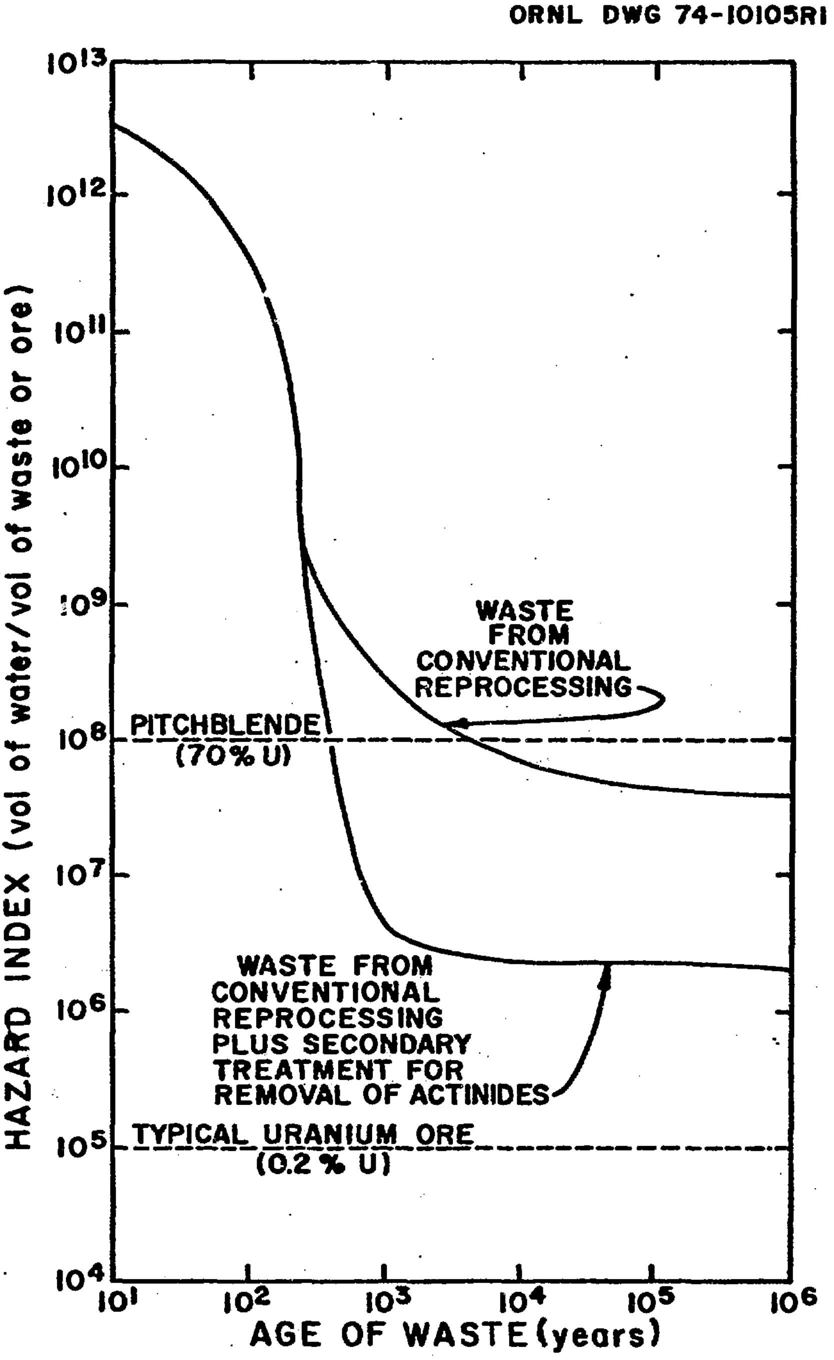
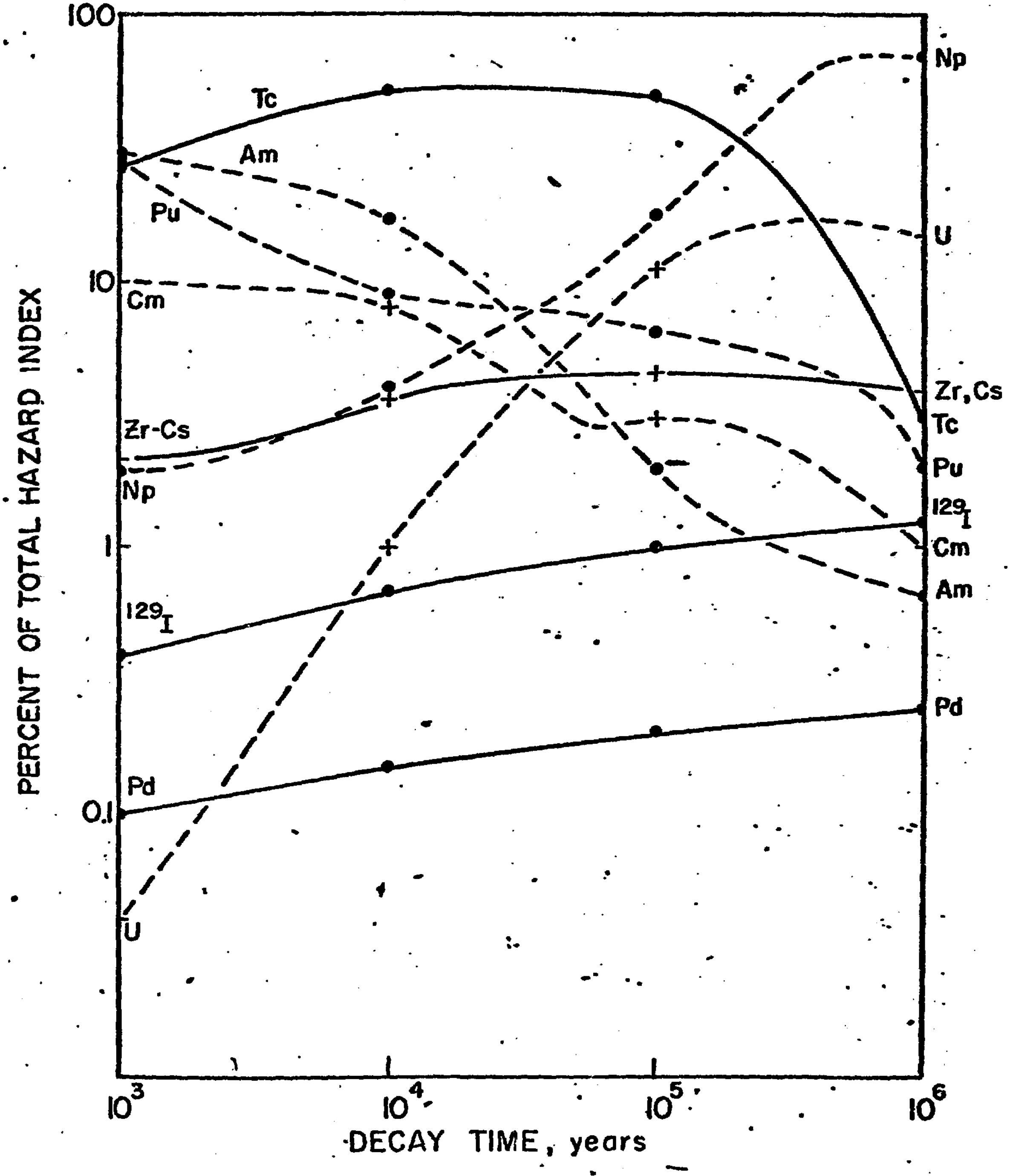


Fig. 1. Effect of age and method of treatment on the hazard index of high-level wastes from LWRs.

Slide 2

ORNL DWG 75-34



Slide 3.

# Actinide Recovery for LWR Fuels

| Element | Goal | Experience |
|---|---|---|
| U | 99.9% | ~99% |
| Np | 95 | ~99 |
| Pu | 99.99 | ~90 |
| Am | 99.9 | — |
| Cm | 99.9 | — |

Slide 4

ORNL DWG 74-3054R

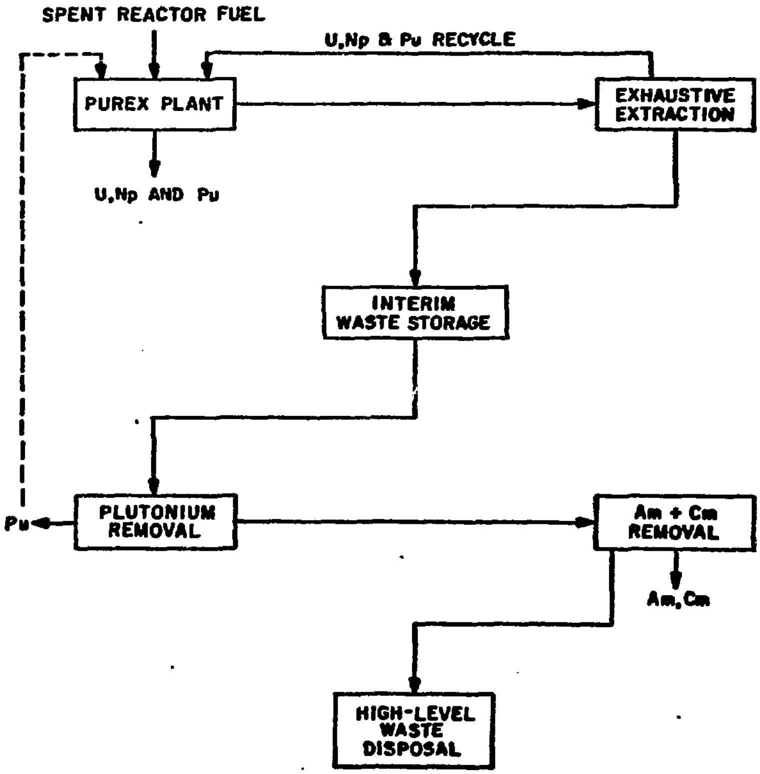


Fig. 8. Conceptual processing sequence for the removal of actinides from LWR reactor fuel.

Slide 5

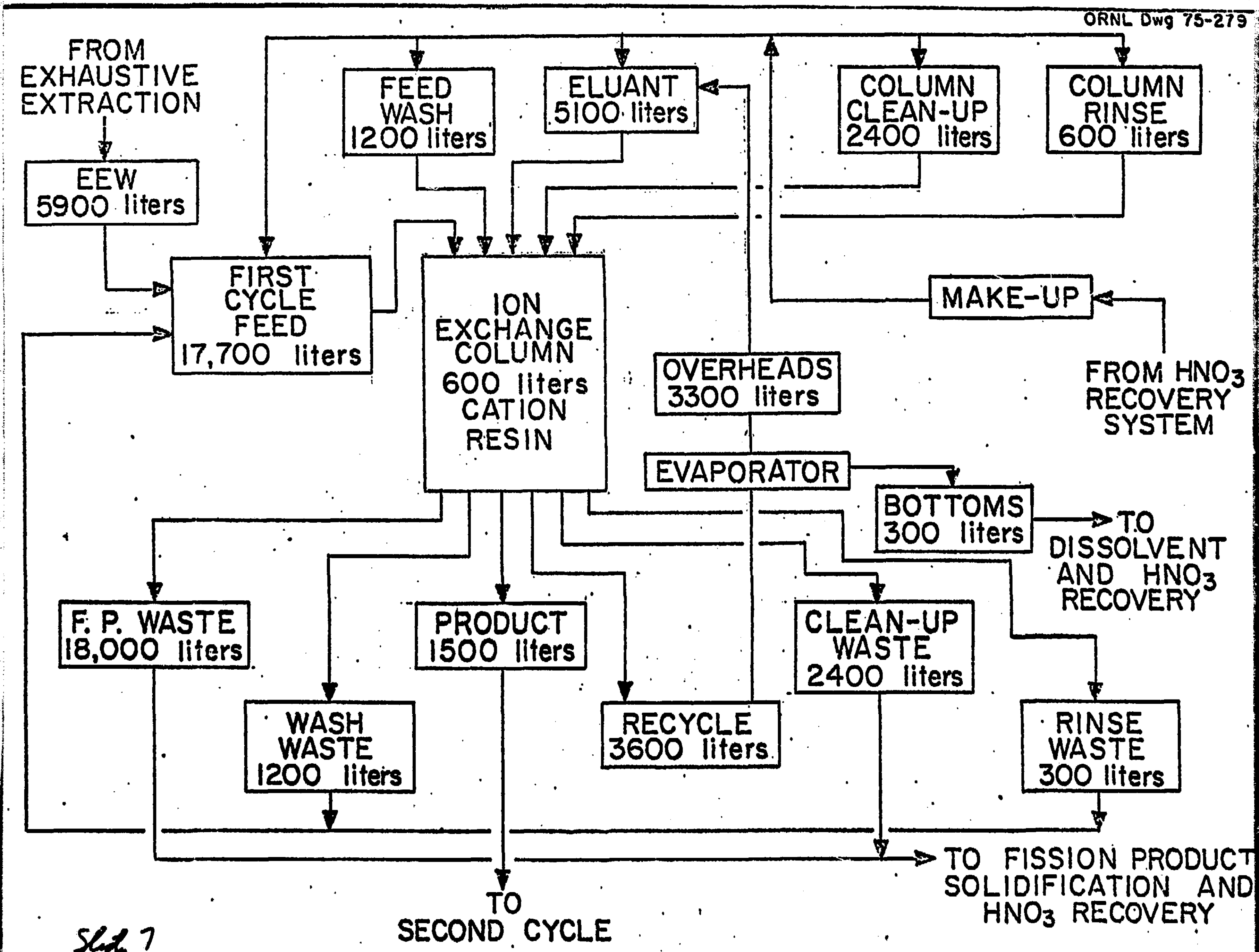
# Fission Product Concentration In HAW
(millimoles per liter)

| | | | | | |
|---|---|---|---|---|---|
| Rb | 1.25 | Ge | 0.002 | Y | 1.7 |
| Cs | 5.9 | Sn | 0.13 | La | 3.0 |
| | | | | Ce | 5.7 |
| Sr | 3.0 | Ag | $4 \times 10^{-4}$ | Pr | 2.7 |
| Ba | 3.9 | Sb | 0.03 | Nd | 9.2 |
| | | | | Pm | 0.06 |
| Zr | 12.9 | Se | 0.21 | Sm | 1.9 |
| Nb | $10^{-5}$ | Te | 1.42 | Eu | 0.36 |
| Mo | 11.4 | | | Gd * | 0.24 |
| | | Br | 0.06 | Tb | 0.004 |
| Tc | 2.7 | I | 0.67 | Dy | 0.022 |
| | | | | Ho | $2 \times 10^{-4}$ |
| Ag | 0.18 | Ru | 6.8 | Er | $6 \times 10^{-5}$ |
| | | Rh | 1.2 | | |
| Cd | 0.24 | Pd | 4.3 | | |

* Stable Gd 18.4

| | | | | | |
|---|---|---|---|---|---|
| In | 0.004 | Fe | 12.2 | U | 13.4 |
| | | Cr | 1.5 | Np | 1.0 |
| | | Ni | 0.6 | Pu | 0.12 |
| | | $PO_4$ | 12.2 | Am | 0.22 |
| | | | | Cm | 0.05 |

Slide 6



ORNL Dwg 75-279

FROM EXHAUSTIVE EXTRACTION

EEW 5900 liters

FIRST CYCLE FEED 17,700 liters

FEED WASH 1200 liters

ELUANT 5100 liters

COLUMN CLEAN-UP 2400 liters

COLUMN RINSE 600 liters

MAKE-UP

FROM $HNO_3$ RECOVERY SYSTEM

ION EXCHANGE COLUMN 600 liters CATION RESIN

OVERHEADS 3300 liters

EVAPORATOR

BOTTOMS 300 liters

TO DISSOLVENT AND $HNO_3$ RECOVERY

F. P. WASTE 18,000 liters

PRODUCT 1500 liters

CLEAN-UP WASTE 2400 liters

WASH WASTE 1200 liters

RECYCLE 3600 liters

RINSE WASTE 300 liters

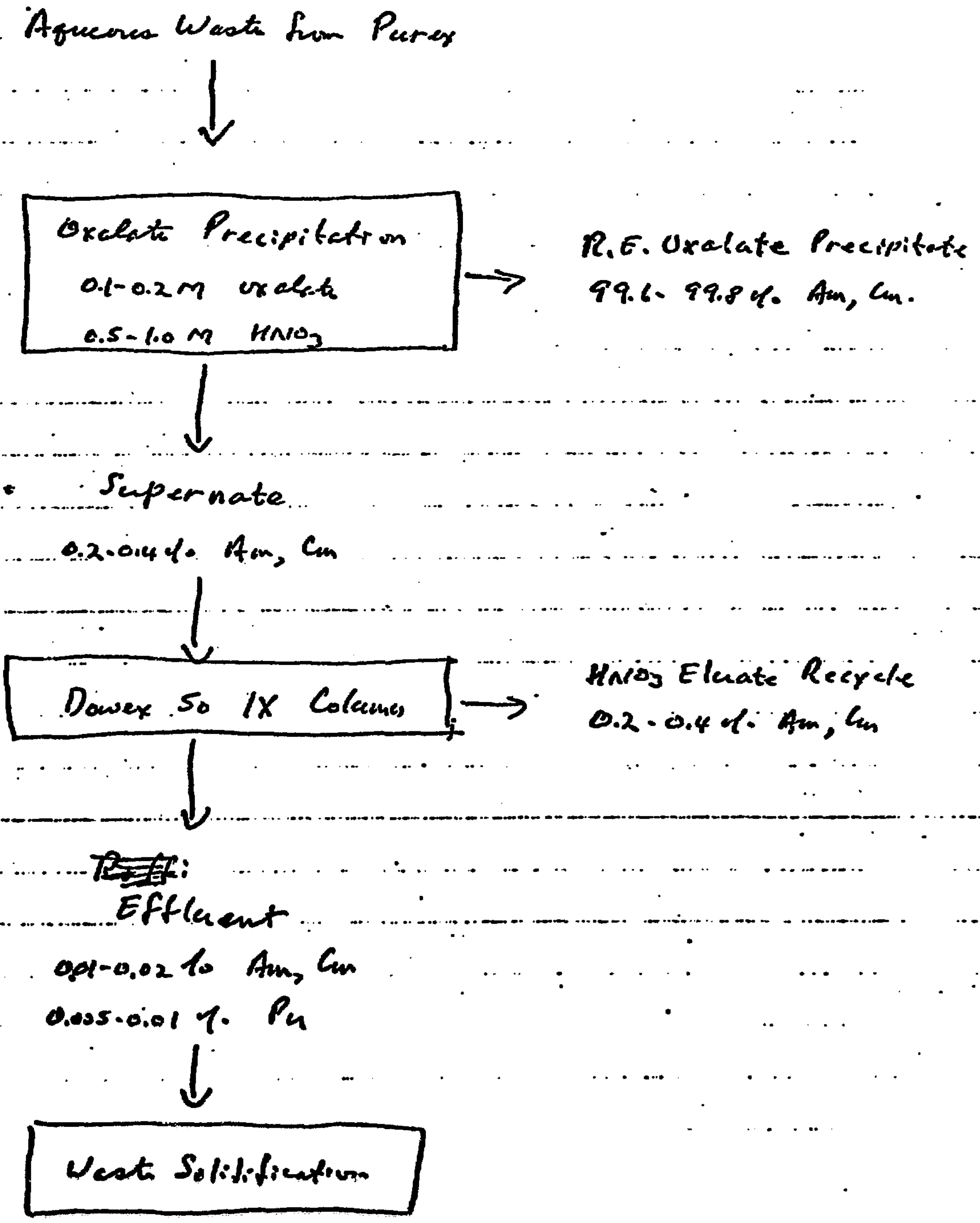
TO FISSION PRODUCT SOLIDIFICATION AND $HNO_3$ RECOVERY

TO SECOND CYCLE

Slide 7

Aug. 20
2 slides
2 Glossy

Oxalate Precipitation - Ion Exchange (OPIX) ← caps



Aqueous Waste from Purex

Oxalate Precipitation
0.1-0.2 M oxalate
0.5-1.0 M $HNO_3$

R.E. Oxalate Precipitate
99.6-99.8 % Am, Cm.

Supernate
0.2-0.4 % Am, Cm

Dowex 50 1X Column

$HNO_3$ Eluate Recycle
0.2-0.4 % Am, Cm

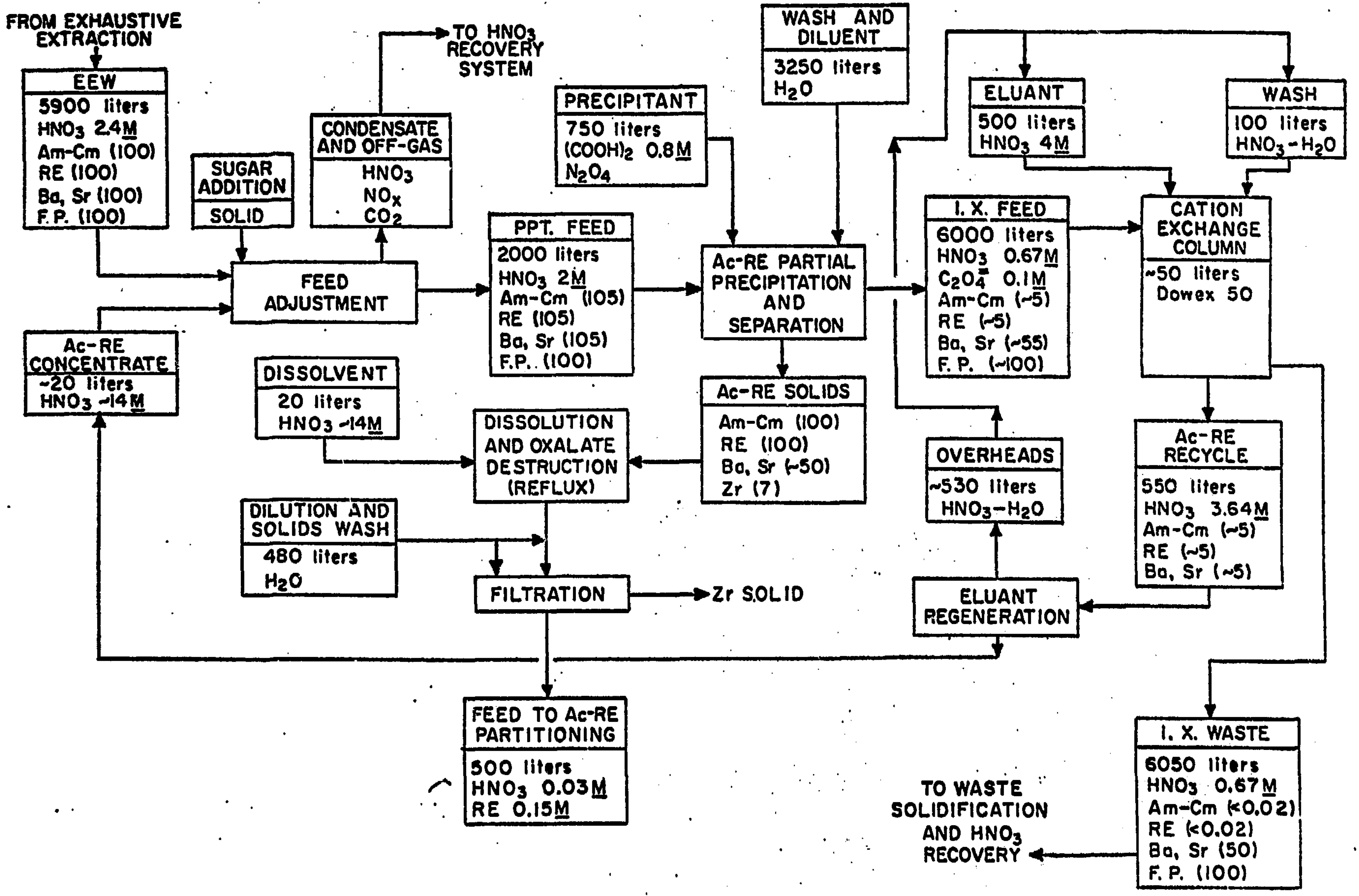
~~Ref~~:
Effluent
0.01-0.02 % Am, Cm
0.005-0.01 %. Pu

Waste Solidification

Slide 8

B-28

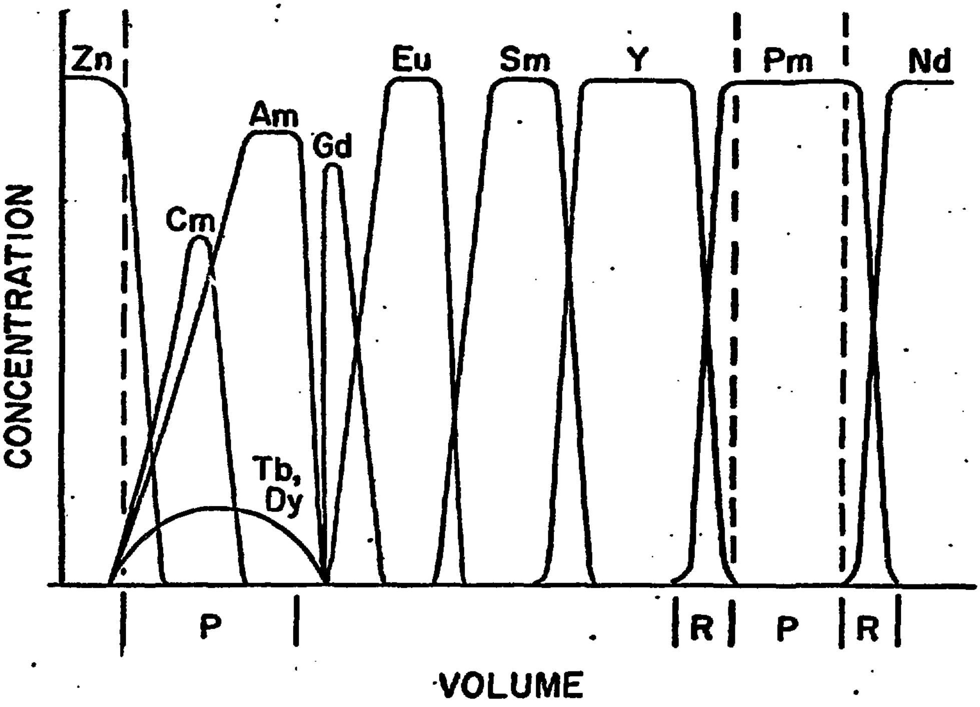
ORNL Dwg 75-12515
R-1



First Cycle of Am-Cm Recovery: Preparation of Am-Cm Partitioning Feed by Partial Precipitation with Cation Exchange of the Supernate.

Slide 9

ORNL DWG 75-72



SIMULATED ELUTION CURVES WITH DTPA

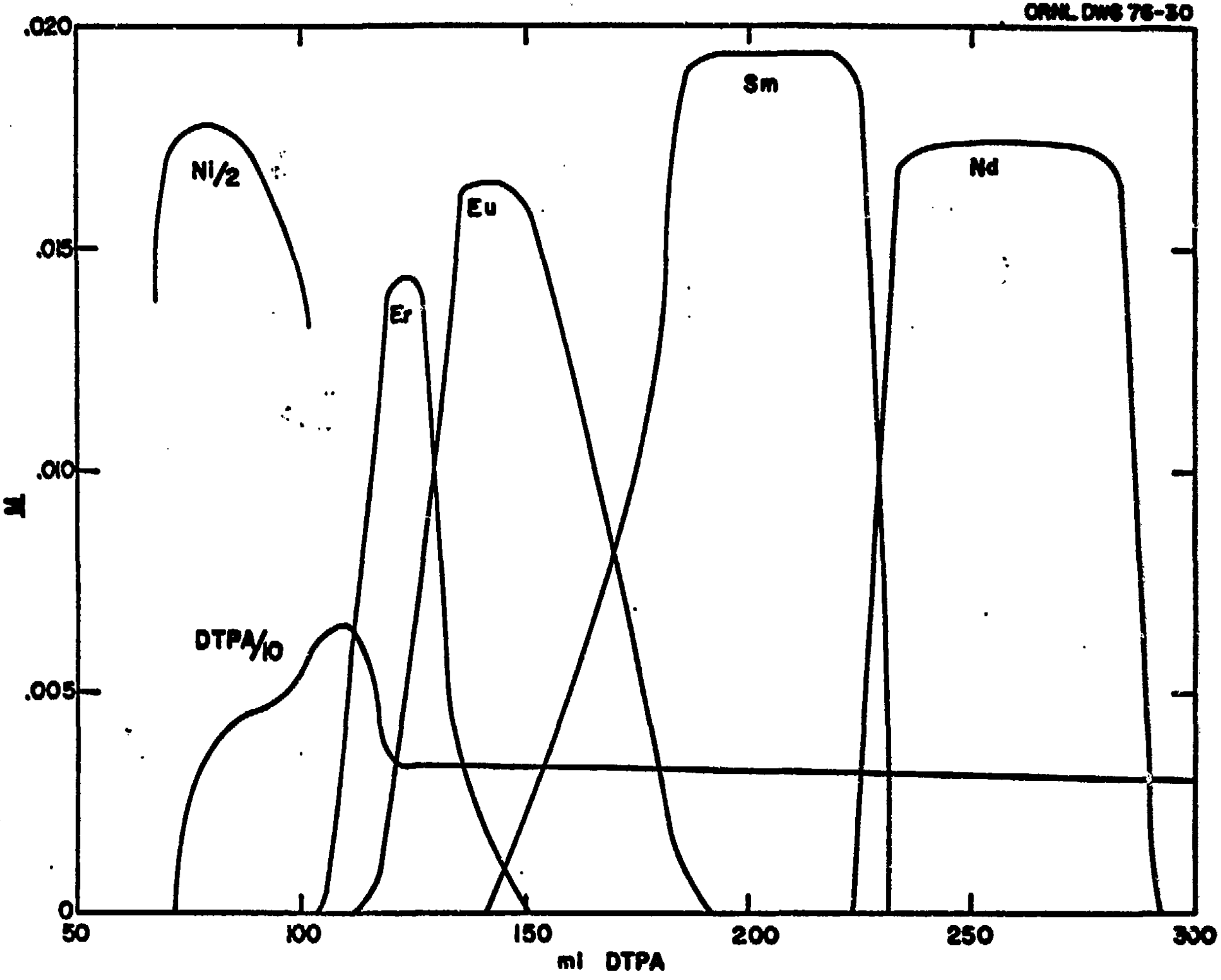
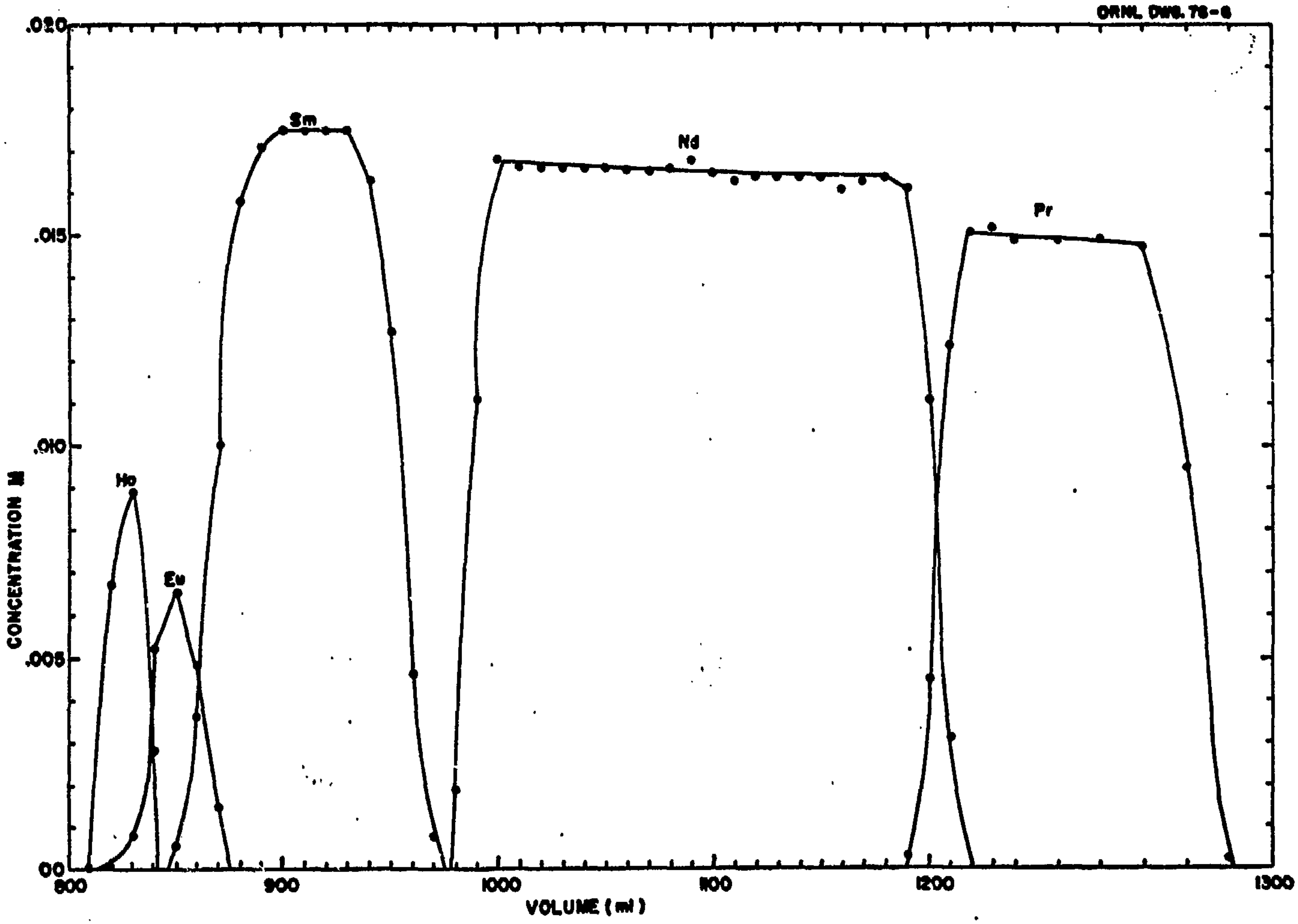
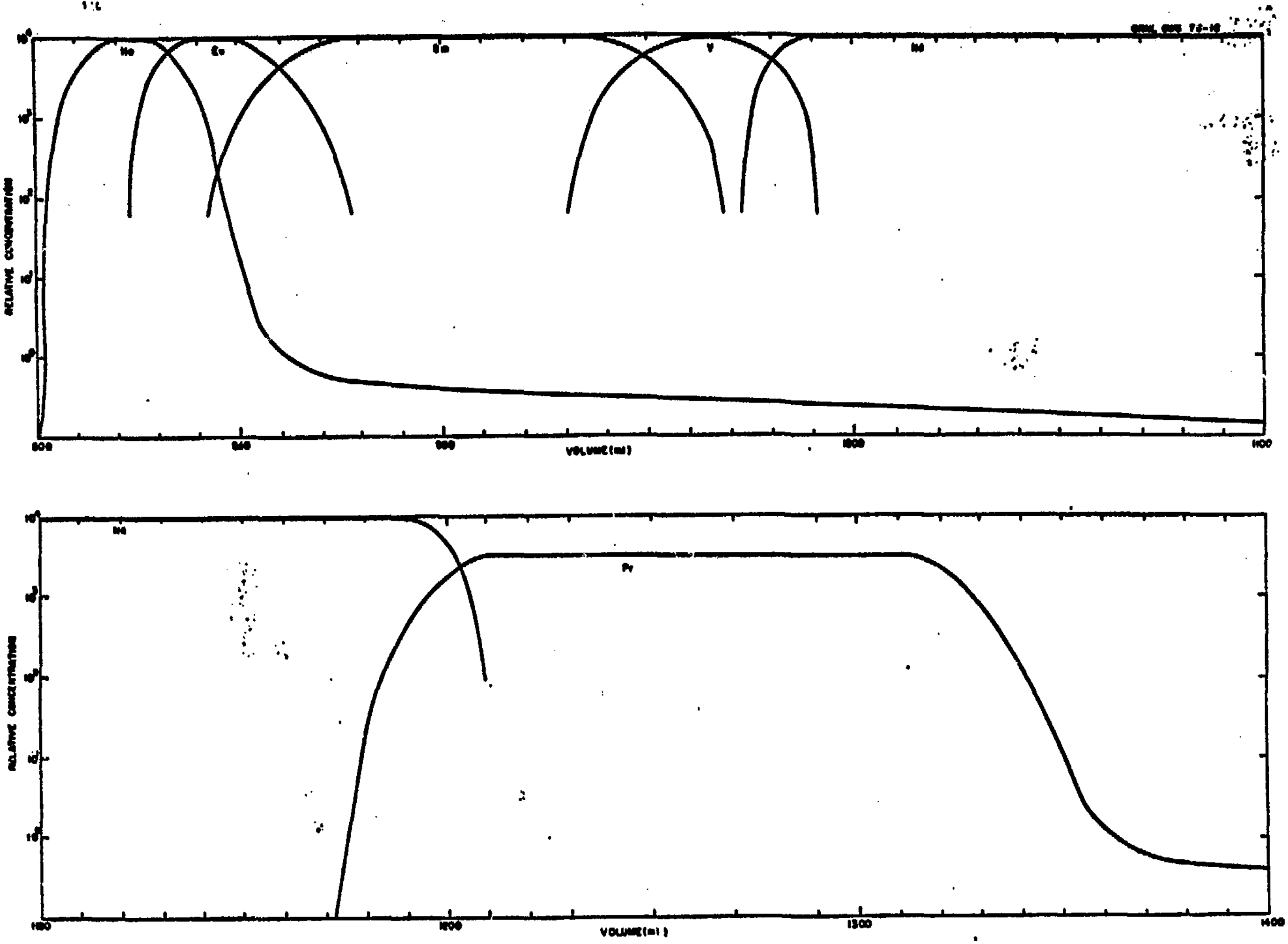
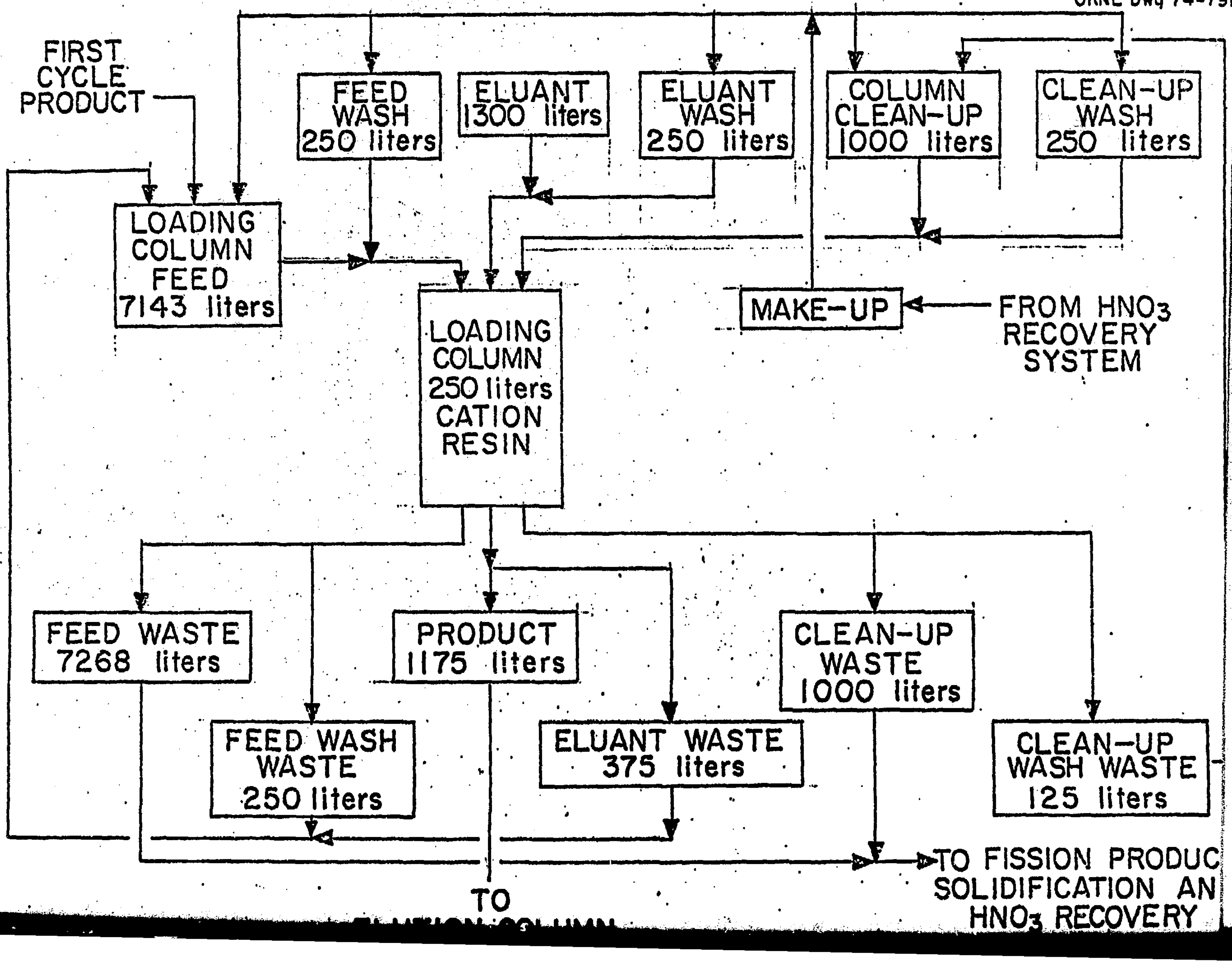
ORNL DWG 76-30
M
.020
.015
.010
.005
0
50
100
150
200
250
300
ml DTPA
Ni/2
Er
Eu
Sm
Nd
DTPA/10

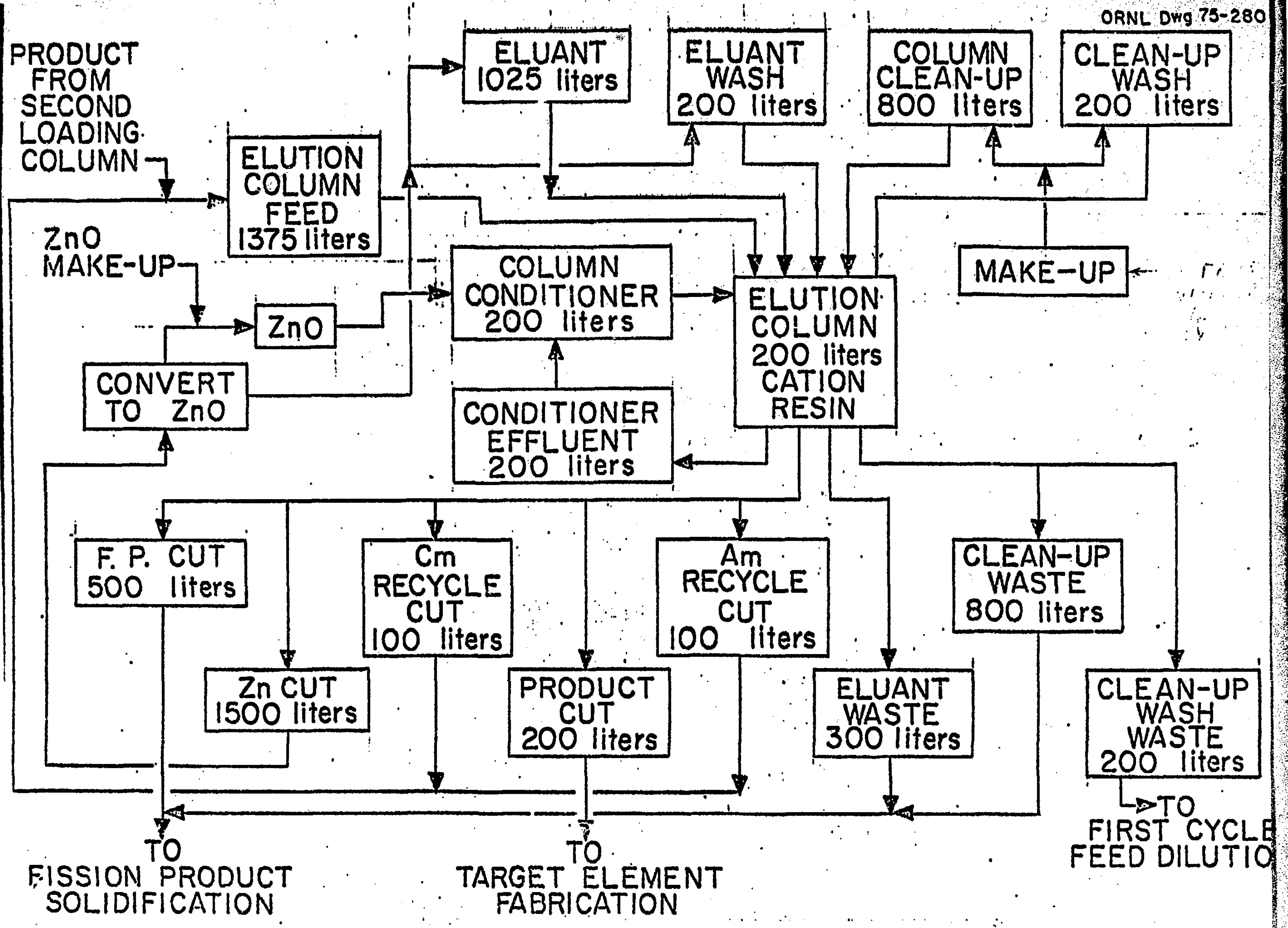
Fig. 11


ORNL DWG. 76-6
CONCENTRATION M
.020
.015
.010
.005
.00
VOLUME (ml)
800
900
1000
1100
1200
1300
Ho
Eu
Sm
Nd
Pr

Slide 12


ORNL DWG 72-10
RELATIVE CONCENTRATION
$10^0$
$10^{-2}$
$10^{-4}$
$10^{-6}$
$10^{-8}$
Ho
Eu
Sm
Y
Nd
800
850
900
1000
1100
VOLUME(ml)
RELATIVE CONCENTRATION
$10^0$
$10^{-2}$
$10^{-4}$
$10^{-6}$
$10^{-8}$
Nd
Pr
1100
1200
1300
1400
VOLUME(ml)


ORNL Dwg 74-791
FIRST CYCLE PRODUCT
FEED WASH 250 liters
ELUANT 1300 liters
ELUANT WASH 250 liters
COLUMN CLEAN-UP 1000 liters
CLEAN-UP WASH 250 liters
LOADING COLUMN FEED 7143 liters
LOADING COLUMN 250 liters CATION RESIN
MAKE-UP
FROM $HNO_3$ RECOVERY SYSTEM
FEED WASTE 7268 liters
PRODUCT 1175 liters
CLEAN-UP WASTE 1000 liters
FEED WASH WASTE 250 liters
ELUANT WASTE 375 liters
CLEAN-UP WASH WASTE 125 liters
TO FISSION PRODUC SOLIDIFICATION AN $HNO_3$ RECOVERY
TO



Am–Cm REMOVAL. SECOND CYCLE IX ELUTION COLUMN