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U^{233} REDUCTION--STUDY FLOW SHEET

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U^{233} REDUCTION--STUDY FLOW SHEET

By

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Plutonium Chemistry Laboratory
Research and Engineering Operation
Chemical Processing Department

September 15, 1964

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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U^{233} REDUCTION--STUDY FLOW SHEET

The attached flow sheet has been prepared for use by the Plutonium Chemistry Laboratory in studies related to the final steps of processing U^{233} nitrate to the metal. It is based entirely on the work of others with uranium processing on this scale.

Several assumptions have been made in setting up the flow sheet. These are:

1. Sufficient time will have elapsed (since the primary separation) for the U^{232} daughter growth to require daughter removal prior to subsequent processing.
2. Primary separation product will contain sufficient metallic impurities to require additional cleanup.
3. Processing will utilize a minimum amount of handling of dry powder.
4. One kilogram batches will be processed (easily converted to other quantities).

A. FLOW SHEET DISCUSSION

The process may be broken down into four major operations. An acid removal step is given in the Appendix, if it should be needed.

1. Daughter Removal

A cation exchange operation is used to remove the Th^{228} daughter of the U^{232} present.(1) Lag storage for about four days results in a minimum gamma radiation field because of the decay of the Th^{228} daughters. Regrowth of the chain will raise the gamma level again, starting about ten days after the ion exchange separation.

The ORNL ion exchange flow sheet(1) was selected instead of the LASL flow sheet(2) because of less complexity in processing the wastes. This flow sheet does not cover the waste and by-product routings, but they obviously must be anticipated. The potential radiation hazard of the ion exchange column after its loading with thorium should be considered if the column is not eluted. Disposal of the column rather than elution of the thorium is proposed.

2. Peroxide Precipitation

A peroxide precipitation is used to separate the uranium from the aqueous solution (and impurities). The operation may be summarized

$$UO_2(NO_3)_2 + H_2O_2 + 2NH_4OH \rightarrow UO_4 \cdot 2H_2O + NH_4NO_3.$$

In practice it involves an initial neutralization with ammonium hydroxide, followed by separate but simultaneous hydrogen peroxide and ammonium hydroxide additions to the feed.(3) The progress of the reaction is followed by a pH meter. The digestion, filtration, and washing steps are not as sensitive as the precipitation.

Peroxide precipitation offers a purification from most metallic ion impurities (but not thorium).(3) Excessive feed impurities have an adverse effect on the precipitation(4) and may have to be compensated for.(5) Details on the procedures and equipment are available.(5)(6)(7) The references quoted do not mention the possible hazards of using hydrogen peroxide, but these should be considered in planning the operation.

3. Conversion To Fluoride

The next processing steps are the interrelated ones of drying, reduction, and hydrofluorination. Temperatures and resulting reactivities are important, but not as severe as those usually considered in large-scale, natural uranium processing.

The flow sheet shown is for a one-vessel (platinum) scheme(7)(8) to reduce the handling of dry powders. Variations are possible, such as the flow sheet using quartz and nickel, with a powder transfer between drying and calcining.(7)(9)

The reactive gases used may be hazardous unless safety precautions are taken. Thus, the hydrogen is diluted to a safe composition with nitrogen. Also, the HF in the off-gases is scrubbed out prior to venting to a stack.(8)

4. Reduction To Metal

A pressure vessel-type reduction is used, with calcium metal as the reduction agent and iodine used as the booster. A magnesia liner is used, and an argon purge of the vessel prescribed.(10)

Since the parameters of pressure vessel reductions are dependent on the size of the pressure vessel and its charge, the flow sheet should be modified to insure good yield when the scale of operation is selected. Considerable information is available on the theory(10) and practice(10)(11)(12) of this operation. Control of the heating-up rate, design of equipment to withstand the temperatures and pressures, prevention of pre-ignitions, etc., all enter into the practice of this operation.

B. NUCLEAR SAFETY

Assumption of the on kilogram batch size was for convenience, and has little relation to a nuclear safety batch limit. Geometry limitations will also be required for one kilogram batches. Such limits may be more restrictive than for plutonium processing.(13)

C. ALTERNATE FLOW SHEETS

This flow sheet was selected on the basis of its well-documented reduction to routine processing of enriched uranium. It is recognized that extensive work has been done on refinements of the large-scale processing of natural and/or depleted uranium; these have not been applied to the small-scale flow sheet. Flow sheets for the direct precipitation of uranium double fluorides are available(14) if equipment or processing problems should become limiting in processing high U^{233} content material.

D. BIBLIOGRAPHY

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(4) R. F. Hibbs and A. E. Sands, "Highly Enriched Or Fully Enriched Uranium Recovery", Reactor Handbook, edited by S. M. Stoller and R. B. Richards, Interscience Publishers, New York, 1961. 2nd Edition, pp. 407-8.

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(6) Patton et al, pp. 235-8.

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(8) Patton et al, pp. 58-60.

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(10) Patton et al, pp. 42-6.

(11) Hibbs and Sands, pp. 409-412.

(12) LA-2245, p. 39.

(13) A. D. Callihan, W. J. Ozeroff, H. C. Paxton, C. L. Schuske, Nuclear Safety Guide, TID-7016, Rev. 1. Atomic Energy Commission. 1961.

(14) E. J. Wheelwright, Hanford Atomic Products Operation (Personal Communication).

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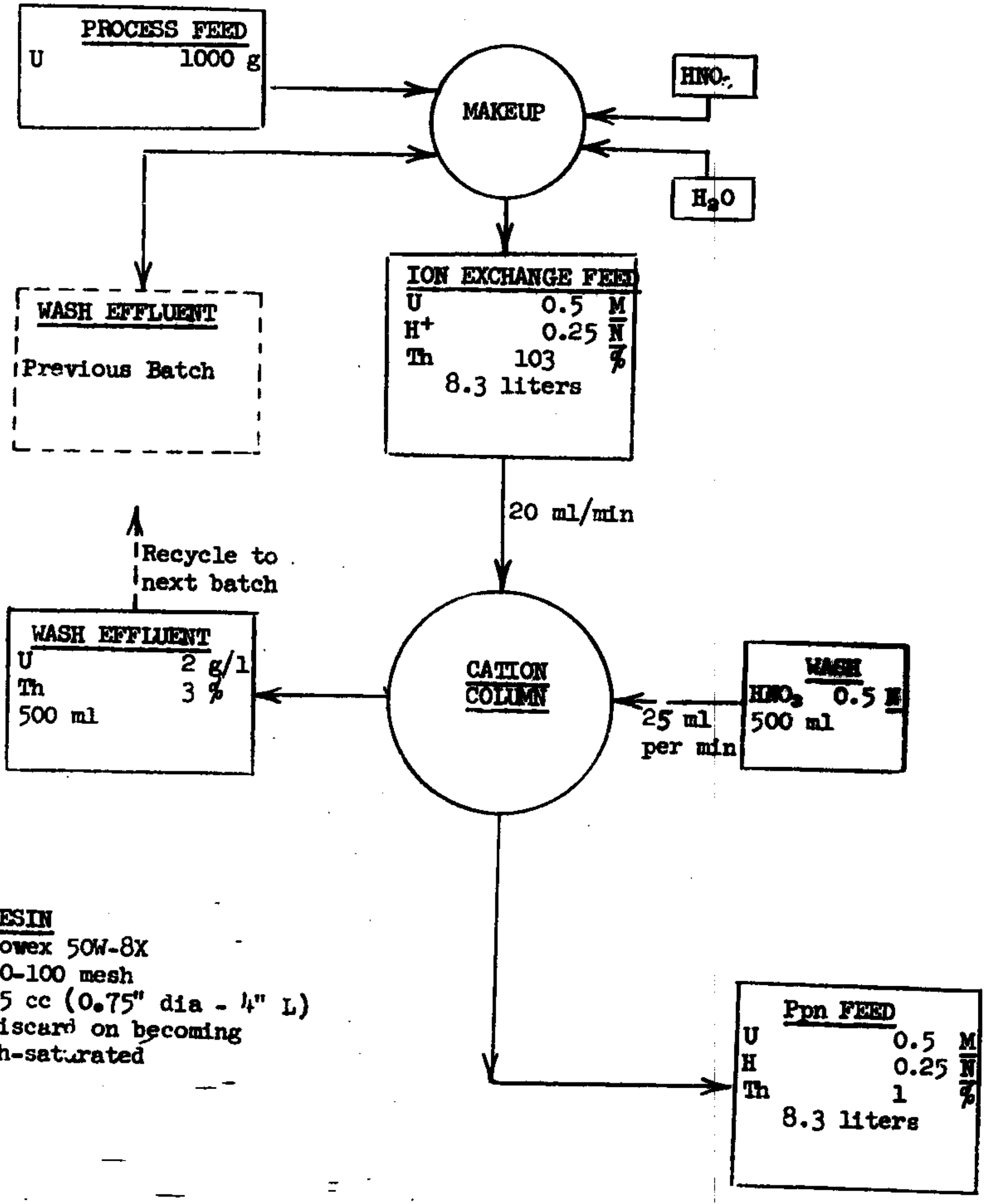
APPENDIX A

ACID REMOVAL FROM THE FEED

Since the possibility exists that the nitrate received exceeds the acidity required for ion exchange de-daughtering, a processing step for acid boil-off may be needed. This would involve concentrating the nitric acid-nitrate system to a molten salt condition, then butting back to a suitable composition with nitric acid and water. A preliminary estimate (based on data in HW-19140) would be that concentrating to a boiling point of 125 C would result in a solution of 5 M uranium, 2 M acid (with a freezing point of 95 C). This could then be adjusted to a suitable feed for the flow sheet by dilution with water.

Such a concentrator would be of value in processing the cation column wash, etc. While waste recovery is not iucluded in the scope of this flow sheet, the equipment involved in the acid removal, plus that of the filtration step, could be used for a rough waste cleanup process utilizing dissolving and ammonium diuranate precipitation.



RESIN
Dowex 50W-8X
50-100 mesh
25 cc (0.75" dia - 4" L)
Discard on becoming
Th-saturated

FIGURE 1

DAUGHTER REMOVAL

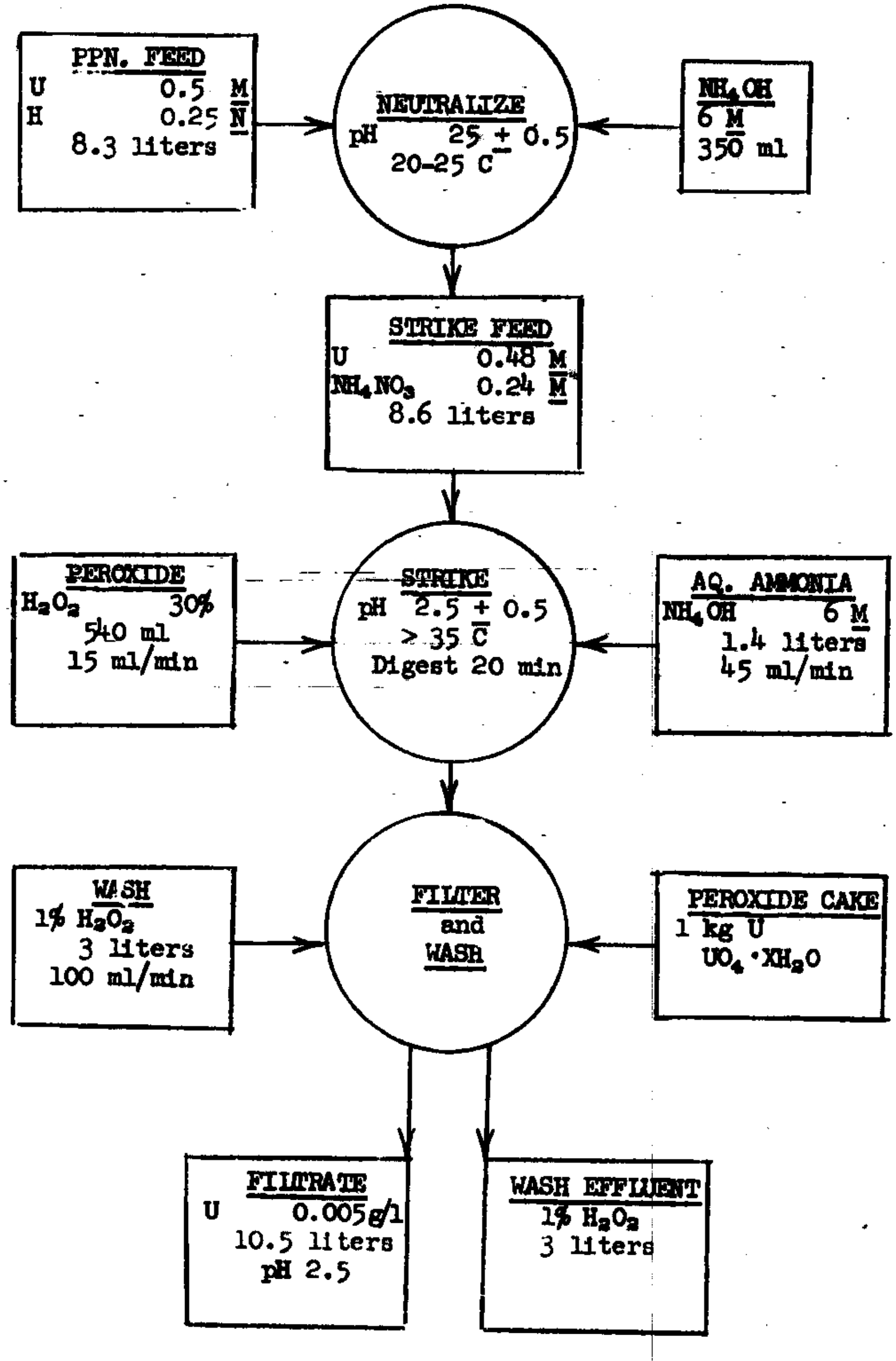


FIGURE 2
PEROXIDE PRECIPITATION

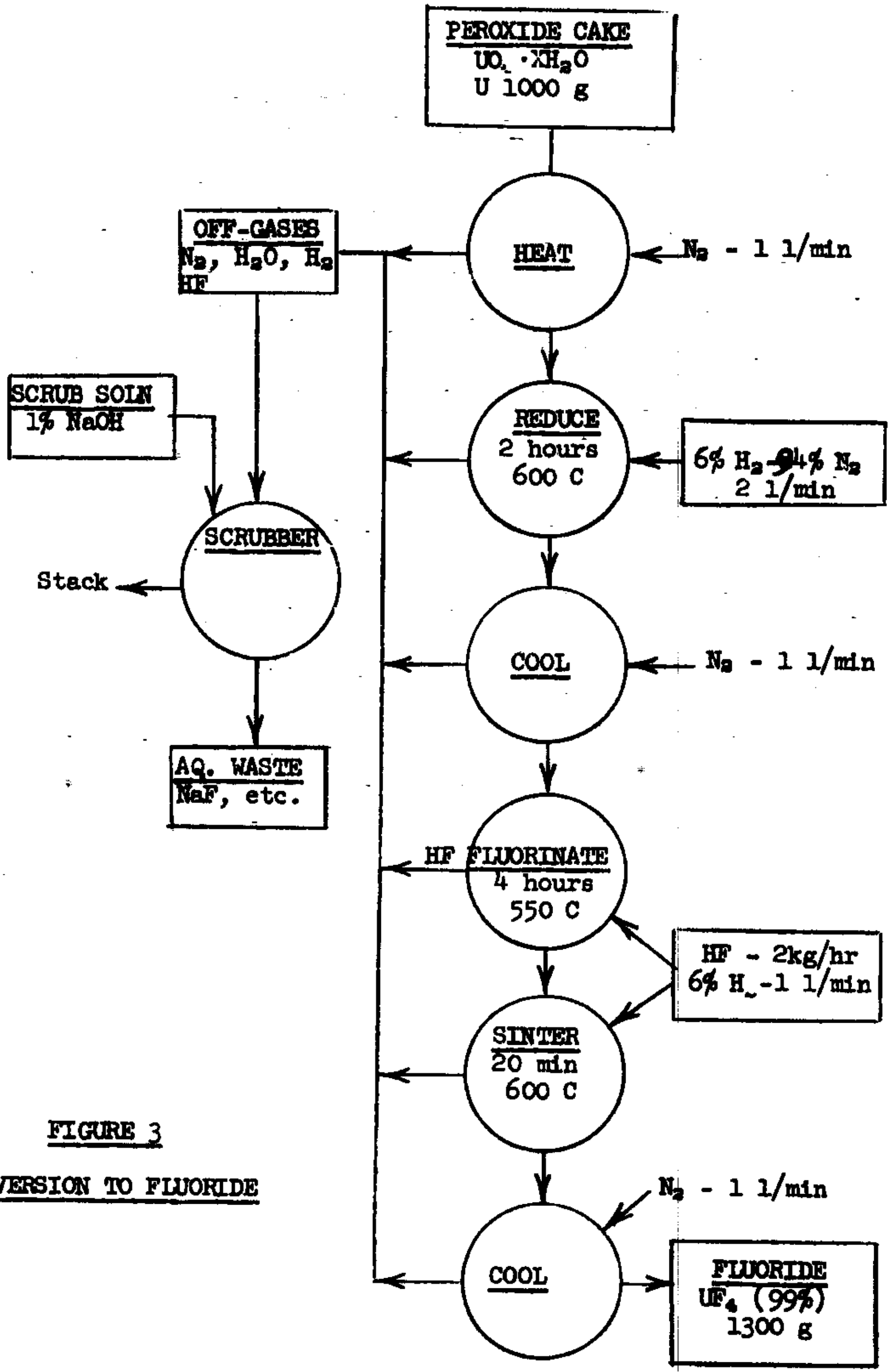


FIGURE 3

CONVERSION TO FLUORIDE

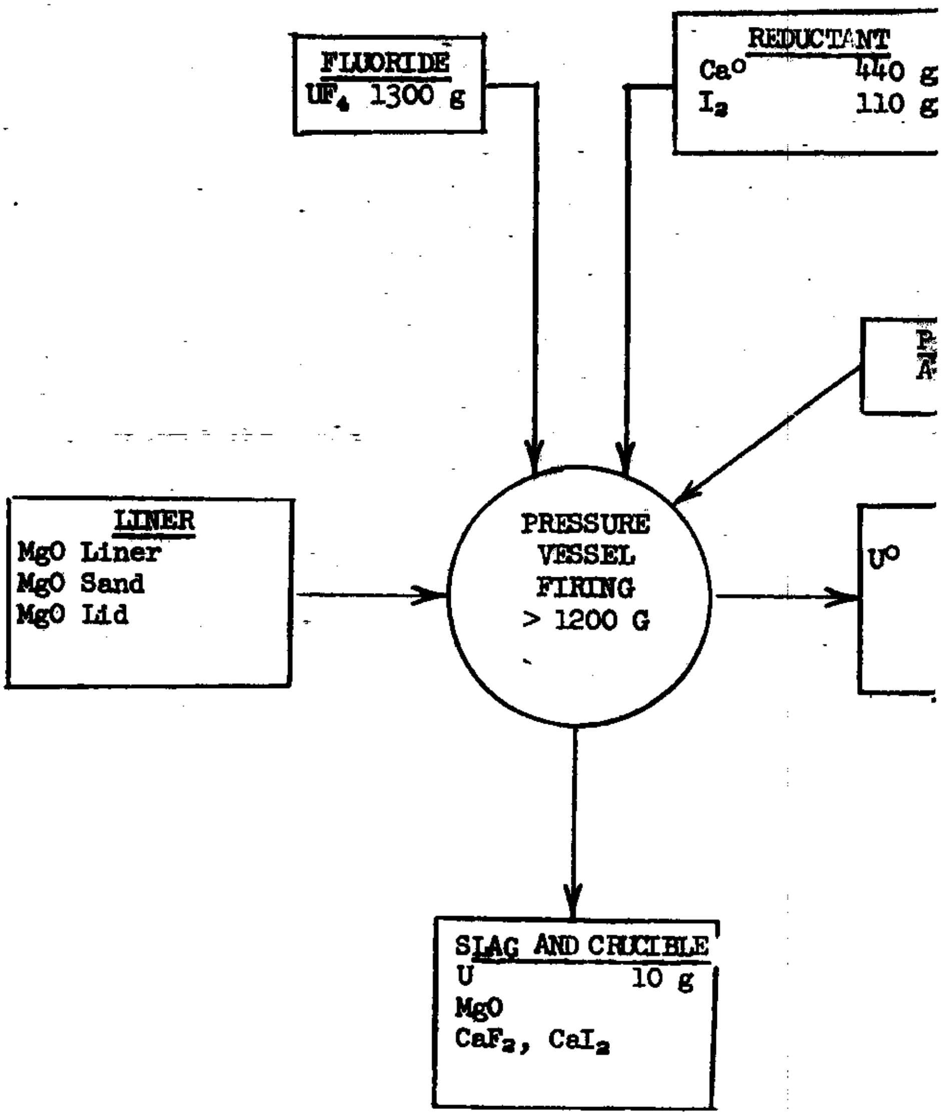


FIGURE 4

PRESSURE VESSEL REDUCTION