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DECONTAMINATION AND MELT DENSIFICATION OF FUEL HULL WASTES

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ABSTRACT

Ongoing work in the United States on treatment of cladding hull residues from nuclear fuel dissolution is described. The report proceeds to the description of the Pacific Northwest Laboratories melt densification and decontamination program. On a laboratory scale, a two-step process, initial treatment with 600°C HF-Ar mixtures followed by aqueous decontaminating, has produced effective decontamination. The Inductoslag process has been selected for densification of the predominately Zircaloy waste stream. The process provides for direct melting of the low density fuel hull residue without intermediate preparation of a consumable electrode. Current efforts are addressed to the design and fabrication of decontamination and melting equipment to be installed in a hot cell and remotely operated.

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The Nature of the Fuel Hull Residue

Most processes proposed for recovery of irradiated UO_2 from sheared fuel bundles leave behind a residue of metallic cladding and fuel hardware. Representative processes include direct nitric acid dissolution, voloxidation in which a preliminary air oxidation of UO_2 pellets to particulate U_3O_8 powder precedes acid digestion, pryochemical dissolution in nitrate salts, and dissolution in liquid N_2O_4 dissolved in polar organic solvents. The Zirflex head-end process in which the Zircaloy clad dissolution is catalyzed by fluoride ion is an exception. The Zirflex process has had limited application, thus far only to reprocessing N-Reactor fuel at the Hanford facility. The Zirflex process or some variant might be applicable to thoria or thorium metal fuel. It can be concluded, however, that in the context of head-end processes, presently proposed for commercial nuclear fuel, metallic dissolver residues will be generated.

The fuel bundle residues recovered from the head-end UO_2 removal process will include short lengths of Zircaloy cladding hulls, internal fuel rod springs, and spacer pellets. They may include as well, fuel bundle support rods, poison rods, massive end fittings, and fuel support grids depending on the extent of fuel disassembly and sorting prior to shearing. The materials are Zircaloy, stainless steel, and Inconel in the approximate weight ratios of 24/4/1 respectively. The precise amounts and ratios of these materials will depend on the reactor type, the vendor and the vintage of the fuel. Metal residues recovered from the uranium extraction head-end will constitute a highly radioactive, transuranic element (TRU) contaminated waste stream of large volume and relatively low density (~1.1 g/ml).[1] The residual activities on the processed fuel hulls are potentially leachable. A certain amount of finely divided Zircaloy metal is often associated with recovered hulls, which may be subject to segregation during transportation of loose hulls and potential ignition.

It is the purpose of this report to consider treatment options for LWR cladding hulls, to review published work currently in progress, and to summarize in somewhat greater detail work at the Pacific Northwest Laboratories with which the author is associated.

Work in Progress

Aside from the PNL program on decontamination and melt densification of cladding hulls which is the principal subject of this presentation, there are several other efforts in progress under Department of Energy (DOE) sponsorship. At the Argonne National Laboratory, V. Treverrow and M. Steindler are developing criteria to assure that fuel hulls are managed without undue risk to either operating personnel or the public. These criteria will emphasize operations at the fuel reprocessing plant in terms of the waste form and packaging. A tentative set of criteria is to be circulated for comments to members of regulatory and energy development agencies and also to potential commercial reprocessors.

Other work at ANL includes an experimental study of TRU decontamination factors which result from the volatilization of Zircaloy hulls (as $ZrCl_4$) treated with HCl or Cl_2. Of the major constituents in Zircaloy hulls, only zirconium is volatilized by HCl at 400°C leaving behind a TRU waste, much reduced in volume for packaging and shipment to a national repository. The separation is somewhat less favorable when Cl_2 is used. The resulting decontaminated $ZrCl_4$ can be converted through a pyrohydrolysis step to ZrO_2 with recovery of the HCl. Alternatively the $ZrCl_4$ might be used to form a zirconate with ion exchange properties for collection of TRU or fission product activities as proposed by H.S. Levine of the Sandia Laboratory. We understand a limited effort continues at Sandia. The process has been recently described in Ref.[2].

The Savannah River Laboratory is currently in the process of detailed study of state-of-the-art reprocessing technology. In the course of this study treatment of cladding hulls has been reviewed under the ground rules that only proven technologies are to be considered. The hull treatment called out is incorporation of the hulls in a concrete grout. M.D. Boersma, SRL, states their process calls for dry addition of the grout to a vibrated hull canister.

The shearing operation is not strictly associated with leached fuel hull handling and treatment. However, the nature of the sheared product, particularly hull lengths, residual UO_2, and fines generated are most relevant to the

treatment process. Work at ORNL is reported in Ref.[3] on shear head-end treatment. Specific comparisons are made of the fines generated from irradiated and non-irradiated fuel cladding during shearing operations. Sheared ends showed smeared metal, ductile tearing, and feather edges for both irradiated and non-irradiated clad. There was no evidence of UZr_3 formation at cladding-fuel interfaces; UZr_3 is an explosion hazard. The shear design did not pinch the cladding, assuring near quantitative acid leach of UO_2.

Although press compactions of oxide-free zirconium alloy scrap and sponge are routinely made, very little is known about the compaction properties of oxidized, irradiated hulls emerging from the chop-leach process. Using press compaction equipment at the U.S. Bureau of Mines at Albany, Oregon, PNL has arranged for the preparation of several compacts at various oxygen levels.[4] The compactions were made in a 10 cm cylinder using a 750 g charge of autoclaved, 2.5 cm lengths of Zircaloy-4 fuel clad tubing. A slow rate of compaction was used to allow monitoring of press ram pressure and displacement. The percent of volume reduction versus compaction pressure is shown in Figure 1. Over a 90% volume reduction was achieved with a compaction pressure of 15,000 psi. Some cladding sections were detached from the compact during ejection from the die. Still other sections detached during a 60 cm drop test. These observations applied irrespective of the extent of oxidation. Fines were generated during compaction, more with the more heavily oxidized cladding sections.

The PNL Decontamination and Melt Densification Program

In Table I, the objectives of the DOE sponsored PNL Fuel Hull Decontamination and Densification Program are described. These objectives, met in their entirety, describe processes by which the dissolver residues can be transformed into an inert, high density waste suitable for long-term storage, or with suitable decontamination procedures, for earth burial. As the technical problems and costs become better defined, options such as decontamination, segregation of fuel hull wastes by material, and melting techniques can be selected or rejected in arriving at a cost effective process.

Table I. PROGRAM OBJECTIVES

- Development of Total Process Leading to Minimum TRU Waste Stream
- Consolidation of Fuel Hulls by Direct Melting
- Development of Decontamination Methods for TRU Element Removal
- Demonstration of Fuel Hull Ingot as a Medium for Tritium Fixation
- Evaluation of Fuel Hull Ingot for Long Term TRU Element Retention
- Cost Comparison of Treatment Alternatives

One obvious method for reducing the volume of TRU waste is the removal of residual fuel and superficial oxide in which the bulk of the activity is absorbed. Before decontamination procedures could be seriously proposed, it was necessary to establish the distribution of TRU elements in a sample of acid leached and irradiated fuel clad. TRU distribution has now been determined for two PWR cladding samples: (a) Saxton Reactor UO_2/PuO_2, ~25,000 MWD/T six years out of the reactor, (b) a high exposure UO_2, ~60,000 MWD/T one year out of the reactor. The analysis did the following:

- Distinguished slowly leachable fraction from nonleachable,
- Determined TRU element fractions within 50-100 μ of the cladding surface,
- Determined a residual TRU content in the metal associated with U or Th impurities in the Zircaloy itself.

The result of the UO_2 element distribution analysis is shown in Figure 2. The base metal TRU is predictable from the neutron exposure and the tramp uranium content. It is noteworthy that current Zircaloy compositional specifications tolerate up to 3.5 ppm uranium. This value exceeds by more than a factor of 10 the concentration of U which will lead to greater than 10 nCi/g TRU after irradiation to normal goal exposure.

The possibility exists that if all traces of superficial contamination can be successfully removed, sufficient decontamination may be accomplished during an optimized melting step to reduce levels of residual TRU below 10 nCi/g.

The Decontamination Process

We have found conventional zirconium etching practice ineffective on specimens oxidized in high temperature water or with oxide films formed at the clad-UO_2 interface after heating and/or irradiation. New methods were required to decontamination without total dissolution of the metal substrate. The most effective procedure has been a pretreatment with 600°C HF followed by an exposure in a solution developed by Meservey:[5]

0.4M	ammonium oxalate
0.16M	ammonium citrate
0.1M	ammonium fluoride
0.3M	hydrogen peroxide

at 90°C for 2 hours.

A detailed description of the decontamination process can be found in Ref.[6]

The action of the gaseous HF is to undercut the oxide layer forming ZrF_4 with possibly some oxyfluoride. Figure 3 is a micrograph of an oxidized sample after the HF treatment showing the oxide undercut by the fluoride layer which grows preferentially at the oxide-metal interface. In Figure 4 an SEM nondispersive X-ray analysis of the specimen confirms the reaction zone below the oxide as zirconium fluoride.

The fluoride layer is quantitatively dissolved in the Meservey solution detaching the oxide in the process. The success of the process depends on the completeness with which the oxide is penetrated by the HF. In our experience, irradiated Zircaloy is more easily descaled than nonirradiated specimens. Presumably because irradiated oxides are less mechanically sound. Table II indicates the activity of a specimen decontaminated in the prescribed fashion is reduced to the level of the base metal activity.

Table II. TRU DISTRIBUTION IN IRRADIATED, ACID LEACHED ZIRCALOY FUEL CLADDING

α Distribution as Determined by Mechanical and Chemical Metal Removal

Source	Leachable Activity In Surface Oxides	Non-Leachable Activity In Surface Oxides	Residual Activity In Cladding Metal
Saxton PWR Mixed Oxide Fuel	9.94×10^{-5} Ci/dm^2	9.88×10^{-5} Ci/dm^2	2.67×10^{-7} Ci/dm^2
High Exposure PWR	8.7×10^{-4} Ci/dm^2	6.7×10^{-4} Ci/dm^2	8.2×10^{-7} Ci/dm^2

α Activity After Decontamination Process

Saxton PWR Mixed Oxide Fuel	3.0×10^{-7} Ci/dm^2
High Exposure PWR	8.2×10^{-7} Ci/dm^2

A small integrated decontamination system has been built and installed in a shielded facility (1706-KEL cave).[7] This mini-scale equipment is principally dedicated to process development in support of higher throughput hot cell experiments to be described below. Decontamination runs have been made on small charges of both irradiated and autoclaved nonirradiated fuel cladding tubing sections. Surface oxides were completely removed. The sum of oxide and metal loss was roughly 3 gms/dm^2 of exposed surface for either irradiated or nonirradiated hulls. Some fine undissolved solids are present in the Meservey wash solutions which can be dissolved in concentrated HF made slightly oxidizing with nitric acid. Reaction rates on the HF reactor have been shown to be relatively insensitive to the rate of stirring which is necessary to shift points of contact between hulls.[4]

Experiments have shown that a small flow of gas through the gas contactor must be maintained to prevent buildup of reaction product hydrogen which hydrides the hot, defilmed Zircaloy surfaces. Careful elimination of water vapor from the HF-Argon mixture in the gas contactor is essential to controlling attack on the metal substrate.[8]

The proposed decontamination scheme seems to satisfactorily meet our defined objectives:

a) About 10% of the cladding hull metal is lost in the decontamination process.

b) Satisfactory surface decontamination levels are achieved on small sample experiments.

c) The secondary waste product can be pyrolized to ZrO_2 plus contaminant oxides which adequately meet the objective of minimum TRU waste volumes.

The Densification Process*

Metals recovered from the dissolver can vary from Zircaloy alone to Zircaloy with 20% stainless steel and Inconel. If melts are to be prepared without descaling, up to 3% zirconium oxide must be accommodated. The necessity of making melts under hot cell conditions implies constraints on potential melting technqiues of which the following are typical:

(1) Direct melting from the chop-leach residues must be possible without prior compaction or double melting.

(2) Significant interaction with crucible materials must be avoided to assure corrosion resistance and mechanical integrity of the resultant ingot, also to minimize additions of contaminated crucibles to the waste stream.

A low melting Zr-S/S-Inconel alloy was anticipated from Zr-Fe, Zr-Ni binary phase diagrams. These results were confirmed in practice. The Zr-10% S/S-5% Inconel melted at about 1100°C versus >1800°C for Zircaloy-4. Induction heated graphite crucible melting of the alloys was demonstrated without excessive interaction with the graphite crucible. Melting of straight Zircaloy produces high graphite crucible-melt interaction at temperatures of 1800-1900°C; melt is saturated with carbon.

A relatively obscure melting technique, the so-called "Inductoslag" process was selected for study, because of its general conformity with hull melting criteria, and because it has been successfully employed in remelt of titanium metal scrap.[9,10] The process employs a split, water cooled copper crucible, the molten metal pool is retained in the crucible by a CaF_2 flux.[11] The contents of the crucible couples to an induction coil. The chop-leach residue along with 1-2% flux is fed from a hopper directly into the crucible. The ingot is continuously withdrawn from the bottom of the crucible. The general layout of the furnace, the feed system and the ingot are shown in Figure 5.

To this point our Inductoslag melts have been made in collaboration with P. G. Clites using an experimental furnace fabricated and used at the U.S. Bureau of Mines' laboratory at Albany, Oregon. We have in the course of these joint studies prepared melts covering most of the range in composition we might expect to encounter in practice (except for radioactivity). Our experience with Inductoslag melting can be summarized in the following.

Melting of Descaled Zircaloy-4 In the course of this demonstration 40 kg of freshly etched Zircaloy-4 tubing were melted in 2-1/2 hours to form a single ingot 10 cm in diameter by 75 cm long. The composition of the ingot after melting was still within specifications for reactor fuel cladding. Uniformity of composition and mechanical properties was excellent. As a proof of fabricability the ingot was refabricated into fuel clad tubing. Sections of the refabricated tubing were autoclaved under standard ASTM conditions.[12] Weight gains were within specifications and a lustrous black surface was developed.

* The melt densification is described in greater detail in Refs.[6,9,10].

Melting of Zr-4, 10 S/S, 5% Inconel The Inductoslag melting of the alloy was somewhat disappointing. The problem is that the process operates at the eutectic melting point with the result that dissolution of the higher melting feed materials is slow. Melting was roughly one-third the rate for Zircaloy-4. Sections of the ingot showed substantial unmelted feed material fixed in a matrix of the eutectic mixture of Zr, Fe, Ni, Cr. Structurally the ingot was quite satisfactory, Figure 6.

Melting of Oxidized Zr-4 Heavily oxidized sections of Zr-4 tubing, up to 3% ZrO_2, were successfully melted into a sound uniform ingot. The as-cast material is very hard and probably unfabricable. However, the experiment is very important in demonstrating that fuel hull densification by melting can be achieved without prior descaling or decontamination. While these properties have not been tested, we are confident satisfactory resistance to corrosion or leaching will be demonstrated.

Furnace Construction An Inductoslag furnace has been designed and built for remote, melt densification of a feed stream of radioactive fuel hulls, Figure 7. The major modifications of the basic Clites and Beall design required for adaptation to hot cell operation include: full length, wide opening door for easy access to furnace internals, a gear driven ingot withdrawal mechanism that provides for maximum ingot length for the furnace height, and a means of independent addition of slag to the melt.

Recent work has included an investigation of methods for remote attachment and detachment of the ingot from the withdrawal mechanism. We are exploring methods for increasing melt rates of mixed Zircaloy-4% Inconel feed stock. Melt rates increased from 4.7 to 25 kg/hr when pure CaF_2 was substituted for the CaF_2-MgF_2 eutectic.

Tritium Absorption and Storage in Zirconium Alloy Ingots The melting of fuel hardware into ingots will release absorbed hydrogen and tritium. The approximately 100 ppm of hydrogen evolved can be reabsorbed into another ingot. The absorption rate and equilibrium pressure of hydrogen over Zircaloy and Zr-(Fe, Ni, Cr) alloy ingots were studied at representative gas pressures and concentration. Both the alloy and Zircaloy-4 absorb hydrogen rapidly enough to be useful for storage of the hydrogen removed from the densified hulls.[6]

HOT CELL DEMONSTRATION OF THE DECONTAMINATION AND MELT DENSIFICATION PROCESS

The Commercial Waste Fixation Program at PNL, when operational, will generate about 250 kg of fuel hull wastes per month as dissolver residues. These cladding hulls will come from PWR fuel irradiated to goal exposure and will be fully prototypic of a reprocessing plant fuel hull waste stream. A supply of hulls should be available by the end of FY 1978. It is our plan to have remotely operable, melt densification and decontamination facilities ready for installation in a hot cell shortly after the cladding hull wastes become available.

An Inductoslag melt furnace has been designed and fabricated for hot cell use. It is currently being installed in a mockup area which duplicates the floor geometry and services available in the 324 Building D Hot Cell. The semi-continuous decontamination process equipment is currently in fabrication with delivery of principal components expected in early December, Figures 8, 9. The completed decontamination facility should be installed in the mockup area by the end of January 1978, Figure 10.

Checkout of the equipment will proceed in two stages. Contact operation and contact equipment adjustment, where required, will represent the first stage in the facility qualification. In the second stage the facilities will be modified for manipulator operation and maintenance. One or more satisfactory operational cycles will be completed before the equipment is disassembled and reinstalled in the 324 Building D Hot Cell. The hot cell is expected to be ready for operation of the melt densification and decontamination process with irradiated fuel hull feed stock by the fall of 1978. We presently propose to operate this facility throughout the Commercial Waste Fixation Demonstration (about one year). Several important, heretofore undetermined characterisitcs of the Inductoslag waste metal ingot will be established. The extent to which

the as-cast ingot is subjected to mechanical spallation of TRU contaminated slag or oxide is unknown. The extent to which the TRU content of the as-cast ingot is subject to leaching is unknown. With those ingots melted from decontaminated fuel hulls, it will be possible to determine if TRU decontamination factors are obtained in the melt through a partitioning process with the flux, through zone refinement or through volatilization of the impurities as fluorides.

The principal purpose of the hot cell demonstration is a proof test of the melt densification process. If the remotely operable melt and decontamination processes function reliably over the course of a year with a throughput of a metric ton or more of an irradiated fuel hull material, we will have achieved the program goals.

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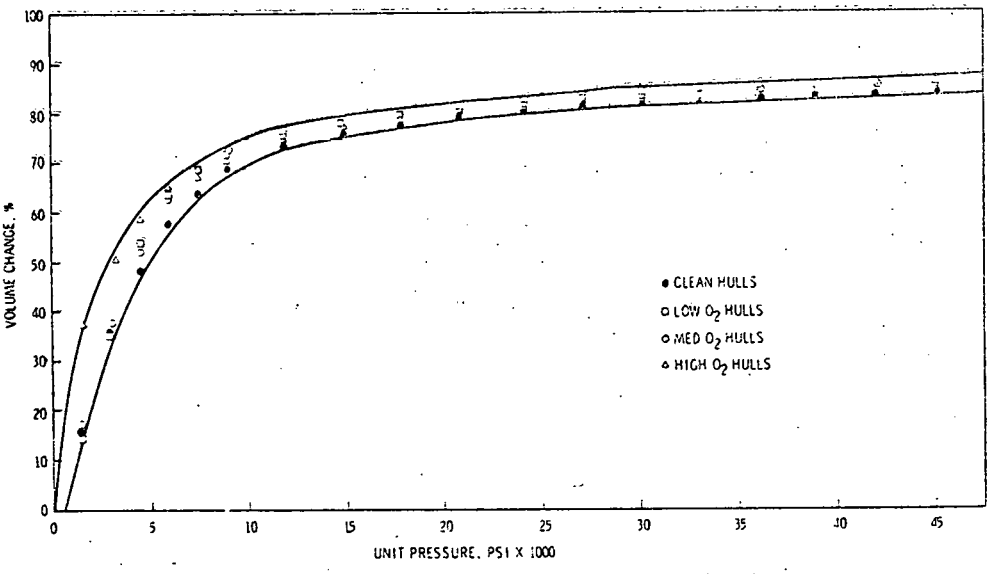


FIG 1. VOLUME REDUCTION ACHIEVED BY PRESS COMPACTION OF CLEAN AND OXIDIZED UNIRRADIATED PWR CLADDING

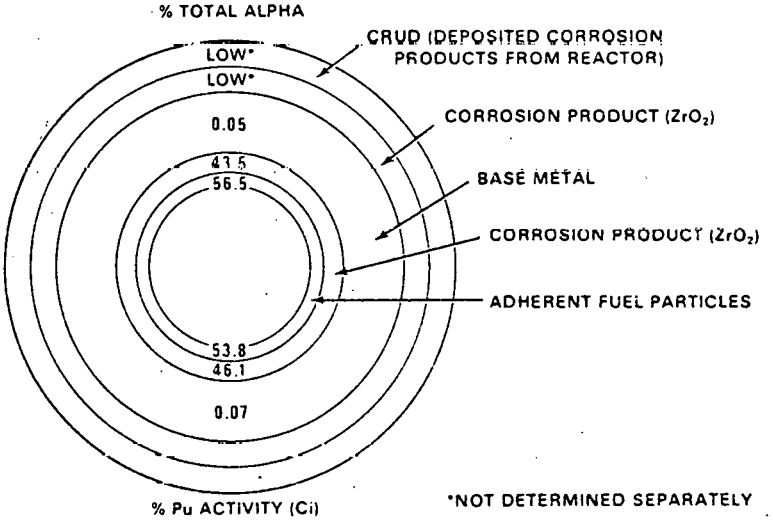
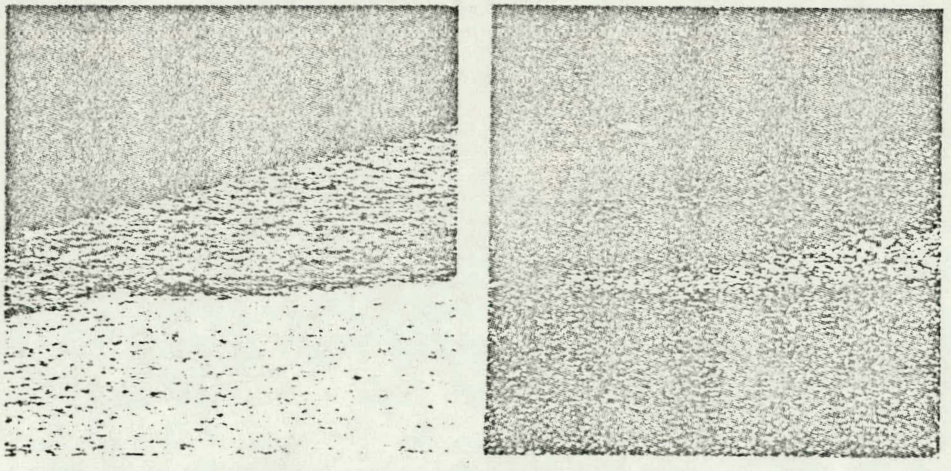


FIG 2. DISTRIBUTION OF TOTAL ALPHA AND PLUTONIUM ACTIVITY IN A PIECE OF PWR UO_2 FUEL CLADDING

500X SEM

FIG 3. SEM OF OXIDIZED ZR-4 AFTER TREATMENT WITH HF AT 600°C



500X Zr 500X F

FIG 4. NONDISPERSIVE X-RAY ANALYSIS OF THE SPECIMEN FROM FIG 3 FOR Zr AND F CONTENT

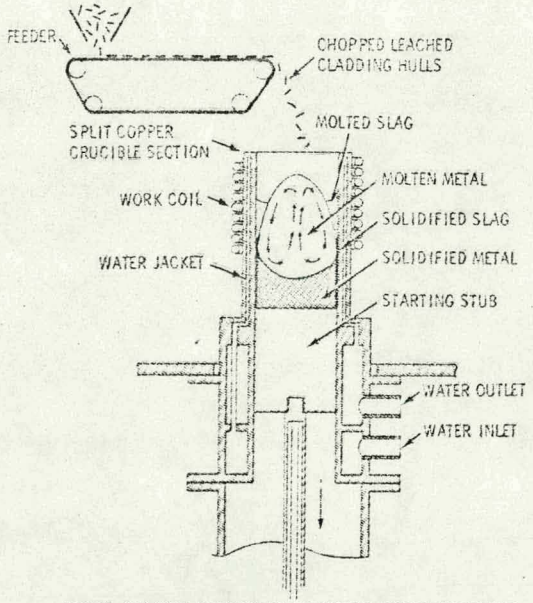


FIG 5. INDUCTOSLAG MELTING PROCESS

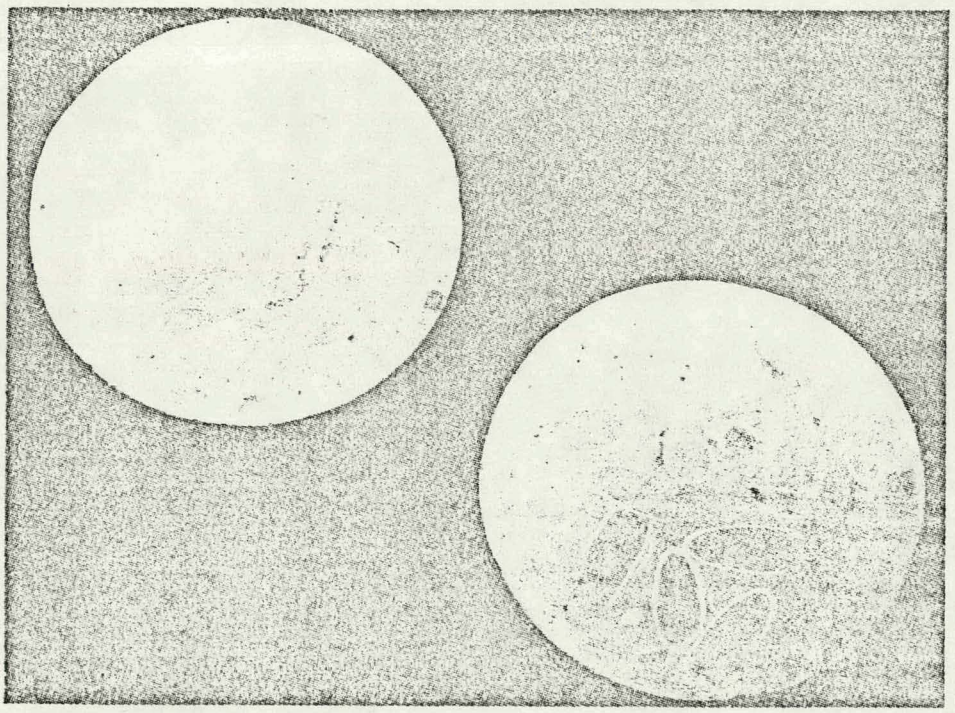


FIG 6. SECTION OF Zr-4 - 10 w/o 304 - 5 w/o INCONEL 718 INDUCTOSLAG MELTED INGOT

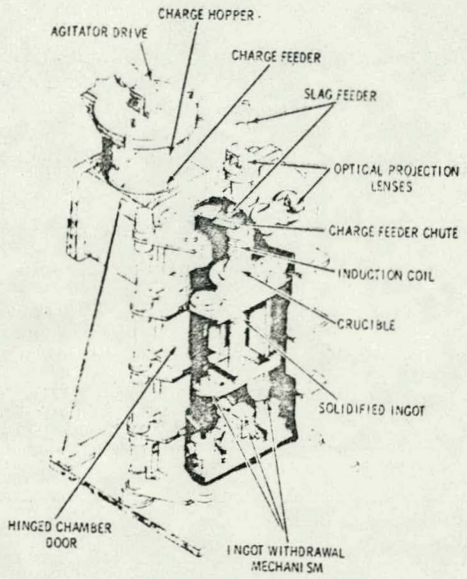


FIG 7. DRAWING OF INDUCTOSLAG MELTING FURNACE DESIGNED AND FABRICATED FOR IN-CELL MELTING OF ACID LEACHED IRRADIATED FUEL HULLS

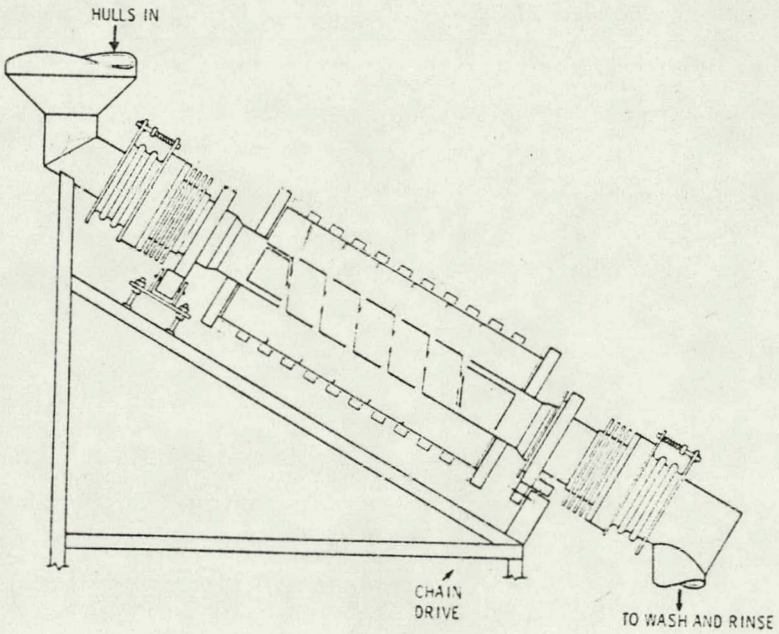


FIG 8. CONCEPTUAL DESIGN OF HF REACTOR

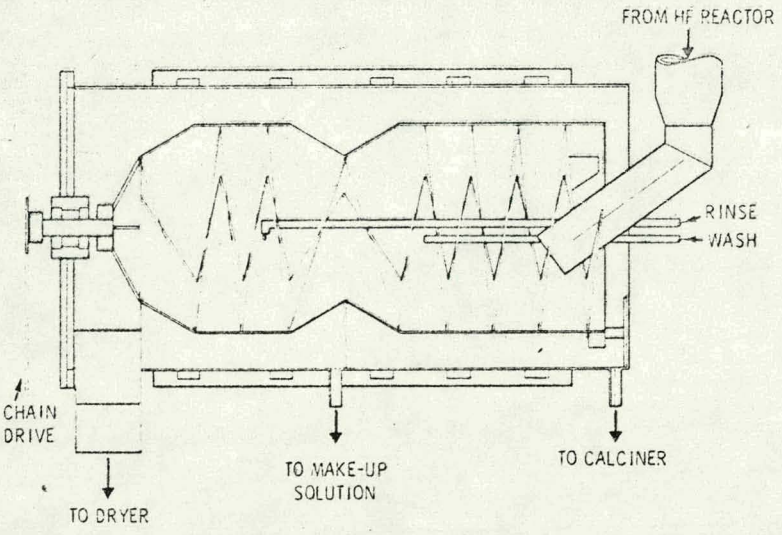


FIG 9. CONCEPTUAL DESIGN OF AQUEOUS WASHER

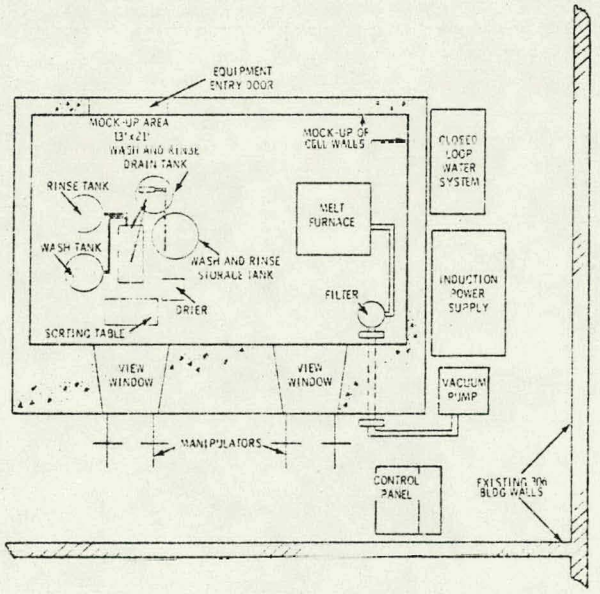


FIG 10. PROPOSED LAYOUT OF HOT-CELL FUEL HULL MELTING AND DECONTAMINATION EQUIPMENT