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PREPARATION OF STAINLESS STEEL, ZIRCONIUM, AND GRAPHITE
CLAD AND BASE REACTOR FUELS FOR SOLVENT EXTRACTION

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ABSTRACT

Chemical, electrolytic, and mechanical head-end techniques for processing stainless steel, zirconium and graphite reactor fuel elements are summarized. The Sulfex (sulfuric acid) and Darex (dilute aqua regia) processes for stainless steel-clad ceramic oxide fuels have received extensive laboratory and cold engineering development and shortly will be tested on a plant scale. Modified Darex processes are being developed for Hastelloy-clad UO_2 -BeO fuels. Both hydrofluoric acid and Zirflex (NH_4F) processes for zirconium fuels have been improved. Dissolution of zirconium alloy fuels in dilute HF allows processing of fuels containing up to 2% uranium. Alloy fuels containing up to 10% uranium can be processed by the Modified Zirflex method. Alternative methods, Grind-Leach, 90% HNO_3 , and combustion-dissolution, for processing graphite-base fuel elements are being studied on a laboratory scale. Supporting studies of the hydrolysis of pure uranium and thorium carbides have also been initiated. Mechanical decladding and chop-leach techniques for several fuel types have been demonstrated.

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PREPARATION OF STAINLESS STEEL, ZIRCONIUM, AND GRAPHITE
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INTRODUCTION

Methods developed for preparing power reactor fuels for solvent extraction fall into three categories: chemical decladding, total dissolution, and mechanical processing. Although several of the techniques have received extensive development in engineering-scale equipment with full-size unirradiated fuels and in hot cells with fully irradiated fuel samples, no processing plant tests on actual irradiated fuels have been run with the exception of total dissolution processes for APPR, STR type, and OMRE fuels at the ICPP (1). A complete review of processing technology was presented in 1959 (1).

AQUEOUS DISSOLUTION OF STAINLESS STEEL-CLAD OR -BASE FUELS

Two processes developed for the dissolution of stainless steel-clad oxide fuels are Darex and Sulfex (1-5). The Sulfex process, dissolution of the stainless steel in boiling 4-6 M H_2SO_4 , is a decladding method for both UO_2 and ThO_2-UO_2 fuels. The oxide cores must be dissolved separately in nitric acid or fluoride-catalyzed nitric acid following the decladding. Darex (dilute aqua regia) reagents may be used for decladding ThO_2-UO_2 fuels and for total dissolution of stainless steel- UO_2 cermet and clad UO_2 , ThO_2-UO_2 , and UO_2-BeO fuels. Nionel and titanium were selected as

the construction metals for the Sulfex and Darex processes, respectively (4). Both processes have received extensive cold engineering study (6-10). The Sulfex process is being considered for use at Savannah River Laboratory (SRL) in the AEC interim processing program while the Darex process will be pilot planted at the Idaho Chemical Processing Plant (ICPP).

Ceramic Oxide Fuels. Both a batch and a continuous Darex process (10) will be tested in the ICPP pilot plant on all types of SS-UO₂ fuel. A batch flowsheet was tested successfully on irradiated Nuclear Ship Savannah (1) and APPR (11) fuel in hot cell runs. In a proposed continuous flowsheet, APPR fuel is dissolved in boiling 5 M HNO₃-2 M HCl followed by continuous chloride stripping with concentrated nitric acid vapor (Fig. 1). Nitric acid recycled from the feed adjustment step is adjusted to 15.6 M with 22.5 M (95%) HNO₃ before it is injected into the stripping column. The use of 95% HNO₃ instead of less concentrated acid allows recovery of most of the chloride in the form of a 4 M HNO₃-2 M HCl recycle acid. Silica present in the fuel can cause plugging of the chloride strip column. Since mechanical removal of silica is undesirable, fluorides have been added to change the character of the silica (12) or to prevent precipitation of silica (13). In current tests with APPR fuel containing a high, ~2.0 wt %, concentration of silicon, the presence of 0.01-0.1 M HBF₄ in the dissolvent did not prevent precipitation but produced a dense easily handled silica (14). Gaseous NO₂ can be used for stripping chlorides instead of nitric acid (5).

Stainless steel-clad UO₂ fuels are readily dissolved in boiling 5 M HNO₃-2 M HCl using a flowsheet similar to that given for APPR fuel. With fuels containing ThO₂-UO₂ cores, the cladding is first dissolved in 5 M HNO₃-2 M HCl and the chloride

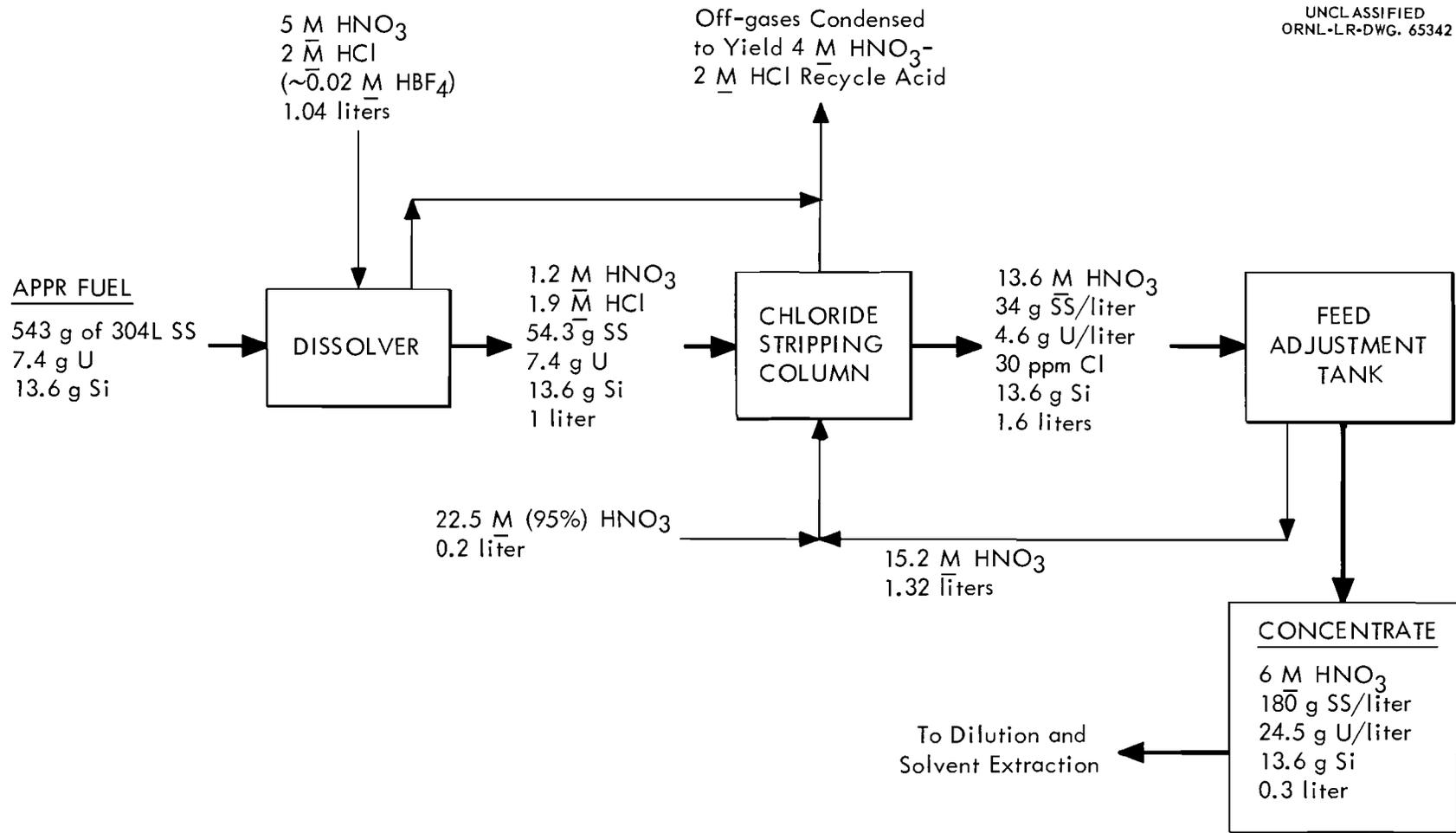


Fig. 1. Darex flowsheet for continuous dissolution and chloride stripping of APPR fuel.

removed from the resulting solution. The acidity of this solution is then adjusted to 11-13 M and sufficient HF or NaF is added to achieve the necessary concentration (about 0.04 M) for dissolution of the core (15).

Darex decladding of stainless steel-clad 95% ThO₂-5% UO₂ (91-95% of theoretical density) fuel specimens was studied as a function of fuel burnup. Uranium decladding losses increased from about 0.2 to 5% as the burnup increased from 0 to about 20,000 Mwd/ton of core (Table 1) (16, 17). Thorium losses were always less than 0.4%. The uranium losses were excessively high for immediate disposal of the decladding solution. Uranium can easily be recovered from these solutions with the acid Thorex extraction process (18). Fragmentation of the fuel at higher burnups contributed to the higher losses; however, the losses were higher than expected on the basis of surface area. Losses from the irradiated fragments (8-20 mesh) were 3-5% whereas losses from -100 mesh unirradiated material of about the same density were only about 0.5%.

Some gas-cooled reactors will contain fuel elements comprised of 70% UO₂-30% BeO pellets clad in Hastelloy-X (46% Ni, 22.5% Cr, 17.2% Fe, and 9.3% Mo). The Hastelloy-X cladding can be dissolved in modified Darex reagents containing 1-5 M HNO₃ and 4 or 5 M HCl (19). Initial rates of dissolution are in the range of 6-28 mg min⁻¹ cm⁻². With simulated fuel samples, the 30-mil claddings were penetrated in about 3 hr in boiling 2 M HNO₃-4 M HCl and about 99.7% of the uranium and 25% of the BeO dissolved in an additional 7 hr of leaching. The final solutions contained 20 g of uranium and 50 g of Hastelloy-X per liter. Hastelloy-clad UO₂-BeO fuels could also be processed by chopping into short sections and leaching with boiling 8-13 M HNO₃. Uranium dissolves quantitatively in less than 10 hr along with 50%

Table 1. Uranium and Thorium Losses to Decladding Solutions for Drex Processing of Irradiated Consolidated Edison ThO₂-UO₂ Fuel Specimens (4,5,16,17)

Specimens declad with boiling 5 M HNO₃-2 M HCl

Final stainless steel concentration: 50 g/liter

Run No. ^a	Pellet Composition			Burnup, Mwd/ton of core	Decladding Time, hr	Losses, %	
	UO ₂ , %	O/U Ratio ^b	Density, g/cc			U	Th
1	9.1	2.0	9.5	0	16	0.17	0.02
2	9.1	2.0	9.5	875	8	0.90	0.40
3	9.1	2.0	9.5	900	8	1.4	0.40
4	9.1	2.0	9.5	970	8	0.54	0.23
5	6.5	2.0	9.1	11,000	3	2.0	0.16
6	4.2	2.0	9.5	14,000	3	3.3	0.20
7	4.2	2.0	9.5	20,000	3	4.7	---
8	4.2	2.0	9.5	20,000	3	4.6	0.12
9	4.2	2.0	9.5	21,800	3	3.2	0.09

^aSintered ThO₂-UO₂ pellets (0.26 in. dia, 0.5 in. high) encased in 20-mil type 304 stainless steel.

^bThe O/U ratio indicates the uranium valence state assuming the thorium to be present as ThO₂.

of the BeO; complete dissolution of BeO requires 30 hr. The UO₂-BeO core can be completely dissolved, however, in less than 15 hr in boiling 8 M HNO₃-0.5 M HF.

The Sulfex process cannot be used for the decladding of fuels clad with Hastelloy-X.

Boiling 4-6 M H₂SO₄ attacks Hastelloy-X at a rate of only about 0.1 mg min⁻¹ cm⁻².

The Sulfex process is applicable to the decladding of stainless steel-clad fuels containing either UO₂ or UO₂-ThO₂ cores. Uranium and plutonium losses on decladding of UO₂ fuel specimens irradiated up to 1440 Mwd/ton of core were less than 0.1% (Table 2) (3), while losses from 95% ThO₂-5% UO₂ specimens irradiated up to 19,000 Mwd/ton were less than 0.4% (Table 3) (4,5,16,17). The slight increase in loss with burnup is attributed to fragmentation of the core.

Table 2. Uranium and Plutonium Losses During Decladding of Irradiated Stainless Steel-Clad UO₂ Yankee Atomic Fuel Pins (3)
 Decladding solution: boiling 6 M H₂SO₄
 Decladding time: 2 hr

Burnup Mwd/ton of U	Losses, %		Pellet Condition
	Uranium	Plutonium	
0	0.005	----	Intact
450	0.003	0.040	Intact
650	0.003	0.009	Intact
800	0.005	0.02	Fragmented
1000	0.03	0.03	Fragmented
1440	0.045	0.052	Fragmented

Uranium-Molybdenum Fuel. Stainless steel-clad U-Mo alloy fuels containing a sodium or NaK bond will probably require mechanical removal of both the cladding and bond because of the hazards involved in the chemical dissolution of the bonding agent (20). The U-Mo alloy core can then be dissolved in nitric acid or nitric acid-

Table 3. Uranium and Thorium Losses to Decladding Solutions for Sulfex Processing of Irradiated Consolidated Edison ThO₂-UO₂ Fuel Specimens (4,5,16,17)

Specimens declad with 200% excess of boiling 4-6 M H₂SO₄

Run No. ^a	Pellet Composition			Burnup Mwd/ton of Core	Decladding Time, hr	Losses, %	
	UO ₂ , %	O/U Ratio ^b	Density, g/cc			U	Th
1	9.1	2.0	9.5	0	16	0.008	0.01
2	9.1	2.0	9.5	620	8	0.07	0.04
3	9.1	2.0	9.5	740	5	0.26	0.18
4	6.5	2.0	9.1	6,000	3	0.03	0.03
5	6.5	2.0	9.1	12,000	3	0.30	0.29
6	4.2	2.0	9.5	14,500	3	0.16	0.03
7	6.5	2.0	9.1	16,600	3	0.16	0.04
8	4.2	2.0	9.5	19,000	3	0.09	0.02

^aSintered ThO₂-UO₂ pellets (0.26 in. dia, 0.5 in. high) encased in 20-mil type 304 stainless steel tubing.

^bThe O/U ratio indicates the uranium valence state, assuming that the thorium is present as ThO₂.

ferric nitrate solution in preparation for solvent extraction (21-23). Iron complexes molybdenum and allows attainment of higher uranium concentrations, other conditions being the same. Alloys containing 3% molybdenum can be dissolved in 6 M HNO₃ or 8 M HNO₃--0.5 M Fe (NO₃)₃ to yield stable solutions that are 3-4 M in nitric and contain 0.6 and 1.0 M uranium, respectively. Phosphate ion can also be used to complex molybdenum; however, its use is not practical since it must be complexed with

iron during solvent extraction. Alloys containing 10% molybdenum can be dissolved in boiling 11 M HNO_3 , allowing molybdic oxide to precipitate. The molybdic oxide, which carries 5-10% of the uranium, is removed by centrifugation, and the acidity of the supernatant solution adjusted prior to solvent extraction. The practicability of direct dissolution of 10% Mo alloy requires engineering demonstration because of the voluminous precipitate formed. The uranium carried by the oxide is recovered after dissolution of the MoO_3 in 5 N NaOH .

Uranium Carbide Fuel. Uranium monocarbide is the core material in another class of sodium- or NaK-bonded stainless steel-clad fuel elements. A potential processing scheme is mechanical removal of the cladding and bonding agent in an inert atmosphere followed by hydrolysis (with either liquid water or steam) of the carbide core. The hydrous oxide produced by the hydrolysis would be dissolved in nitric acid in preparation for solvent extraction. Pure uranium monocarbide hydrolyzed at temperatures of 25-100°C yields 93 ml (STP) of gas per gram of sample consisting of 86 vol % methane, 11 vol % hydrogen, 1.8 % ethane, and lesser quantities of C_3 - to C_7 -hydrocarbons (24). All the carbon present in the carbide appears in the gaseous products. Preliminary experiments indicate that the hydrolysis of ThC is similar to that of UC. When mixtures of UC, U_2C_3 , and UC_2 were hydrolyzed, the volume of gas evolved per gram decreased to about 32 ml/g as the C/U atom ratio increased to 1.6, and the amount of carbon appearing in the gaseous products decreased to about 50%. The nonvolatile carbon remained partly as an insoluble wax and partly as unidentified water-soluble species. Direct dissolution of UC cores in nitric acid does not appear attractive in that the carbon remaining in solution, about 50%, primarily as organic acids, may constitute a hazard and complicate solvent extraction and waste disposal.

AQUEOUS DISSOLUTION OF ZIRCONIUM-CLAD OR -BASE FUELS

Ceramic Oxide Fuels. Zirconium- or Zircaloy-clad uranium oxide fuels may be declad with boiling 6 M NH_4F -1 M NH_4NO_3 (Zirflex process) and the oxide core dissolved in nitric acid (25-27). The clad is dissolved at an average rate of about $10 \text{ mg min}^{-1} \text{ cm}^{-2}$ as long as the fluoride/zirconium mole ratio is greater than 7. The stability of the decladding solution is also dependent on the F/Zr ratio, with the zirconium solubility at 25°C decreasing from about 1 to 0.1 M as the F/Zr ratio increases from 6 to about 25 (25,27). With ammonium nitrate present, the dissolver off-gas is essentially pure ammonia. If the ammonia is not completely removed from the system, a sludge of hydrous zirconium oxide is formed. In 1- and 6-in.-dia dissolver tests at F/Zr charge ratios of 6.5, relatively solids-free solutions containing 0.7-0.8 M Zr were produced with both 4.5 and 6 M NH_4F containing 0.5 M NH_4NO_3 by either complete withdrawal or rectification and reflux of the overhead condensate (5). With specimens irradiated up to 15,750 Mwd/ton, maximum uranium and plutonium losses to the decladding solutions were about 0.1 and 0.08%, respectively (4,28) (Table 4). The irradiated pellets were fractured but the total amount or rate of irradiation did not affect the degree of fracturing significantly. However, the fragmentation was less than with $\text{ThO}_2\text{-UO}_2$ fuel since less than 0.3% of the UO_2 was finer than 10 mesh.

Decladding of zirconium-clad UO_2 fuel in nitric acid-hydrofluoric acid solutions was also studied (29). However, attack of the UO_2 core by the terminal solution (0.25 M HNO_3 -2 M HF -0.44 M Zr) was relatively high, about 0.1% per hour.

The Zirflex process may also be applicable to zirconium-clad $\text{ThO}_2\text{-UO}_2$ fuels. Uranium losses were 0.2 and 0.4% for decladding periods of 3 and 5 hr, respectively

(15) with unirradiated ThO₂ fuel specimens (8.3 g/cc) containing 4.2% UO_{2.7}. Since this is only 83% of theoretical density, losses should be lower with high density pellets containing stoichiometric UO₂.

Table 4. Uranium and Plutonium Losses on Zirflex Decladding of Zircaloy-2-Clad PWR Fuel Pins (4,28)

Each specimen declad with boiling 6 M NH₄F-1 M NH₄NO₃

Time: 1-3 hr

UO₂ density: 96% of theoretical

Run No.	Fuel Burnup, Mwd/ton	Decladding Loss, %		Condition of Fuel Pellets
		Uranium	Plutonium	
1	0	0.01	---	Intact
2	0	0.08	---	Intact
3	159	0.001	0.006	Fractured ^a
4	217	0.015	0.03	Fractured ^a
5	580	0.03	0.05	---
6	1,270	0.11	0.07	---
7	1,750	0.04	0.08	---
8	15,750	0.04	0.007	Fractured ^b
9	15,750	0.04	0.03	Fractured ^b

^aLess than 0.3% finer than 10 mesh; irradiation rate ~5.0 Mw/ton U

^bSpecial UO₂, less than 0.1% finer than 10 mesh; irradiation rate ~45 Mw/ton U

Zirconium Alloy Fuels. Zirconium-uranium alloy or hydride fuels can be dissolved in either hydrofluoric acid (30) or ammonium fluoride-ammonium nitrate-hydrogen peroxide (Modified Zirflex process)(31). Hydrofluoric acid is used at present with the dissolution being conducted in Monel vessels. After dissolution nitric acid and aluminum nitrate are added to the solution to obtain conditions suitable for recovery of the uranium by solvent extraction. Generally, dissolution is achieved in boiling 10 M HF but it can be accomplished with 4.8 M HF. Use of the latter reagent allows dissolution of U-Zr alloys containing up to 2 wt % uranium without exceeding the UF_4 solubility limit (32). Zircaloy-2 and zirconium-uranium alloys can also be dissolved at average rates of ~5 mils/hr in 1 M HNO_3 to which HF was added continuously to maintain the free fluoride at <0.1 M (33c,d). Short-term corrosion rates of 309Cb stainless steel were satisfactorily low.

The Modified Zirflex process (31) is an improvement over the HF system in that only stainless steel vessels are required and no hydrogen is evolved during dissolution. Either batch or continuous dissolution is satisfactory. The hydrogen peroxide in the dissolvent oxidizes tetravalent uranium to the more soluble hexavalent state thereby preventing precipitation of UF_4 even when alloys containing 10% uranium are dissolved. Uranium-zirconium alloys can also be dissolved in $NH_4F-H_2O_2$ solutions containing no ammonium nitrate (34).

Zirconium-clad U-10% Mo fuel can be completely dissolved by dissolution of the zirconium in 0.075 M HF followed by addition of 3 M HNO_3 --0.075 M $Al(NO_3)_3$ to dissolve the core (33). A dilute system is maintained to prevent precipitation of molybdic oxide. Stainless steel (309Cb) appears to be a satisfactory material of construction.

Limited tests show that zirconium-uranium alloy fuels can be dissolved in titanium equipment using strong nitric acid, chromate ion, and fluoboric acid, singly or in combination, to inhibit corrosion of the vessel (35). The most promising solvent investigated was refluxing 3 M HNO_3 -0.4 M HBF_4 -0.6 M Cr(III) -0.4 M Cr(VI) -0.46 M Zr . Zircaloy-2 dissolution rates were $10 \text{ mg min}^{-1} \text{ cm}^{-2}$. A stable product containing 0.36 M Zr was obtained after addition of aluminum nitrate to complex fluoride. In 24-hr tests titanium corrosion specimens formed protective films and showed small weight gains.

GRAPHITE-BASE FUELS

Processing methods being evaluated for the recovery of uranium and thorium from graphite-base fuels are the Grind-Leach (36,38), 90% HNO_3 (37,38), and combustion-dissolution (38) processes. Graphite fuel elements can be placed in either of two categories; 1) dispersion fuels containing small, uncoated uranium and/or thorium oxide or carbide particles dispersed in a graphite matrix; and 2) coated particle fuels containing 100- to 400-micron oxide or carbide particles each coated with Al_2O_3 or pyrolytic carbon dispersed in the graphite matrix. Fuel elements from either category may be coated with such materials as SiC , ZrC , or pyrolytic carbon.

The Grind-Leach process (mechanical powdering followed by nitric acid leaching) is applicable to all fuel types. With uncoated dispersion fuels, grinding to 16 mesh and leaching for about 10 hr with boiling 15.8 M HNO_3 results in recovery of greater than 99% of the uranium when the uranium content of the fuel is greater than about 5%. Recoveries are only about 85% from fuel containing 1% uranium. Dispersion fuels containing both uranium and thorium must be leached with

fluoride-catalyzed nitric acid to ensure complete uranium and thorium recovery. Fuels containing coated particles must be ground fine enough (~200 mesh) to ensure crushing of all the particles to obtain complete recovery during leaching. Fuels coated with SiC or ZrC present special problems because of the abrasive properties of the coatings.

Treatment of dispersion graphite fuels with boiling 90% (21.5 M) HNO₃ results in simultaneous disintegration and leaching of the fuel. Coated fuels require rough crushing prior to the acid treatment. Recoveries from fuels containing only uranium are usually greater than 99% when the uranium content of the fuel is greater than about 2% but decrease to ~96% when the uranium content decreases to 0.7%. Generally two, successive 4-hr leaches (3.5 liters of acid per kg of fuel) are sufficient. Thorium leaches more slowly than uranium; hence, fuels containing both uranium and thorium require multiple leaching if high recoveries are to be obtained. Recoveries are equally high from graphitized (fired above 2400°C) or ungraphitized (fired below 1200°C) fuels although the graphitized fuels disintegrate more readily in 90% HNO₃. Disintegration and leaching in 90% HNO₃ also occur at 25°C but, generally, the recoveries are lower. In tests with slightly irradiated (0.001% burnup) fuel specimens, about 50% of the long-lived fission products remained in the graphite residue even when uranium recovery was quantitative. Although fuels containing coated fuel particles are disintegrated by 90% HNO₃, they cannot be processed by this method since the acid does not penetrate pyrolytic carbon or Al₂O₃ coatings.

The combustion-dissolution process involves burning the fuel in oxygen and leaching the oxide residue with nitric acid. This process is applicable to all types

of graphite-base fuels except those containing Al_2O_3 -coated fuel particles. Rough crushing of fuels coated with SiC or similar materials will be required prior to combustion and some loss of uranium to the residue can be expected. Addition of fluoride ion to the leachant is particularly effective in freeing uranium from siliceous residues. Up to 95% of the ruthenium was volatilized in tests on low burnup fuels during combustion.

ELECTROLYTIC DISSOLUTION

Electrolytic dissolution is being developed as a general method for dissolution of reactor fuels in nitric acid. Generally, the fuel rests in a niobium (high overvoltage, valve metal) basket anode submerged in nitric acid (33,39,40). However, in a new dissolver design, the Series dissolver, the fuel does not contact either electrode but becomes an induced electrolytic cell in the solution between the electrodes (41). Aluminum, uranium, iron, chromium, and nickel dissolve whereas most of the zirconium, tin, molybdenum, graphite, and silicon are converted to sludges. Dissolution of ceramics such as $\text{ThO}_2\text{-UO}_2$ or BeO-UO_2 in fluoride containing systems may not be practical because of electrode corrosion problems. Important development problems include maintaining anode-fuel contact and minimizing arcing in the basket system, removal of insoluble sludges, slivers, and heels from the dissolver, chemical and stray electrical current corrosion of dissolver, and recovery of uranium from sludge after disintegration of U-Zr alloy fuel.

At the Idaho Chemical Processing Plant (ICPP) about 24 alloys ranging from stainless steels to aluminum and Hastelloys have been successfully dissolved and both Zircaloy-2 and zirconium-uranium alloys disintegrated in laboratory scale batch and continuous dissolvers using a niobium anodic basket (40). A critically safe pilot plant

5,000 amp unit is being designed for installation at the ICPP pilot plant (42). A perforated 1/8-in. thick, 5-1/8 in. i.d. x 10 ft high niobium anode, with 1/8 in. holes and 28% free area is contained in a 1/8-in. thick 7 in. i.d. x 10 ft high niobium cathode tank. The concept of the "Series" dissolver was successfully demonstrated in laboratory scale tube dissolvers with 8 M HNO₃ (41). Dissolution rates up to 2.5 and 0.9 mg min⁻¹ cm⁻² were obtained for stainless steel and aluminum, respectively, at ~110 volts and 0.64 mg min⁻¹ cm⁻² for zirconium at 75 volts. Advantages of this system include elimination of the electrode contact-arc problem, use of higher voltage, and easily replaceable electrodes. Scaleup and material of construction problems remain to be defined.

In laboratory scale work at the Savannah River Laboratory (SRL) (33), in which fuel specimens were generally attached to an anode, successful fuel dissolution or disintegration was demonstrated, i.e., stainless steel and Zr-2 clad UO₂, U-10% Mo, APPR, Al clad U-Al alloy, and graphite - 14% U. Uranium loss to the residues was generally <0.2% although nitric acid leaching was used in the case of U-Mo and graphite residues. About 11-52% of the uranium is lost to the residue from disintegration of low U-Zr fuels and cannot be recovered by HNO₃ leaching. Hence, electrolytic dissolution is not considered a satisfactory processing method for Zr-U alloy. Corrosion of 304 and 309 SS welded samples in solutions containing 20-30 g of SS/liter and HNO₃ was 2 mils/yr at 90°C in the presence of nitrogen oxides formed during dissolution (33).

Two prototype "cold" pilot plant dissolvers with 500 and 5000 ampere capacities have been successfully demonstrated at SRL in initial experiments on stainless steel

and Zr-2 clad UO_2 rods and aluminum and stainless steel rods, respectively (33). The 5000 ampere unit (33) consists of a 5 in. x 12 in. x 5 ft long niobium V bottom metal strip basket suspended in a 6-ft dia x 7 ft 304 SS tank. The anode basket is surrounded by a perforated 10.5 in. x 16 in. niobium cathode. Anode contact is maintained by a hammer striking the anode periodically. Aluminum dissolved in 8 M HNO_3 at a rate of 0.38 g/amp-hr at a current of 3600 amps at 10-25 volts and stainless steel in 4.3 M HNO_3 at approximately 0.6 g/amp-hr at 2000 amperes and 12 volts. Severe arcing between basket and stainless steel rods, which occurred in initial runs, was eliminated by reducing the voltage to 12 V, replacing the V bottom with a flat 1/2" niobium plate, separating the stainless steel rods above the liquid level from the anode with a stainless steel insert, and shutting off the current whenever the hammer struck to re-establish anodic contact.

CHLORIDE VOLATILITY PROCESSES

Chloride volatility processes are being developed at ORNL, BNL, ICPP, and ANL for volatilizing structural material from nuclear fuels while leaving the fertile and fissile material in a form which can be either dissolved in nitric acid in preparation for solvent extraction or treated with fluorine to produce uranium hexafluoride (43-47). Laboratory results indicate that recovery of fertile and fissile material is nearly quantitative and that reaction rates are satisfactory (Table 5) and wall grate corrosion rates are low for fuels containing zirconium, niobium, molybdenum and aluminum. Only hydrochlorination of zirconium has been extensively demonstrated on an engineering scale. No aqueous processes have been proposed for two of the fuels listed, niobium and 36% UO_2 -64% ZrO_2 (3rd PWR seed). Stainless

Table 5. Reaction and Corrosion Rates in High Temperature Gas-Solid Reactions

Fuel Material	Reagent	Volatile Product	T, °C		Corrosion Rate, mils/mo		Reaction Rate, mg min ⁻¹ cm ⁻²
			Wall	Grate	Wall	Grate	
Zr	HCl	ZrCl ₄	350	600	0.1	1	5
Nb	Cl ₂	NbCl ₅	200	300	0.00	0.04	10
U-10% Mo	15% HCl- air	MoO ₂ Cl ₂	100	400	0.00	0.05	12
Al	HCl	Al ₂ Cl ₆	200	300	0.01	0.05	10
SS	Cl ₂	FeCl ₃	300	600	0.06	1.5	1
34% UO ₂ - 64% ZrO ₂	15% CCl ₄ - N ₂	ZrCl ₄	350	585	1	6	3

steel reacts only slowly at temperatures at which metal containers can be used. The materials selected for corrosion rate tests were Haynes-25 (wall) and Nichrome V (grate). Development work using fluidized beds is underway at Brookhaven National Laboratory (47) and Argonne National Laboratory.

MECHANICAL PROCESSING

Two mechanical methods for processing spent power reactor fuels are being studied at Oak Ridge National Laboratory (49,54), (a) decladding of NaK or Na bonded fuels and (b) shearing and leaching of stainless steel or Zircaloy-2 clad fuels.

Mechanical processing methods as an aid or substitute for chemical methods has the following advantages:

1. Additional fuel types could be processed in existing stainless steel equipment.
2. Removal of inert structural metals prior to the dissolution step would increase

the capacity of existing plants for fissile and fertile metal and waste storage facilities would be minimized by storage of the inerts as metal.

3. Breaking of fuel cores by shearing would shorten the dissolution time because of the increased surface area exposed to acid dissolvents.

4. Decladding of liquid metal bonded fuel and disposal of the NaK or Na separately prevents them from being charged to a dissolver where an explosive reaction with acid could occur.

Mechanical decladding of NaK bonded stainless steel clad fuel was successfully demonstrated on 26 SRE Core I fuel clusters which survived the temperature excursion (48). Evaluation of chop-leach processing is continuing using a shear, conveyor, continuous leacher complex with a capacity of ~7 kg U/hr for stainless steel clad- UO_2 fuel. The equipment has passed operability acceptance tests and is ready for life tests with prototype unirradiated fuels. Chop and leach processing should have wide application to a variety of nuclear fuels. A cost comparison of a chop-leach vs. a Sulfex head end system for processing stainless steel clad UO_2 fuel at a rate of 800 metric tons U/yr showed lower capital and operating costs by ~20% and ~50%, respectively (50). The greatest saving was in waste disposal, i.e., a factor of 20. Demonstration of the chop-leach process will probably be performed with irradiated fuels at the Idaho Chemical Processing Plant following successful engineering development at Oak Ridge National Laboratory.

At Hanford Atomic Products Operation, size reduction of unirradiated fuels has been studied using a 40 ton vertical hydraulic shear with a male V moving blade (51)

as well as disassembly by hacksawing (52) or slitting (53). An underwater chop-leach complex was carried through the design stage (1). Tests on irradiated fuels are not planned.

Decladding of SRE Core I Fuel. An equipment complex for mechanically decladding SRE Core I fuel was designed and fabricated (49) in 1958-1959 and acceptance testing (54) in the ORNL Segmenting Facility (Fig. 2) was completed and spent SRE Core I fuel mechanically processed (55) by September 1961. A color movie is available (58). The SRE Core I fuel consists of clusters, 105.5-in. long, of 7 elements or rods containing 2.7 percent enriched uranium slugs in thin walled, 0.010 in., 304 stainless steel tubular cladding, 92-5/16-in. long by 0.790-in.-o.d. The active fuel length is 72 in. consisting of 12 slugs, 0.750-in.-dia by 6.0-in. long, of unalloyed uranium thermally bonded to the clad by a 0.010-in. NaK eutectic annulus. At the end of the column is a helium filled space, approximately 18 in. high, which allows expansion of the NaK bond and serves as a reservoir for fission gases.

About 1.8 metric tonnes of fuel consisting of 175 tubular fuel rods were mechanically declad, steam cleaned, recanned and placed in dry storage at rates of 2 kg U/hr to 9.2 kg U/hr with negligible loss of uranium and plutonium. A pictorial presentation of portions of the decladding process is presented in Figs. 3 through 8.

Hydraulic expansion of the clad and expulsion of the slugs was effective on 16% of the rods, slugs from 77% were physically dislodged by a mechanical screw, and 7% had to be processed in an auxiliary roller cutter unit and the clad peeled off by remote manipulators. The unexpected hardness of the stainless steel cladding appears to have resulted from work hardening. The hardening prevented expansion of the cladding,

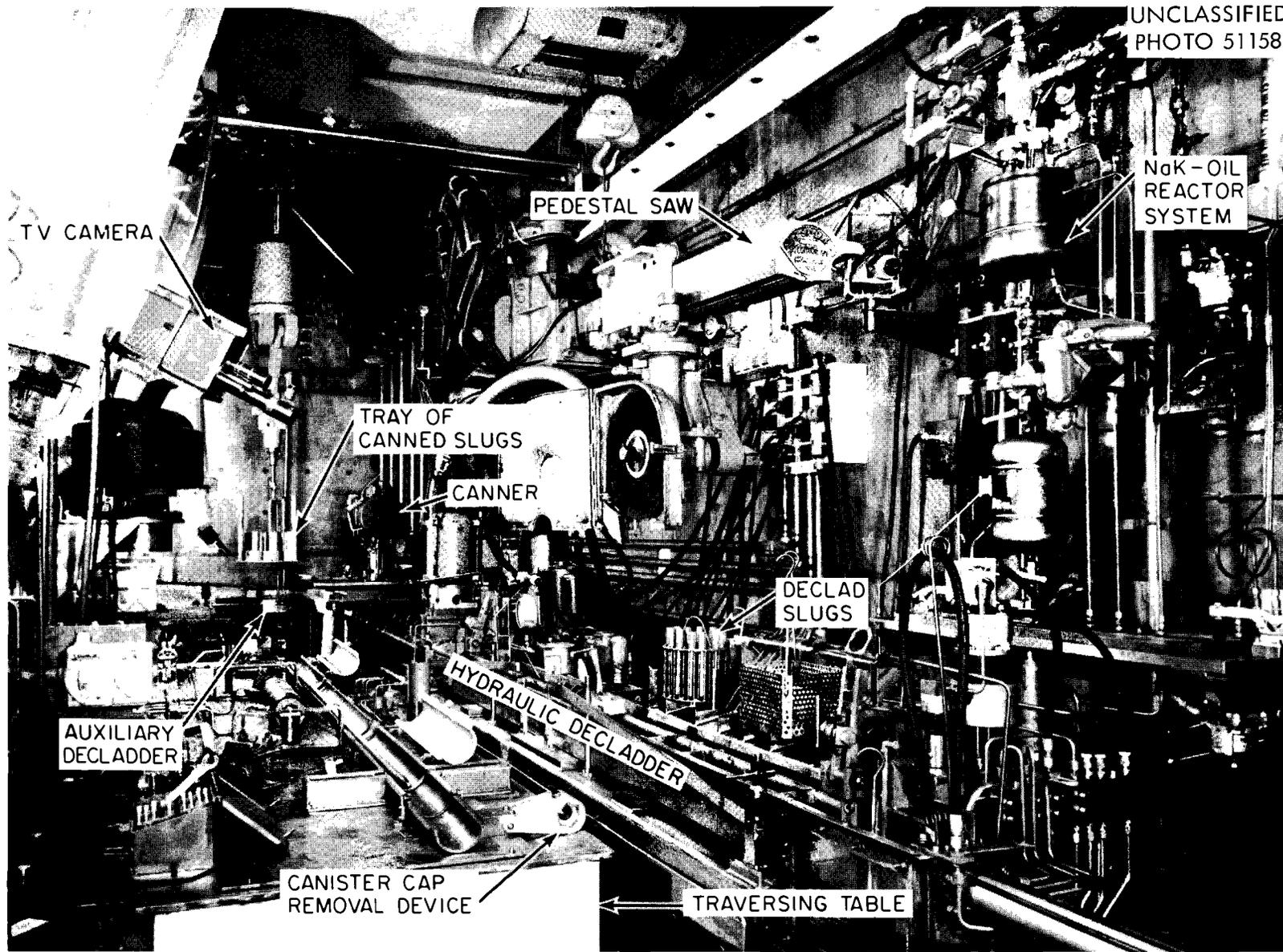


FIG. 2. MECHANICAL PROCESSING EQUIPMENT FOR DECLADDING SRE CORE I FUEL (INTERIOR VIEW, CELL A) ORNL SEGMENTING FACILITY.

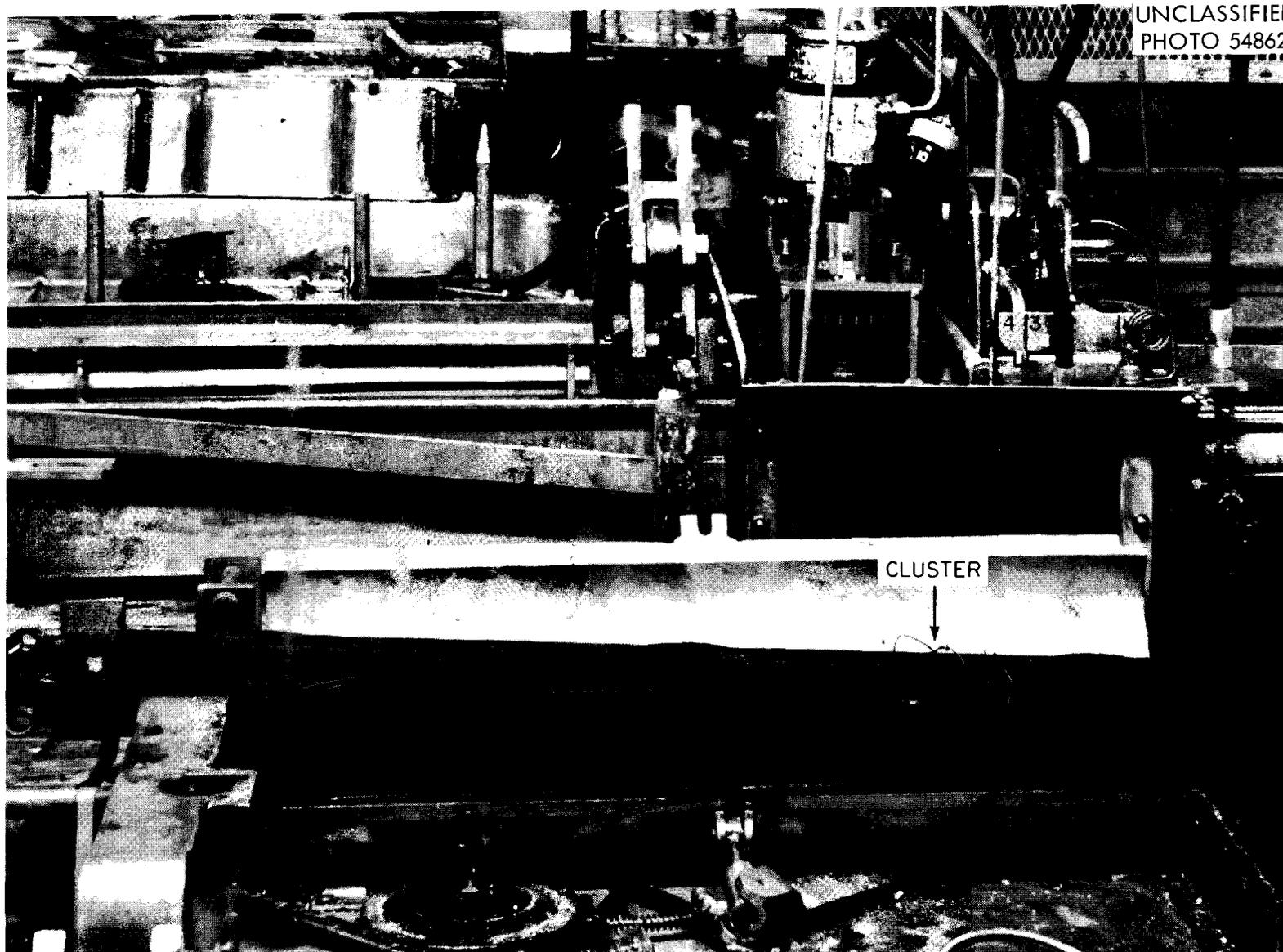


FIG. 3. SRE CORE 1 CLUSTER IN SAW TROUGH PREPARATORY TO REMOVAL OF INERT ENDS BY ABRASIVE DISC SAWING. HYDRAULIC DECLADDING UNIT IN BACKGROUND.

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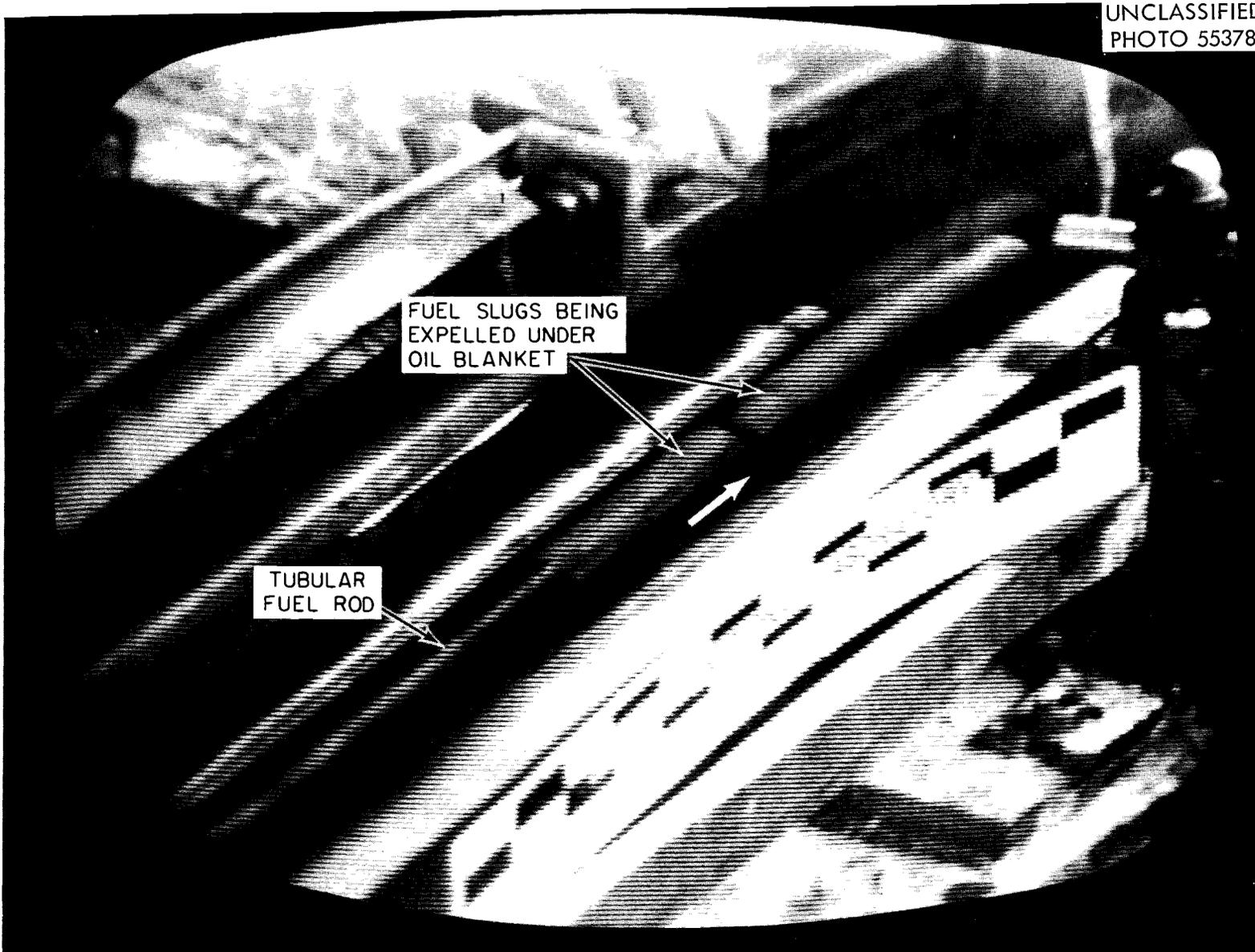


FIG. 4. EXPULSION OF SRE CORE I FUEL SLUGS FROM STAINLESS STEEL TUBULAR FUEL JACKET BY AN INTERNAL MECHANICAL SCREW (PHOTOGRAPH FROM TELEVISION SCREEN).

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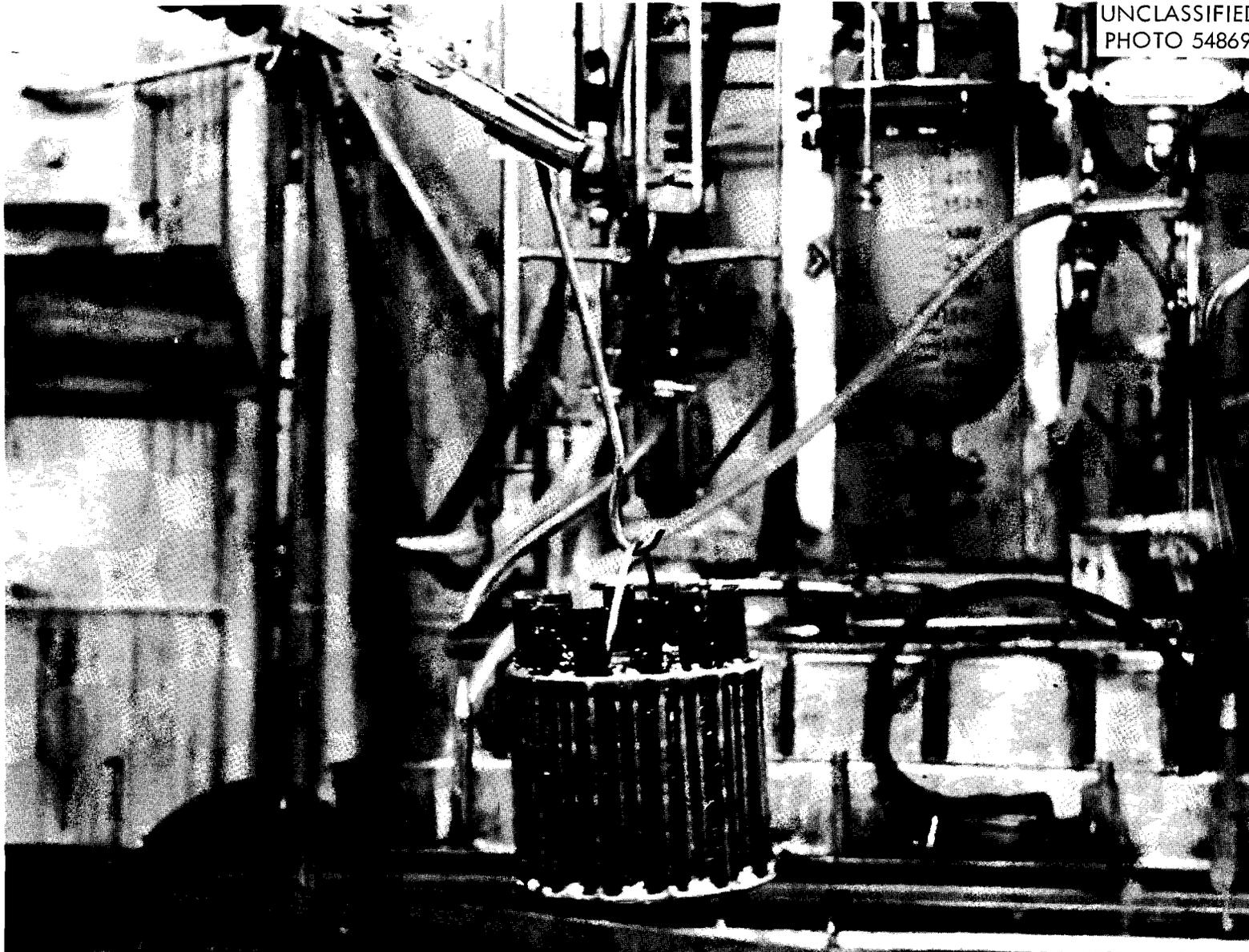
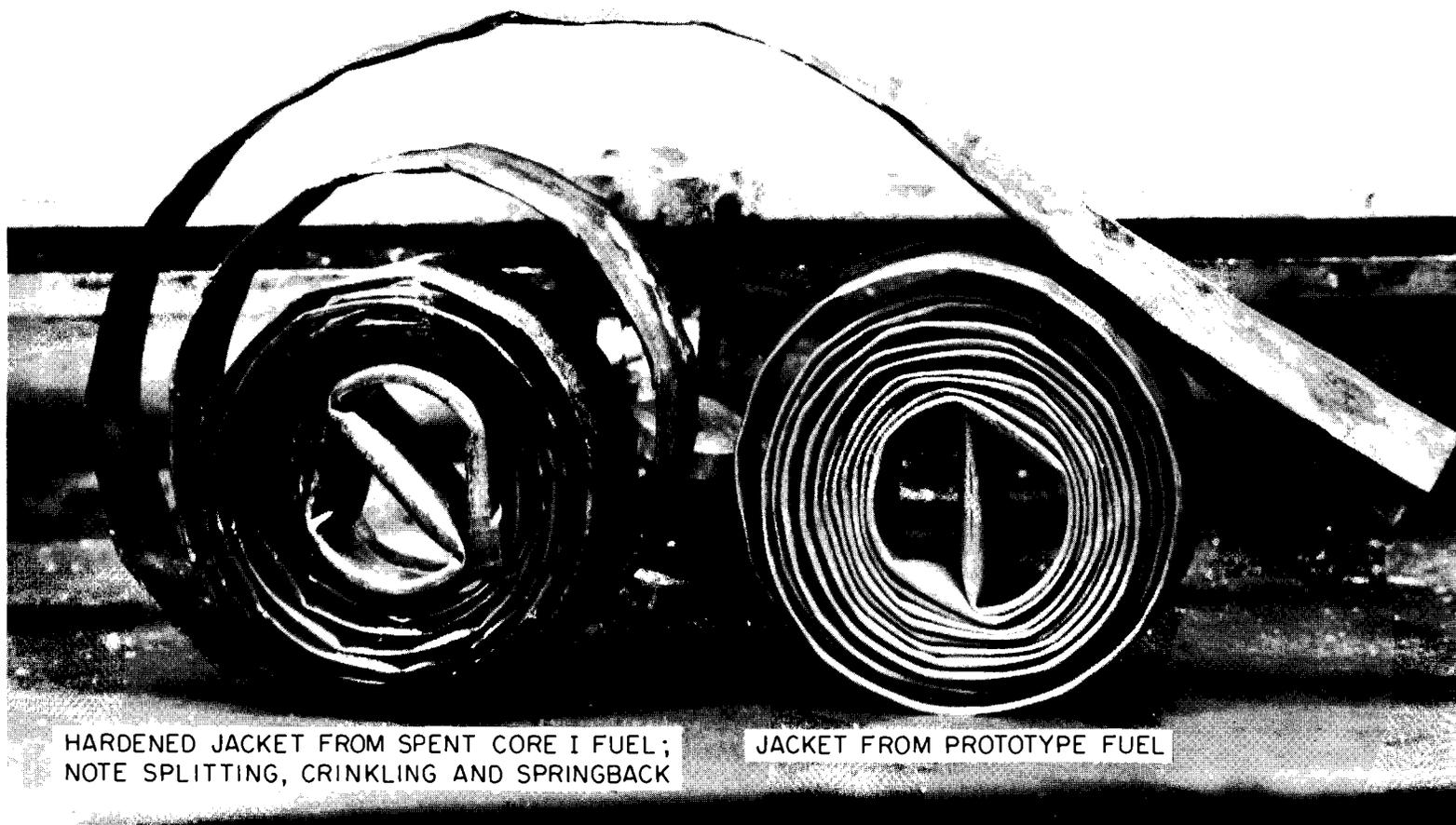


FIG. 5. SLUGS FROM ONE SRE CORE I FUEL ROD BEING TRANSFERRED TO STEAM CLEANER.
NOTE: GLOBULES OF NaK CLINGING TO OILY SURFACES OF URANIUM SLUGS.

OAK RIDGE NATIONAL LABORATORY

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HARDENED JACKET FROM SPENT CORE I FUEL ;
NOTE SPLITTING, CRINKLING AND SPRINGBACK

JACKET FROM PROTOTYPE FUEL

FIG. 6. COMPARISON OF 304 STAINLESS STEEL JACKET PROCESSED FROM SRE CORE I FUEL COMPARED TO A MORE DUCTILE PROTOTYPE JACKET.

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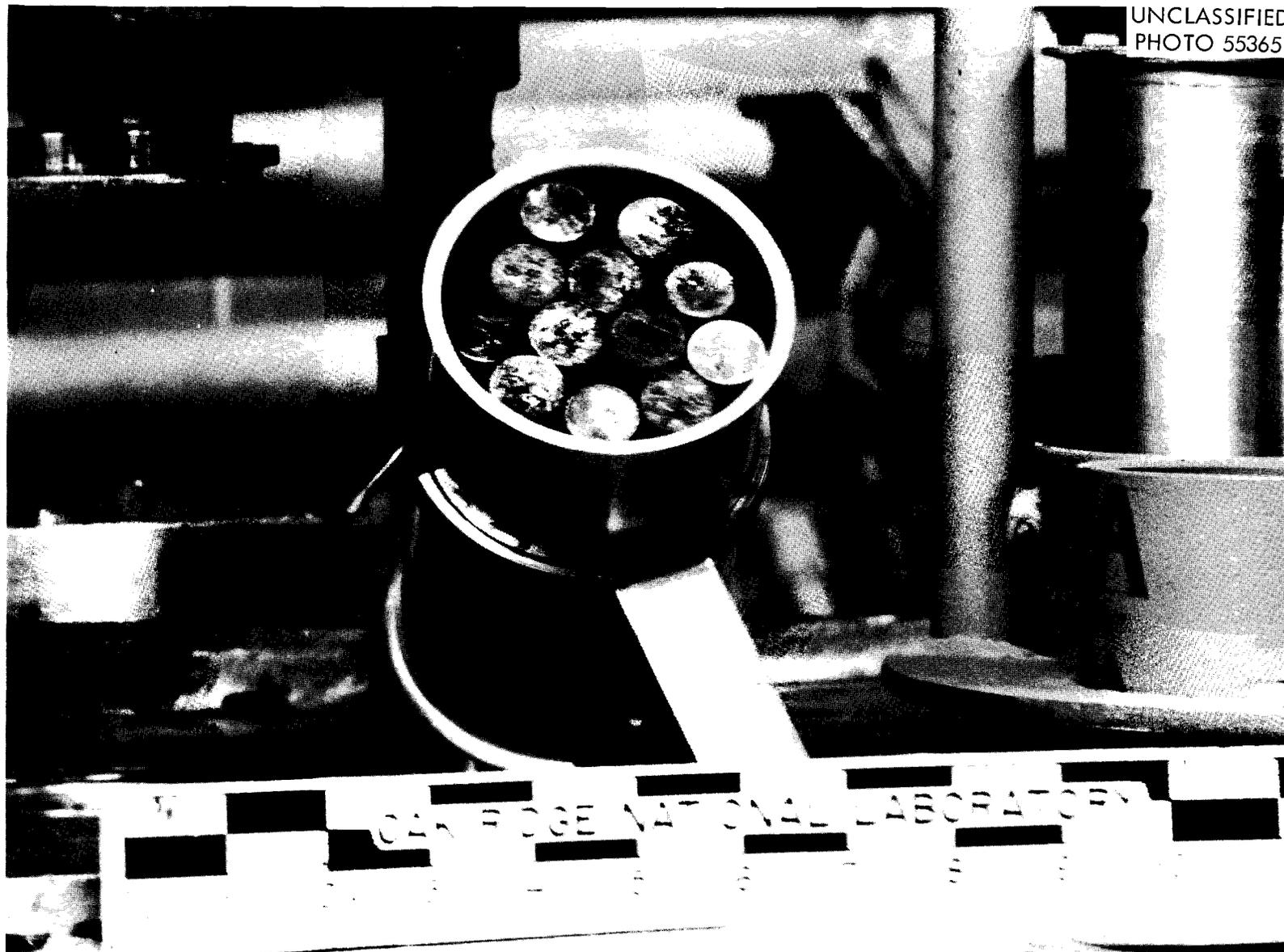


FIG. 7. STEAM CLEANED SLUGS FROM ONE SRE FUEL ROD (~10 kg) JUST PRIOR TO SEALING OF ALUMINUM CAN.

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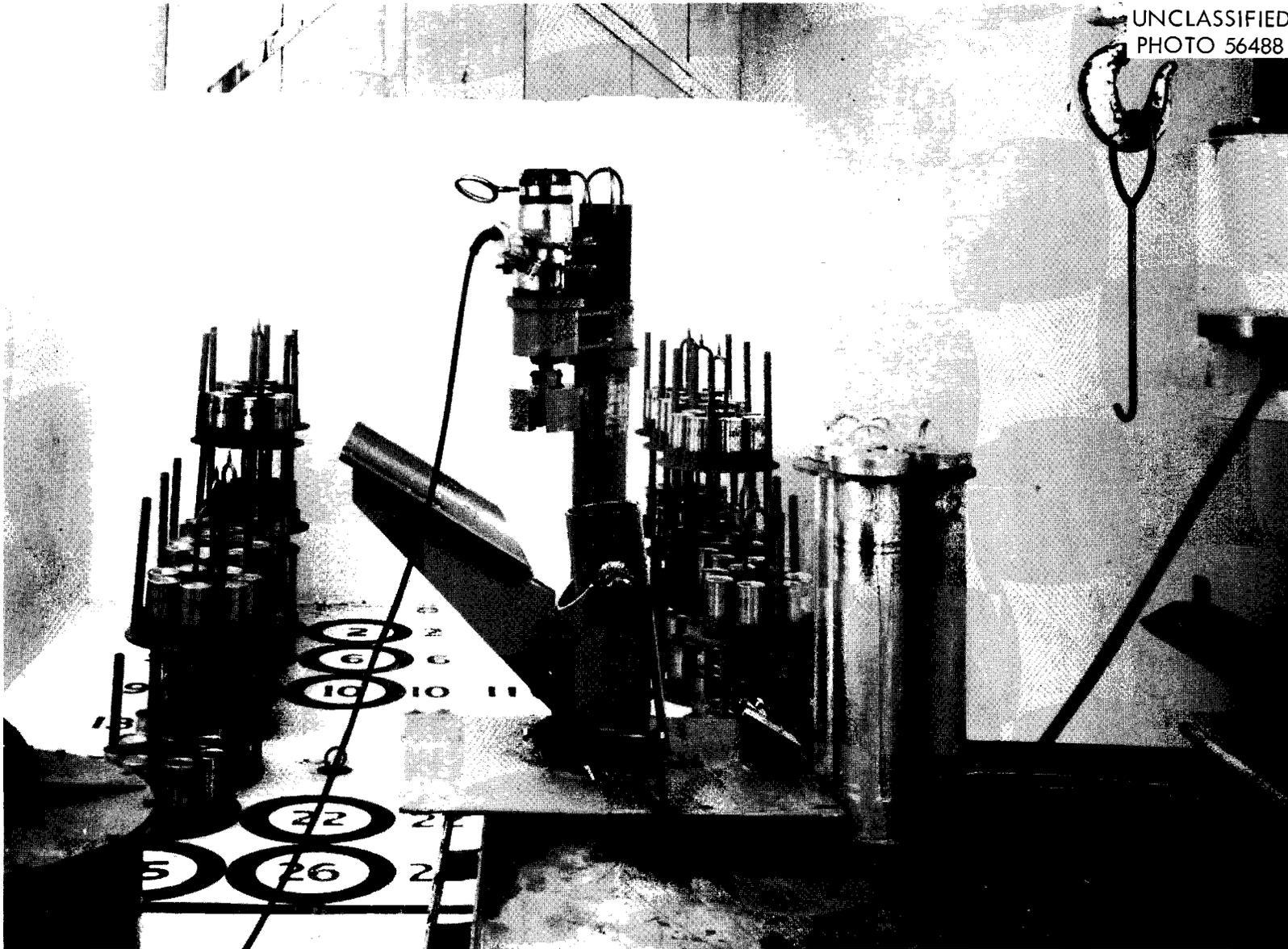


FIG. 8. DEJACKETED, CLEANED, CANNED, AND STORED FUEL SLUGS IN CRITICALLY SAFE STORAGE RACKS AWAITING SHIPMENT IN CANISTERS (IN FOREGROUND) TO PROCESSING SITE.

planned as the primary decladding method. Generally, fuel slugs were pitted, slightly bent, swollen and elongated. The NaK (22% Na, 78% K) eutectic bond was pasty (probably oxidized) and the 18 liters collected and destroyed by steam contained about 1 curie of Cs-137.

Waste volumes were small. Liquid collected from NaK destruction and steam cleaning of slugs was ~ 0.33 gal/kg U processed. Solid stainless steel waste, inert ends, spacer wires, and clad amounted to ~ 0.07 kg/kg U processed.

Although unexpected difficulties were encountered because of the reactor incident, decladding of liquid metal bonded fuels is considered to be feasible and practical. Shear and leach, however, may prove to be a more versatile and universal method which may be essentially independent of the metallurgical properties of spent fuels and reactor events.

Shear and Leach. The chop-leach complex being evaluated at ORNL is shown in Fig. 9 and a chemical flowsheet, based on small scale studies (57), in Fig. 10. The complex is designed to continuously chop and leach ~ 7 kg U/hr as stainless steel clad UO_2 . The cost of the custom built remotely operated stainless steel shear and controls was \$185,000 and the stainless steel spiral inclined rotary feeder and spiral inclined rotary leacher with centrifuge about \$40,000 each.

The shear, designed to cope with particulate and acid fume problems, produces desirable discrete pieces of tubular fuel assemblies for nitric acid leaching of the cores. Tests with prototype fuel, Fig. 11, and a stepped blade produced product (56) about 1 in. long except for the very last cut of the six foot long assembly which was about 1-1/2 to 2 in. long. About 18% of the core porcelain was dislodged and $\sim 1\%$

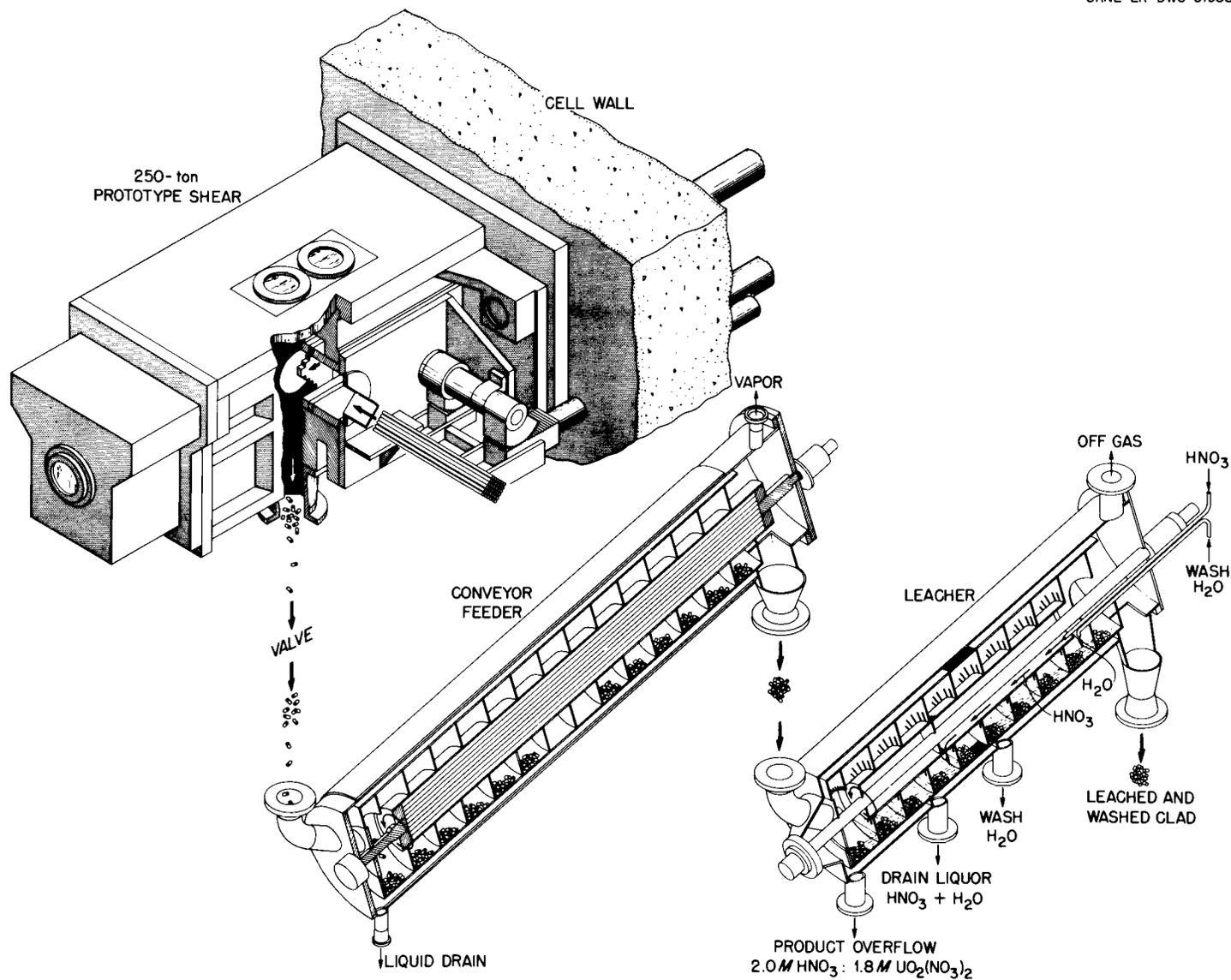


FIG. 9. SHEAR AND LEACH COMPLEX.

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- BASED:
1. CHOP 1 UO₂-FILLED MARK 1
PROTOTYPE EVERY NINE HOURS.
2. USE 4 HOUR LEACHING PERIOD-
I.E. FEED 1 FLITE PER HOUR.

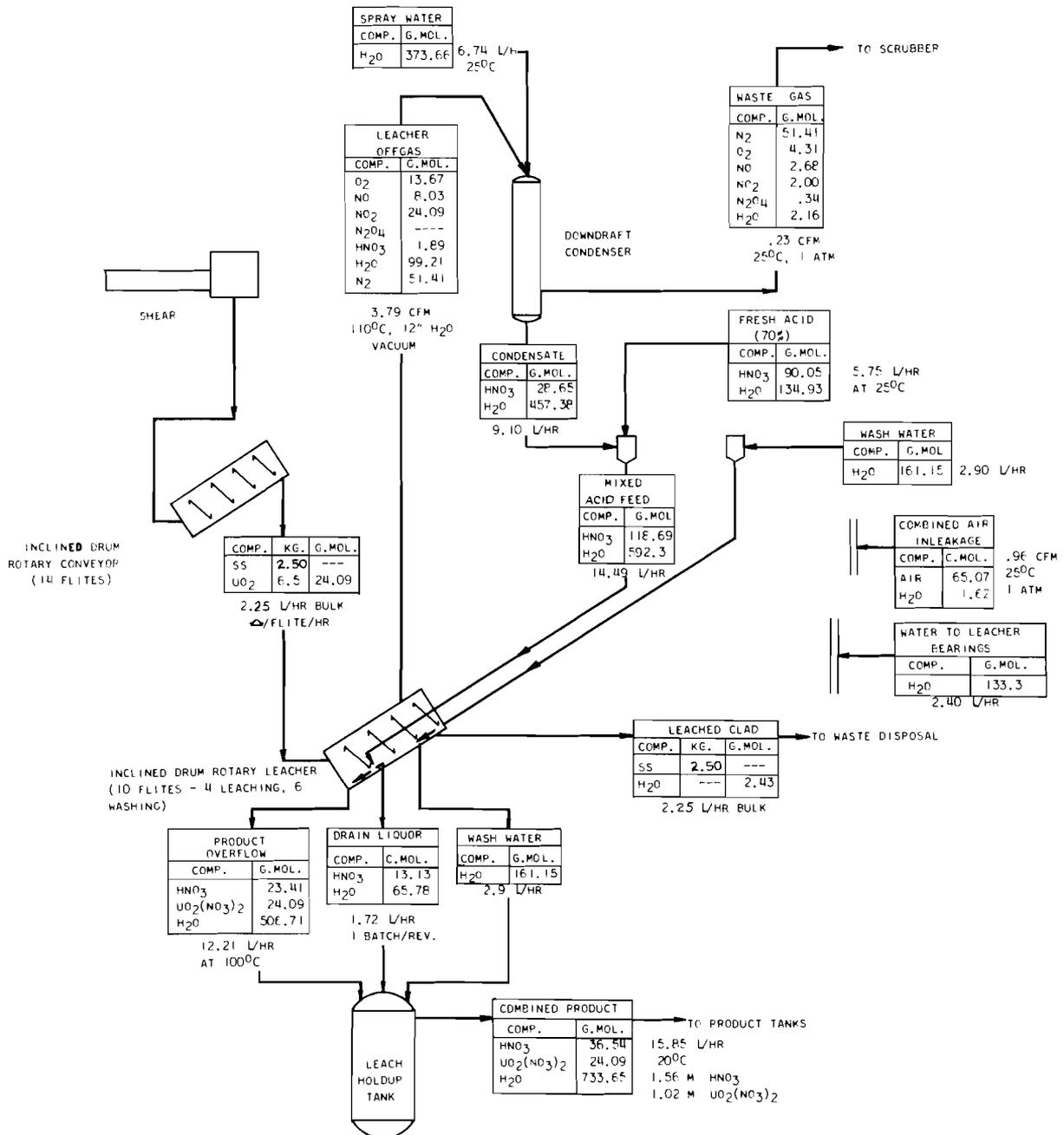


FIG. 10. MATERIAL BALANCE FLOWSHEET SHEAR AND LEACH.

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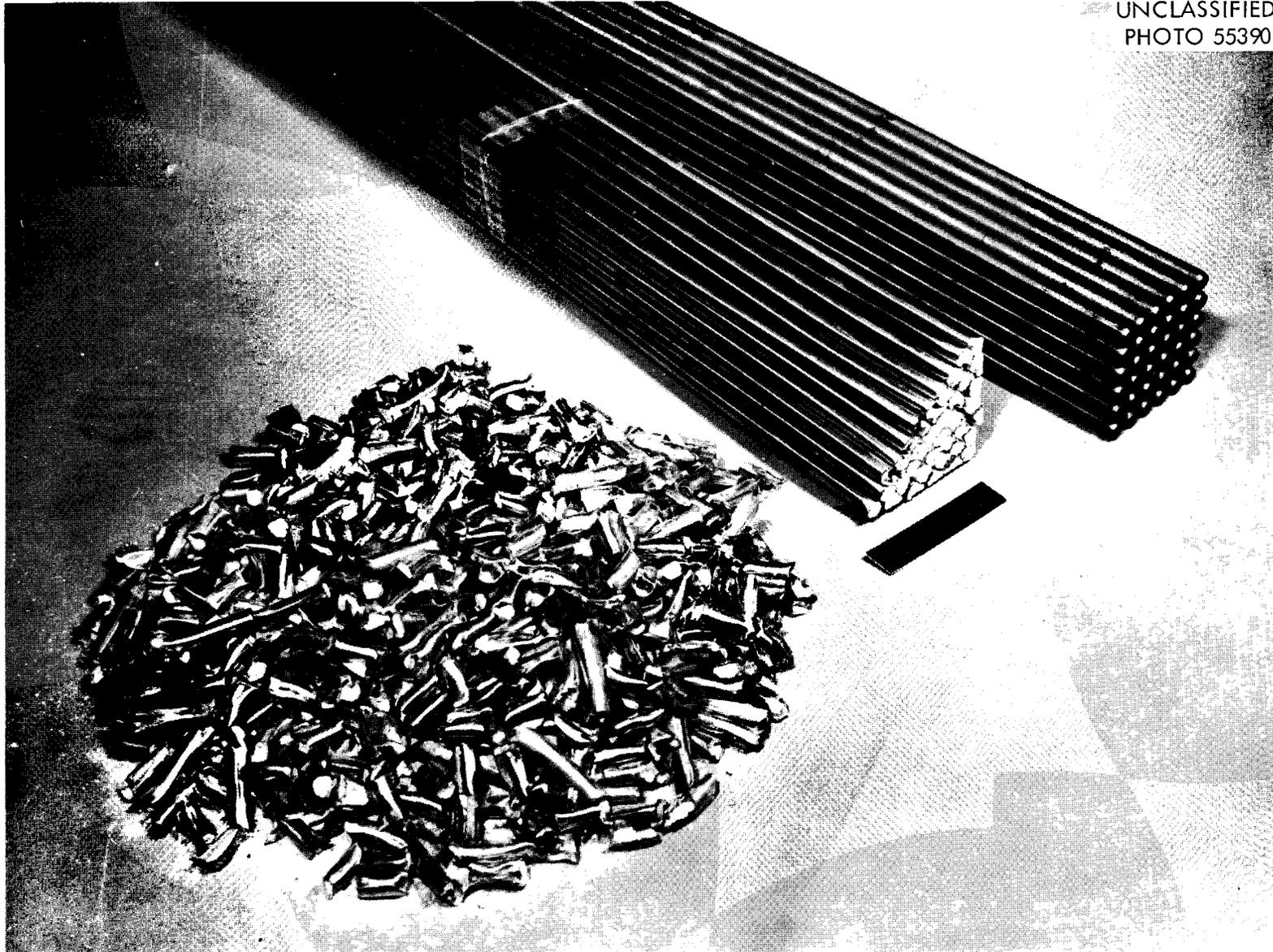


FIG. 11. ORNL MARK I PROTOTYPE FILLED WITH PORCELAIN BEFORE AND AFTER SHEARING WITH STEPPED BLADE COMPARED WITH PRODUCTS OF SHEARING A COMPLETE ASSEMBLY 72 INCHES LONG.

of the stainless turned into magnetic fines ~ 2000 to $< 44 \mu$ in size. The ferrules were flattened and torn from the assembly. Blade wear after about 1000 cuts was negligible.

The operation of the leacher was predicted in small scale batch tests (57), Fig. 12. Prototype fuel has been assembled for full scale tests during 1962 with stainless steel clad UO_2 , ThO_2 and UO_2-ThO_2 , and with Zircaloy-2 clad UO_2 .

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CONDITIONS

7M HNO₃ 30.3 ML/MIN.
UO₂ PELLETS (PWR REJECTS, 0.360 IN. O.D. X 0.370 IN. LONG,
ρ = 10.1 GMS/CC) 600 GMS/BATCH HNO₃/UO₂ MOLE RATIO
= 5.74

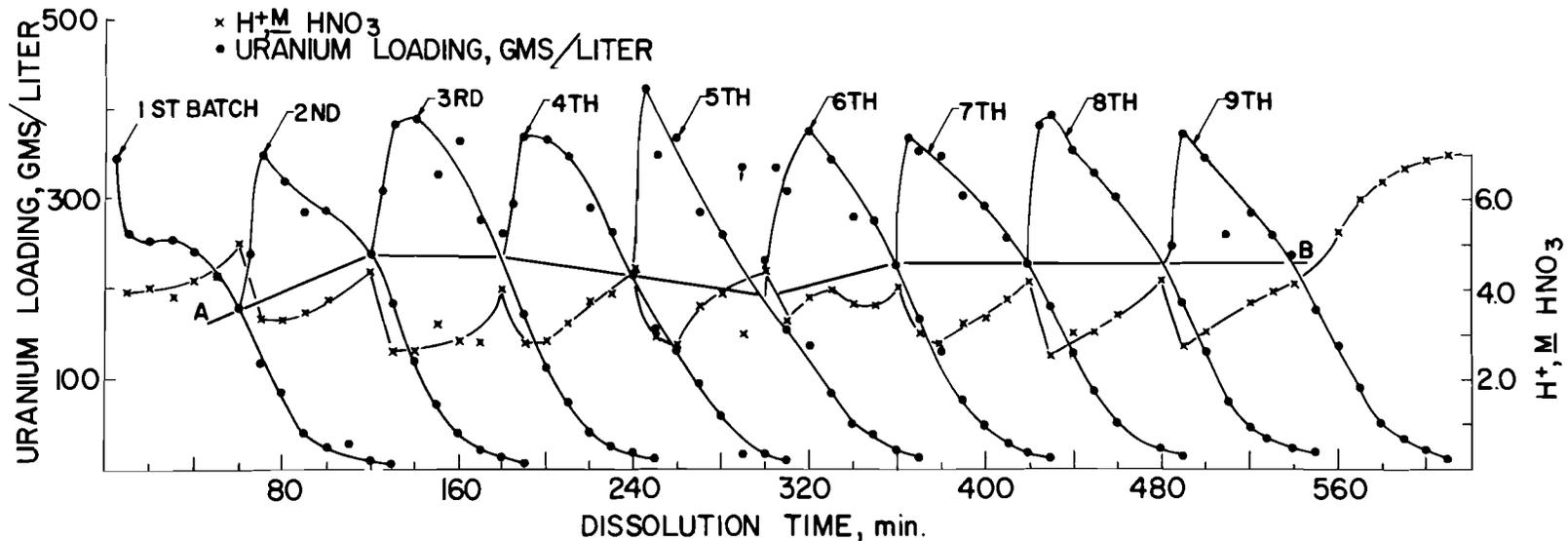


FIG. 12. URANIUM LOADING AND H⁺ AS A FUNCTION OF DISSOLUTION TIME FOR FOUR-STAGE LEACHER MODEL; NOTE: DISSOLUTION OF NINE BATCHES OF UO₂ PELLETS BASED ON 4-HOUR DISSOLUTION TIME.

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