UNCLASSIFIED

(CLASSIFICATION)

GENERAL ELECTRIC

HANFORD ATOMIC PRODUCTS OPERATION – RICHLAND, WASHINGTON

DOCUMENT NO.
HW-65290

COPY NO. [redacted]

DATE
April 13, 1960

ISSUING FILE

TITLE

THE USE OF LOW TEMPERATURE ACIDIC FLUORIDE SOLUTIONS FOR PREFERENTIAL DECLADDING OF ZIRCALOY-CLAD UO_2 FUELS

AUTHOR

R. F. Haness

ROUTE TO	PAYROLL NO.	LOCATION	FILES ROUTE DATE	SIGNATURE AND DATE
300 File				

UNCLASSIFIED

(CLASSIFICATION)

300 Files

UNCLASSIFIED

HW-65290

54-3000-039 (9-58) AEC-GE RICHLAND, WASH.

HANFORD ATOMIC PRODUCTS OPERATION
GENERAL ELECTRIC COMPANY
RICHLAND, WASHINGTON

[redacted]
4-13-60

REPORT OF INVENTION

A.E.C. CASE NO.

G. E. CASE NO.

TO: R. E. Burns

I: ATTACHED HERETO IS A DESCRIPTION OF WHAT MAY BE AN INVENTION IN:

The use of low temperature acidic fluoride solutions for preferential decladding of Zircaloy-clad UO_2 fuels.

II: THE NAME, TITLE OR POSITION, WORKS LOCATION, AND PERMANENT ADDRESS OF THE INVENTOR(S) IS:

R. F. Maness, Senior Engineer
Development & Corrosion Chemistry, H.L.O., 326 Bldg., 300 Area.
624 Basswood, Richland, Washington.

III: EVIDENCE AS TO WHEN AND WHERE THE INVENTION WAS MADE CAN BE FOUND IN THE FOLLOWING LISTED WRITTEN OR PICTORIAL MATERIAL (NOTEBOOK, FILE REPORTS OR DRAWINGS, ETC.):

Notebook HWN-2221

IV: THE APPROXIMATE DATE OF THE FIRST ENTRY IN SAID WRITTEN OR PICTORIAL MATERIAL DESCRIBING OR SHOWING SAID INVENTION IS:

March 18, 1960

V: PERSONS WHO COULD TESTIFY AS TO WHEN AND WHERE THE INVENTION WAS MADE INCLUDE THE FOLLOWING:

L. H. Williams
W. L. Walker
R. E. Burns

SIGNED (SUPERVISOR)	DATE	DEPARTMENT
		Development & Corrosion Chemistry Operation Hanford Laboratories Operation

NOTE: SUGGESTIONS FOR PREPARING THE INVENTION DESCRIPTION ARE CONTAINED ON THE REVERSE SIDE OF THIS FORM.

UNCLASSIFIED

UNCLASSIFIED

HW-

Distribution:
1-6. R. K. Sharp
7. L. P. Bupp
8. O. F. Hill
9. R. E. Burns
10. R. F. Maness
11. 300 Files

April 13, 1960

INVENTION REPORT

THE USE OF LOW TEMPERATURE ACIDIC FLUORIDE SOLUTIONS FOR PREFERENTIAL DECLADDING OF ZIRCALOY-CLAD UO_2 FUELS

This report concerns what may be an invention in the use of low temperature nitric acid - hydrofluoric acid solutions to preferentially declad Zircaloy-clad UO_2 fuels.

Current processes for dissolving Zircaloy cladding include neutral fluoride solutions (NH_4F-NH_4NO_3) for preferentially decladding uranium or uranium dioxide fuels and acid fluoride solutions for total dissolution of such fuels as Zircaloy-clad U-Zr alloy. In the interest of simplicity of operation (no ammonia removal problem), it may be desirable to preferentially declad Zircaloy-clad uranium dioxide fuels with acid fluoride solution. Satisfactory Zircaloy dissolution rates, relatively low container corrosion rates and low loss of fuel core to the decladding solution may be obtained with hydrofluoric acid solutions containing low concentrations of nitric acid when the dissolution is performed at low temperature ($\leq$ 75C). This observation constitutes the possible invention claimed in this report. Data are presented in the following paragraphs to support this claim.

Instantaneous dissolution rates of Zircaloy-2 in 0.25 M HNO_3 - HF solutions are shown in Table I as a function of temperature and "free fluoride" concentration. An initial fluoride concentration of three molar is required to penetrate the scale of heavily oxidized Zircaloy. The nitric acid requirement for dissolution of the tin present in Zircaloy-2 is $<$ 0.25 M and $>$ 0.10 M. Zirconium dissolves in acid fluoride solution to form ZrF_4 and liberates about 200,000 cal/mole zirconium dissolved. No applied heat is necessary to initiate or maintain reaction. The low initial temperature reduces container corrosion to a minimum. Higher temperatures may be tolerated as reaction proceeds and the free fluoride concentration is reduced. Typical corrosion data are given in Table II.

WITNESSED:
This _____ day of _____, 1960.

_____

_____

INVENTED BY:

_____

_____
(Date)

Uranium dioxide losses to simulated decladding solutions are shown in Table III. These data show core losses become excessive only at nitric acid concentrations above 0.25 molar.

WITNESSED:
This _____ day of _____, 1960.

_____

_____

INVENTED BY:

_____

_____
(Date)

Table I

Instantaneous Dissolution Rates of Zircaloy-2
Effect of Temperature and Free Fluoride Concentration

Conditions: One-minute exposures. Initial solution contained 0.25 M HNO_3.

Free Fluoride, M* (F - 4 Zy)	Temp., °C.	Zircaloy-2 Dissolution Rate, Mils/Hour
3.0	25	108
2.0	25	55
2.0	50	120
1.5	25	31
1.5	50	55
1.0	25	12
1.0	50	18
1.0	Boiling	80
0.5	25	2
0.5	50	5
0.5	Boiling	17
0.1	Boiling	2

*Defined as total molarity of fluoride minus four times the molarity of dissolved zirconium.

WITNESSED:
This _____ day of _____, 1960.

_____

_____

INVENTED BY:

_____

_____
(Date)

Table II

Hastelloy F* Corrosion Rates in Acid Fluoride Solutions

Solution	Temp. °C.	Corrosion Rate, Mils/Month
1) 0.25 M HNO_3, 2 M HF	25	0.2
2) 0.25 M HNO_3, 2 M HF	50	1.0
3) 0.25 M HNO_3, 3 M HF	25	0.3
4) 0.25 M HNO_3, 3 M HF	50	2.0
5) 0.25 M HNO_3, 2 M HF, 0.27 M Zy	Boiling	1.4
6) 0.25 M HNO_3, 2 M HF, 0.44 M Zy	Boiling	0.3

*Vacuum melted (0.01 C.)

WITNESSED:
This _____ day of _____, 1960.

_____

_____

INVENTED BY:

_____

_____
(Date)

Table III

UO_2 Losses in Acid Fluoride Decladding Solution
Sintered UO_2 Pellets

Conditions: Exposure to boiling solutions for 20 to 180 minutes.
UO_2 pellets heavily etched with nitric acid prior to use.

Solution	UO_2 Loss, Weight Percent/Hour
1) 0.5 M HNO_3, 2 M HF, 0.40 M Zr	0.9
2) 0.25 M HNO_3, 2 M HF, 0.44 M Zr	0.1
3) 2 M HF, 0.46 M Zr	0.01
4) 0.25 M HNO_3, 3 M HF	0.1
5) 0.25 M NH_4NO_3, 2 M HF, 0.40 M Zr	0.1

WITNESSED:
This _____ day of _____, 1960.

_____

_____

INVENTED BY:

_____

_____
(Date)