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FLUORINATION OF INCINERATOR ASH BY HYDROFLUORINATION OR AMMONIUM BIFLUORIDE FUSION FOR PLUTONIUM RECOVERY*

By

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S.J. Kent

NSR ENHANCEMENTS: PYROCHEMICAL PRETREATMENTS

OBJECTIVE: ENHANCE Pu RECOVERY AT LOWER LIQUID VOLUMES

DESIGN CRITERIA:

Pu RECOVERY EFFICIENCY – 98% ON SINGLE PASS
WITH < 25% REQUIRING REPROCESSING

OPTIONAL FLOWSHEETS...

HYDROFLUORINATION (WET/DRY)
AMMONIUM BIFLUORIDE (NH_4HF_2) FUSION

"COMPETING TECHNOLOGIES"...

SILVER CATALYZED DISSOLUTION
CASCADE DISSOLVERS

FLUORINATION OF INCINERATOR ASH AT LANL
JUNE 13 TO AUGUST 8, 1988

SRL PARTICIPANTS

SAMUEL D. FINK
SARA J. KENT
JOHN H. GRAY (CONSULTANT)

LANL PARTICIPANTS

PYROCHEMISTY (MST-13)

STUART A. APGAR, III
DAVID F. BOWERSOX (LIAISON)
JOEL D. WILLIAMS (SUPERVISION)

AQUEOUS PROCESSING (MST-12)

ELAINE ORTIZ
PAMELA K. NYSTROM
JAMES J. BALKEY (LIAISON)
ROBERT BEHRENS (CONSULTANT)
TOM BLUM (CONSULTANT)

ANALYTICAL (CLS-1)

THOMAS MARSHALL (WET CHEMISTRY)
NELSON STALNAKER (Pu ANALYSES)
JOEL DAHLBY (SUPERVISION/CONSULTANT)

PRINCIPLE OBJECTIVES

DETERMINE RELATIVE EFFEICIENCIES OF AMMONIUM BIFLUORIDE (NH_4HF_2) FUSION AND HYDROFLUORINATION PRETREATMENTS

IDENTIFY ENGINEERING CONCERNS FOR PROCESSES

INCREASE KNOWLEDGE OF CHEMISTRY OF PROCESS

BORROW FROM LANL EXPERIENCE AND EQUIPMENT DESIGN FOR OFFGAS SCRUBBING

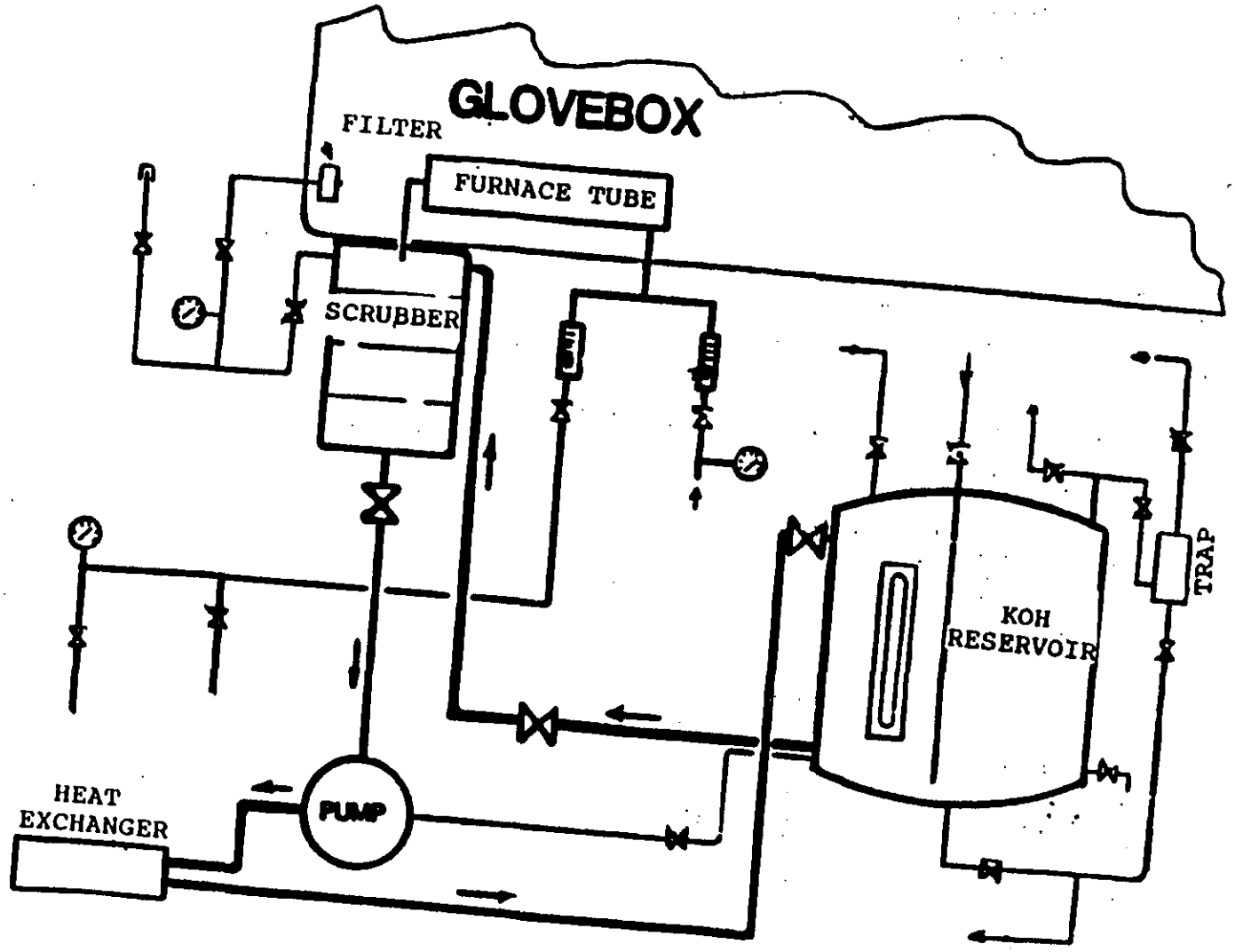

Figure 1. Equipment schematic (taken from Reavis and Apgar[1]).

PYROCHEMICAL OPERATING CONDITIONS

HYDROFLUORINATION...

BASIS: OPTIMAL OXIDE CONDITIONS (TRACY RUDISILL)
LANL EXPERIENCE (STU APGAR; JIM REAVIS)

OBJECTIVES: FORM PuF_4 TO IMPROVE DISSOLUTION
REMOVE Si AS SiF_4

DRY 30 MIN AT 200°C UNDER Ar FLOW
HEATED TO 600°C
GASES: HF (400 g/hr); 0_2 (320 g/hr)
REACTION TIME 4 HR (6 IN ONE CASE)

NH_4HF_2 FUSION...

BASIS: SRL EXPERIENCE (JOHN GRAY)

OBJECTIVES: FORM PuF_4 TO IMPROVE DISSOLUTION
REMOVE Si AS SiF_4

NH_4HF_2/ASH MASS RATIO EXAMINED 0.75-1.0

LOW TEMPERATURE

150 TO 165°C
REACTION TIME 3 HR

HIGH TEMPERATURE

310 TO 320°C
REACTION TIME 3-6 HR (UNTIL MINIMAL OFFGAS)

AQUEOUS PROCEDURE

BASIS: SRL EXPERIENCE (RON ROMAN, JOHN GRAY)

RINSE...

OBJECTIVE: REMOVE CHLORIDE & FREE FLUORIDE

CONDITIONS...

HNO_3 ACID	1 OR 2 MOLAR
TEMPERATURE	BOILING VS. AMBIENT

DISSOLUTION...

OBJECTIVE: DISSOLVE > 98% OF Pu CONTENT

CONDITIONS...

HNO_3 ACID	8 OR 10 MOLAR
$AL(NO_3)_3$	0.3 OR 0.4 MOLAR

$AL(NO_3)_3$ USED TO: COMPLEX FREE FLUORIDE
COMPLETE PuF_4 DISSOLUTION
IMPROVE FILTRATION

ASH FEEDSTOCK CHARACTERIZATION

DESCRIPTION...

10kg LANL INCINERATOR ASH
GROUND AND WELL BLENDED

< 88 micron	5.97%
88-177 micron	19.99%
177-354 micron	26.16%
> 354 micron	47.89%

COMPOSITION (WEIGHT %)...

Pu	17.72%
Cl	9.8%
C	1.8%
H	0.3%
Si	10.0%
Fe	15.0%
Al	2.0%
Mg	7.0%
Ca	5.0%
K	5.0%
Na	5.0%

WEIGHT LOSS ON IGNITION 11.3%

DISSOLUTION BEHAVIOR...

"HISTORICAL" VALUES...

Pu CONTENT 16.7%
Pu RECOVERY (SINGLE PASS) AVG. 55.6%

(RANGE: 30.7-85.8%)

THIS MATERIAL...

Pu RECOVERY (SINGLE PASS) 81.1%

HYDROFLUORINATION RESULTS

DURING HYDROFLUORINATION...

Cl REMOVAL	99.6%
Si REMOVAL	99.5%
Pb REMOVAL	100.0%
P REMOVAL	100.0%
NET WIEGHT LOSS	5.3%

OFFGAS LINE WEIGHT GAIN 0.43-2.87 g/100 g ASH
(7.0-42.9% OF EVOLVED WEIGHT)

SLIGHT CRUSTING AND ADHERING PROBLEM WITH MATERIAL

FLUORINE UTILIZATION...

AMOUNT OF ORIGINAL F IN SOLIDS AFTER TREATING 2.9%

BASED UPON NET WEIGHT OF MATERIAL...

REACTION >80% "COMPLETE" AFTER 2 HR
REACTION 100% :COMPLETE" AFTER 4 HR

ACID DISSOLUTION...

Pu RECOVERY EFFICIENCY 92 +/- 3%

NH_4HF_2 FUSION RESULTS

DURING FUSION (OVERALL)...

Cl REMOVAL	82.1%
Si REMOVAL	9.7%

AFTER LOW TEMPERATURE...

OFFGAS LINE WEIGHT GAIN	0.0-1.4 g/100 g ASH (0.0-14.1% OF EVOLVED WEIGHT)
HARD CAKE PRODUCED	

AFTER HIGH TEMPERATURE...

OFFGAS LINE WEIGHT GAIN	???????? (54.6% OF EVOLVED WEIGHT)
	0.5 G/MIN
	3 WT % Si; 19.2 WT% F; 42.2 WT% N
	NO MATERIAL IF T (LINE) > 250^{o}C
NO CAKING IF MATERIAL GROUND	

FLUORINE UTILIZATION...

AMOUNT OF ORIGINAL F IN MATERIAL AFTER FUSION	56.4%
AMOUNT TO OFFGAS AS SiF_4	

ACID DISSOLUTION...

Pu RECOVERY EFFICIENCY	98 +/- 5(?)%

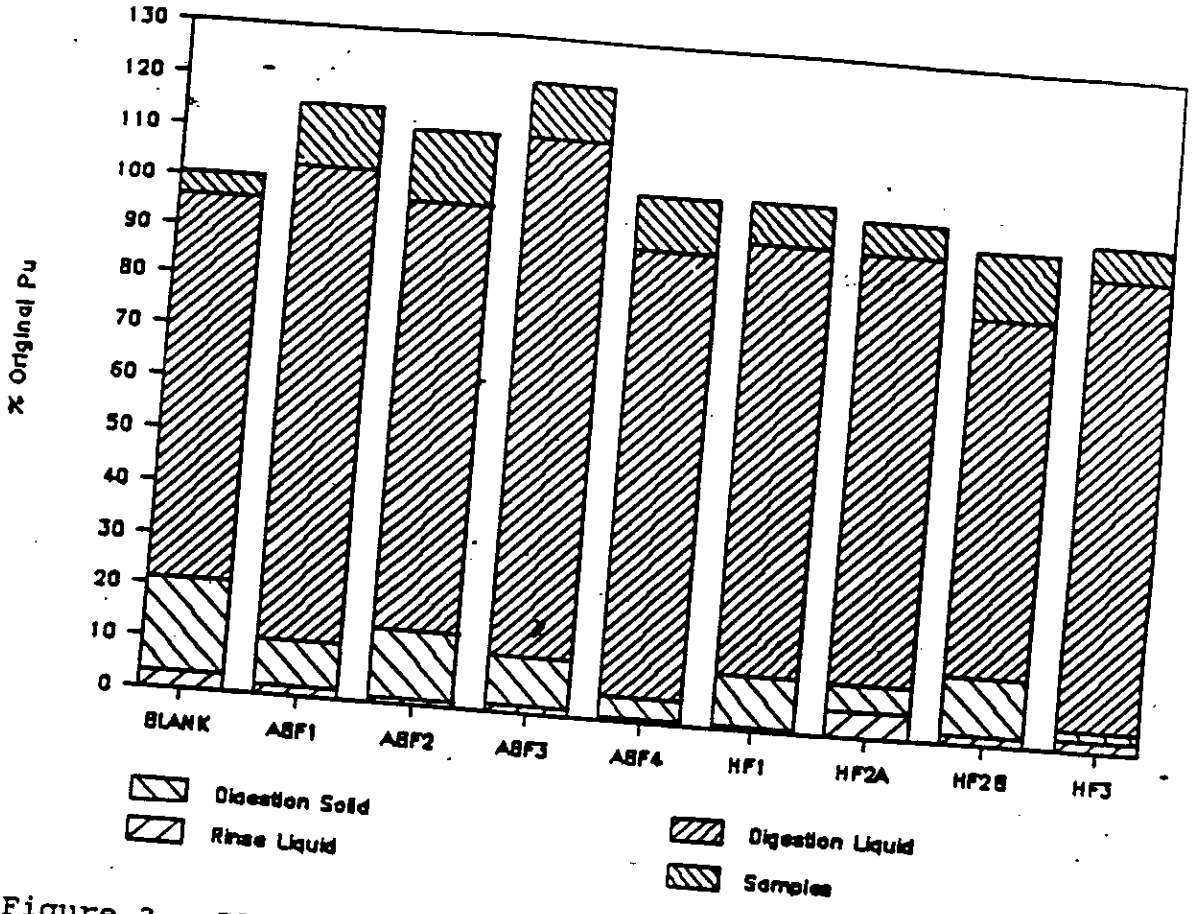

Figure 3. Plutonium material balances.

EQUIPMENT DEVELOPMENT EFFORT

EED...

BRUCE GOODWIN	REACTOR SELECTION
DAVE STEWARD	OFFGAS SCRUBBER
DAN MAESTAS	HEIR APPARENT

246-F INSTALLATION..

SCOTT TROTTER

ESD/ETC...

GEORGE SCHURR	REACTOR SELECTION
JIM DUNSON	OFFGAS CONCERNS

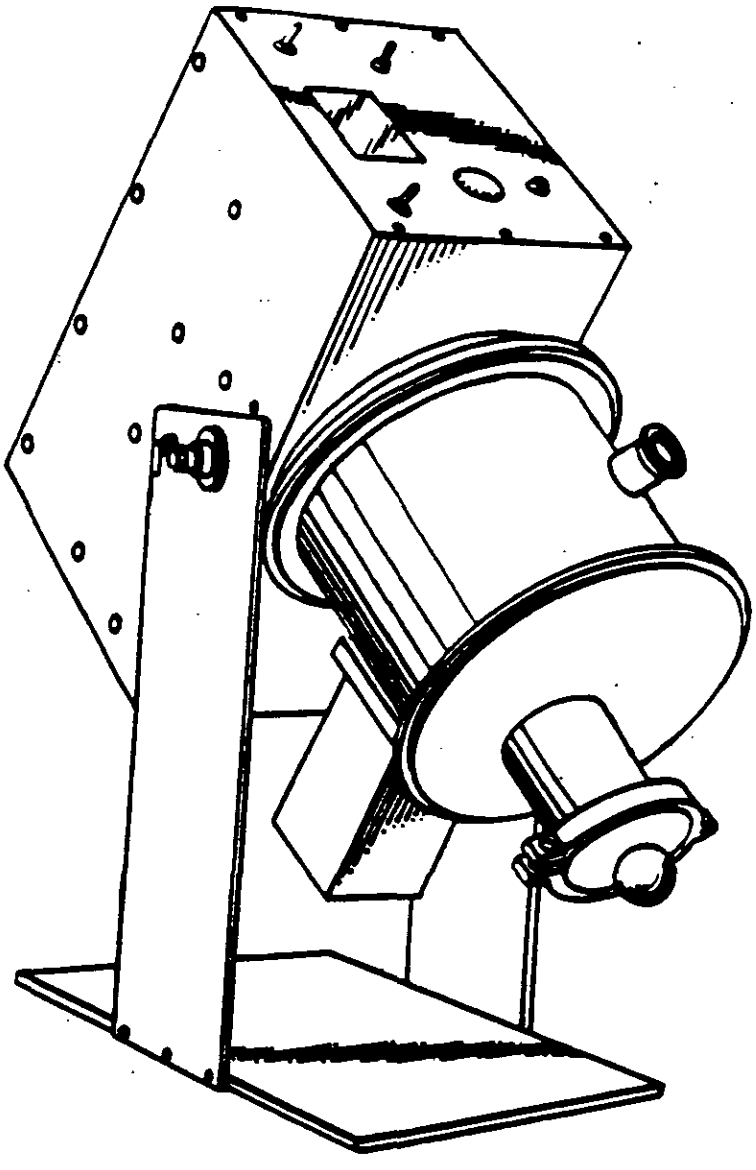

FIGURE 2