ORIGINAL

Rockwell Hanford Operations

SUPPORTING DOCUMENT

Number	SD-WM-PTR-003
Rev. Ltr./Chg. No.	Rev. 0
Page	1 of 16
Total Pages	16

PROGRAM: WASTE ENCAPSULATION

Document Title: Process Test Report for Silver Decontamination of Strontium in the Waste Encapsulation and Storage Facility (WESF)

Baseline Document ☐ Yes ☒ No

WBS No. or Work Package No. WE42C

Key Words: Strontium, Silver, Strontium Fluoride, WESF, Process Test, Impurity, Encapsulation, Ammonia

Prepared by (Name and Dept. No.) K.S. Kalkofen 65920 — Kimberly S. Kalkofen — Date 7/25/84

See reverse side for additional approvals

THIS DOCUMENT IS FOR USE IN PERFORMANCE OF WORK UNDER CONTRACTS WITH THE U.S. DEPARTMENT OF ENERGY BY PERSONS OR FOR PURPOSES WITHIN THE SCOPE OF THESE CONTRACTS. DISSEMINATION OF ITS CONTENTS FOR ANY OTHER USE OR PURPOSE IS EXPRESSLY FORBIDDEN.

Abstract

Silver decontamination of strontium in WESF through use of ammonia complexation of silver was successful in that WESF strontium processing could be continued. Ninety-nine percent removal of silver contamination in B Plant eliminates the need for any future ammonia complexation in WESF.

*	Distribution	Name	Mail Address
*	LLL	Adams	MO-400/200E
	JF	Albaugh	2750E/200E
*	WB	Barton	271B/200E
	JS	Buckingham	222S/200W
*	LL	Buckley	2750E/200E
*	RF	Carlstrom	MO-400/200E
*	EK	Carter	MO-400/200E
*	JC	Fulton	271B/200E
	KA	Gasper	271B/200E
	RL	Hibbard	271B/200E
*	RW	Higbee	271B/200E
*	KS	Kalkofen	231-Z/200W
*	JH	Kessner	MO-400/200E
*	DL	Lamberd	MO-400/200E
*	JH	Rasmussen	MO-400/200E
	IE	Reep	271B/200E
*	RH	Rieck	271B/200E
	JP	Sloughter	2704S/200W
*	DK	Steiner	MO-400/200E
*	MW	Stevenson	MO-400/200E
*	CS	Sutter	MO-400/200E
	TB	Veneziano	2750E/200E
*	RL	Weiss	222S/200W
*	ST	Willett	271B/200E
*	Central Files (2)		
	Department of Energy, Richland Operations Office		
	NT	Karagianes	Fed/700
*	JK	Wukelic	Fed/700

(Continued on reverse side)

*COMPLETE DOCUMENT (No asterisk, title page/summary of revision page only)

L. D. Randal, MSA-CRM, 6/12/2019

Approved for Public Release;
Further Dissemination Unlimited

Release Stamp

OFFICIALLY RELEASED
SEP 4 10 59 AM '84

Prepared By: _____

Used By: _____

Rockwell Hanford Operations

Page	Number	SUPPORTING DOCUMENT
2	SD-WM-PTR-003	

Approvals

- [x] L E Rogers 8/9/84 — Program Office
- [x] [signature] for B. — Research and Engineering
- [x] RW Higher 8/8/84 — Plant Operations
- [ ] Health, Safety and Environment
- [ ] Quality Assurance
- [ ] Training
- [ ] End Function
- [ ] End Function
- [ ]
- [ ]
- [ ]
- [ ]
- [x] MW Stevenson — Approval Authority

* Distribution	Name	Mail Address

TABLE OF CONTENTS

	PAGE
SUMMARY	4
INTRODUCTION	4
RESULTS AND DISCUSSION	9
pH Adjustment	9
Increased Caustic Addition	9
Processing Time Constraint	10
Filtrate Rework	10
Product Purity	10
Equipment Failure/B Cell Maintenance	11
REFERENCES	16
TABLES	
I. Process Test Evaluation Summary for Silver Decontamination of Strontium in WESF	12
II. Filtrate Sample Results for Process Test	15
FIGURES	
1. SrF_2 Flowsheet	6
2. Modified SrF_2 Flowsheet	7
3. TK-B-1 Feed Sample Results	8

PROCESS TEST REPORT FOR SILVER DECONTAMINATION OF STRONTIUM IN THE WASTE ENCAPSULATION AND STORAGE FACILITY (WESF)

SUMMARY

The strontium fluoride (SrF_2) process test, incorporating the use of ammonium hydroxide (NH_4OH) for silver complexation, was initiated on March 6, 1984 and completed on July 10, 1984. During the process test, 4.2 megacuries of strontium were processed in 32 runs with minimal processing problems and relatively few equipment failures. A total of 51 product capsules and 42 waste capsules were produced. More waste capsules than usual were produced because of processing difficulties introduced by the silver impurity. Although the process test proved succesful in that WESF was allowed to continue strontium processing, the addition of NH_4OH will not be implemented into the strontium fluoride flowsheet. B Plant has experienced great success in removing 99 percent of the silver from the strontium feed through addition of NaCl during the caustic strike process (Ref. 1). Ammonium hydroxide addition for silver complexation will not be required in future Waste Encapsultion and Storage Facility (WESF) campaigns.

INTRODUCTION

Beginning in mid-January 1984, with the caustic strike 83-2 product, WESF experienced major processing problems as a result of tremendous black solid formation in strontium feed during pH adjustment. It was impossible to run the strontium fluoride process because of severe line and filter pluggage. The sticky, dark gray material was unacceptable as SrF_2 product because of obvious impurity contamination. Through laboratory and engineering tests, the impurity was found to be silver at a molarity of 1.69×10^{-2} M. The results from a feed sample analysis are shown in figure 3. This silver formed a dark colored silver oxide (AgO) precipitate during the pH adjustment of the strontium nitrate ($Sr(NO_3)_2$) feed received from B Plant.

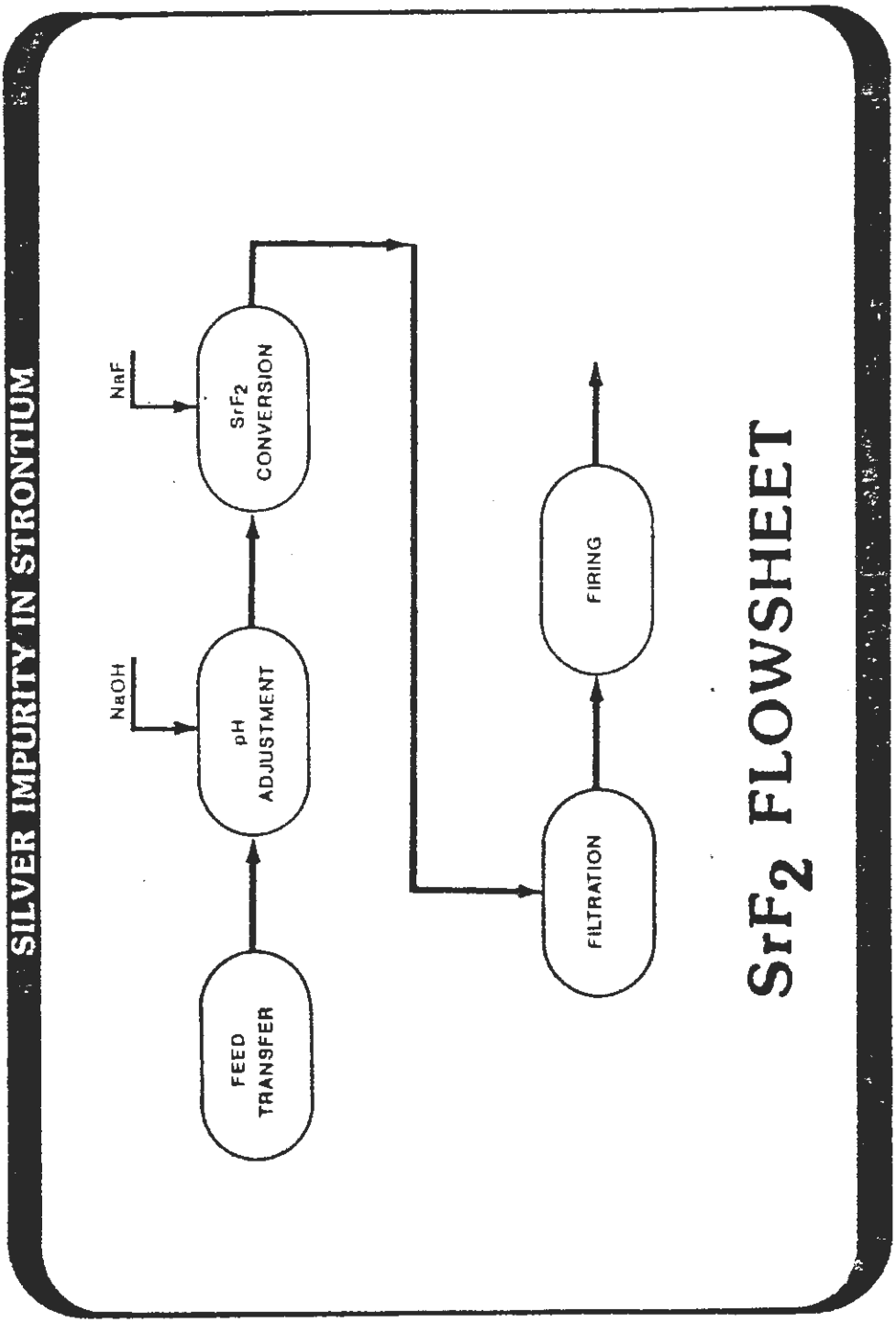
Silver contamination probably originated during PUREX silver reactor charging. This silver material, when spilled, was routed with other PUREX waste to Tank Farms. During PAS processing of this waste at B Plant, the silver followed the strontium through centrifugation and solvent extraction in a +1 or +2 oxidation state. Silver precipitated as Ag_2SO_4 with strontium sulfate during sulfate precipitation and as Ag_2CO_3 during metathesis. While silver would be expected to precipitate during caustic strike and be removed from the strontium, lab studies indicate that significant quantities of silver can remain in the strontium supernatant. Residual amounts of ammonia in semi-purified strontium may have prevented silver precipitation and removal during caustic strike.

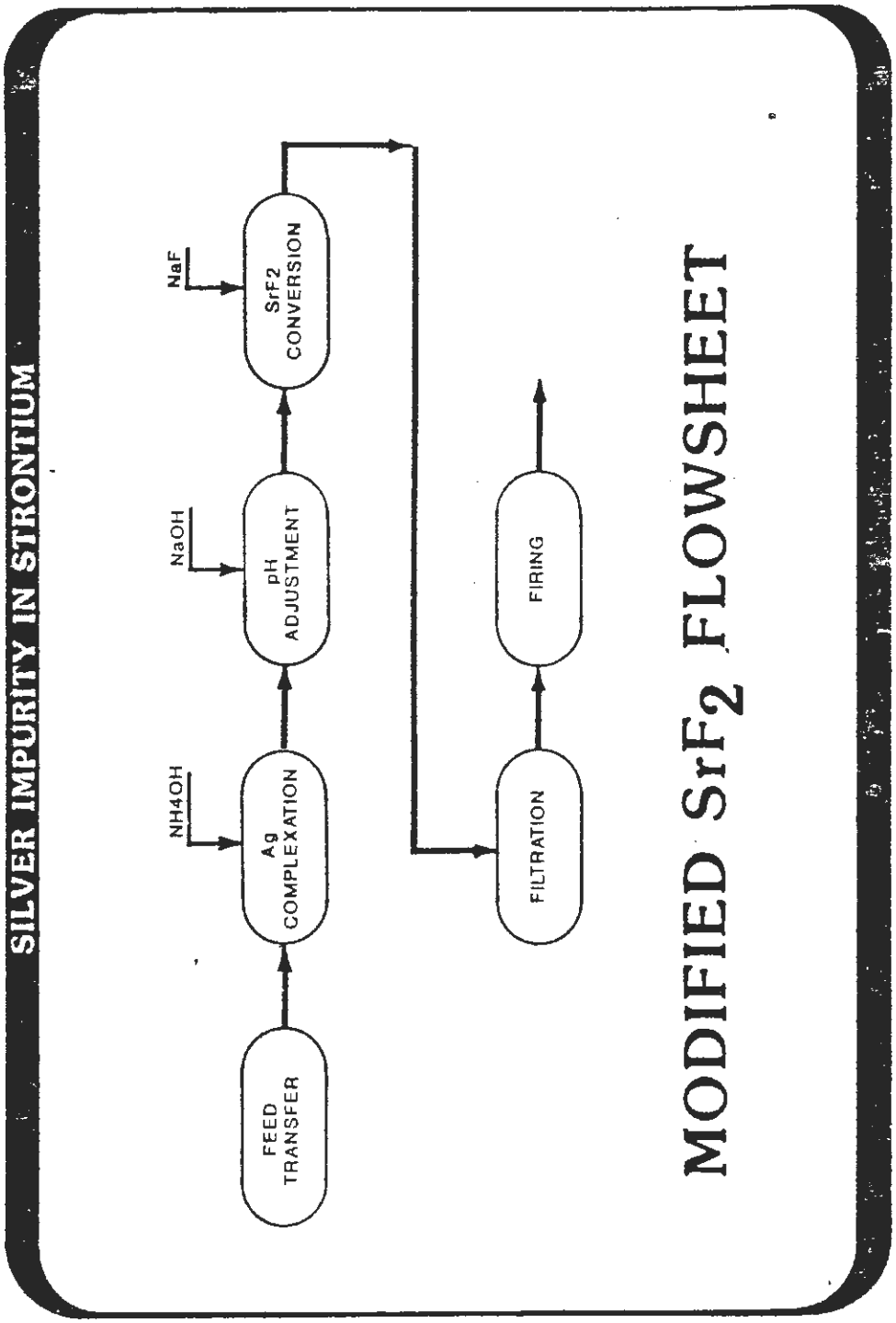
To make feasible continued WESF strontium processing, four immediate processing options were identified by the chemical laboratory:

- Acidic SrF_2 Precipitation (WESF)
- AgO Precipitaion /Decantation (B Plant)
- AgCl Precipitation /decantation (B Plant)
- $Ag_x(NH_4)_y$ Complexation (WESF)

Consideration was given to the overall effectiveness of the individual processing options as well as to process flowsheet compatibility, time cycle, and any potential safety hazards. Preliminary in-cell and laboratory tests showed that all four processing alternatives were effective in precipitating/complexing the silver. From the standpoint of flowsheet compatibility and time constraint, ammonia complexation of silver at WESF proved most feasible. The safety concerns of ammonia use in B cell were addressed (Ref. 2), specifically K-3 filter pluggage, ammonium nitrate formation, hazardous silver compound formation, ammonia impacts on capsule integrity and the levels of ammonia used. No signficant safety hazards related to these areas were found.

During laboratory tests, it was found that the silver could be complexed sufficiently in a 1 to 1 ammonia to silver mole ratio. Ammonia, in the form of NH_4OH was added to the $Sr(NO_3)_2$ feed before the pH adjustment with NaOH (Figure 1). This resulted in only one additional step to the original SrF_2 flowsheet (Figure 2). A process test procedure, PTP-E-995-00001, incorporating the use of NH_4OH into the SrF_2 process was written (Ref 3). The $Sr(NO_3)_2$ solution in TK-39-5 (CS-83-2) was processed in 32 runs under this process test.


SILVER IMPURITY IN STRONTIUM
NaOH
NaF
FEED TRANSFER
pH ADJUSTMENT
SrF2 CONVERSION
FILTRATION
FIRING
SrF2 FLOWSHEET



MODIFIED SrF_2 FLOWSHEET

TK-B-1 FEED SAMPLE RESULTS

RUN #84-9

Sr Concentration: 1590 Ci/L

pH: 2.1

Visual: Clear, No Solids

Element	Molarity
Ag	1.69×10^{-2}M
H^+	2.5×10^{-1}M
Al	$<3.13 \times 10^{-3}$M
Ba	6.1×10^{-2}M
Ca	1.79×10^{-2}M
Cd	$<1.79 \times 10^{-4}$M
Cr	$<1.93 \times 10^{-4}$M
Fe	1.28×10^{-3}M
Mg	1.84×10^{-3}M
Mn	$<7.32 \times 10^{-3}$M
Na	4.73 M
Pb	$<9.7 \times 10^{-4}$M
Sr	2.84×10^{-1}M

FIGURE 3

RESULTS AND DISCUSSION

Results of the process test are summarized in Table I and II. Table I provides the overall summary of the test through documentation of each run. Table II summarizes the effectiveness of silver complexation, accuracy of pH adjustment, and other trends exemplified in filtrate sample results. The only criteria established for this process test was the ability of WESF to process strontium nitrate into an encapsulatible strontium fluoride without experiencing major processing difficulties. This objective was achieved. There were, however, some operational difficulties encountered during this process test. These difficulties are documented below.

pH ADJUSTMENT

In normal strontium processing at WESF, $Sr(NO_3)_2$ feed is adjusted to pH = 8.5 for neutralization and subsequent prevention of HF formation. HF is corrosive to stainless steel, the material of the tanks and lines in B Cell. At a pH $\geq$ 11, strontium begins to precipitate as $Sr(OH)_2$ rather than SrF_2. A ph = 8.5 guarantees neutralization of the feed and precludes $Sr(OH)_2$ precipitation.

For this process test, it was decided to adjust the feed to pH = 7 to ensure neutralization but to prevent as much AgO precipitation as possible. It was observed that the quantity of AgO precipitate increases with increased NaOH addition.

During the process test, insufficient caustic addition (pH<4) resulted in rework batches. It was surmized that the free H^+ competed with strontium for the fluoride ion allowing the soluble $Sr(NO_3)_2$ to pass into the filtrate. Excess caustic addition (pH>7) resulted in more AgO precipitation and the possibility of $Sr(OH)_2$ formation at pH>11.

INCREASED CAUSTIC ADDITION

The $Sr(NO_3)_2$ solution in TK-39-5 had a very high H^+ concentration (H^+ = 0.64M). This feed solution to WESF required more than 2000 grams (NaOH) per run to neutralize the H^+. In an effort to speed pH adjustment and minimize TK-B-5 volume, the molarity of the caustic used was increased from 0.1 M to 4.0 M. This measure improved processing in that larger runs could be processsed within TK-B-5 volume constraints. However, the higher concentration introduced more potential for operator error as it was easy to either under- or overshoot the desired pH of 7. This is seen in the pH results of the four TK-B-4 filtrate samples taken during the process test (Table II). Operator exposure to high radiation levels during sample load-out to the laboratory prevented more sampling.

PROCESSING TIME CONSTRAINT

During processing with NH_4OH, it was discovered that the $Ag_x(NH_4)_y$ complex degrades over time, wherein the free Ag ion forms the dark colored AgO precipitate. It is not known what causes this dissociation as the phenomenon was never duplicated with the "cold" laboratory sample. Radiolytic heat and/or radiation effects may be responsible. In an attempt to overcome this problem, NH_4OH addition was doubled, then tripled over stoichiometric requirements. This showed little effect. Operations was informed to commence with pH adjustment, NaF addition, digestion, and filtration as quickly as possible after NH_4OH addition so as to minimize AgO precipitation. Minimizing the time between steps helped to reduce AgO precipitations.

FILTRATE REWORK

As can be seen from Table II, the pH adjustment step in the SrF_2 process was difficult to perform correctly. Operators found themselves having to pH adjust quickly because of the time constraint with AgO precipitation, but also having to adjust correctly to a pH of 7. Five rework batches were required as a result of insufficient caustic addition. The $Sr(NO_3)_2$ feed received from B Plant had a very high H^+ concentration. Unneutralized H^+ competes strongly for fluoride ion (Ref. 4), allowing strontium to pass into the filtrate as the soluble $Sr(NO_3)_2$. The filtrate must be reworked to remove the strontium as a solid strontium fluoride.

PRODUCT PURITY

Because of insufficient ammonia complexation of silver and subsequent AgO precipitation, the SrF_2 product from this process test does contain silver contamination. According to sample results, only 16 to 31 percent of the silver in the $Sr(NO_3)_2$ feed was accounted for in the filtrate (Table II). Conversely, essentially all of the ammonia was accounted for in the filtrate. It is doubtful that all of the remaining silver was contained in the filter cakes. TK-B-4 filtrate samples were not neccesarily representative of the tank contents since silver precipitates with time as AgO and would not be seen in the sample analysis. It is estimated that 20 percent of the silver in the feed remains in the SrF_2 product. Silver is not corrosive and should have no effect on capusle integrity.

Fired SrF_2 product was often hardened and difficult to remove from the furnace boats. Air chiseling was required for product removal and breakup. Because of filter and line pluggages, the demineralized water back wash of the filter cake was sometimes in feasible. When the back wash is not performed, high sodium levels are observed in SrF_2 filter cake. Sodium nitrate contributes to hardened SrF_2 product and consequent difficult product handling.

EQUIPMENT FAILURE/B CELL MAINTENANCE

WESF experienced more equipment failures than usual during this process test. Most of the equipment problems centered around filtration. Filtration manifold pluggages were frequent as were failed manifold valves. Sticky AgO precipitate was the cause of this pluggage. Caustic valves also failed more often. This may be attributed to the 40 fold increase in caustic concentration for pH adjustment of the feed.

The most costly and noticeable failure was filter cartidge loss due to pore pluggage. AgO precipitate and high $NaNO_3$ resulting from no demineralized water back wash plugged the $\leq$20 micron filter cartridge pores. These plugged pores prevented a good vacuum and successful filtration. Historically, a set of four filters averages 8 strontium runs before plugging. During this process test, a set of four filters averaged only three runs before plugging.

The WESF clean cell policy was much more difficult to abide by during this process test because of the nature of the silver impurity. In trying to flush lines, water would be spilled on the B cell deck and floor and to the sump. Neither NaOH nor HNO_3 were effective in dissolving and rinsing away the AgO spilled in B cell. B cell was eventually cleaned through periodic dry sweeping and disposal in waste drums.

TABLE I

PROCESS TEST EVALUATION SUMMARY FOR SILVER DECONTAMINATION OF STRONTIUM IN WESF

Run No.	Date Transferred	Transfer Volume (ℓ)	Sr (M)	Ag (gmoles)	NH_4OH (gmoles)	NaOH Addition (gmoles)	NaF Addition (grams)	Processing Comments
84-5 (A)	3/06/84	20	0.31	0.40	0.44	58.4	1000	Processing Improved
84-5 (B)	3/07/84	50.3	0.31	1.01	1.10	32	1500	Product: Light gray
84-6	3/08/84	74.9	0.31	1.50	1.80	28	2500	
84-7	3/13/84	75.3	0.34	1.65	1.92	19.2	2500	B-5-N plugged Rework required 255 ci/ℓ in TK-B-4
84-8	3/19/84	74.5	0.38	1.83	2.14 (requested)	29.4	3000	NH_4OH inadvertently not added. Severe AgO precipitation.
84-9	3/29/84	80	0.38	1.95	2.50	NA	3500	Rework required - 53 ci/ℓ pH = 1.54 in TK-B-4
84-10	3/31/84	80	0.38	1.95	2.50	NA	4000	Dark colored product
84-11	4/02/84	80.5	0.38	1.96	3.01	NA	4000	Good pH, good off-white product
84-12	4/04/84	85	0.38	2.08	3.20	NA	4000	Off-white product
84-13	4/06/84	84.7	0.38	2.07	3.20	NA	3500	Good, off-white product.

TABLE I
(CONT.)

Run No.	Date Transferred	Transfer Volume (ℓ)	Sr (M)	Ag (gmoles)	NH_4OH (gmoles)	NaOH Addition (gmoles)	NaF Addition (grams)	Processing Comments
84-14	4/13/84	90	0.27	1.57	3.20	NA	3000	Good, white product
84-15	4/16/84	94.6	0.32	1.95	3.76	NA	3500	Filtering problems
84-16	4/18/84	95	0.32	1.96	3.76	NA	3500	
84-17	4/30/84	80	0.38	1.96	4.32	NA	4000	Rework required
84-18	5/03/84	85	0.38	2.08	4.32	NA	4000	Filtering problems because of time constraint
84-19	5/07/84	90	0.38	2.20	4.32	NA	4000	Filtered well
84-20	5/11/84	94	0.34	2.06	4.32	80	4000	Filtering problems
84-21	5/14/84	90.5	0.34	1.96	6.08	NA	4000	
84-22	5/21/84	90.5	0.38	2.19	6.08	18	4000	Rework required 747 ci/ℓ in TK-B-4
84-23	5/24/84	90.5	0.38	2.19	6.08	NA	4000	Some filtering problems
84-24	5/29/84	90.3	0.38	2.19	7.60	NA	4500	Processed okay gray product
84-25	5/30/84	90	0.38	2.18	7.60	88.4	4000	Light gray product

TABLE I
(CONT.)

Run No.	Date Transferred	Transfer Volume (ℓ)	Sr (M)	Ag (gmoles)	NH_4OH (gmoles)	NaOH Addition (gmoles)	NaF Addition (grams)	Processing Comments
84-26	5/31/84	90	0.38	2.18	7.6	NA	4000	Lines plugged, filtering took 16 hours
84-27	6/04/84	90	0.38	2.18	7.6	96	4000	B5N plugged
84-28	6/06/84	92	0.38	2.23	7.6	76	4000	Top filter manifold plugged
84-29	6/07/84	92	0.38	2.23	7.6	NA	4000	Filters #1 & #3 plugged. Rework required because filter pot burst
84-30	6/12/84	90	0.38	2.18	7.6	20	4000	Filter cake almost white. Rework required
84-31	6/25/84	90	0.38	2.18	7.6	42	4000	Filtered slowly. NH_4OH/NaF addition time was too long
84-32	6/26/84	90	0.38	2.18	7.6	66	4000	Filter cake very hard
84-33	6/28/84	90	0.34	1.95	7.6	NA	3500	Dilute feed from TK-39-5 filtered slowly, lines plugged
84-34	7/03/84	90	0.28	1.56	7.6	64	3000	2nd dilute run
84-35	7/05/84	90	0.23	1.36	7.6	37.6	2500	3rd dilute run
84-36	7/09/84	82	0.19	1.02	7.6	7.0	2000	Last dilute run TK-39-5 is below dip leg

TABLE II

FILTRATE SAMPLE RESULTS FOR PROCESS TEST

TK-B-4 Sample No.	Run No.	Adjusted pH	Ag (%complexed)	NH_3 (%Recovered to filtrate)	Sr (ci/ℓ)
B2948	84-5A	8.4	20	100+% *	4.8
B2965	84-5B	11.4	16	24	6.9
B3423	84-9	1.54	31	97	53
B4552	84-22	0.90	—	—	747

* 110% based on sample result calculations.

REFERENCES

1. SD-WM-PTR-006, "Process Test Report for Silver Decontamination of Strontium in B Plant", July 13, 1984, S.T. Willett.

2. Letter 65920-84-047, March 6, 1984, S.M. Joyce to D.L. Lamberd, "Safety Concerns of Ammonia Use in B Cell".

3. PTP-E-995-00001, "Prepare Strontium Fluoride" (Procedure), March 6, 1984, K.S. Kalkofen.

4. Letter 65453-81-353, November 10, 1981, J.R. Jewett to S.T. Willett, "Fluoride Monitoring in the Waste Encapsulation and Storage Facility (WESF) Strontium Process".

5. PFD-E-903-00001, "Waste Encapsulation and Storage Facility Strontium Fluoride Flowsheet", Revised March 1984, K.S. Kalkofen.

6. SD-WM-PTP-006, "Process Test for Silver Decontamination of Strontium in B Plant", April 1984, S.M. Joyce.

7. Letter 65920-84-056, March 15, 1984, S.M. Joyce to J.S. Buckingham and W.B. Barton, "Silver - Strontium Separation in B Plant".