ACC. NO. 120044

DPST-83-932

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

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MEMORANDUM

October 19, 1983

TO: M. A. EBRA

FROM: R. E. EIBLING, B. A. HAMM
REE BAH

DEMONSTRATION OF IN-TANK SLUDGE PROCESSING PART II.
EFFECT OF PROCESSING ON RADIONUCLIDES

INTRODUCTION

The scope and cost of the Defense Waste Processing Facility have been significantly reduced by adding in-tank sludge processing to the process flowsheet. A demonstration of in-tank processing was recently completed and the achievement of the major goals described in a previous memo.[1] This memo describes the effect of in-tank sludge processing on the radionuclides in the waste. This memo will also identify those areas that will require further work both before and during the next scheduled in-tank sludge processing batch.

SUMMARY

In-tank processing of sludge:

- o Did not change the distribution of radionuclides between sludge and supernate during aluminum dissolution.
- o Produced some dissolution of Se-79, Tc-99, Sb-125, and Eu-154, 155 during washing.

Quantification of the partition ratios will require improved analytical methods or procedures.

- o Analyses of Sr-90, Se-79, and Tc-99 in solids need to be improved. Analytical results for these radionuclides on duplicate samples currently vary by as much as four orders of magnitude.
- o Methods are needed for low level gamma emitters in supernate.
- o Consistent reporting of all radionuclides detected during gamma spectrum analysis is needed.
- o The rare earths such as Eu or Ce should not be determined on solids dissolved by the acid bomb procedure.

DISCUSSION

The key processes relative to the radionuclides are aluminum dissolution and sludge washing. Each of these will be discussed after a review of the sample analyses procedures is given. Included with each discussion will be chronological tables of the measured results.

I. Experimental Procedure

A complete description of the sampling schedule, in-tank sampling procedure and high level cells sample handling procedure was given in DPST-83-638. Therefore, the only procedures that shall be described are related specifically to chemical analysis. These analytical procedures include sample dissolution for solids analysis.

After sample preparation in the shielded cells, the samples are transferred to Analytical Development Division in four-milliliter vials. Liquid samples are monitored for activity and diluted to acceptable radiobench handling levels. Solids are dissolved by either of two specified procedures.

Acid bomb dissolution consists of placing 200 milligrams of solids in a Parr bomb, adding both hydrochloric and hydrofluoric acid and heating to about 250°C. The liquid is then diluted volumetrically to 100 ml and monitored to see if further dilution is required.

Sodium peroxide fusion dissolves 500 milligrams of solids by fusing with 5 grams of sodium peroxide followed by addition of HCl and dilution to 200 ml. Samples of the final solutions are analyzed by the required method and reported in activity/ml. For supernate samples the result can be used directly. Results for solids are corrected for dissolution and are expressed as activity/gram solids.

Radionuclide analyses are of three different types. Gamma-emitting fission products are analyzed by gamma spectroscopy. For high levels of gammas such as Cs-137 the result is reported with no further work. Trace levels of other fission products are usually swamped by the cesium spectrum and cesium must be removed prior to analysis. Phosphotungstic acid is used to precipitate the cesium and the precipitate is removed before counting.

Fission products that emit beta particles require individual separation procedures to enable accurate liquid scintillation counting. Plutonium is extracted separately and the alpha particles counted.

II. Experimental Results

A. Aluminum Dissolution

The goal of the aluminum dissolution phase of the demonstration was to dissolve 75 percent of the aluminum in sludge. Another goal was to determine if aluminum dissolution would alter the portion of the radionuclides that were insoluble. For that reason, as many radionuclides as possible were monitored while sodium hydroxide was added and the tank was heated to 85°C. Table II.A.1 gives the tank volume, volume percent solids, density and weight percent insoluble solids. Tables II.A.2 and II.A.3 specify the amount of soluble and insoluble radionuclides found during sludge sampling. In general, the sample results varied over a wide range making analysis of the chemistry difficult.

No detectable trends were observed during the aluminum dissolution process. This conclusion is based on both soluble and insoluble Cs, Pu, Sr, Tc, and Se. For Ru-106 it is based on soluble data and for Eu and Sb it is based on solids data. Conclusions were not possible for Co-60 since very few results were reported for samples from either aluminum dissolution or sludge washing steps. Figure II.A.1 is an example of the solids data for Eu-154 and reveals both the wide range of results and the lack of a trend. The graph also illustrates that Eu analysis by acid bomb dissolution is consistently lower than that by sodium peroxide fusion dissolution. Such a result suggests that insoluble rare earth fluorides can be formed during acid bomb dissolution and therefore, rare earths should be analyzed by peroxide fusion dissolution.

B. Washing and Settling

After aluminum dissolution the sludge was washed to remove the soluble salts and Cs-137. The goal was to reduce the soluble salts to less than 2% of the sludge on a dry weight basis. During this process other radionuclides could be transferred to the supernate and would then go through the salt decontamination process. Both soluble and insoluble forms of the radionuclides were monitored during the washing process. Tables II.B.1 and II.B.2 list the results found for soluble and insoluble radionuclides respectively. In general, the data shows large scatter thus making the analysis difficult. Averaging the data does not improve the picture because the sample analysis varied over orders of magnitudes. The source of the scatter could have been in the shielded cells sample preparation procedure or in the analytical procedures used by the Analytical Development Division.

Soluble radionuclides will follow dilution during washing if no further dissolution occurs. Figure II.B.1 compares Cs-137 found with the predicted level based on dilution. By this analysis Cs, Pu, and Sr follow dillution and are not being dissolved from the waste.

In contrast the graphs for Se-79 and Tc-99 shown in Figures II.B.2 and II.B.3 indicate dissolution of the radionuclide from the sludge. A final value for Se is not shown since the level was below our detection limits by current methods. The solids data for these two nuclides has so much scatter it is not possible to confirm the result based on a reduction in the insoluble levels.

Ruthenium was not reported in either the solids or the liquids during washing and will require improved methods in the future. Solids analysis for Eu and Sb reveals an overall decrease in the insoluble levels. Figures II.B.4 and II.B.5 display log (curies) versus the process step number where 4 is predissolution, 7 was post dissolution, 10 was after first wash, 13 was after second wash, and 18 was after the final wash. Antimony is probably present as the anion, antimonate. A search of the literature confirmed that Europium solubility increases from pH 12 to pH 14.[2] Confirmation of either dissolution could not be verified by supernate analyses since neither were reported by Analytical Development Division.

QUALITY ASSURANCE

The Quality Assurance Program that covers the in-tank demonstration support is described in DPSTQA-82-2-59. Throughout the demonstration, results were recorded on written procedure sheets or in technical notebooks. To improve the quality of data, chemical analyses were done on multiple samples and the results averaged. In some cases different methods of analysis were applied. Technical notebooks used during the demonstration were DPSTN-3381, 4009, and 4024.

REE,BAH:pmc
Att
#5

REFERENCES

1. HAMM, B. A., EIBLING, R. E., and FOWLER, J. R., "Demonstration of In-Tank Sludge Processing Part I. Aluminum Dissolution, Sludge Washing and Settling Results," DPST-83-668, July 12, 1983.

2. KRAGTEN, J., Atlas of Metal-Ligand Equilibria in Aqueous Solution, 272-273, 1978.

TABLE II.A.1

PHYSICAL PROPERTIES

Sample ID	Tank Volume Liters X 10^6	Volume Percent Solids	Density kg/l	wt% Insoluble Solids
5A-1	1.06	40.0	1.17	10.6
5A-2	1.06	37.1	1.20	10.1
5B	1.16	----	----	----
5C	1.58	24.3	1.23	7.8
5D	1.68	18.4	1.23	6.8
5E	1.96	14.6	1.25	4.1
5F	2.13	15.0	1.25	4.3
5G	2.19	15.7	1.25	4.0
5H	2.29	14.3	1.26	3.3
5I	2.33	12.1	1.22	2.8
5J	2.36	10.0	1.23	3.2
5K	2.39	10.0	1.22	2.7
5L	2.41	8.6	1.24	2.7
5M	2.44	9.9	1.24	2.4
5N	2.46	8.5	1.24	2.1

TABLE II.A.2

SOLUBLE RADIONUCLIDES DURING Al DISSOLUTION

Sample	Se-79 Curies	Sr-90 Curies	Tc-99 Curies	Ru-106 Curies	Cs-137 Curies	Pu Curies
5A-1	---	---	---	---	---	---
5A-2	---	---	---	---	---	---
5B	---	---	---	---	---	---
5C	---	---	---	---	---	---
5D	5.45	---	117	10000	12500	15.0
5E	1.27	2760	182	206	268000	14.7
5F	1.52	---	122	11900	251000	---
5G	23.0	6420	93.1	165	321000	16.3
5H	1.32	1590	204	249	347000	22.9
5I	1.29	1880	121	229	354000	20.9
5J	1.82	4890	110	215	194000	19.7
5K	3.80	3880	103	219	303000	18.5
5L	2.59	3610	157	276	313000	17.8
5M	1.31	1800	147	233	356000	16.7
5N	2.54	13600	660	246	341000	19.6

TABLE II.A.3

INSOLUBLE RADIONUCLIDES DURING Al DISSOLUTION

	Se-79		Sr-90		Tc-99	
Sample	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies
5A-1	---	31.6	---	7.81E+3	---	298.
5A-2	401.	35.6	4.50E+5	8.89E+3	195.	12300.
5B	76.0	25.9	3.96E+5	4.25E+3	165.	40.4
5C	---	---	---	---	---	---
5D	106.	80.6	6.25E+6	2.23E+6	442.	431.
5E	69.6	37.1	1.99E+6	2.56E+6	3590.	537.
5F	70.1	530.	1.86E+6	3.20E+6	448.	355.
5G	53.2	64.6	8.26E+5	2.37E+6	1430.	215.
5H	52.2	39.9	1.71E+6	2.50E+6	448.	249.
5I	49.2	19.7	4.63E+5	2.70E+6	155.	323.
5J	52.3	54.2	1.68E+6	1.67E+6	484.	741.
5K	61.4	24.3	2.03E+6	3.18E+6	110.	148.
5L	50.5	22.3	4.65E+6	4.79E+6	319.	126.
5M	---	42.1	---	1.67E+6	---	639.
5N	---	43.4	---	3.40E+6	---	1110.

TABLE II.A.3, cont'd

INSOLUBLE RADIONUCLIDES DURING Al DISSOLUTION

	Sb-125		Cs-137		Eu-154*	
Sample	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies
5A-1	---	916.	---	56300.	---	30100.
5A-2	6120.	1150.	38700.	43000.	15600.	27800.
5B	5290.	512.	47400.	67200.	6440.	28200.
5C	---	---	---	---	---	---
5D	7370.	6520.	62000.	5760.	23600.	38800.
5E	---	---	---	---	33000.	37000.
5E	7070.	5840.	1880.	60800.	11900.	2150.
5E	---	382.	---	---	---	34100.
5F	7530.	6540.	44300.	74100.	12500.	41000.
5F	---	---	---	---	---	25200.
5G	6380.	3980.	23800.	70900.	24700.	179000.
5H	---	2200.	30100.	57100.	24800.	31000.
5H	---	---	---	---	---	31200.
5I	6090.	---	22500.	52500.	3540.	30400.
5I	4140.	---	---	---	---	33300.
5J	7980.	---	32800.	60200.	26300.	37000.
5J	---	---	---	---	---	36900.
5K	7120.	---	25000.	59400.	5060.	30800.
5K	7890.	---	---	---	---	33900.
5L	6840.	8360.	53800.	62300.	15700.	49900.
5L	---	---	---	---	---	40400.
5M	---	2450.	---	62300.	---	14800.
5M	---	---	---	---	---	38500.
5N	---	---	---	6510.	---	4330.
5N	---	---	---	---	---	34900.

* Eu-155 was also detected and reported although not listed here.

TABLE II.A.3, cont'd

INSOLUBLE RADIONUCLIDES DURING Al DISSOLUTION

	Pu	
Sample	Acid Curies	Na_2O_2 Curies
5A-1	---	1980.
5A-2	9150.	29700.
5B	11200.	49000.
5C	---	---
5D	9790.	11700.
5D	---	---
5E	3970.	3890.
5E	---	---
5E	---	---
5F	81.2	12900.
5F	---	---
5G	8490.	10600.
5H	7340.	2230.
5H	---	---
5I	2010.	9660.
5I	---	---
5J	1070.	10800.
5J	---	---
5K	2140.	4080.
5K	---	---
5L	1520.	---
5L	---	---
5M	---	4720.
5M	---	---
5N	---	---
5N	---	---

TABLE II.B.1

SOLUBLE RADIONUCLIDES DURING SLUDGE PROCESSING

Sample†	Se-79 Curies	Sr-90 Curies	Tc-99 Curies	Cs-137 Curies	Pu Curies
4-T1	17.4	291.	45.4	164000	2.74
4-T2	9.70	623.	48.4	189000	3.80
7-A	1.37	1500.	33.2	73000.	7.86
7-A	---	---	---	69700.	---
7-ASA-7A	0.327	3150.	54.0	91700.	2.41
7-ASA-7B	1.73	2720.	67.3	89900.	4.46
10	0.357	322.	8.01	5830.	0.166
13	0.177	584.	1.80	2280.	0.135
18-B	---	22.2	---	190.	---
18-R1	---	28.1	0.543	173.	0.142
18-R2	---	21.4	0.677	177.	0.0992

† The initial number of the sample code corresponds to the step of the demonstration that the sample was collected. Step 18 is identified as Step 16 in SRP documents.

TABLE II.B.2

INSOLUBLE RADIONUCLIDES DURING SLUDGE PROCESSING

	Se-79		Sr-90		Tc-99	
Sample†	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies
4-AD-A	153.	41.3	2590000.	3070000.	762.	2260.
4-ASA-42A	---	48.8	---	2530000.	---	---
4-ASA-42B	---	47.7	---	62800.	---	324.
4-T1	379.	3.50	262000.	1510000.	630.	272.
4-T2	784.	31.6	847000.	562000.	805.	988.
4A	88.6	233000.	142000.	2070000.	151.	504.
4B	48.4	365.	57400.	1770000.	134.	375.
4C	89.9	26.8	129000.	1580000.	115.	346.
7A	39.5	37.3	1070000.	1180000.	797.	1060.
7-42AW	22.4	12.6	1530000.	3020000.	---	115.
7-42BW	---	1.90	3030000.	2630000.	234.	24.
7-ASA-7A	---	33.7	---	12800.	---	429.
7-ASA-7B	---	26.0	---	2430000.	---	---
10	58.2	3.97	58200.	855.	134.	232.
13	38.8	11.4	530000.	924000.	22.5	68.4
13	---	35700.	126000.	157000.	8.86	265.
18-B	---	15.3	109000.	1240.	42.0	115.
18-R1	10.5	13.7	65300.	300.	2270.	6540.
18-R2	---	8.28	17600.	308.	99.6	---.

† The initial number of the sample code corresponds to the step of the demonstration that the sample was collected. Step 18 is identified as Step 16 in SRP documents.

TABLE II.B.2

INSOLUBLE RADIONUCLIDES DURING SLUDGE PROCESSING

	Sb-125		Cs-137		Eu-154*	
Sample†	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies	Acid Curies	Na_2O_2 Curies
4-ASA-42A	---	---	---	25300.	---	---
4-ASA-42B	---	---	---	22900.	---	---
4-AD-A	6860.	5220.	---	---	19300.	29700.
4-42A		---	---	---	---	21800.
4-42A		---	---	---	---	39100.
4-42B		---	---	---	---	21600.
4-42B		---	---	---	---	35300.
4-T1	7640.	6280.	19100.	52300.	10300.	35500.
4-T1	---	---	20700.	89900.	25000.	41400.
4-T1	---	---	---	---	8350.	32800.
4-T2	4890.	5780.	33600.	9350.	36000.	32800.
4-T2	---	---	206000.	48900.	40300.	34700.
4-T2	---	---	---	---	44700.	38300.
4A	6420.	5960.	12800.	51900.	---	37600.
4A	---	---	---	---	---	34700.
4B	6030.	4900.	10700.	57200.	---	32600.
4B	2510.	---	---	---	---	30800.
4C	6930.	4070.	22900.	56800.	---	28100.
4C	7440.	---	---	---	---	28600.
7A	5750.	---	42400.	45700.	17200.	40100.
7A	---	---	---	---	---	40900.
7-42AW	4380.	4740.	11600.	370000.	3850.	23400.
7-42AW	3520.	---	---	---	5560.	23100.
7-42BW	3820.	3050.	11700.	318000.	5030.	17500.
7-42BW	3900.	---	---	---	4020.	18200.
7-ASA-7A	---	---	---	---	---	19000.
7-ASA-7A	---	---	---	---	---	17600.
7-ASA-7B	---	---	---	68100.	---	39700.
7-ASA-7B	---	---	---	---	---	41700.
10	581.	103.	26500.	46900.	16600.	1770.
10	554	---	---	---	---	24400.
13	6510.	2930.	21300.	29000.	8270.	20900.
13	6400.	3020.	19900.	27300	---	18800.
13	6380.	---	---	---	---	18400.
13	6280.	---	---	---	---	20800.
18-B	2800.	---	6230.	23400.	---	18200.
18-B	3030.	---	---	---	---	16200.
18-R1	2940.	---	6730.	27300.	---	18000.
18-R1	3030.	---	---	---	---	16300.
18-R2	3400.	---	5180.	23700.	168.	18100.
18-R2	2890.	---	---	---	---	---

* Eu-155 was also detected but is not reported here.

† The initial number of the sample code corresponds to the step of the demonstration that the sample was collected. Step 18 is identified as Step 16 in SRP documents.

TABLE II.B.2, cont'd

INSOLUBLE RADIONUCLIDES DURING SLUDGE PROCESSING

	Pu	
Sample†	Acid Curies	Na_2O_2 Curies
4-AD-A	6690.	8850.
4-ASA-42A	---	12100.
4-ASA-42B	---	11600.
4-T1	7410.	7620.
4-T2	15500.	10300.
4A	4100.	9700.
4B	3620.	10300.
4C	4770.	9440.
7A	7890.	11800.
7-42AW	10100.	9880.
7-42BW	18900.	10100.
7-ASA-7A	---	9970.
7-ASA-7B	---	6260.
10	33000.	9700.
13	2700.	10200.
13	2930.	8880.
18-B	12900.	8540.
18-R1	14300.	8640.
18-R2	10600.	9030.

† The initial number of the sample code corresponds to the step of the demonstration that the sample was collected. Step 18 is identified as Step 16 in SRP documents.

FIGURE II.A.1

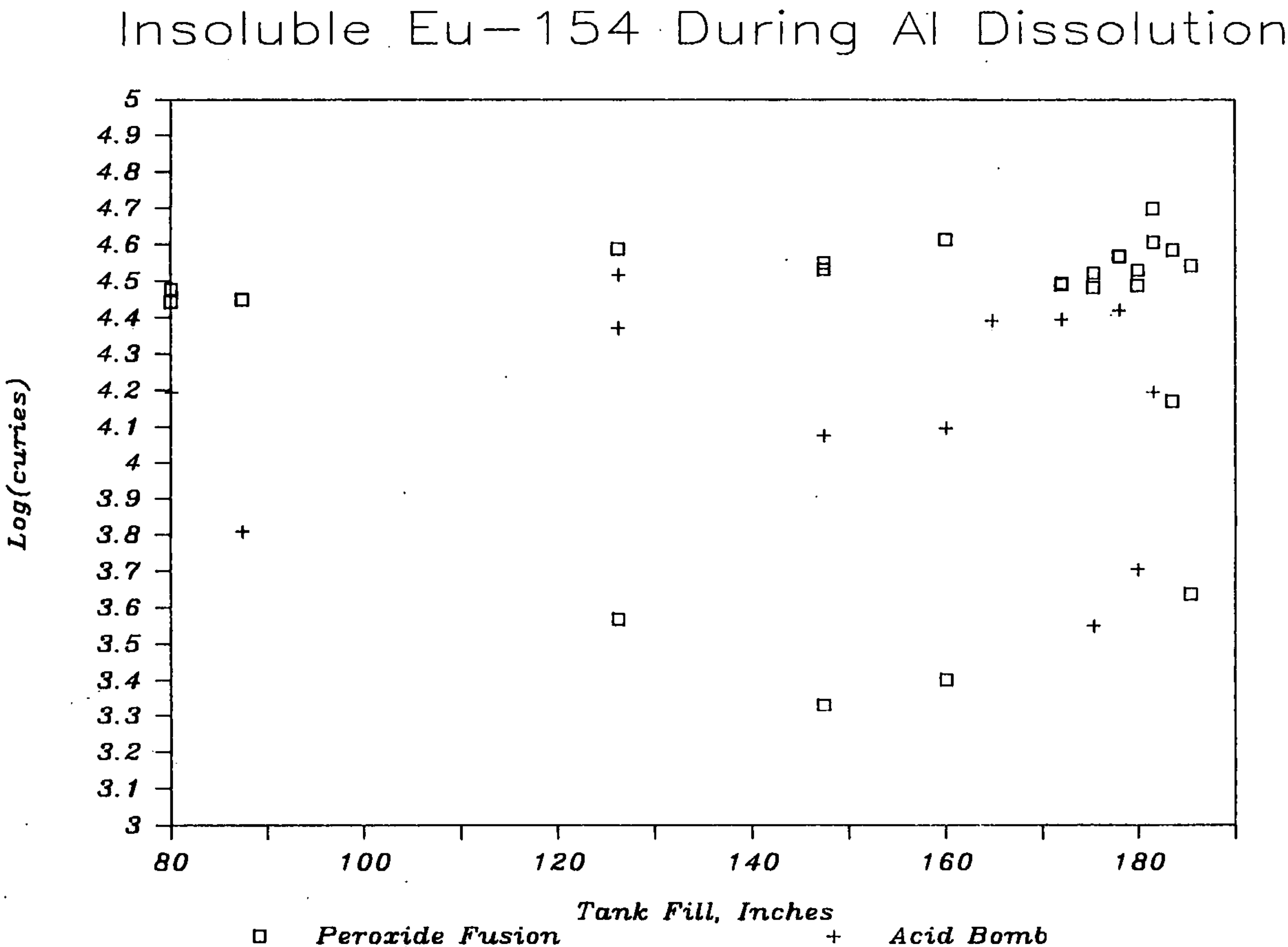
Insoluble Eu-154 During Al Dissolution
Log(curies)
5
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3
80
100
120
140
160
180
Tank Fill, Inches
Peroxide Fusion
Acid Bomb

FIGURE II.B.1

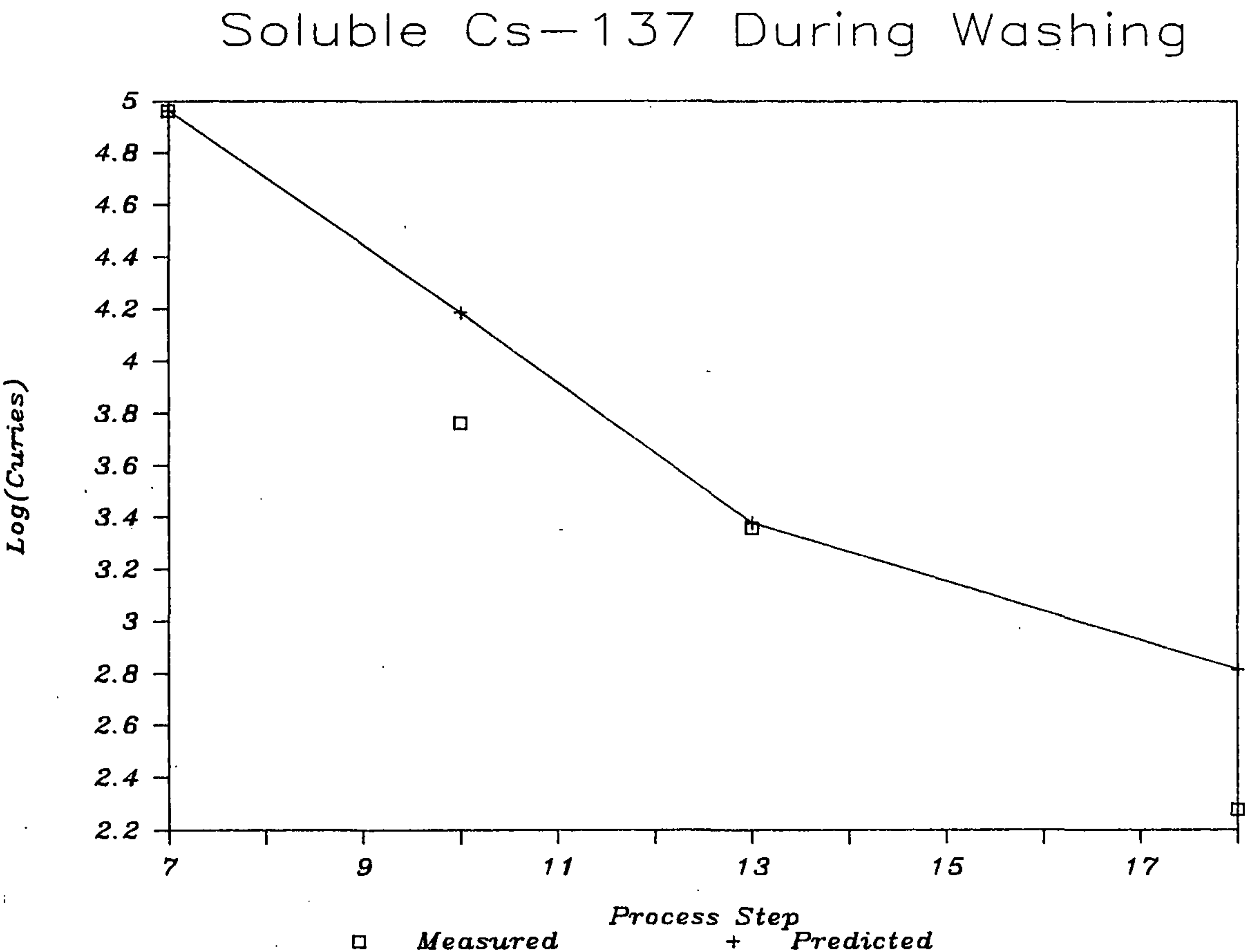
Soluble Cs—137 During Washing
Log(Curies)
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
7
9
11
13
15
17
Process Step
□ Measured
+ Predicted

FIGURE II.B.2

Soluble Se-79 During Washing

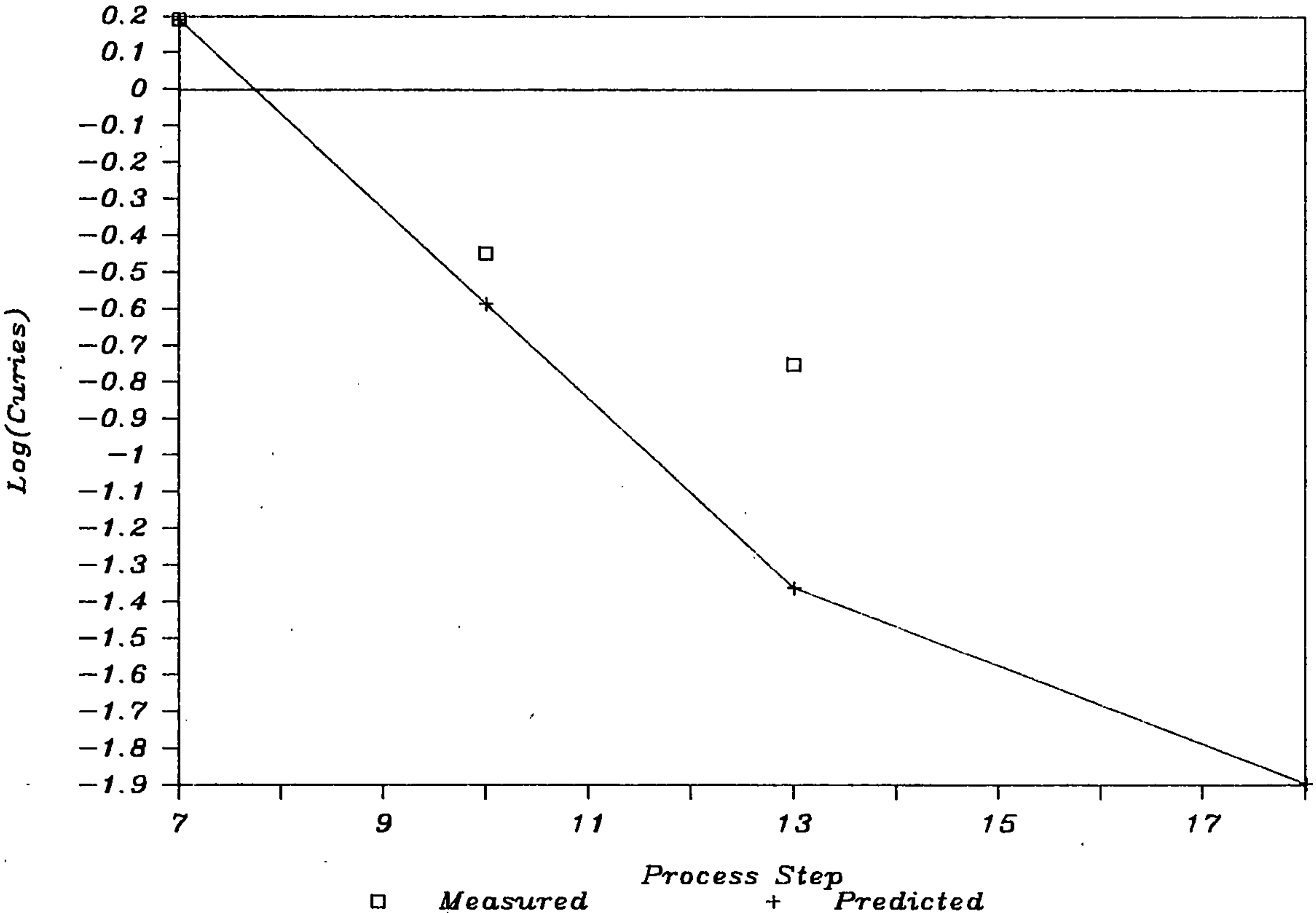

FIGURE II.B.3

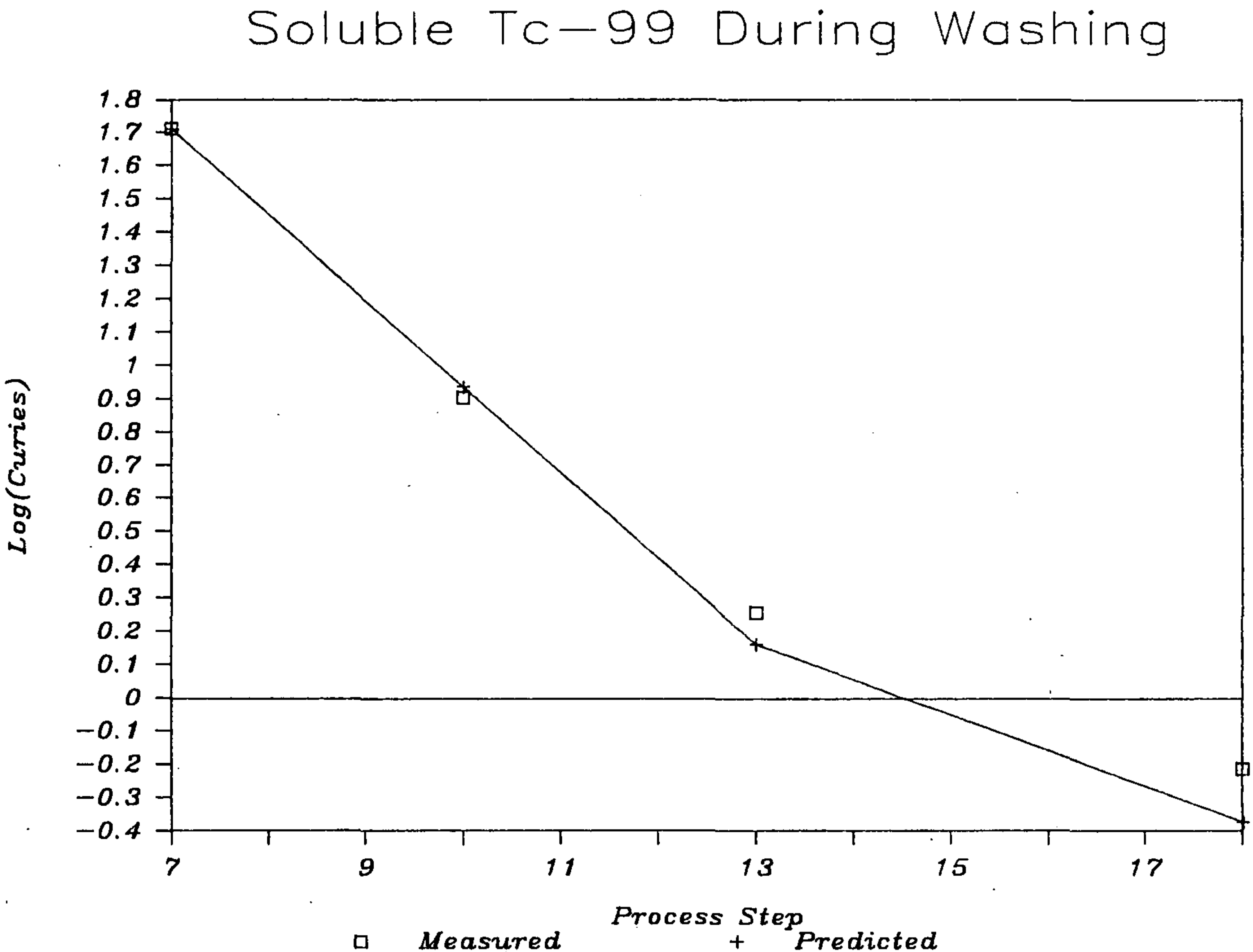
Soluble Tc—99 During Washing
Log(Curies)
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
−0.2
−0.3
−0.4
7
9
11
13
15
17
Process Step
□ Measured
+ Predicted

FIGURE II.B.4

Insoluble Eu−154 During Washing

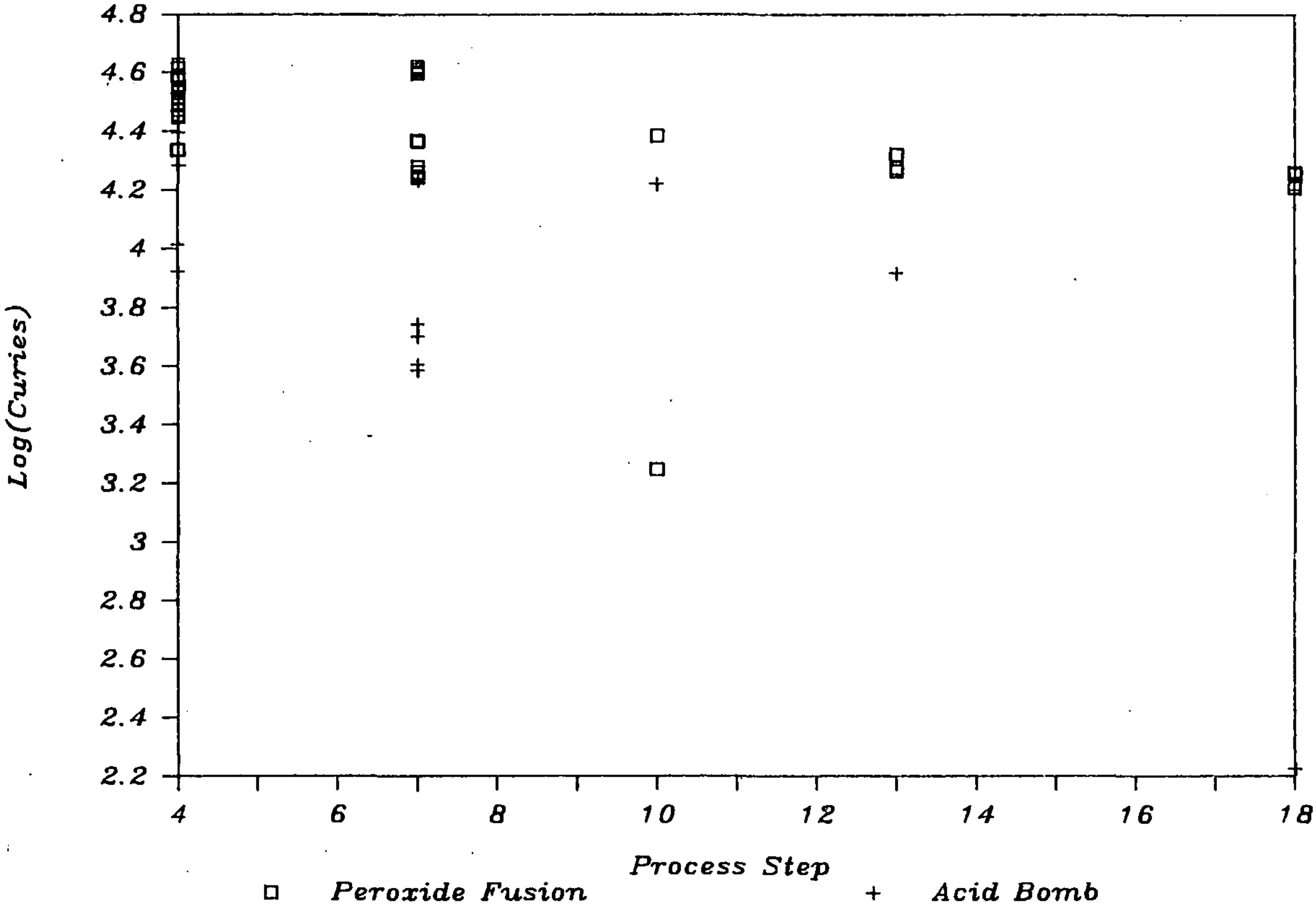

FIGURE II.B.5

Insoluble Sb-125 During Washing