[redacted]

LAMS-883

Series A

This is copy 5 of 20 copies.

23 May 1949

This document contains 25 pages.

PROGRESS OF LIQUID WASTE DISPOSAL STUDIES

Work done by:

C. W. Christenson
M. B. Ettinger
W. R. Kennedy
G. G. Robeck
Bert Schnapp
J. F. Newell

Report written by:

J. F. Newell
C. W. Christenson

[redacted]

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C. W. Christenson POSITION Chief, I.W.S.
DATE 8-13-54

7814

LAMS 863

Progress of Liquid Waste Disposal Studies

A series of experiments was reported in LAMS-863 on the use of inert materials and coagulants for removing plutonium from waste solutions. It was stated that treatment consisting of chemical coagulation, sedimentation and filtration appeared to have attractive possibilities for reducing the plutonium concentration in liquid laboratory wastes. It was also stated that further study would be necessary to determine the feasibility of the process in the presence of plutonium complexing agents.

Contained in this report are data from the following experiments:

1. Coagulation studies on Technical Area Waste.
2. Effect of fluorides on plutonium removal by coagulation.
3. Study of citrates as a complicating factor.

Investigation of Coagulant Efficiencies

The primary purpose of these studies is directed toward developing a method of treating wastes from the Technical Area. Thus, to obtain a more representative measure of various coagulant efficiencies, a number of daily composite samples collected from the Technical Area discharge were combined. Analysis of the combined sample showed the following characteristics:

Plutonium concentration - 4500 Counts/Minute/Liter

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified [redacted]
BY AUTHORITY OF DC 4-50 25
BY C. W. Christian POSITION Chief, D.W.S.
DATE 8-23-54

pH - 3.0

Total Solids - 650 ppm (46% Ash)

Acidity - 444 ppm as CaO

The experiments performed on the combined sample are briefly described in the following paragraphs.

Use of Ammonia and Ferric Chloride

Because the use of this combination of chemicals might be expected to produce a minimum weight and volume of sludge, their use in effecting a carrier precipitation was investigated.

1500 ml samples of the combined wastes previously described were treated with ferric chloride (20 ppm $FeCl_3$) using ammonia to adjust the pH. Samples were stirred about 10 minutes and filtered through No. 2 Whatman fluted filter paper. 1000 ml samples were taken for analyses. Floc formation in each case was slight. This treatment was investigated with the pH at three different levels. At pH 5.3 the residual plutonium in the filtered effluent was 1350 C/M/L. At pH 8.3 and 9.5 it was 63 and 61 C/M/L respectively. For comparison, ammonia alone was added to adjust the pH to 9.3. Filtered effluent from this treatment showed a residual of 80 C/M/L. The suspended solids in the coagulated mixtures varied with the pH and ranged from 40 to 85 ppm. These data are presented in detail in Table I.

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified [redacted]
BY AUTHORITY OF DCL-5025
BY C. V. Christensen POSITION Chief, I.W.S.
DATE 8-13-54

[redacted]

Table I

Coagulation Studies on Combined Technical Area Composite Waste Using Ammonium Hydroxide and Ferric Chloride

Material Treated	Coag & Amount	Alkali	Adjusted pH	Pu Concentration in C/M/L		Susp. Solids after Coag.	
				Untreated	Treated	Tot.	%Ash
Mixed Composite Technical Area Wastes	None	NH_4OH	9.5	4500	69	65	53.8
	20ppm $FeCl_3$	NH_4OH	5.3	4500	1350	40	25.0
	20 ppm $FeCl_3$	NH_4OH	8.3	4500	63	83	50.6
	20 ppm $FeCl_3$	NH_4OH	9.5	4500	61	85	62.4

The results obtained indicate fair plutonium removal at pH values of 8.3 and 9.5. The fact that substantially the same results were obtained using ammonia alone indicates that the sample itself must carry material which acts as a suitable carrier for Pu at pH values in the vicinity of 9.0. As compared to other precipitation processes investigated using the combined Technical Area waste, this procedure was less effective for Pu removal. Since the primary objective is to secure a highly effective removal of Pu, further investigation of this treatment has been dropped. Also, as a secondary objective, this method is not effective in removing fluorides from solution.

Use of Lime and Ferric Chloride

Another series of experiments on the combined waste was conducted using ferric chloride with lime as the alkali.

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DOE-5025
BY G.W. Christian POSITION Chief, D.W.S.
DATE 8-13-54

[redacted]

The study procedure was similar to that described for the ferric chloride-ammonia work. In each case a heavy floc was formed after only a few minutes stirring. At pH values of 6.1, 8.4 and 9.9 the plutonium residual in the filtered effluent varied from 7 to 31 C/M/L. For comparative values in an experiment with lime alone, the plutonium residual in the filtered effluent was 7 C/M/L. The suspended solids in the flocculated mixture varied from 725 to 850 ppm. These data are presented in Table II.

Table II

Coagulation Studies on Combined Technical Area Composite Waste Using Lime and Ferric Chloride

Material Treated	Coag & Amount	Alkali	Adjusted pH	Pu Concentration in C/M/L		Susp. Solids After Coag.	
				Untreated	Treated	Tot.	%Ash
Mixed Composite Technical Area Wastes	None	Lime	9.4	4500	6	--	--
	20 ppm $FeCl_3$	Lime	6.1	4500	14	850	90.3
	20 ppm $FeCl_3$	Lime	8.4	4500	31	725	87.4
	20 ppm $FeCl_3$	Lime	9.9	4500	7	865	87.6

Table II indicates that the treatment with ferric chloride and lime followed by filtration effected uniformly satisfactory reduction in the Pu content. Since lime alone at pH 9.4 also effected a very good Pu removal, the presence of heavy metals or other "carrier" materials in the waste is again demonstrated. The amounts of precipitate produced were

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL 5025
BY G. W. Christen POSITION Chief I.W.S.
DATE 8-13-54

[redacted]

 [redacted]

relatively high. But the fact that this treatment worked well over a wide pH range more than offsets this disadvantage. Also, lime is effective in removing excess fluorides from solution.

Use of Lime and Alum

The same type of experiment was repeated using 43 ppm of hydrated alum. Lime was used to adjust the pH of the several samples studied. In each case a heavy floc was formed after only a few minutes stirring. At pH values of 4.2, 5.9, and 8.8 the plutonium residual in the filtered effluent varied from 10 to 16 C/M/L. In one experiment at pH 7.3 the plutonium residual was 75 C/M/L. This higher count was probably due to poor filtration or an error in the analysis. The suspended solids in the flocculated mixture varied from 660 to 864 ppm.

Table III

Coagulation Studies on Combined Technical Area Composite Waste Using Lime and Alum

Material Treated	Coag.& Amount	Alkali	Adjusted pH	Pu Concentration in C/M/L		Susp. Solids after Coag.	
				Untreated	Treated	Tot.	%Ash
Mixed Composite Technical Area Wastes	43ppm Hydr. Alum	Lime	4.2	4500	10	660	87.0
	43ppm Hydr. Alum	Lime	5.9	4500	16	673	88.4
	43ppm Hydr. Alum	Lime	7.3	4500	75	844	88.0
	43ppm Hydr. Alum	Lime	8.8	4500	10	864	86.8

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C. W. Christensen POSITION Chief, I.W.S.
DATE 8-13-54

[redacted]

 [redacted]

It will be noted that the alum-lime treatment was successful over a wide pH range. Solids in the flocculated mixture did not differ significantly from that produced by the lime-ferric chloride treatment.

Use of Sodium Hydroxide and Ferric Chloride

The above experiment was repeated in the same manner using 20 ppm $FeCl_3$ as the coagulant and sodium hydroxide as the alkali. At pH values of 7.1 and 9.9 the filtered effluent showed 10 C/M/L and 45 C/M/L of plutonium respectively. The floc formed was not nearly as voluminous as when lime was used. The suspended solids in the mixed liquor was 68 ppm and 138 ppm respectively. These data are presented below in Table IV.

Table IV

Coagulation Studies on Combined Technical Area Composite Waste Using Sodium Hydroxide and Ferric Chloride

Material Treated	Coag. & Amount	Alkali	Adjusted pH	Pu Concentration in C/M/L		Susp. Solids After Coag.	
				Untreated	Treated	Tot.	%Ash
Mixed Composite Technical Area Wastes	20ppm $FeCl_3$	NaOH	7.1	4500	10	68	50
	20ppm $FeCl_3$	NaOH	9.9	4500	45	138	63.8

It will be noted that the treatment with ferric chloride and caustic soda resulted in satisfactory Pu removal and yielded less solids than the treatments using lime. In operation of a treatment process caustic soda would also have the advantage

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY G. W. Christens POSITION Chief, IWS.
DATE 8-13-54 [redacted]

 [redacted]

over lime because of relative ease in feeding small controlled amounts.

Effect of Fluorides on Treatment

Portions of the combined composite waste were fortified with 500 and 1000 ppm of fluoride in the form of sodium fluoride. Each sample was treated with lime and ferric chloride at pH 7.7 and pH 10.5. The filtered effluents showed very low plutonium counts. As could be expected the suspended solids in the mixed liquor was higher than without the fluoride, being 900 and 1100 at the two pH values. Etching of the porcelain casseroles during the analytical procedure was evidence that a considerable amount of fluoride remained throughout the treatment process. It will be noted also, that the increase in suspended solids observed is much less than would have resulted with complete fluoride removal as calcium fluoride. The failure of the process to give more complete removal of fluoride may be attributed to inadequate amounts of calcium ion to precipitate greater amounts of the fluoride. One experiment was conducted using ferric chloride and ammonia at pH 9.5 on the fluoride fortified waste. The plutonium concentration in the filtered effluent was 125 C/M/L. A smaller amount of floc was formed and the suspended solids in the mixed liquor was 250 ppm. The results are shown in Table V.

It was evident from the above experiments that almost any flocculation was efficient in removing plutonium from this combined composite waste. To determine which flocculant was

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C.W. Christensen POSITION Chief, IWS
DATE 8-13-54

[redacted]

 [redacted]

Table V

Coagulation Studies on Combined Technical Area Composite Waste Fortified with Fluorides

Material Treated	Coag.& Amount	Alkali	Adjusted pH	Pu Concentration in C/M/L		Susp.Solids After Coag.	
				Untreated	Treated	Tot.	%Ash
Mixed Composite Technical Area Wastes plus 500 ppm Fluoride	10ppm $FeCl_3$	Lime	7.7	4500	30	870	89
Mixed Composite Technical Area Wastes plus 500 ppm Fluoride	10ppm $FeCl_3$	Lime	10.7	4500	13	1140	87
Mixed Composite Technical Area Wastes plus 1000 Fluoride	10ppm $FeCl_3$	Lime	7.9	4500	34	942	89.5
Mixed Composite Technical Area Wastes plus 1000 ppm Fluoride	10ppm $FeCl_3$	Lime	10.3	4500	14	1075	88.3
Mixed Composite Technical Area Wastes plus 1000 ppm Fluoride	20ppm $FeCl_3$	NH_4OH	9.5	4500	125	249	79.1

better, as well as the effective agent in the removal of plutonium, several experiments were run on distilled water spiked with about 67,000 C/M/L of plutonium. As was expected the formation of floc in distilled water was very difficult and in most cases non-existent. From the limited number of experiments conducted it can be concluded that a very definite floc formation is necessary before appreciable amounts of

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified [redacted]
BY AUTHORITY OF DC4-5825
BY C. W. Christensen POSITION Chief, IWS
DATE 8/13-54

plutonium can be removed from the Technical Area waste solution; and that higher pH values (above 9.0) are needed for good removals.

The necessity of a definite floc was evidenced by superiority of ferric chloride over alum and the superiority of lime over sodium hydroxide. For comparative purposes, sodium hydroxide alone was used without any coagulant in one experiment at pH 11.5. Since there was no floc formation a filter aid was added before filtration. No reduction of plutonium concentration was found in the filtered effluent. In other cases where no appreciable floc was formed and filter aids were used no appreciable reductions of plutonium concentration were noted in the filtered effluent.

Some of the above experiments were repeated in tap water with ground tufa added for turbidity. Floc formations were much better, resulting in significantly better plutonium removals. However, higher pH values were needed for treating tap water and distilled water solutions than for treating the technical area wastes.

Selection of Flocculant

Time does not permit the complete investigation of all of the factors involved in flocculation nor does it permit the investigation of all of the coagulants available. On the basis of the results from the limited amount of preceding work it was decided to limit the remainder of the work to an investigation of ferric chloride and lime. Ferric chloride was chosen

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C.W. Christensen POSITION Chief, I.W.S.
DATE 8-13-54

[redacted]

because it appeared to give a heavier, more rapidly settling floc than the alum. Lime was chosen because it appeared to assist in floc formation as well as removal of fluorides. Since fluoride removal is necessary for protection of well water supplies in this area, it is planned to insure complete precipitation by the addition of more calcium in the form of calcium chloride. These two coagulants, it will be noted, give the largest amount of sludge but, generally, the best removal of plutonium. The large amount of sludge is a disadvantage. Some thought was given to a two stage treatment by removing the Pu with iron and either sodium hydroxide or ammonia followed with lime and calcium chloride for fluoride removal. However, since calcium fluoride is a very good carrier for the plutonium, the second stage treatment would result in a large amount of sludge containing a smaller, but significant amount of plutonium.

It should be emphasized that the selection of ferric chloride and lime as the chemicals to be investigated for treatment of Technical Area wastes was not based on any outstanding qualities or performance in plutonium removal. The deciding factor was the need to treat the waste for fluoride removal as well as to remove its plutonium content. With an adequate supply of calcium ion present, it would appear possible to simultaneously reduce both the plutonium content and the fluoride content of the waste to satisfactory levels in one relatively simple treatment

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C. W. Christensen POSITION Chief, IWS
DATE 8-13-54

[redacted]

process. This possibility is most attractive and indicated the further investigation of treating Technical Area wastes with ferric chloride and lime.

Treatment of Technical Area Wastes with Lime and Ferric Chloride

Composite samples of Technical Area wastes were collected during the working hours on eleven different days, one sample was composited of the overnight flow for February 17-18, and one sample was collected representing the weekend flow for February 11-14. A sample of the previously described combined Technical Area wastes was included in this experiment.

The mechanics of the experiment included the addition of 20 ppm of iron (ferric chloride) to act as the coagulant, then adjusting the pH to about 9.5 with lime. The plutonium concentrations in the untreated samples varied from 118 C/M/L to 5350 C/M/L. After the lime and ferric chloride treatment, the concentration remaining in the filtered effluent varied from a minimum of 2 C/M/L to a maximum of 37 C/M/L.

There is always a possibility that these wastes will contain a much higher concentration of plutonium than was present in the samples tested. Accordingly, each of the above samples was spiked with 63,000 C/M/L of plutonium and the coagulation procedure was repeated. The results were, in the main, satisfactory. One-half of the results obtained were less than 100 C/M/L. The overnight and weekend samples were the least amenable

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified [redacted]
BY AUTHORITY OF DCL-50-25
BY C. W. Christen POSITION Chief, DWS
DATE 8-23-54

 [redacted]

to treatment, the results in these cases being 916 C/M/L and 631 C/M/L respectively. These samples were treated again with 100 ppm of Fe instead of 20 ppm resulting in a residual count of 196 C/M/L and 238 C/M/L. The sample on February 15 and the overnight sample were treated with 20 ppm Fe, 200 ppm sodium fluoride and 200 ppm calcium chloride which treatment considerably decreased the residual count.

The above work indicates that serial coagulation may be necessary to consistently maintain a plutonium concentration less than 70 C/M/L in the final effluent.

It was pointed out in LAMS-863 that, when working with spiked distilled water, it was possible to reduce the plutonium concentration from 100,000 C/M/L to 125 C/M/L with only 20 ppm of Fe and lime. In distilled water the amount of floc was, comparatively, very small. This work has been repeated with essentially the same results. It is not understood, at present, why the results on weekend and overnight samples (which contain very little dissolved solids) should have been so poor.

Table VI shows the characteristics of these wastes and the results of the treatment with lime and ferric chloride.

The data contained in Table VI show the following interesting observations:

1. The average of suspended solids of the flocculated mixtures (372 ppm) is about 25% of the average of total solids (1295 ppm) contained in the untreated waste. This indicates that coagulation may produce less solids than would an

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DC 4-5-24
BY C. W. Christensen POSITION Chief L.W.S.
DATE 8-13-54 [redacted]

TABLE VI
Treatment of Technical Area
Wastes with Lime and Ferric Chlori

19	pH	Total Solids ppm	Total Solids %Ash	Suspended Solids ppm	Suspended Solids %Ash	Acidity ppm as CaO	Phosphates ppm	Nitrates ppm	Fluorides ppm	Chlorides ppm	Plutonium Concentration C/M/L	Pu in F After Treatme with Fe and Ca
ined		6054	46.2	21	28.2	444	----	----	----	----	4500	20
4	2.6	2184	84.0	25	12.0	329	----	----	----	----	2200	6
7	2.6	856	46.7	13	23.2	368	----	----	----	----	1440	4
8	2.9	449	41.8	13	22	337	----	----	----	----	1540	2
9	3.0	378	59.4	18	8.5	296	----	----	----	----	1650	
10	3.1	357	51.9	20	0	234	----	----	----	----	1440	
11	3.2	351	54.9	20	13	194	----	----	----	----	5350	16
and	8.1	893	72.7			3.4	0.2	3	4	36	118	4
14	2.6	5094	84.3	17	35	353	0.1	3, 26	100	64	2350	6
15	3.3	358	55.5	24	20	162	0.4	67	130	33	2400	21
.6	2.5	592	58.0	9	4.3	287	0.5	19	120	35	850	37
.7	3.0	372	50.6	19	17	144	0.1	122	100	52	1100	29
'-18	8.1	212	54.7	15	47.4	2.8	0.2	3	4	31	160	8
.8	3.9	896	75.1			48	0.1	5	90	44	2030	19
		1235	51.3	18	10.6	298	0.23	563	100	42	1815	13

(1) 35 C/M/L with 100 ppm $FeCl_3$
(2) 196 C/M/L with 100 ppm $FeCl_3$
(3) 205 C/M/L with 100 ppm $FeCl_3$
530 C/M/L with 20 ppm $FeCl_3$+200p
(4) 238 C/M/L with 100 ppm $FeCl_3$
396 C/M/L with 20 ppm $FeCl_3$+200p

The laundry uses up to 7 pounds per day in clean-
vats. It is estimated that 17,000 gallons per

TABLE VI
reatment of Technical Area
es with Lime and Ferric Chloride

Chlorides ppm	Plutonium Concentration C/M/L	Pu Concentration in Filt. Eff. C/M/L: After Treatment with $FeCl_3$ and CaO	Pu Concentration in Filt. Eff. C/M/L: 63,000 C/M/L and treated with $FeCl_3$ and CaO	Susp. Solids in Flocculated Mixture: Gms	Susp. Solids in Flocculated Mixture: Ash	Lbs. Dry Sludge per 1000 gal. Waste	gal. wet sludge per 1000 gal. of Waste (from Imhoff Cone)
----	4500	20					
----	2200	6	173				
----	1440	4	21	47	80	2.06	45
----	1540	2	312[1]	93		5.69	36
----	1650	8	196	62		5.57	13
----	1440	5	88	87		1.39	9.5
----	5350	16	117	160		3.75	10
36	118	4	631[2]	186		3.88	12
64	2360	6	49	185		1.62	
33	2400	21	295[3]	185		4.04	60
35	850	37	60	140		2.83	11
52	1100	29	94	114		3.68	11
31	160	8	916[4]	109		1.74	
44	2030	19	212	[illegible]		0.69	7.1
				183		1.36	11
42	1815	13		172		3.09	20.5

35 C/M/L with 100 ppm $FeCl_3$
96 C/M/L with 100 ppm $FeCl_3$
05 C/M/L with 100 ppm $FeCl_3$
30 C/M/L with 20 ppm $FeCl_3$+200ppm NaF + 200 ppm CaO
38 C/M/L with 100 ppm $FeCl_3$
96 C/M/L with 20 ppm $FeCl_3$+200ppm NaF + 200 ppm CaO

 [redacted]

evaporation process for these wastes. It will be noted that the total solids of the untreated waste was 8184 ppm and 5094 ppm on February 4 and 14, respectively. The corresponding suspended solids in the flocculated mixtures was 247 ppm and 485 ppm.

2. The data show an average of 20.5 gallons of wet sludge produced by coagulation per 1000 gallons of waste, representing about 3.09 pounds of dry solids per 1000 gallons of waste. This is an overall reduction from 8330 pounds of waste liquid to 3.09 pounds of dry radioactive solids.

3. The fluoride content is excessively high from a public health standpoint to permit discharge into a receiving stream or into the ground. Adequate lime treatment will precipitate the fluorides from solution and may aid in removing the plutonium.

4. During the working hours the pH characteristics are predominately in the 2.0 to 4.0 range, whereas the night and weekend flows are in the normal range of the water supply 7.8 to 8.3. The average acidity for the waste in this study was 228 ppm in terms of CaO. As expected the acidity was very low during the night and weekend flows.

Citrates as a Complicating Problem

Citrates are used in may ways at Los Alamos.

1. The laundry uses up to 7 pounds per day in cleaning out tubs and vats. It is estimated that 17,000 gallons per

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DC 4-5025
BY C. W. Christensen POSITION Chief, IWS.
DATE 8-13-54 [redacted]

 [redacted]

day of waste originate from this source. On this basis, a daily composite sample should show approximately 50 ppm of citrate. Spot discharges would be predicted to show a much higher figure.

2. In the DP West area 30 pounds of citric acid and 20 pounds of sodium citrate are consumed weekly. These materials are used in the preparation of decontaminating solutions and find their way into the wastes from the area. It is estimated that these wastes might show 200 ppm of citrates.

Citrates are used because they are an excellent solvent and complexing agent for plutonium. Accordingly, it was anticipated that in wastes containing citrates, difficulties might be encountered with otherwise satisfactory plutonium removal processes.

To investigate this possibility, 100 ppm of citric acid was added to four samples of the Technical Area wastes. The ferric chloride-lime precipitation process was then applied to these samples. Either no precipitate, or a highly unsatisfactory precipitate resulted. Next, difficulties were encountered in filtration. It was found necessary to refilter the liquid through the same paper several times in order to secure a clear filtrate. Finally, as shown by the results given in Table VII, the removal of plutonium was very poor.

[redacted]

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C.W. Christen POSITION Chief, L.W.S.
DATE 8-13-54

[redacted]

TABLE VII

Removal of Pu from Tech Wastes ($FeCl_3$ - Lime treatment) with 100 ppm Citric Acid Added

Date Sampled	Initial Pu C/M/L	Pu After Treatment C/M/L
2-15-49	2400	1050
2-16-49	850	460
2-17-49	1100	1050
2-18-49	2030	1320

Removal of citrates from distilled water and/or tap water was studied by various procedures. For the most part these data are not too satisfactory. Filter aids were required, complicating the question of which agent was responsible for any removal of plutonium noted. In general, extreme difficulty was encountered in the production of floc using either ferric chloride or alum in the presence of citrate. This may be attributed to the complexing action of the citrate which either partially or completely held the coagulating metal ion in solution.

On this basis, it seemed apparent that if plutonium were to be removed from a waste containing appreciable quantities of citrate, it would be necessary to either remove or destroy the citrate, or select a "carrier" which would function in the presence of citrate.

The removal of citrate seems a very poor possibility. It forms no common highly insoluble salt. Its solubility in water is so great, and it complexes with so many metallic ions, that removal by extraction with an organic solvent does not

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DC 4-5125
BY C. W. Christensen POSITION Chief, LWS
DATE 8/3-54

 [redacted]

appear to be a likely process.

The destruction of the material appears to be a more practical step. Citrates are readily oxidized or synthesized into cell structure by micro-organisms. They can also be oxidized by cold premanganate or by permanganate and bromine in acid solution.

Experimental Study of Citrate Removal by Chemical Oxidation

Preliminary attempts were made to oxidize citrates with chlorine. As gauged by persistance of the ability to hold iron in solution, little or no citrate oxidation was effected. The chlorine oxidation was tried at laboratory temperature over a wide pH range with no apparent success.

Oxidation by permanganate was studied next. In a low pH range with small amounts of $MnSO_4$ added as a catalyst, it was immediately apparent that the permanganate was attacked. Manganese dioxide was obviously a product of the oxidation. Further the iron sequestering ability of the solution was gone. The possibility of permanganate oxidation with or without carrier precipitation was accordingly investigated. The technique used was as follows: 101,000 C/M of Pu were added to 1500 ml of tap water. The permanganate and coagulant to be used were then added. Sulfuric acid was next added to adjust the pH to the desired level and the mixture stirred for a period of about 1 hour. Lime slurry was then added to adjust the pH of the mixture to the level desired for coagulation. The solution was

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C. W. Christensen POSITION Chief, DW. S.
DATE 8-13-54

 [redacted]

stirred, settled, filtered through a fluted paper and analyzed for plutonium. Results and conditions of this experiment are reported in Table VIII.

The type of processing required by the treatment with permanganate in acid solution followed by precipitation in alkaline solution is not too desirable. However, there is definite indication that the method should work. Further study of this method is indicated, especially if other less complicated methods do not prove satisfactory. Evaluation of the pH range in which the method will function is especially indicated. It may be noted that Table VIII indicates that the iron functioned satisfactorily in connection with permanganate oxidation, that the alum was much less efficient, and finally that the precipitated manganese dioxide alone apparently did a very poor job of carrying the Pu down.

The use of calcium fluoride as a carrier in the presence of citrate has been investigated. 200 ppm of citrate were added to tap water. Variable amounts of sodium fluoride were then added to different portions of the solution. Calcium chloride in quantity roughly equivalent to the fluoride was added concurrently, 20 ppm of $FeCl_3$ were then added. Calcium hydroxide slurry was used to bring the pH up to 9.5 and the mixture stirred gently for approximately 30 minutes.

Results of this series of tests are shown in Table IX. It is apparent that as a plutonium carrier in the presence of citrates, calcium fluoride shows some promise. However,

CHANGED TO Unclassified
DC 4-5025
BY C. W. Christensen POSITION Chief, I. W. S.
DATE 8-13-54

TABLE VIII

Removal of Plutonium in the Presence of Citrate by $KMnO_4$ Oxidation, followed by Coagulation and Filtration

Material Treated	$KMnO_4$	Time of Stirring	pH of Oxidation	Alkali	pH of Coagulation	Coagulant	Catalyst	Res Pu C/M/L
1500 ml tap water, 101,000 C/M of Pu, 20 ppm $FeCl_3$, 250ppm citric acid, 2 ml 20% H_2SO_4	0.82g	1.5 hrs.	2.3	$Ca(OH)_2$	9.9	$FeCl_3$	2 drops 20% $MnSO_4$	50
1500 ml tap water, 101,000 C/M of Pu, 13 ppm $Al_2(SO_4)_3$	0.82g	1.5 hrs.	2.2	$Ca(OH)_2$	9.5	$Al_2(SO_4)_3$	do	6,730
1500 ml tap water, 101,000 C/M of Pu, 250 ppm Citric acid, 2 ml 20% H_2SO_4	0.82g	1.5 hrs.	2.2	$Ca(OH)_2$	9.5	none	do	28,900

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DC4-5025
BY C.W. Christen POSITION Chief, L.W. 8.
DATE 8-13-54

[redacted]

the precipitates obtained settled very poorly and the supernatants were left turbid. Filtration was slow and difficult. Several passes through one fluted filter paper were required in order to secure a clear filtrate. It is possible that calcium fluoride might be a satisfactory carrier. However, practical difficulties in connection with its use are indicated to be very considerable. Accordingly, the further investigation of calcium fluoride as a plutonium carrier in the presence of citrate is being held in abeyance.

TABLE IX

Removal of Pu added to Tap Water (68,000 C/M/L) Using a Calcium Fluoride Carrier (1/2 hour stirring, filtration through paper in all cases)

Trial No.	Chemicals Added $FeCl_3$	NaF	$CaCl_2$	Lime	Residual Pu C/M/L
1	20 ppm	50	50	to pH 9.8	26,700
2	20 ppm	100	100	to pH10.1	8,950
3	20 ppm	200	200	to pH10.2	2,550
4	20 ppm	400	400	to pH10.1	950

An alternative carrier contemplated is tribasic calcium phosphate. Only one check of this material to be described later, has been undertaken. The number of carriers which might be investigated is almost unlimited. However, from the standpoint of material cost, only a limited number of materials can be given serious consideration. It is planned to investigate

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C. W. Christen POSITION Chief, I. W. S.
DATE 8-13-54

 [redacted]

the possible use of a number of metals such as lead, bismuth, tin, titanium and molybdenum. These metals presumably would be tested as carriers in the form of the precipitate resulting from alkaline hydrolysis.

Destruction of Citrates by Biological Agents

Biological oxidation has shown some indications that it may prove adequate as a citrate removal process. Some very good activated sludges have been produced and maintained in the laboratory using citric acid as the principal organic food. Specific tests, to be described later, have indicated some preliminary promise that biological oxidation may prove adequate for citrate removal, either as a treatment or as a preliminary citrate reduction step applied before chemical precipitation. The possibilities of anaerobic destruction should also be investigated.

Investigation of DP West Wastes

A number of preliminary investigations were carried out on samples or prepared solutions into which citrate was introduced. However, it was deemed that more value would be obtained from work with some of the actually occurring citrate bearing wastes. Accordingly, steps were taken to secure waste samples from the DP West Area.

The first sample secured was taken February 23, and consisted of a series of small grab portions composited over a 15 minute period. This sample contained large amounts of synthetic detergent. On the basis of subsequent behavior and characteristics, the presence of considerable quantities of

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DC4-5025
BY C. W. Christensen POSITION Chief, I.W.S.
DATE 8-13-54

citrates was inferred.

A brief summary of some of the characteristics and behavior of this waste is given below.

I. Appearance and superficial examination: Waste was an opalescent cloudy solution with little suspended matter. It was obviously heavily laden with a synthetic detergent. (Suds formed on slight agitation and persisted in acid or limed solution.)

II. Analytical Values

pH - 7.3 B.O.D. - 250 ppm
Total solids - 828 ppm; Ash 30.6%
Pu - 22,000 C/M/L

III. Results of Several Pu Removal Procedures.

(1) $FeCl_3$ and lime. No formation of floc observed up to pH 9.5 Analysis not attempted.

(2) 2000 ppm of activated carbon added, stirred for 3 1/2 hours, filtered. Residual plutonium concentration was 2340 C/M/L.

(3) Chlorination (600 ppm) for 1 hr. contact period. 100 ppm $FeCl_3$ plus lime slurry. No floc or ppt. formed. 300 ppm NaF and $CaCl_2$, 50 ppm alum, pH adjusted to 9.5 with lime. Residual plutonium concentration in filtered effluent was 2000 C/M/L.

(4) 2/3 grams per liter $KMnO_4$, 20 ppm $FeCl_3$, H_2SO_4 added to bring pH down to 2.5. Stirred for 1-1/2 hrs. Lime slurry added to raise pH to 9.5, settled and filtered. Residual plutonium concentration was 28 C/M/L.

(5) 200 ppm of PO_4 added as Na_3PO_4. A small amount of lime added to raise pH to 10.0. Solution was stirred 30 minutes and filtered through paper. Residual plutonium concentration was 1550 C/M/L.

(6) 4 liters of sample was added to 1 liter of citrate specialized activated sludge and aerated for 24 hours. The activated sludge was allowed to settle from the mixture. One portion

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C.W. Christman POSITION Chief, L.W.S.
DATE 8-18-54

of the supernatant was filtered and analyzed for plutonium. The residual plutonium concentration was 1090 C/M/L. A second portion of the supernatant was flocculated with 20 ppm $FeCl_3$ and lime at pH 9.5. The residual plutonium concentration was 647 C/M/L.

In order to prevent misunderstanding of the relative value of the several treatments tried some comments appear to be in order.

(1) The precipitates resulting in steps 3 and 5 were extremely difficult to filter. In terms of plant operation such precipitates would be almost unmanageable.

(2) The fact that the waste was treated with activated sludge does not mean that an activated sludge process could be contemplated in connection with such a waste. The tendency of the waste to form large amounts of foam on aeration would preclude such a possibility. The sludge treatment was undertaken to get an index of the sort of results which might be obtained by the use of trickling filters. No attempt was made to remedy possible lack of nutritional elements in the waste. In spite of this fact a very considerable reduction in citrates must have occurred, as evidenced by the fact that after the biological treatment a good floc was readily obtained using iron and lime.

This group of citrate studies has represented only preliminary exploratory work. Further work is in progress. The lines of attack indicated for the immediate future are:

(1) Further study of the characteristics of DP West wastes.

(2) Further study of biological oxidation

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified
BY AUTHORITY OF DCL-5025
BY C. W. Christensen POSITION Chief, I.W.S.
DATE 8-13-54

 [redacted]

applied to this waste.

(3) Further study of citrate oxidation by permanganate.

(4) Continued search for a carrier which will remove Pu satisfactorily in the presence of citrates.

CLASSIFICATION CANCELLED (OR CHANGED) TO Unclassified [redacted]
BY AUTHORITY OF DOE-5425
BY G. W. Christman POSITION Chief, D.W.S.
DATE 8-13-54