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PRESOLIDIFICATION TREATMENTS
OF DECONTAMINATION WASTES

Report No. 81-468-K

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ABSTRACT

Unsatisfactory leaching performance of several solidified decontamination solutions indicated a need for presolidification treatments to reduce the water sensitivity of the active chemicals. Chemical treatments examined in this work include pH adjustment, precipitation and oxidation-reduction reactions. The reactions involved in these treatments are discussed. The most suitable presolidification treatment for each decontamination solution has been identified. Further research is needed to test the effectiveness of these treatments.

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740632-355-043	837.83	February 25, 1982	81-468-K



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EXECUTIVE SUMMARY

The intent of this work was to examine presolidification treatments of decontamination wastes which, if untreated, give solidified waste products with unfavourable leaching performance. The most suitable presolidification treatment(s) for each decontamination solution investigated are discussed.

Bituminized alkaline permanganate wastes experienced swelling under water immersion conditions in the first year of testing. To obviate this problem, permanganate solutions should be acidified to pH 8.0 and then reacted with Turco 4521A prior to immobilization.

Turco 4512 solution should be treated with aluminum chloride solution at pH 6.0 to precipitate aluminum complexes which contain Al-OH-Al and Al-PO₄-Al linkages.

Bituminized sodium carbonate/sodium bicarbonate wastes showed pronounced volume change shortly after immobilization. This problem may be circumvented by reacting these wastes with calcium hydroxide to form calcium carbonate (solubility equals 0.0014 g/100 cc at 298 K) prior to immobilization. In analogy with barium carbonate solidified wastes, it is expected that calcium carbonate waste would not develop any swelling or show any volume change under immersion conditions.

Turco 4521A and Peroxcit solutions contain reactive chemicals such as oxalate and citrate ions. These solutions should be treated first with calcium hydroxide for the precipitation of calcium oxalate and then reacted with hydrogen peroxide to oxidize oxalate and citrate ions remaining in solution to carbon dioxide and water.

Further research is required to evaluate the effectiveness of the recommended presolidification treatments. This will involve comparing the leaching performance of treated and untreated simulated wastes in various matrices.

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To Mr. F.J. Kee
Director of Research

PRESOLIDIFICATION TREATMENTS OF DECONTAMINATION WASTES

1. INTRODUCTION

Recently Williamson/1/ reported that aqueous radioactive wastes containing permanganate ions or anhydrous reactive chemicals such as peroxide bicarbonate which had been bituminized with hard asphalt, developed cracks and became swollen under water immersion conditions. This swelling is due to water penetration into the solidified wastes and subsequent reactions with water sensitive salts. To improve the physical characteristics and leaching performance of the affected waste products, presolidification treatments prior to immobilization are required. A literature survey of presolidification treatments of decontamination wastes revealed no suitable data are available. This study was undertaken to investigate, develop and evaluate presolidification treatments which will result in solidified waste forms with improved water resistance, low leachability, low corrosion rates to containers, minimum volume and minimum cost/2/.

2. RESULTS AND DISCUSSION

Decontamination solutions investigated in this work are summarized in Table 1. These solutions have been divided into four categories.

- 2.1 Alkaline permanganate solutions.
- 2.2 Phosphate and metaphosphate containing solutions.
- 2.3 Peroxide bicarbonate solutions.
- 2.4 Oxalate and citrate containing solutions.

Detailed chemical composition and discussion of areas of application of these decontamination solutions have been reported elsewhere/3,4,5,6/.

TABLE 1

CHEMICAL COMPOSITION OF DECONTAMINATION SOLUTIONS

No.	Category	Code Name or Abbreviation	Chemical Composition	Solute Percentage	g/L	Molarity M	pH																																																																						
1	Alkaline permanganate solutions	Alkaline permanganate	KMnO ₄ NaOH	23	30	0.19	13.0																																																																						
				77	100	2.5		2	Phosphate or metaphosphate containing solutions	Turco 4512	H ₃ PO ₄	85	50.0	0.43	1.4	100	10.0	0.016	10.0	Calgon	Na ₆ P ₆ O ₁₈	50	5.0	0.0082	6.5	25	2.5	0.0082	Pickering Solution	Na ₆ P ₆ O ₁₈ Na ₂ C ₁₅ H ₂₃ SO ₃ Na ₂ C ₁₀ N ₂ H ₁₄ O ₈	25	2.5	0.0074		100	10	0.027	9.0	3	Carbonate-bicarbonate solutions	Peroxide bicarbonate	Na ₂ CO ₃ ·10H ₂ O NaHCO ₃ H ₂ O ₂	57	72.4	0.25	9.8	27	34.3	0.41	16	20.3	0.60				4	Oxalate and citrate solutions	Turco 4521A	(NH ₄) ₂ HC ₆ H ₅ O ₇ H ₂ C ₂ O ₄	66	33	0.15	4.0	34	17	0.19		Peroxcit	H ₂ C ₂ O ₄ C ₆ H ₈ O ₇ H ₂ O ₂	54	51	0.56	1.0	33	31	0.16	13
2	Phosphate or metaphosphate containing solutions	Turco 4512	H ₃ PO ₄	85	50.0	0.43	1.4																																																																						
				100	10.0	0.016	10.0																																																																						
		Calgon	Na ₆ P ₆ O ₁₈	50	5.0	0.0082	6.5																																																																						
				25	2.5	0.0082																																																																							
		Pickering Solution	Na ₆ P ₆ O ₁₈ Na ₂ C ₁₅ H ₂₃ SO ₃ Na ₂ C ₁₀ N ₂ H ₁₄ O ₈	25	2.5	0.0074																																																																							
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		Peroxcit	H ₂ C ₂ O ₄ C ₆ H ₈ O ₇ H ₂ O ₂	54	51	0.56	1.0																																																																						
				33	31	0.16																																																																							
				13	12	0.36																																																																							

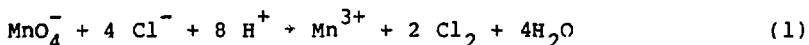
Presolidification treatments examined in this work are pH adjustment, precipitation reactions, oxidation-reduction reactions and a combination of these treatments, ie, pH adjustment followed by either oxidation-reduction or precipitation reactions. Advantages associated with these treatments include the formation of harmless products such as water and carbon dioxide in addition to solid products which should contain most of the activity. It should be noted that all experiments were carried out at room temperature and all samples were prepared as described in Appendix 1.

2.1 Treatment of Alkaline Permanganate Solutions

Permanganate ions are easily reduced (depending on the pH) to manganese (II) species and/or manganese dioxide by oxidizable organic ligands such as oxalate and citrate ions or by inorganic ions ie, ferrous (II) cations. This fact suggests that Turco 4521A (a decontamination solution containing a mixture of oxalate and citrate ions in the ratio of 1.25 to 1) may be employed for the destruction of permanganate ions. Prior to investigating treatment with Turco 4521A, the fundamental chemistry associated with the destruction of permanganate ions by pH adjustment followed by reaction with oxalate and citrate ions was examined.

2.1.1 Reduction of Permanganate Ions by pH Adjustment

The nature of permanganate species in solution is pH sensitive. At pH 13, the predominant species is permanganate ions. On acidification to pH 8, however, a dark brown precipitate of manganese dioxide is formed. The choice of acid used for neutralization is important. In this work, it is suggested that sulfuric acid be used as this acid contains twice the number of protons as hydrogen chloride, thus only half the volume of acid is required. Furthermore, in the absence of reducing agents, ie, oxalate ions, chloride ions are easily oxidized to corrosive and toxic chlorine gas as illustrated in Equation 1/8/.



The pH level of 8.0 was chosen because it is a desirable pH for acceptable immobilization of permanganate wastes in asphalt or water extendible resins (WER).

The results tabulated in Table 2 show that pH adjustment is an inefficient presolidification treatment as only 8% of permanganate ions are destroyed. This finding led to the investigation of permanganate ion destruction by pH adjustment and subsequent addition of oxalate and citrate ions.

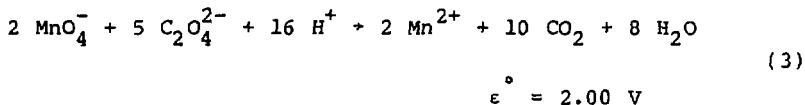
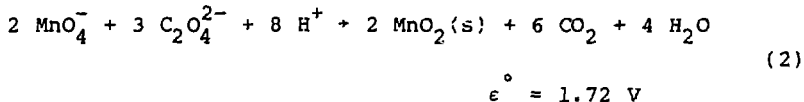
TABLE 2

PERCENTAGE OF PERMANGANATE IONS DESTROYED AT PH=8.0

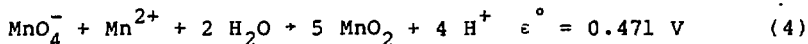
Weight of Permanganate, g	Vol, mL	PH	Weight of MnO_2 (g)	Moles of Manganese Dioxide	% of Permanganate Ions Destroyed
3.0083	150	8.2	0.1394	0.0016	8.4
3.0183	150	8.1	0.1444	0.0016	8.4
3.0500	150	7.8	0.1616	0.0019	9.8
			Aver.=0.1485	Aver.=0.0017	Aver.=8.9

2.1.2 Treatment of Permanganate Ions by Oxalate Ions

Typical permanganate/oxalate reactions are summarized in Equations 2 and 3/7,8/.



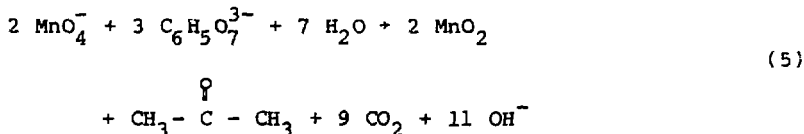
In the presence of excess permanganate ions the predominant product is solid manganese dioxide as shown in Equation 4.



To investigate the effect of oxalate to permanganate ratios on the weight of solid manganese dioxide formed and on the residual concentration of both manganese and oxalate ions in solution at pH = 8.0 a series of solutions containing oxalate to permanganate ratios of 0.5, 1.0, 1.5, 2.0 and 2.5 were studied. Variations of these parameters with oxalate to permanganate ratios are summarized in Table 3 and depicted in Figures 1 and 2. These data suggest that maximum solid manganese dioxide is obtained from solutions containing oxalate to permanganate molar ratio of 2 to 1. Support for this finding is based on the observation that the residual percentages of both manganese and oxalate ions in solution at 2 to 1 molar ratio are 0.0015 and 1.9 respectively.

2.1.3 Treatment of Permanganate Ions by Citrate Ions

Reactions of citrate ions with permanganate ions are more complex than oxalate-permanganate reactions due to the fact that oxidation of citrate ions may yield several by-products such as acetone and/or partially decarboxylated citrate ions as shown in Equation 5.



Duplicate runs of solutions containing 0.28, 1.0, 1.5, 2.0 and 2.5 citrate to permanganate molar ratio were analyzed to ascertain the weight of solid manganese dioxide formed and residual percentages of both total manganese and citrate ions in solution.

TABLE 3
PERCENTAGE OF MANGANESE AND OXALATE IONS, REMAINING IN SOLUTION
AT VARIOUS OXALATE TO PERMANGANATE MOLAR RATIOS AT PH=8.2±0.1

No.	Weight of Oxalate(g)	Weight of Permanganate (g)	$C_2O_4^{2-}:MnO$ Mole Ratio	Wt. of MnO_2 (g)	Mn Remaining In Solution (mg/L)	% Mn Remaining In Solution	$C_2O_4^{2-}$ Remaining In Solution (mg/L)	% $C_2O_4^{2-}$ Remaining In Solution
1	0.8851	3.0075	0.517	0.6617	3190	16.97	500	9.0
2	1.7727	3.0312	1.03	1.3826	2200	11.90	705	6.6
3	2.5711	3.0840	1.47	1.6744	1040	6.07	685	4.8
4	3.4570	3.0181	2.00	2.3003	0.26	0.0015	380	1.9
5	4.3700	3.0742	2.54	2.1424	1.46	0.007	2120	8.2

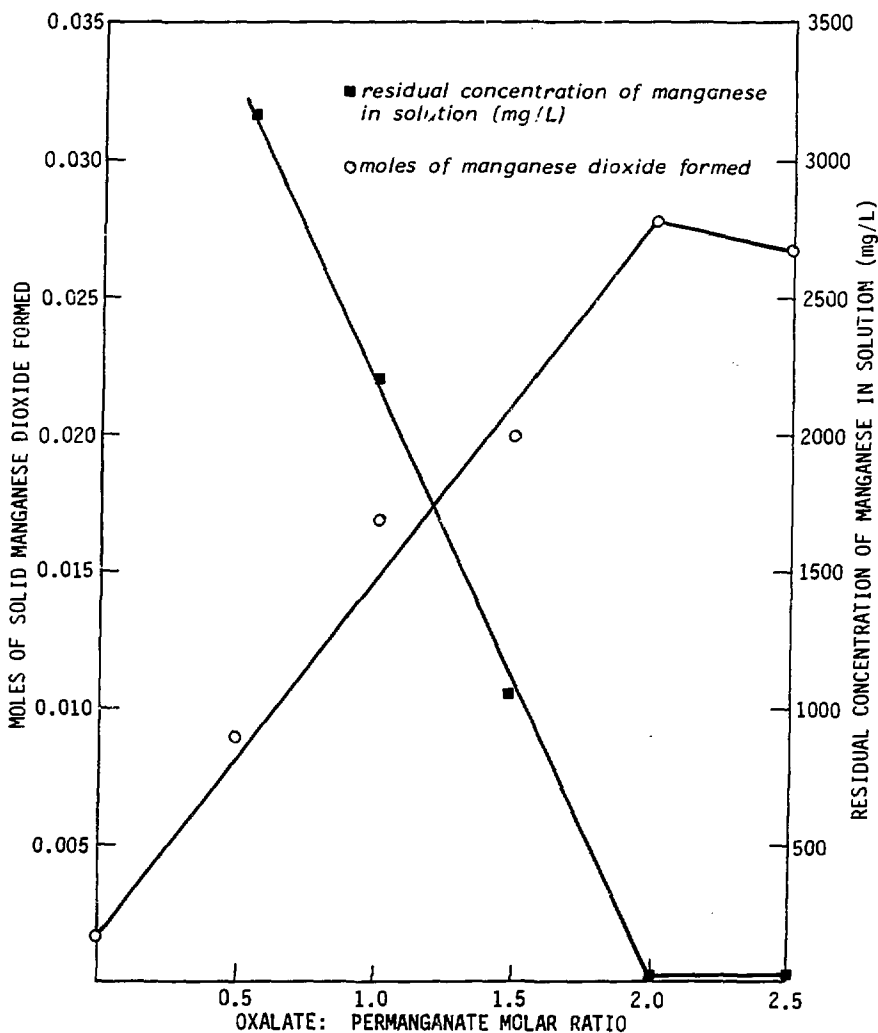


FIGURE 1

SOLID MANGANESE DIOXIDE AND THE RESIDUAL CONCENTRATION OF MANGANESE IN SOLUTION AT VARIOUS OXALATE/PERMANGANATE MOLAR RATIOS

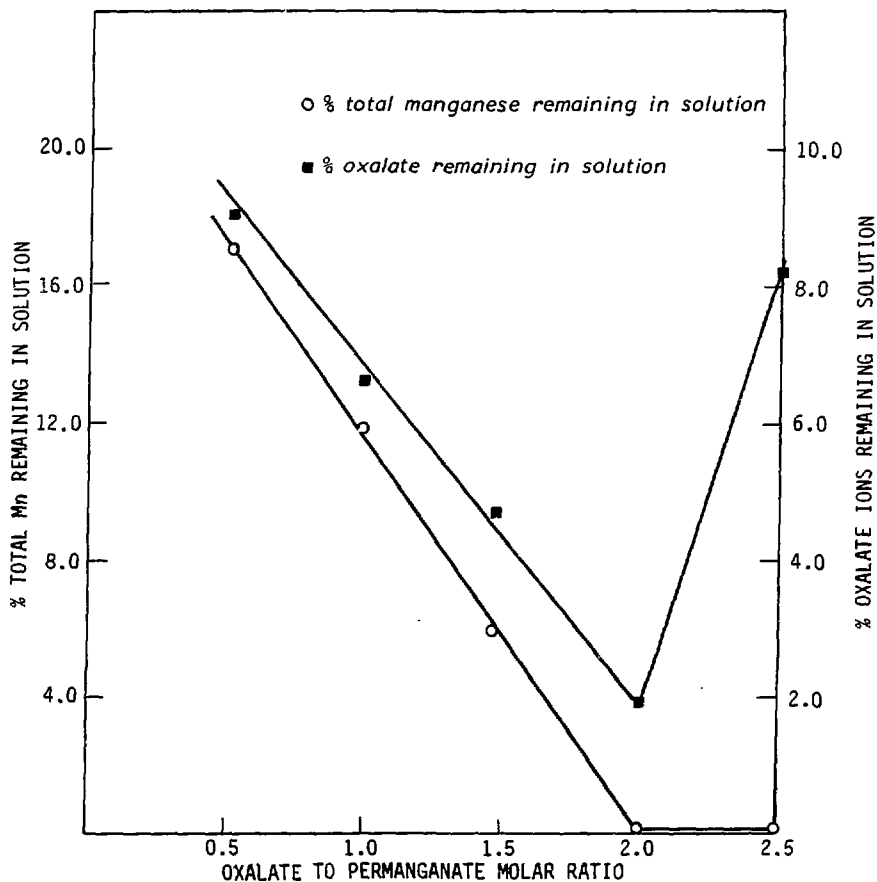


FIGURE 2

PERCENTAGE MANGANESE AND PERCENTAGE OXALATE REMAINING IN SOLUTION AT VARIOUS OXALATE TO PERMANGANATE MOLAR RATIOS AT pH 8.2±0.1

Variations of these parameters with citrate to permanganate molar ratio (Z) are presented in Tables 4 and 5 and displayed in Figures 3 and 4. Figure 3 shows that solutions containing citrate to permanganate molar ratio of 1 to 4 resulted in 99.9% permanganate destruction with 0.1% and 13% respectively of manganese and citrate ions in solution. As shown in Figure 4 increasing the citrate to permanganate ratio to greater than 1 to 4 is of no benefit and results only in higher residual concentrations of citrate ions in solution.

According to Equation 5, maximum destruction of permanganate ions is expected for solutions containing Z ratio of 3 to 2. The experimental results showed maximum permanganate destruction occurred at a Z ratio of 0.28 indicating possible formation of manganese citrate complexes and partially decarboxylated citrate ions.

2.1.4 Treatment of Permanganate Ions by Reaction With Turco 4521A Solutions

The earlier experimental work showed that permanganate solutions can be successfully treated with either oxalate or citrate ions. This observation led to the use of Turco 4521A for the destruction of permanganate ions. Typical values for manganese dioxide formed and residual oxalate and citrate in solution are given in Table 6. These data suggest that:

- Excess permanganate ions in solution resulted in maximum precipitation of manganese dioxide.
- The amount of manganese dioxide formed was the highest at citrate to permanganate molar ratio of 0.28 to 1 and then decreased as the ratio increased.
- No precipitate was detected for solutions containing oxalate to permanganate ratio >6 and citrate to permanganate ratio >2.
- Maximum oxalate and citrate destruction occurred for solutions containing oxalate to permanganate molar ratio of 3 to 1 and a citrate to permanganate molar ratio of 0.28.

These observations suggest that permanganate ions can be destroyed by mixing alkaline permanganate with Turco 4521A in a one to one volume ratio.

2.1.5 Treatment With Ferrous Ammonium Sulfate

Treatment of permanganate ions with ferrous sulfate solutions involves reduction of permanganate ions to manganese (II) and oxidation of ferrous (II) to ferric (III) as given in Equation 6/10/:

TABLE 4

**WEIGHT OF SOLID MANGANESE DIOXIDE AND PERCENTAGE OF MANGANESE CITRATE
REMAINING IN SOLUTION AS A FUNCTION OF MOLAR RATIOS AT PH= 8.0**

No.	Wt. of Citrate (g)	Wt. of Permanganate (g)	$C_6H_5O_7^{3-} : MnO_4^-$ Mole Ratio	Wt. of MnO_2 Formed (g)	Mn Remaining In Solution (mg/L)	% Mn Remaining In Solution	$C_6H_5O_7^{3-}$ Remaining In Solution (mg/L)	% Citrate Remaining In Solution
1	1.1884	3.0027	0.276	2.8644	16.4	0.082	900	11.4
2	4.3134	3.0087	1.04	2.2887	116	0.60	7200	25.9
3	6.4782	3.0094	1.50	2.0909	530	2.8	15800	39.0
4	8.5738	3.0427	1.97	0.9302	1490	8.6	20000	40.8
5	10.7559	3.0225	2.48	0.0799	720	4.0	22000	34.8

TABLE 5

WEIGHT OF SOLID MANGANESE DIOXIDE, PERCENTAGE OF MANGANESE AND PERCENTAGE OF CITRATE IONS
REMAINING IN SOLUTION AT VARIOUS CITRATE TO PERMANGANATE RATIOS pH = 8.0

No.	Wt. of $C_6H_5O_7^{3-}$ (g)	Wt. of MnO_4^- (g)	$C_6H_5O_7^{3-}:MnO_4^-$ Mole Ratio	Wt. of MnO_2 Formed (g)	Mn Remaining in Solution (mg/L)	% Mn Remaining In Solution	Citrate Remaining In Solution (mg/L)	% Citrate Remaining In Solution
1	1.1932	3.0198	0.276	3.4240	10.6	0.070	900	15.1
2	4.3135	3.0067	1.00	2.0917	122	1.01	4600	26.7
3	6.4611	3.0158	1.50	1.4283	400	2.52	12000	35.3
4	8.5730	3.0493	1.96	1.1394	1390	10.2	13800	36.2
5	10.7615	3.0360	2.48	0.2817	2000	17.1	15000	36.2

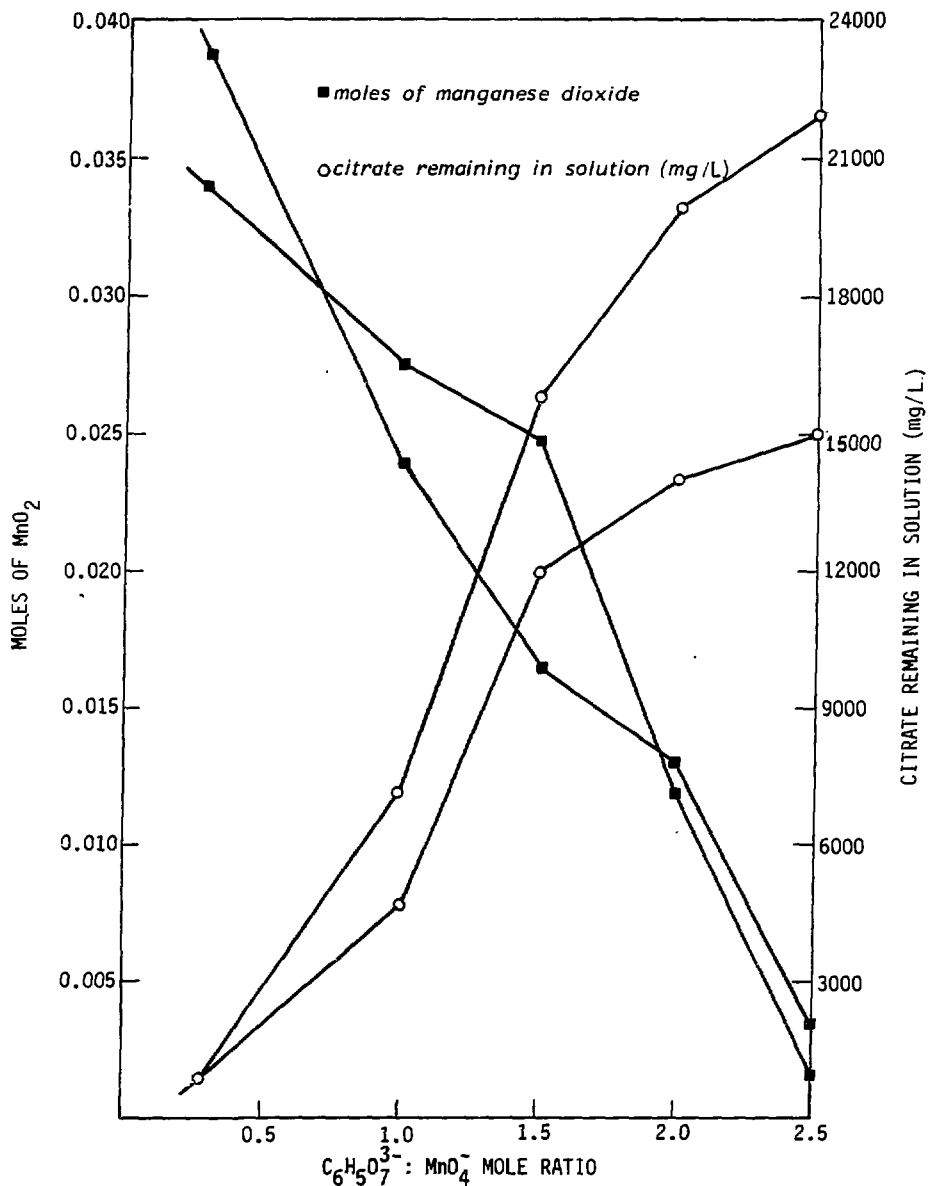


FIGURE 3

MANGANESE DIOXIDE AND RESIDUAL CITRATE IN SOLUTION AT VARIOUS CITRATE TO PERMANGANATE RATIOS

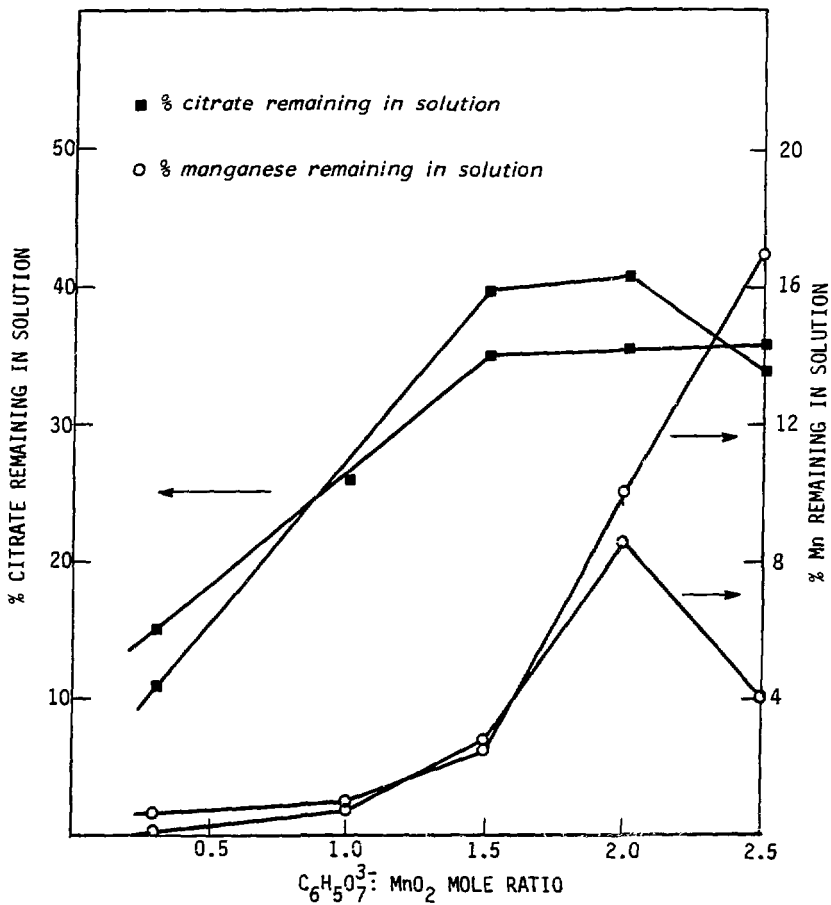


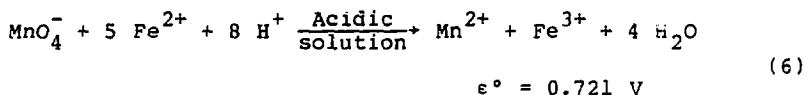
FIGURE 4

PERCENTAGE CITRATE REMAINING IN SOLUTION AT VARIOUS
 $C_6H_5O_7^{3-} : MnO_2$ RATIOS
 pH = 8.1 ± 0.1

TABLE 6

OXALATE & CITRATE DESTRUCTION AT VARIOUS OXALATE TO PERMANGANATE AND CITRATE TO PERMANGANATE RATIOS.
 PERMANGANATE CONCENTRATION = 0.189 MOLES PER L, OXALATE = 0.156 MOLE PER L AND CITRATE = 0.0532 MOLES PER L

No.	Vol. of Permanganate mL	Vol. of Citrate and Oxalate, mL	Moles of Permanganate	Oxalate to Permanganate Ratio	Citrate to Permanganate Ratio	Total Volume mL	Initially Present (mg/L)	Oxalate Remaining In Solution (mg/L)	% Oxalate Destroyed	Initially Present (mg/L)	Citrate Remaining In Solution (mg/L)	% Citrate Destroyed	Moles of Manganese Dioxide
1	20	20	0.0038	0.82	0.28	40.8	6686	2700	60	5027	1750	65	0.0055
2	10	25	0.0019	2.05	0.70	35.5	9670	2300	76	6923	2250	67	0.0028
3	10	50	0.0019	4.12	1.4	67.2	10214	5700	44	7481	4500	40	0.0025
4	5	37.5	0.00095	6.13	2.10	48.8	10444	6000	43	7715	5500	29	0.0028
5	5	10	0.00095	1.64	2.80	15.2	9038	2500	72	6619	2200	67	0.0013
6	5	75	0.00095	12.3	4.10	96.6	10664	6800	36	7830	9250	63	-----
7	5	125	0.00095	20.4	7.0	130.0	13132	7000	47	9748	10250	76	-----
8	1	50	0.00019	41.0	14.0	53.8	12746	7500	41	9627	11000	34	-----



Equation 6 indicates that the theoretical equivalent point is reached if the molar ratio of ferrous (II) ions to permanganate ions is 5 to 1. The experimental results presented in Table 7 point out that the equivalent point was reached when 51.17 mL of ferrous (II) solutions were added. This volume is equal to 0.0051 mol of ferrous (II) ions which corresponds to a ferrous to permanganate ratio of 5.4 to 1. The discrepancy between the theoretical and experimental ratios is attributed to over-titration.

A comparison of presolidification treatments for alkaline permanganate wastes is given in Table 8. The results obtained in this work suggest that the recommended presolidification treatment involves mixing equal volumes of permanganate solutions with Turco 4521A and if precipitation is incomplete a solution containing a mixture of oxalate and citrate ions in the ratio of 3 to 1 should be added. Details of this procedure are given in Appendix 2.

2.2 Treatment of Phosphate and Metaphosphate Containing Solutions

2.2.1 Phosphoric Acid Solution (Turco 4512)

Phosphoric acid solutions treated with aluminum chloride will precipitate phosphate and/or hydroxide ions as aluminum complexes. The effect of both pH and phosphate to aluminum (III) molar ratio (R) on the weight of aluminum complexes formed was investigated at R values of 0.8, 1.6 and 3.2 and pH levels of 6.0, 7.0 and 8.0. The weight of solid aluminum phosphate/aluminum hydroxide and the residual concentration (mg/L) of both aluminum and phosphate ions in solution were determined. The results are summarized in Table 9 and exhibited in Figures 5 and 6. Based on these data the following observations can be made:

1. The residual concentration of aluminum ions in solution increased from less than 1.0 mg/L at pH 6 and R = 0.8 to 11 mg/L at pH 7.4 and R = 0.8.
2. The residual concentration of phosphate ions in solution also increased from 33 mg/L at pH 6 and R = 0.8 to 194 mg/L at pH 8.0 and R = 0.8.
3. At each pH level investigated, the residual concentrations of both aluminum and phosphate ions in solution were always lowest in the presence of excess aluminum. These observations are in agreement with the results reported by Hsu/11/ which showed that the optimum pH range for aluminum

TABLE 7
VOLUMES OF 0.1N FERROUS AMMONIUM SULFATE REQUIRED
TO TITRATE 5.0 mL SAMPLES OF 0.19 M PERMANGANATE SOLUTIONS

No.	Vol. of MnO_4^- mL	Moles of $\text{MnO}_4^- \times 10^4$	Vol. of Fe^{2+} mL	Moles of $\text{Fe}^{2+} \times 10^3$	$\text{Fe}^{2+}:\text{MnO}_4^-$ Ratio (exp)	$\text{Fe}^{2+}:\text{MnO}_4^-$ Ratio (Theor.)
1	5.0	9.49	51.24	5.12	5.4	5
2	5.0	9.49	51.04	5.10	5.4	5
3	5.0	9.49	51.58	5.16	5.4	5
4	5.0	9.49	50.84	5.08	5.5	5
5	5.0	9.49	51.13	5.11	5.4	5

TABLE 8
COMPARISON OF PRESOLIDIFICATION TREATMENTS
FOR ALKALINE PERMANGANATE SOLUTIONS

No.	Presolidification Treatments	Advantages	Disadvantages	Recommended Treatment
1	pH adjustment	simple	Low percentage of permanganate destruction.	
2	Oxalate addition	<ol style="list-style-type: none"> 1. forms solid manganese dioxide which contains most of the activity. 2. The pH after treatment is 8 which is required for acceptable immobilization. 	<ol style="list-style-type: none"> 1. The volume increased by about 40%. 	
3	Citrate addition	<ol style="list-style-type: none"> 1. forms solid manganese dioxide. 2. The pH after treatment is 8 which is required for acceptable immobilization. 	<ol style="list-style-type: none"> 1. The volume increased by about 40%. 	
4	Turco 4521 A	<ol style="list-style-type: none"> 1. Already available as a second step decontaminant. 2. Contains oxalate and citrate ions and thus forms solid manganese dioxide. 	<ol style="list-style-type: none"> 1. May require the addition of extra oxalate and citrate because some of the oxalate and citrate originally present in solution may have been reacted with the oxide film during decontamination operations. 	Recommended
5	Titration with ferrous sulfate	Easy to perform.	<ol style="list-style-type: none"> 1. The volume increase may reach 40%. 2. The titration is conducted in acidic solution. Thus sodium hydroxide must be added to adjust the pH to 8.0 for immobilization. 	

TABLE 9

TREATMENT OF ACID SOLUTIONS WITH ALUMINUM CHLORIDE AT VARIOUS
pH LEVELS AND PHOSPHATE TO ALUMINUM MOLAR RATIOS

Sample No.	Moles of $PO_4^{3-} \times 10^3$	Moles of $Al^{3+} \times 10^3$	pH	PO_4^{3-} / Al^{3+} Molar Ratio	PO_4^{3-} Remaining In Solution (mg/L)	Weight of Aluminum Percipitate (g)	Al Remaining In Solution (mg/L)
1	1.59	2.0	5.95	0.795	33	0.2361	<1
2	3.18	2.0	5.95	1.59	740	0.2704	<1
3	6.36	2.0	5.95	3.18	2300	0.3056	<1
4	1.59	2.0	7.10	0.795	57	0.2496	<1
5	3.18	2.0	6.95	1.59	510	0.2247	10
6	6.36	2.0	7.00	3.18	2200	0.2788	24
7	1.59	2.0	8.05	0.795	194	0.2710	11
8	3.18	2.0	7.40	1.59	800	0.2670	35
9	6.36	2.0	7.65	3.18	2440	0.2902	16

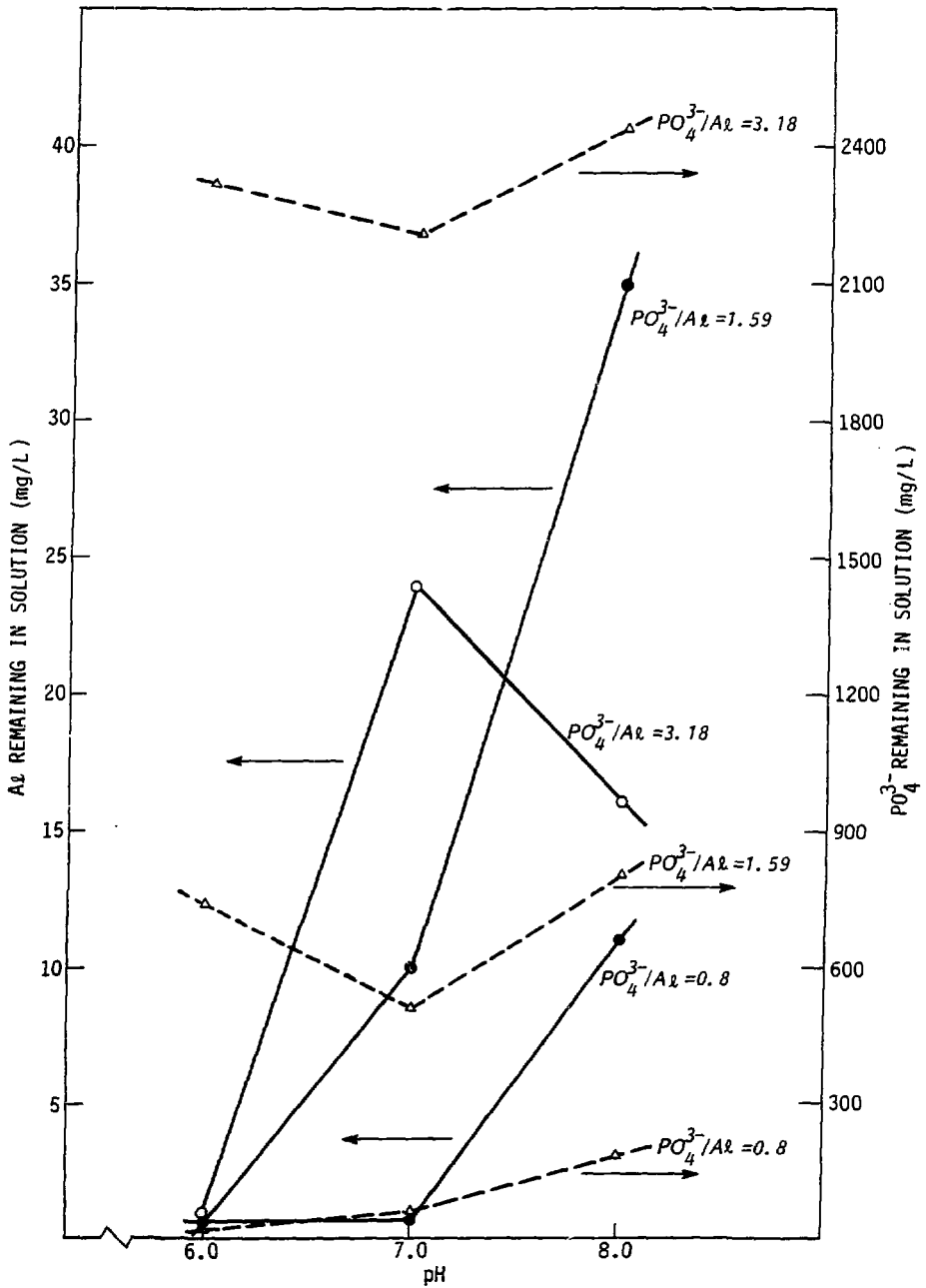


FIGURE 5

RESIDUAL CONCENTRATION OF ALUMINUM AND PHOSPHATE IN SOLUTION

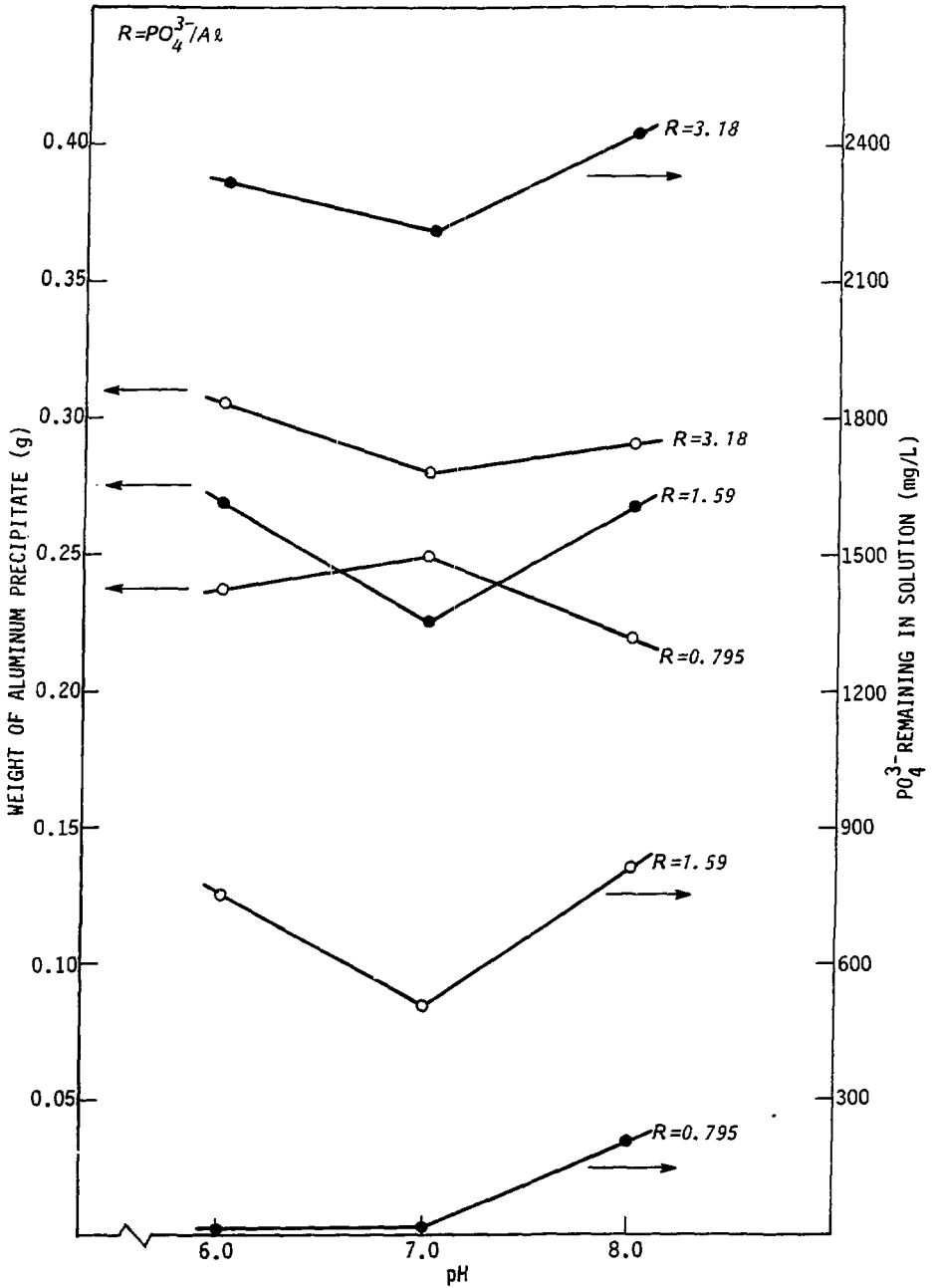


FIGURE 6

WEIGHT OF ALUMINUM PRECIPITATE AND RESIDUAL CONCENTRATION OF PHOSPHATE IN SOLUTION AT VARIOUS pH LEVELS

phosphate precipitation in aluminum chloride-sodium dihydrogen phosphate systems is pH 6 to 8.

4. At each pH level, the residual concentration of both aluminum and phosphate ions increased sharply with increased initial phosphate concentration ($R > 1$).

These observations may be explained on the basis that phosphate precipitation is controlled by formation of Al-OH-Al and Al-PO₄-Al linkages rather than aluminum hydroxide and aluminum phosphate individually. At low pH and in the presence of excess aluminum, the product formed is dominated by Al-OH-Al linkages whereas in the presence of excess phosphate, Al-PO₄-Al linkages predominate/11,12,13/.

The data presented in Table 9 show that complete phosphate removal from Turco 4512 solutions can be achieved by reaction with aluminum chloride at pH 6.0.

2.2.2 Treatment of Sodium Tripolyphosphate Solutions (STPP)

Two treatments for STPP solutions were considered. The first is to react STPP solutions with aluminum chloride as described in Section 2.2.1 and the second involves reacting STPP solutions with a mixture of aluminum chloride and calcium nitrate. The following observations can be considered on the basis of the experimental results given in Tables 10 and 11 and displayed in Figures 7, 8 and 9.

- Precipitates are not formed from solutions containing excess TPP in the pH range 9.0 to 6.0.
- A white precipitate is formed from solutions containing excess aluminum in the pH range studied. This precipitate is thought to contain only Al-OH-Al linkages because aluminum tripolyphosphate is water soluble.
- As found with the Turco 4512 treatment, maximum precipitation occurred for solutions containing excess aluminum at pH 6.0.
- The weight of solid calcium and aluminum hydroxide increased as the pH increased to 8.0, whereas the residual concentration of both calcium and aluminum ions in solution decreased with increasing pH.

The preceding observations indicate that no benefit is obtained from presolidification treatments of TPP solutions with either aluminum chloride or a mixture of aluminum chloride and calcium nitrate as essentially all TPP ions remain in solution as shown in Table 12.

TABLE 10
 WEIGHTS OF ALUMINUM PRECIPITATE FORMED AT
 VARIOUS pH LEVELS AND TRIPOLYPHOSPHATE (TPP)
 TO ALUMINUM MOLAR RATIOS.

No.	Moles of TPP	Moles of Aluminum	pH	TPP to Aluminum Ratio	Wt. of Precipitate (g)	Aluminum Remaining In Solution (mg/L)
1	0.001	0.002	6.25	0.50	0.0638	340
2	0.002	0.002	6.00	1.00	-----	---
3	0.004	0.002	6.55	2.00	-----	---
4	0.001	0.002	7.25	0.50	0.0329	380
5	0.002	0.002	7.00	1.00	-----	---
6	0.004	0.002	7.15	2.00	-----	---
7	0.001	0.002	9.05	0.50	0.0277	440
8	0.002	0.002	9.00	1.00	-----	---
9	0.004	0.002	8.90	2.00	-----	---

TABLE 11

RESIDUAL CONCENTRATION OF ALUMINUM AND CALCIUM IONS AT VARIOUS
 NITRATE TO ALUMINUM AND CALCIUM TO ALUMINUM RATIOS
 pH LEVELS = 7.0 AND 8.0 AND THE TPP TO ALUMINUM RATIO IS 0.5 to 1.0

No.	TPP to Aluminum Molar Ratio	Nitrate to Aluminum Ratio	Calcium to Aluminum Ratio	pH	Wt. of Precipitate (g)	Residual Concentration of Aluminum (mg/L)	Residual Concentration of Calcium (mg/L)	TPP to Calcium Ratio
1	0.5	2.0	1.0	8.0	0.0636	208	32	0.5
2	0.5	4.0	2.0	7.9	0.0946	225	84	0.25
3	0.5	1.0	0.5	7.9	0.0464	340	30	1.0
4	0.5	2.0	1.0	7.0	0.0112	396	78	0.5
5	0.5	4.0	2.0	6.9	0.0172	326	138	0.25
6	0.5	1.0	0.5	6.9	0.0066	410	39	1.00

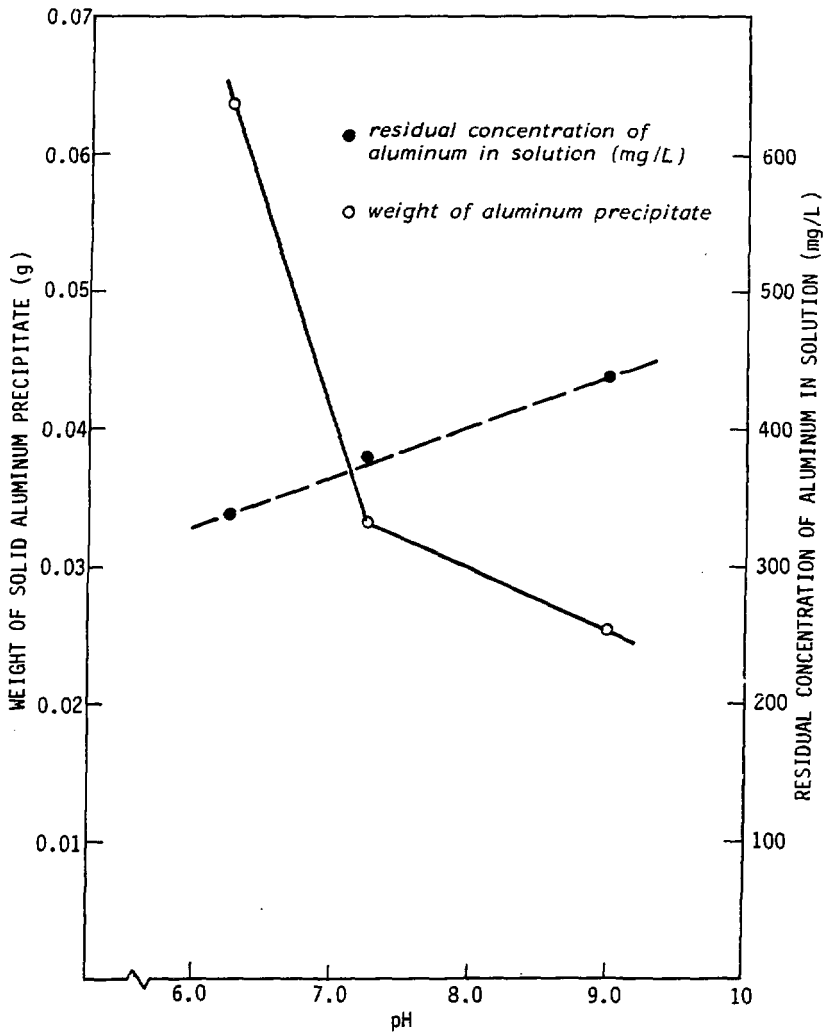


FIGURE 7

WEIGHT OF ALUMINUM TPP AND THE RESIDUAL CONCENTRATION OF ALUMINUM IN SOLUTION AT VARIOUS pH LEVELS
 x = RESIDUAL CONCENTRATION OF ALUMINIUM IN SOLUTION (mg/L)

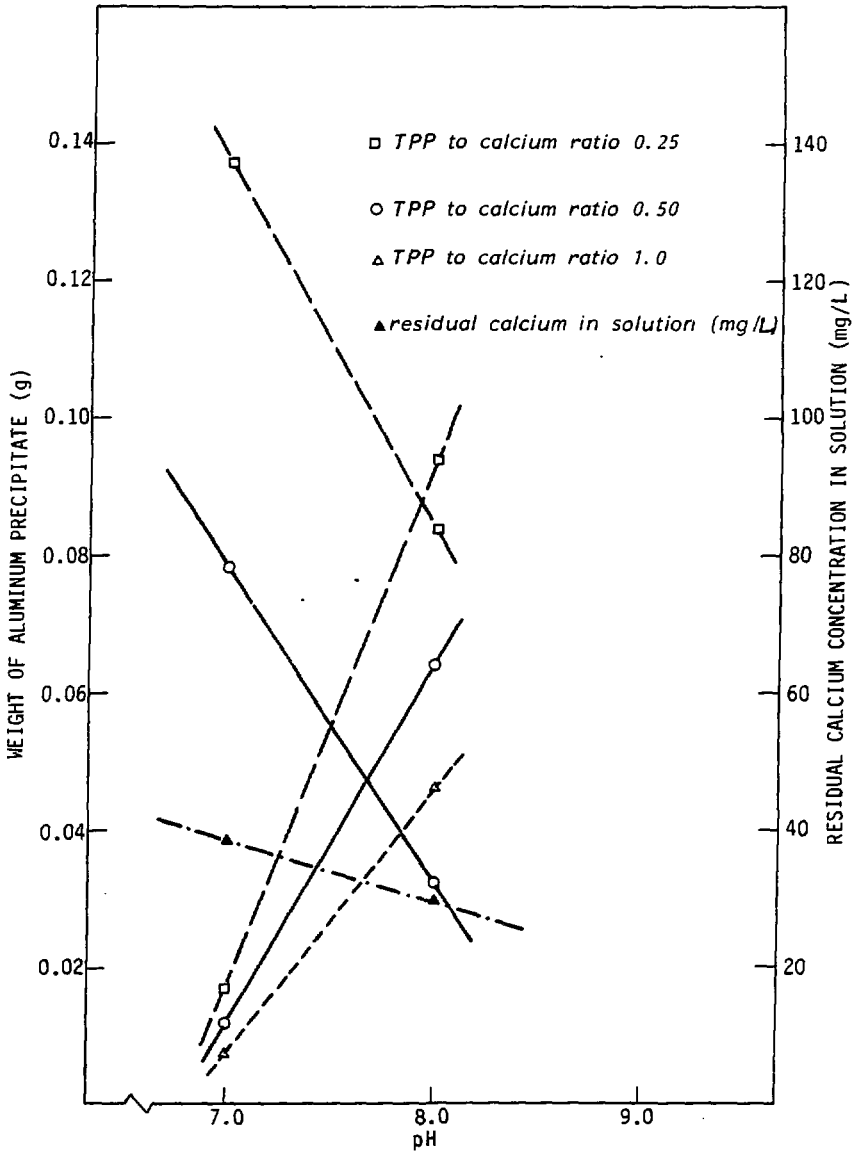


FIGURE 8

WEIGHT OF ALUMINUM PRECIPITATE AT VARIOUS pH LEVELS AND CALCIUM TO ALUMINUM RATIO

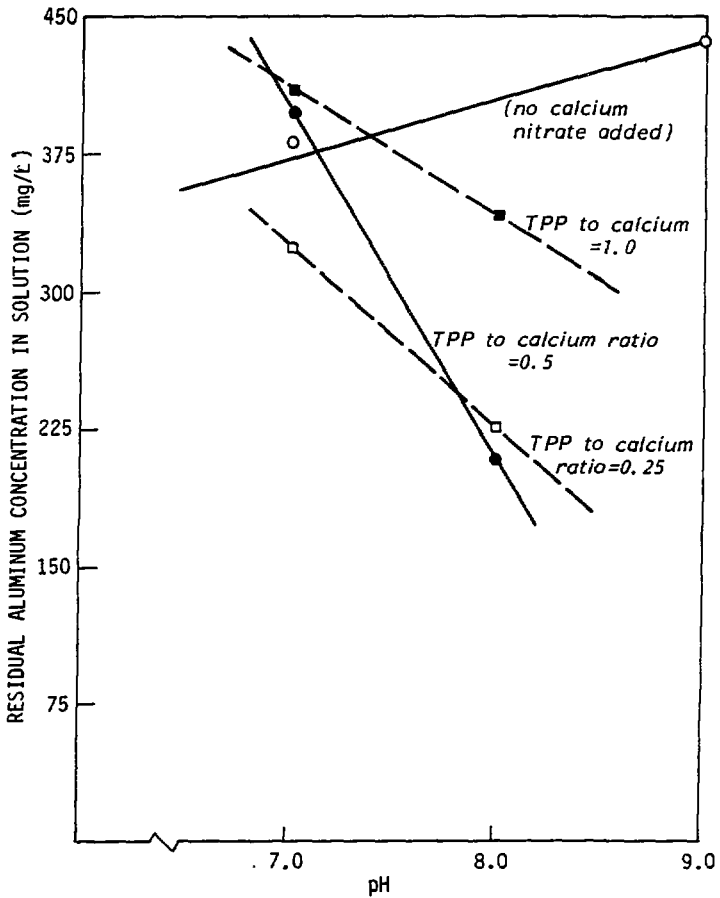


FIGURE 9
RESIDUAL CONCENTRATION OF ALUMINUM IN SOLUTION
AT VARIOUS pH LEVELS
TPP TO ALUMINUM RATIO IS 0.5

TABLE 12

ADVANTAGES AND DISADVANTAGES OF PRESOLIDIFICATION TREATMENTS OF TURCO 4512 & SODIUM TRIPOLYPHOSPHATE (STPP)

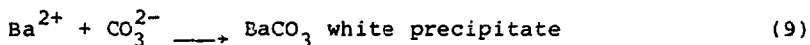
No.	Decontamination Solution	Presolidification Treatment (s)	Advantages	Disadvantages	Recommended Treatment
1	Turco 4512	Addition of aluminum chloride at various pH levels.	Formation of a precipitate containing Al-OH-Al and Al-PO ₄ -Al linkages, which would contain most of the activity.	The pH of the final product may require pH adjustment to 8.0.	Reaction with aluminum chloride at pH 6.0.
2	STPP	<ol style="list-style-type: none"> 1. Reaction with aluminum chloride at pH levels 6.0, 7.0 and 9.0. 2. Reaction with a mixture of aluminum chloride and calcium nitrate. 	The stability range of the precipitate formed was extended to higher pH levels.	<p>Inefficient removal of tripolyphosphate from solution.</p> <p>Inefficient removal of tripolyphosphate ions from solution.</p>	

2.3 Treatment of Peroxide Bicarbonate Solutions

Decontamination solutions containing carbonate-bicarbonate ions can be treated with barium chloride to form barium carbonate and nitric or hydrochloric acid to produce carbon dioxide, sodium nitrate and sodium chloride respectively. An advantage of barium chloride treatment is that solidified barium carbonate wastes have already been found to have favourable leaching performance/1/.

2.3.1 Treatment With Barium Chloride

When the peroxide bicarbonate solution was treated with barium chloride, the number of moles of barium carbonate formed was less than the theoretically expected value. This discrepancy is attributed to the formation of soluble barium bicarbonate in addition to barium carbonate as illustrated in Equations 8 and 9.

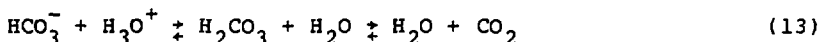


Evidence in support of barium bicarbonate formation is the existence of equilibria between carbonate and bicarbonate species at pH 6.38 and 10.32 as shown in Equations 10 and 11/14/



2.3.2 Treatment With Hydrochloric or Nitric Acids

Carbonate-bicarbonate ions are readily destroyed by hydrochloric or nitric acid as shown in Equations 12 and 13:



Complete neutralization of bicarbonate-carbonate samples was achieved by addition of either acid and confirmed when carbon dioxide gas ceased to evolve (see Table 13). A comparison of presolidification treatments for bicarbonate-carbonate solutions is summarized in Table 14.

2.4 Turco 4521A and Peroxycit Solutions

2.4.1 Treatment With Permanganate Solutions

As discussed in Section 2.1, citrate and/or oxalate ions can be destroyed by reaction with permanganate solutions. However, it is important to note that Turco 4521A or Peroxycit solutions should be added slowly to permanganate solutions to avoid

TABLE 13
PRESOLIDIFICATION TREATMENTS OF
PEROXIDE BICARBONATE SOLUTIONS (100 mL)

Description	Presolidification Treatment		
	Barium Chloride	Hydrogen Chloride	Nitric Acid
Weight of reactants (g)	12.5	---	---
Moles of reactants	0.06	---	---
Volume mL	---	10.8	11.2
Weight of product (g)	9.196	---	---
Moles of products	0.05	0.064	0.067
Products formed	Barium carbonate	Sodium chloride	Sodium Nitrate
	Barium bicarbonate	Water	Water
	Sodium chloride	Carbon dioxide	Carbon dioxide

TABLE 14
COMPARISON OF PRESOLIDIFICATION TREATMENTS
FOR PEROXIDE BICARBONATE SOLUTIONS

No.	Presolidification Treatment	Advantages	Disadvantages	Recommended Treatment
1	Reaction with barium chloride	Formation of barium carbonate which has been found to yield solid wastes with high water resistance .		Reaction with barium chloride at pH 6.5.
2	Acidification with nitric acid	Formation of innocuous compounds such as water and carbon dioxide.	Nitrate ions are very reactive towards oxidizing agents.	
3	Reaction with hydrochloric acid	Formation of innocuous compounds such as water and carbon dioxide.	Chloride ions are readily oxidized to chlorine gas by oxidizing agents.	

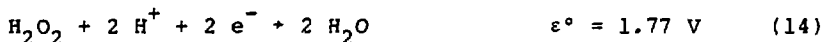
spattering. This problem, however, can be alleviated by using other oxidizing agents such as hydrogen peroxide.

2.4.2 Treatment With Hydrogen Peroxide

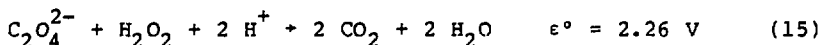
To investigate the impact of pH and hydrogen peroxide concentration on the degree of destruction of oxalate and citrate ions in Turco 4521A and Peroxcit solutions, it is first necessary to study this effect for solutions containing either oxalate or citrate ions.

2.4.2.1 Treatment of Oxalate Ions by Hydrogen Peroxide

The pH of solutions each containing 25.0 mL of 0.19 M oxalate and various volumes of 0.20 M hydrogen peroxide was adjusted to 1.6, 6.8, 10.0 and 12.0. Variations of the percentage of oxalate ions destroyed with pH are summarized in Table 15 and displayed in Figure 10. At pH \geq 7.0 the percentage of oxalate ion destroyed was about 30% and this value was found to be insensitive to pH changes in the range 7.0 to 12.0. As the pH was lowered to 1.6, the percentage of oxalate ions destroyed increased to about 60%. This increase may be explained on the basis that the reduction of hydrogen peroxide to water is acid catalyzed as shown in Equation 14/14/.



The overall reaction between oxalate and hydrogen peroxide is given in Equation 15.



The results obtained in this work suggest that solutions containing oxalate to peroxide molar ratio of approximately one to one experienced maximum oxalate destruction at pH 1.6. This observation is in agreement with Equation 15 which shows that maximum carbon dioxide formation is obtained if the oxalate to peroxide molar ratio is one to one. The principal advantage of this treatment is the formation of water and carbon dioxide whereas the disadvantages include a volume increase of about 100%.

2.4.2.2 Treatment of Citrate Ions by Hydrogen Peroxide

The procedure followed in this section is similar to that described in Section 2.4.2.1 except that the pH of the citrate solutions was adjusted to 5.10, 7.0, 9.0 and 12.0. The residual concentrations of citrate ions in solution were determined by ion chromatography. The obtained results are summarized in Table 16 and plotted in Figure 11. This figure shows that maximum citrate destruction (28%) occurred for solutions containing citrate to hydrogen peroxide molar ratio of 0.38 to 1 at pH 7.0. As the pH increased to 12, the average percentage of citrate ions destroyed decreased to 5%.

TABLE 15

PERCENTAGE OF OXALATE IONS DESTROYED BY HYDROGEN PEROXIDE AT VARIOUS pH LEVELS
 HYDROGEN PEROXIDE = 0.20 M, OXALATE = 0.19 M AND TEMPERATURE = 298 K

No.	Vol. of Oxalate mL	Vol. of NaOH mL	Vol. of Hydrogen Peroxide mL	pH	Total Volume (mL)	Oxalate Initially Present (mg/L)	Oxalate Remaining in Solution (mg/L)	% Oxalate Destroyed
1	25	---	10	1.6	35	12214	5500	55
2	25	---	25	1.6	50	8550	3000	65
3	25	---	50	1.6	75	5700	2500	56
4	25	33.81	10	6.8	68.81	6075	4350	28
5	25	34.32	25	6.8	84.32	4957	3500	29
6	25	34.12	50	6.8	109.12	3831	2700	30
7	25	34.00	10	10.0	69	6058	4200	31
8	25	34.15	25	10.0	84.15	4967	3300	34
9	25	34.30	50	10.0	109.3	3824	2600	32
10	25	7.01	10	12.0	42.0	9950	6900	31
11	25	7.00	25	12.0	57.0	7333	5000	32
12	25	7.10	50	12.0	52.1	5091	3500	31

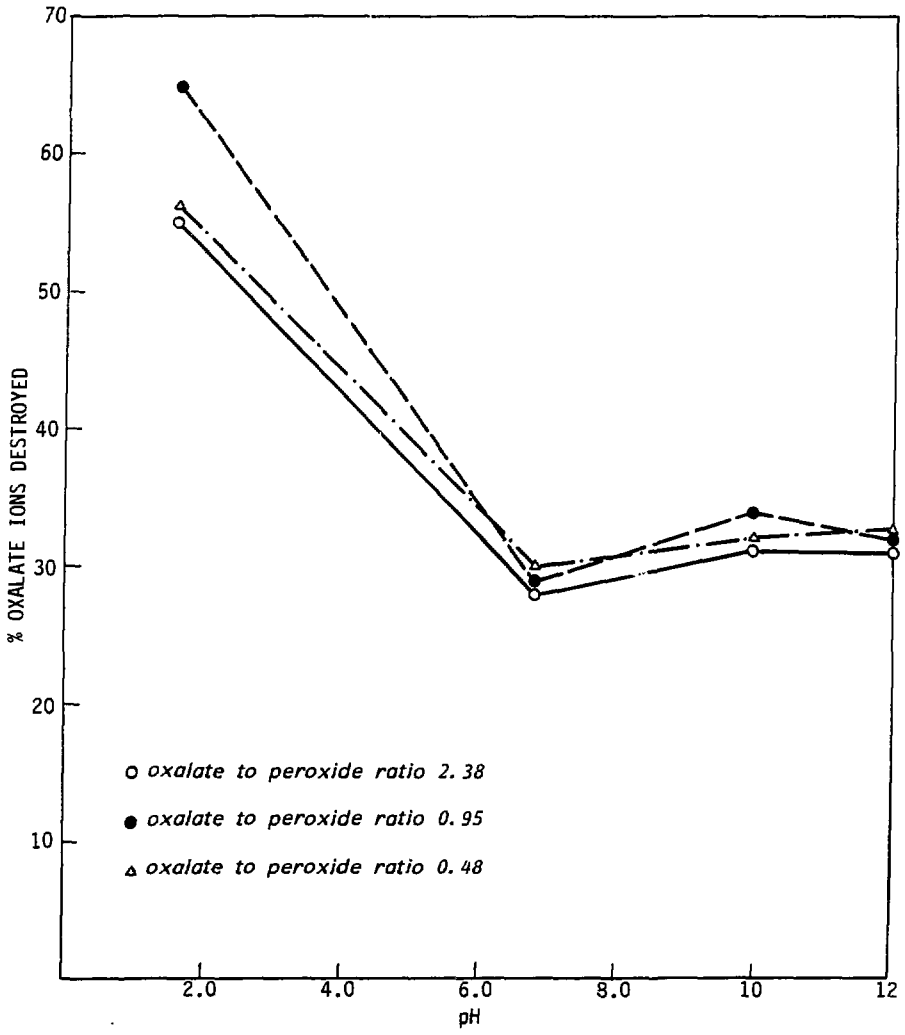


FIGURE 10

PERCENTAGE OF OXALATE IONS DESTROYED AT VARIOUS pH LEVELS

TABLE 16

PERCENTAGE OF CITRATE IONS DESTROYED BY HYDROGEN PEROXIDE
SOLUTIONS AT VARIOUS pH LEVELS
HYDROGEN PEROXIDE = 0.2 M, CITRATE = 0.15 M AND TEMPERATURE = 298 K

No.	Vol. of Citrate (mL)	Vol. of Sodium Hydroxide Added (mL)	Vol. of Hydrogen Peroxide (mL)	Total Volume mL	pH	mg/L of Citrate Initially Present	mg/L of Citrate Remaining	% Citrate Destroyed	Citrate to Hydrogen Peroxide Ratio
1	25	---	10	35	5.12	20250	19250	4.9	1.9
2	25	---	25	50	5.10	14175	13750	3.0	0.75
3	25	---	50	75	5.10	9450	8500	10.0	0.375
4	25	3.75	10	38.75	7.00	18290	17500	4.3	1.9
5	25	3.65	25	53.65	7.05	13211	117500	11.0	0.75
6	25	3.62	50	78.62	7.00	9015	6500	27.9	0.375
7	25	5.00	10	40.00	9.00	17719	16250	8.3	1.9
8	25	4.18	25	54.18	9.05	13081	11000	15.9	0.75
9	25	5.90	50	80.90	9.00	7963	7000	12.1	0.375
10	25	11.80	10	46.80	12.0	15144	15000	0.95	1.9
11	25	12.10	25	62.10	12.1	11413	11000	3.6	0.75
12	25	11.90	50	86.90	12.1	8156	7500	8.0	0.375

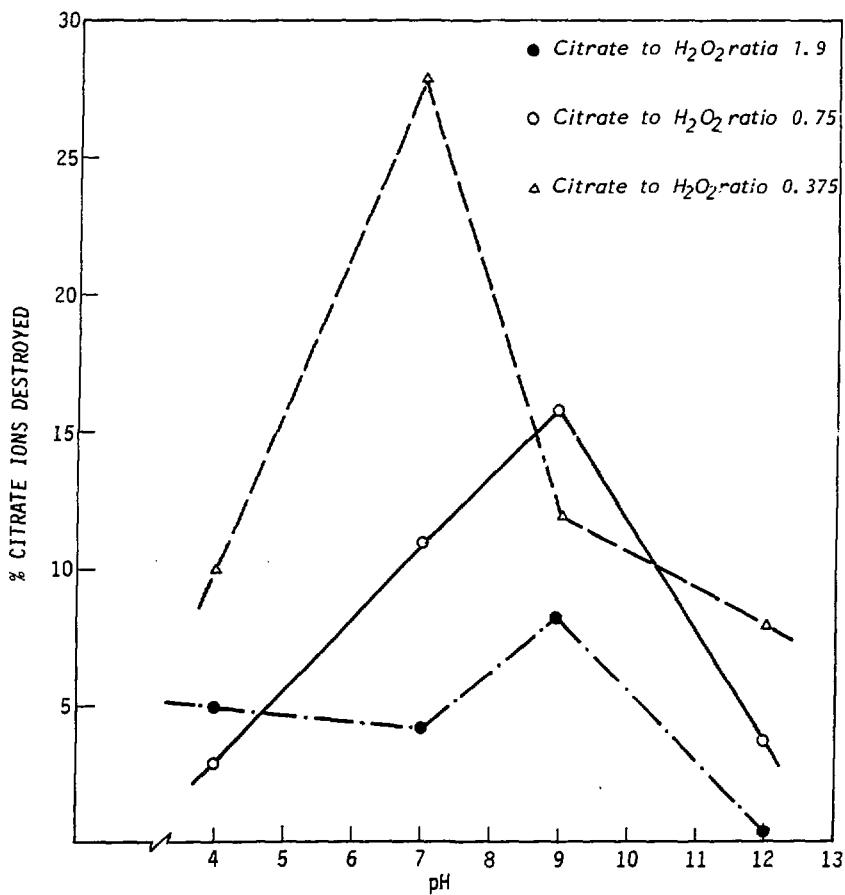


FIGURE 11

PERCENTAGE CITRATE IONS DESTROYED AT VARIOUS pH LEVELS
TEMPERATURE = 298 K

TABLE 17

PRESOLIDIFICATION TREATMENT OF PEROXCIT SOLUTION
BY CALCIUM HYDROXIDE. CITRATE = 0.16 M, OXALATE = 0.56 M
AND HYDROGEN PEROXIDE = 0.36 M. pH = 1.3

Volume of sample, mL	200	
Moles of oxalate	0.112	
Moles of citrate	0.032	
Weight of calcium hydroxide		9.0 g
Moles of calcium hydroxide		0.12
Weight of calcium precipitate		16.67 g
Moles of calcium oxalate [assuming precipitate is calcium oxalate]		0.12
% of oxalate converted to calcium oxalate		100 %

TABLE 18

PRESOLIDIFICATION OF PEROXCIT SOLUTION BY BARIUM HYDROXIDE
 CITRATE = 0.16 M, OXALATE = 0.56 M AND HYDROGEN PEROXIDE = 0.36 M

Volume of sample, mL	200	
Moles of oxalate	0.112	
Moles of citrate	0.032	
Weight of barium hydroxide, g		2.05
Moles of barium hydroxide		0.012
Weight of barium precipitate, g		1.89 g
Moles of solid barium oxalate		0.0083
% of oxalate converted to barium oxalate		67 %

TABLE 19

COMPARISON OF PRESOLIDIFICATION METHODS FOR PEROXCIT SOLUTIONS.

No.	Presolidification Treatment	Advantages	Disadvantages	Recommended Treatment
1	Addition of calcium hydroxide	<ol style="list-style-type: none"> 1. Formation of solid calcium oxalate. 2. 100% efficiency. 3. Relatively inexpensive. 	<ol style="list-style-type: none"> 1. 25% increase in volume. 	Recommended Treatment
2	Addition of barium hydroxide	<ol style="list-style-type: none"> 1. Formation of solid barium oxalate. 	<ol style="list-style-type: none"> 1. 25% increase in volume. 2. 67% efficiency. 3. More expensive than calcium hydroxide. 	

As reported in Section 2.4.2.1 this treatment also produces harmless compounds such as water and carbon dioxide.

2.4.3 Treatment of Peroxcit Solutions

The results reported in Sections 2.4.2.1 and 2.4.2.2 indicate that hydrogen peroxide can be used for the destruction of either oxalate or citrate ions. Based on these data it is also expected that both Peroxcit and Turco 4521A can be treated with hydrogen peroxide at room temperature.

In this section two additional treatments for the destruction of Peroxcit are examined. These treatments involve reaction with calcium or barium hydroxide to yield calcium and barium oxalate respectively. Two sets of typical data are shown in Tables 17 and 18. Based on these data it is seen that calcium hydroxide treatment is more efficient than that of barium hydroxide. This is because complete oxalate precipitation was achieved by calcium whereas only 67% of oxalate was precipitated by barium hydroxide.

Because of the similarities between the chemical composition of Turco 4521A and Peroxcit, it is expected that Turco 4521A may also be treated with calcium hydroxide. A comparison of presolidification treatments for Peroxcit solutions is tabulated in Table 19.

Finally, a summary of all recommended presolidification treatments along with their preferred procedures is described in Appendix 2.

3. CONCLUSIONS

An investigation of presolidification treatments for radioactive decontamination wastes has identified processes that can be applied to individual solutions prior to immobilization to obtain stable solid wastes with suitable water resistant characteristics. Recommended treatments for each solution are as follows:

Alkaline Permanganate

Adjust pH, then precipitate permanganate as manganese dioxide by reaction with Turco 4521A solution. This allows two commonly used decontamination solutions to be combined in a treatment appropriate to both.

Turco 4512

Precipitate phosphate as aluminum complexes containing Al-OH-Al and Al-PO₄-Al linkages by reaction with aluminum chloride at pH 6.0.

Peroxide Bicarbonate Solution

React with barium chloride to precipitate barium carbonate which yields immobilized wastes with favourable leaching performance.

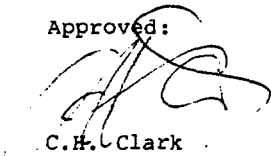
Peroxcit/Turco 4521A Solutions


Treat with calcium hydroxide to form solid calcium oxalate. Decant supernatant and treat with hydrogen peroxide for the destruction of citrate and oxalate ions remaining in solution.

Additional research is required to evaluate the benefits associated with the above presolidification treatments. This will involve investigating the leaching performance of treated and untreated simulated wastes in various matrices.

Approved:

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MAH:njm

REFERENCES

1. Williamson, A.S. Performance of Bituminized Aqueous Radioactive Wastes. Presented at the IAEA Seminar on the Management of Radioactive Wastes From Nuclear Power Plants. Karlsruhe, Federal Republic of Germany. 5-9. October 1981.
2. Moghissi, A.A., H.W. Godbee, M.S. Ozker and M.W. Carter. Nuclear Power Waste Technology. The American Society of Mechanical Engineers, New York, NY, 1978. p 284.
3. Ayres, J.A. Editor. Decontamination of Nuclear Reactors and Equipment. The Ronald Press Company. New York, NY, 1970. Chapter 5.
4. Spekkens, P. Chemical Decontamination - A Literature Survey. Research Report No. 81-11-R.
5. Choppin, G.R., R.L. Dillon, B. Griggs, A.B. Johnson, J.F. Remark and A.E. Martell. Literature Review of Dilute Chemical Decontamination Processes for Water-Cooled Nuclear Reactors. EPRI-NP-1033, March 1979.
6. Perrigo, L.D. and J.R. Divine. Decontamination Methods PNL-SA-7770, May 23, 1979.
7. Spekkens, P. Decontamination of Moderator Heat Exchanger Tubing From Pickering NGS. Research Report No. 79-105-H.
8. Cotton, F.A. and G. Wilkinson. Advanced Inorganic Chemistry. 3rd Ed. Interscience Publishers. New York, NY, 1972. Chapter 25.
9. Zegger, J.L. and G.P. Pancer. A Chemical Methods for Nuclear Reactor Decontamination, Nuclear Engineering, Part VIII, Chemical Engineering Progress Symposium Series, Vol 56, No 28, pp 66-71, American Institute of Chemical Engineers, 1960.
10. Vogel, A.I. A Textbook of Quantitative Inorganic Analysis. 3rd Ed. Longmans. New York, NY. 1961.
11. Pa Ho Hsu. Water Research. 9, 1155 (1975).
12. Pa Ho Hsu. Adv. Chem. Ser. 73, 115 (1968).
13. Pa Ho Hsu. Environ. Letter. 5, 115 (1973).
14. Robert C. Weast, Editor. Handbook of Chemistry and Physics. 61st Edition. The Chemical Rubber Co. Cleveland. 1980-81.

APPENDIX 1

Experimental Section

A) PREPARATION OF SAMPLES

2.1.1 Permanganate Solutions

The pH of three 100.0 mL samples each containing 3.0 g of potassium permanganate was adjusted to 8.0 by addition of 1:3 sulfuric acid solution. The samples were left unstirred overnight, and then any precipitate formed was filtered out, dried and brought to constant weight.

2.1.2 Permanganate - Oxalic Acid Solutions

Fifteen grams of potassium permanganate were dissolved in 500.0 mL of distilled water containing 50.0 g of sodium hydroxide. The pH was adjusted to 8.0 by addition of 6.0 M hydrogen chloride. The solution was divided into five equal parts to which 0.85 g, 1.81 g, 2.57 g, 3.45 g and 4.25 g of oxalic acid were added respectively. The samples were left unstirred for two days, then filtered through a 0.45 μ m membrane. The precipitate was dried to constant weight. The filtrate was saved for two weeks and any precipitate formed during this period was filtered out, dried and weighed. Finally, the residual concentration of both manganese and oxalate ions in the filtrate was determined by atomic absorption spectrophotometry and ion chromatography.

2.1.3. Potassium Permanganate - Diammonium Hydrogen Citrate Solutions

Diammonium hydrogen citrate with a mass of 1.19 g, 4.30 g, 6.45 g, 8.60 g and 10.75 g of were dissolved in five 100.0 mL samples each containing 10.0 g of sodium hydroxide and 3.0 g of potassium permanganate. The pH of each sample was adjusted to 8.0 (if necessary) by addition of 1.0 N sodium hydroxide. All samples were left unstirred for two days and then filtered through a 45 μ m membrane. The precipitates were dried and weighed. The supernatant liquid was saved for two weeks and any precipitate formed was filtered, dried and weighed. Finally, the residual concentration of both manganese and citrate ions in solution were determined by atomic absorption spectroscopy and ion chromatography. It should be noted that this experiment was repeated twice.

2.1.4 Treatment With Turco 4521A Solutions

Volumes of 20.0 mL, 10.0 mL, 10.0 mL, 5.0 mL, 5.0 mL, 5.0 mL, 5.0 mL and 1.0 mL of potassium permanganate solutions containing 30.0 g/L were transferred into eight beakers. Then 20.0 mL, 25.0 mL, 50.0 mL, 37.5 mL, 10 mL, 75.0 mL, 125.0 mL and 50.0 mL of a solution containing a mixture of oxalate and citrate ions (14.0 g of oxalate and 12.0 g of citrate per litre) were added to the permanganate solutions respectively. The pH of each sample was adjusted to 8.0. The solutions were left unstirred for two days and then any residue formed was filtered, through a 0.45 μ m

membrane, dried and weighed. The residual concentrations of both oxalate and citrate ions in solution were determined by ion chromatography.

2.1.5 Potassium Permanganate - Ferrous Ammonium Sulfate Solutions

Three 25.0 mL samples of potassium permanganate solutions containing 30.0 g/L were transferred into three beakers. Twenty-five millilitres of (1:5) sulfuric acid and 5.0 mL of concentrated phosphoric acid were added to each sample prior to titration with ferrous ammonium sulfate solution (19.6 g/L).

2.2.1 Phosphoric Acid (Turco 4512) - Aluminum Chloride Solutions

Nine 10.0 mL samples of aluminum chloride solutions containing 2.7 g/L were transferred into nine beakers and divided into three groups. Then, 10.0 mL, 20.0 mL and 30.0 mL of 0.159 M phosphoric acid were added to each group. The pH of the three groups was adjusted to 6.0, 7.0 and 8.0 respectively by addition of 0.1 N sodium hydroxide. All solutions were allowed to stand for three hours and then centrifuged. The precipitate was washed with ethanol (60% by volume), dried and weighed. The residual concentration of aluminum in solution was determined by atomic absorption spectroscopy and that of phosphate ions by ion chromatography.

2.2.2 Treatment of STPP With Aluminum Chloride

The experimental procedure described in Section 2.2.1.1 was followed in this section except that 12.5 mL, 25.0 mL and 50.0 mL of 0.082 M sodium tripolyphosphate were used instead of phosphoric acid. Any precipitate formed was filtered, dried and weighed. The residual concentration of aluminum in solution was determined by atomic absorption spectroscopy.

2.2.3 Treatment With Aluminum Chloride and Calcium Nitrate

Six 120.0 mL samples of aluminum chloride solution containing 2.7 g/L were transferred into six beakers. 25.0 mL of 0.082 M STPP solution were added to each beaker. Ten millilitres, 20.0 mL and 5.0 mL of 0.02 M calcium nitrate were then added to the first three beakers. The pH of these three solutions was adjusted to 7.0 by addition of 0.1 N sodium hydroxide. To beakers four through six, the same volumes of calcium nitrate were added but the pH was adjusted to 8.0. All solutions were left unstirred for three hours. Any precipitate formed was removed by centrifugation, dried and weighed. The residual concentration of both calcium and aluminum in solution were determined by atomic absorption spectroscopy.

2.3 Treatments of Peroxide Bicarbonate Solutions

Seventy-two grams of sodium carbonate decahydrate were dissolved in 750.0 mL of distilled water containing 34.0 g of sodium hydrogen carbonate and 15.0 mL of 17.5% (by volume) hydrogen peroxide. The mixture was then diluted to 1.0 L. Three 100.0 mL samples were transferred into three beakers. Twelve and one-half grams of barium chloride were dissolved in the first beaker, whereas the solutions in the second and third beakers were neutralized with 5.9 M hydrogen chloride and 6.0 M nitric acid respectively. The residue formed in the first beaker was filtered, dried and weighed.

2.4.2.1 Treatment of Oxalate Solutions by Hydrogen Peroxide at Various pH Levels

Twelve 25.0 mL samples of oxalate solutions containing 17.0 g/L were transferred into twelve beakers. The samples were divided into four groups. One hundred millilitres, 25.0 mL and 50.0 mL of hydrogen peroxide (3.5% by volume) were added to each group. The pH levels of the groups were adjusted to 1.6, 6.8, 10.0 and 12.0 respectively. The solutions were left unstirred for two weeks and then analyzed for the oxalate content by ion chromatography.

2.4.2.2 Citrate - Hydrogen Peroxide - Sodium Hydroxide Solutions

The procedure outlined in Section 2.4.2.1 was adopted for the preparation of citrate-hydrogen peroxide-sodium hydroxide solutions except that the concentration of citrates was 33.0 g/L and the pH of solution in Group 1 through 4 was adjusted to 5.15, 7.0, 9.0 and 12.0 respectively.

2.4.3 Peroxcit Solutions

Fifty grams of oxalic acid, 31.0 g of citric acid and 7.0 mL of 17.5% hydrogen peroxide were dissolved in 500.0 mL of distilled water and then the mixture was diluted to 1.0 L. Two 200.0 mL samples were transferred into two beakers. Nine grams of calcium hydroxide were added to the first beaker whereas 2.05 g of barium hydroxide were added to the second beaker. Any precipitate formed was filtered, dried and brought to constant weight.

B) EXPERIMENTAL MEASUREMENTS

Residual concentrations (mg/L) of total manganese, aluminum and calcium in solution were determined by atomic absorption spectroscopy.

Residual concentrations of oxalate, citrate and phosphate ions in solution were determined by ion chromatography.

APPENDIX 2

Recommended Procedures for the Most Suitable
Presolidification Treatments of Decontamination Solutions

APPENDIX 2.A

Presolidification Treatment of Alkaline Permanganate Solutions

- | <u>Step</u> | <u>Operation</u> |
|-------------|---|
| 1. | Adjust pH to 8.0 by slowly adding 6.0 M sulfuric acid.
Note: 6.0 M acid solution is prepared by adding concentrated sulfuric acid to equal volumes of water. |
| 2. | Mix equal volumes of Turco 4521A and alkaline permanganate solution.
NOTE: Add Turco 4521A to permanganate solution slowly. |
| 3. | Allow mixture to stand for 72 hours. |
| 4. | Check for complete precipitation by adding a solution containing a mixture of oxalate and citrate ions.
NOTE: Composition of this citrox solution is: oxalic acid 14.0 g/L and citric acid 12.0 g/L. |
| 5. | Check activity of the supernatant liquid. |
| 6. | If activity is acceptable, pump off solution and immobilize the remaining slurry.
NOTE: If activity is high, immobilize the supernatant liquid and the residue. |

APPENDIX 2.B

Presolidification Treatment of Phosphoric Acid Solutions (Turco 4512)

<u>Step</u>	<u>Operation</u>
1.	Mix equal volumes of Turco 4512 and aluminum chloride solution containing 3.0 g/L.
2.	Adjust pH to 6.0 by addition of sodium hydroxide (80 g/L).
3.	Allow to stand for 4 hours.
4.	Insure complete precipitation by adding more aluminum chloride.
5.	Check activity of supernatant liquid.
6.	If activity is acceptable, pump off solution and immobilize slurry.
7.	If activity is high, immobilize both the supernatant and the precipitate.

APPENDIX 2.C

Presolidification Treatment of Peroxide Bicarbonate Mixture

<u>Step</u>	<u>Operation</u>
1.	Dissolve 12.0 g of barium chloride in each litre of peroxide bicarbonate solution.
2.	Adjust pH to 6.0 (if necessary) by addition of 6.0 M sulfuric acid. NOTE: Carbon dioxide evolves upon addition of acid. Add acid slowly.
3.	Check activity of the supernatant liquid.
4.	If activity is acceptable, pump solution off and immobilize the remaining slurry.
5.	If activity is high, immobilize the supernatant liquid and the residue.

APPENDIX 2.D

Presolidification Treatment of Peroxcit Solutions

<u>Step</u>	<u>Operation</u>
1.	Dissolve 45.0 g of calcium hydroxide in each litre of Peroxcit solution.
2.	Allow solution to stand for three hours.
3.	Check for complete precipitation by addition of more calcium hydroxide. This is done by taking a sample of the supernatant liquid and adding a small amount of calcium hydroxide. If a precipitate forms add more calcium hydroxide; if no precipitation takes place assume precipitation is complete.
4.	Check activity of supernatant liquid.
5.	If activity is acceptable, decant supernatant liquid and immobilize slurry.
6.	If activity is high, add 100 mL of hydrogen peroxide (5% by volume) to each 2.5 L of Peroxcit solution.
	NOTE: Add hydrogen peroxide solution slowly because carbon dioxide gas is evolved.
7.	Immobilize the supernatant liquid and the residue.

APPENDIX 2.E

Presolidification Treatment of Turco 4521A Solution

The presolidification treatment described in Appendix 2.D is also recommended for Turco 4521A because Turco 4521A and Peroxcit solutions have essentially the same chemical composition.

