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DE84003088**PHYSICAL-CHEMICAL TREATMENT OF TAR SAND
PROCESSING WASTEWATER**

Task No. 3 - Dewatering of Foamate Residuals
Task No. 4 - Leaching Potential of Sludges
Task No. 5 - Summary of Economic Considerations

Final Report

By
Paul H. King

November 1983**Work Performed Under Contract No.: DE-AS20-81LC10678**

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Laramie Project Office
Laramie, Wyoming

By
University of Arizona
Tucson, Arizona

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Laramie, Wyoming 82071

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I. INTRODUCTION

The Tar Sand processing wastewater treatment program currently being conducted by the U. S. Department of Energy, Laramie Energy Technology Center, has been successful in identifying appropriate chemical treatment processes which can be employed to treat wastewaters generated from in-situ extraction methods to levels compatible with most environmental and industrial standards. In the overall research program attention has been given to both steam driven as well as combustion-based extraction processes. In work done at both the University of Arizona and Virginia Polytechnic Institute and State University, the propriety of a chemical treatment step, either chemical coagulation or flotation, for suspended solids removal from a representative steam driven wastewater (TS-1S) has been demonstrated.

Two previous reports have been submitted under contract DE-AS20-81LC10678 awarded to the University of Arizona. The first of these reports (July, 1982) summarized the results of an extensive parametric study of chemical coagulation of TS-1S wastewater. In that work, ferric chloride was found to be an especially suitable coagulant for this application. Appropriate coagulant dosage, pH, and mixing conditions were defined, and a preliminary economic evaluation of the cost of coagulation was described. The second report (April, 1982) focused particularly on the management of sludges resulting from the chemical coagulation process. Because of its superiority as a coagulant, primary attention in that report was given to an evaluation of potential dewatering techniques for ferric chloride sludge produced from coagulation of TS-1S wastewater.

This report describes the remaining work conducted under the subject contract. In particular, three tasks are involved:

1. An evaluation of the dewatering properties of residuals generated by flotation/foam fractionation treatment of TS-1S wastewater. The primary research defining appropriate wastewater treatment schemes of this type was conducted by Dr. G. Boardman at Virginia Polytechnic Institute and State University. Residuals were provided to the University of Arizona by LETC.
2. An evaluation of the leachate potential of both chemical coagulation and flotation/foam fractionation sludges using a method specified by LETC.
3. A preliminary economic analysis comparing selected sludge disposal options and summarizing previously reported economic analysis of chemical treatment alternatives.

II. DEWATERING OF FOAMATE RESIDUALS

Two sets of foamate samples were provided to the University of Arizona for evaluation under the subject contract. The first samples, received in early October, 1982, were dilute in nature and could not be dewatered directly. These samples were subjected to chemical coagulation and direct filtration, and some work was accomplished on the resultant sludges. This first phase of the foamate work is discussed below in the section titled "Dilute Foamate: Coagulation, Direct Filtration and Specific Resistance Determination". The second set of foamate samples was received in November, 1982. Results of dewatering studies for these sludges are described in the section titled "Dewatering of Concentrated Foamate".

Dilute Foamate: Coagulation, Direct Filtration and Specific Resistance Determination

The first samples provided by LETC for study under this phase of the contract were described as a polymer based foamate and were analyzed by the methods noted in our previous reports. The results were:

Suspended solids	336. mg/l
pH	7.18
TOC (filtered)	37.2 mg/l

The dilute nature of this foamate was immediately evident and direct concentration of the solids by either vacuum filtration or gravity drainage was clearly infeasible. After discussion with LETC personnel, it was determined that coagulation of the foamate would be attempted in an effort to concentrate the suspended solids to the extent that a dewatering process could be employed with a reasonable chance of success. In the meantime, LETC officials sought to obtain more concentrated foamate samples.

Alum and ferric chloride were employed as coagulants for the dilute foamate samples. A jar test procedure similar to that described in the final report on Task No. 1 was utilized. A Phipps and Bird six paddle stirring apparatus was used with 400 ml samples placed in 600 ml beakers. Two runs were accomplished for each coagulant. In each case a two-minute rapid mixing period at 100 rpm was followed by 30 minutes of flocculation at 30 rpm and 60 minutes of quiescent settling. Run No. 1 represented a broader range of coagulant dosages. Run No. 2 narrowed the range of dosages to the level indicated as most appropriate from Run No. 1. Results of these studies are given in Tables 1 and 2.

TABLE NO. 1. RESULTS OF RUN NO. 1: BROAD DOSAGE RANGE
FOR COAGULATION OF DILUTE POLYMER FOAMATE

<u>Alum Dosage, mg/l</u>	100.	150.	200.	250.	300.	350.
pH	6.2	5.7	4.8	4.5	4.4	4.3
TOC, mg/l	33.8	30.9	28.6	28.9	29.5	30.0
Suspended Solids, mg/l	14.	20.	17.	42.	43.	71.
<u>Ferric Chloride Dosage, mg/l</u>	100.	150.	200.	250.	300.	350.
pH	6.1	4.8	3.7	3.3	3.2	3.0
TOC, mg/l	28.2	22.7	23.1	24.2	23.5	25.0
Suspended Solids, mg/l	6.	9.	8.	7.	10.	16.

TABLE NO. 2. RESULTS OF RUN NO. 2: NARROW DOSAGE RANGE
FOR COAGULATION OF DILUTE POLYMER FOAMATE

Alum Dosage, mg/l	25.	50.	75.	100.	125.	150.
pH	7.2	7.0	6.6	6.3	6.1	5.8
TOC, mg/l	36.3	34.5	33.3	32.5	31.3	30.6
Suspended Solids, mg/l	108.	98.	8.	3.	6.	11.
<hr/>						
Ferric Chloride Dosage, mg/l	25.	50.	75.	100.	125.	150.
pH	7.2	6.9	6.5	6.0	5.9	4.9
TOC, mg/l	7.2	6.9	6.5	6.0	5.9	4.9
Suspended Solids, mg/l	89.	68.	3.	6.	2.	3.

The sludges produced during the coagulation process were subject to evaluation to the extent possible in the light of the limited quantities available. Using most of the remaining raw foamate to produce sufficient sludge, the following samples were obtained:

1. Alum sludge, 40 ml volume, 2.1% solids, produced from coagulation of dilute foamate at 200. mg/l alum dosage.
2. Ferric chloride sludge, 80 ml volume, 0.8% solids, produced from coagulation of dilute foamate at 150. mg/l ferric chloride dosage.

The volume of alum sludge was insufficient to determine a value for specific resistance of this material using the conventional method described previously in the final report on Task No. 2. The initial rate of dewatering in a Buchner funnel test at a vacuum of about 18 inches of mercury was about 0.5 ml per second and was similar to the initial rate observed for the ferric chloride sludge. Sufficient ferric chloride sludge was available to complete a single Buchner funnel test. A calculated specific resistance of 2.1×10^{-3} m/kg was obtained.

One final test was conducted on the raw polymer foamate in an effort to simulate possible results of direct filtration of this material without coagulant addition. Filtration was driven by a vacuum of 18 inches of mercury and the following filter media were employed:

1. Millipore HA (0.45 μ m)
2. Millipore SM (5 μ m)
3. Whatman No. 3
4. Whatman No. 30
5. Whatman No. 40
6. Whatman No. 42
7. Whatman GF/C
8. S&S No. 589 (white ribbon)

Results of this study indicated that in each case filtration was relatively rapid and similar filtered effluent was obtained. Suspended solids were entirely removed, as expected. Filtrate TOC was 37. mg/l and total solids ranged from 500 to 540 mg/l.

The dilute foamate studies indicated that sludge concentration and dewatering can be accomplished utilizing a chemical coagulation process, preferably employing ferric chloride as opposed to alum. However, the added expense of this step is clearly an over-riding consideration. It would appear that one major goal in the development of a flotation/foam fractionation process for initial treatment of TS-1S type wastewaters is the ability to produce a foamate that is sufficiently concentrated to allow direct dewatering to occur without the additional coagulation step. With this consideration in mind further efforts were directed towards dewatering of the more concentrated foamates described in the following section.

Dewatering of Concentrated Foamate

A second series of polymer-based foamate samples was received from LETC during November, 1982. Although the samples differed significantly from one another, they were uniformly more concentrated than the dilute samples discussed in the previous section, and it was thus possible, following initial characterization, to proceed directly to dewatering studies. Results of this work are given in the following sections:

Characterization of foamate: Initial characterization focused on two foamate batches, hereinafter referred to as Barrel A and Barrel B. In addition, substantially smaller reconcentrated samples of apparently collapsed foam were also studied. This material had the appearance of "oil balls", and is hereinafter referred to as "Reconcentrated Foamate". The results of the initial characterization experiments are given in Table 3.

TABLE NO. 3. RESULTS OF INITIAL CHARACTERIZATION
OF CONCENTRATED FOAMATE SAMPLES

<u>Parameter</u>	<u>Barrel A</u>	<u>Barrel B</u>	<u>Reconcentrated Foamate</u>
pH	7.32	7.62	7.83
TOC (filtered)	34.75	36.89	48.92
Total Solids	14,252	5,288	47,616
Suspended Solids	8,324	4,552	52,024

The relatively concentrated nature of these samples as compared to the dilute foamate previously described is immediately evident. Nonetheless, suspended solids levels in the range of 0.5 to 0.8 percent as indicated for both Barrels A

and B are still not as concentrated as would be desirable for influent to typical sludge dewatering processes. The reconcentrated foamate sample analyzed had an approximate solids concentration of 5. percent, a more desirable level. However, as indicated by the comparison of suspended solids with total solids, it was difficult to obtain a representative sample of reconcentrated foamate due to the nonhomogeneous nature of this material. These values should thus be considered as approximate.

Dewatering by gravity drainage: Sand bed drying under the influence of gravity can be simulated in small tubes. Using the method described previously in the final report on Task No. 2, a sample taken from Barrel A was applied at a depth of 6.0 inches to a column containing 4.0 inches of gravel overlain by 8.0 inches of sand. The diameter of the column was 3.8 inches. Results are given in Table 4.

The data indicate that while drainage water is rapidly released under these conditions, substantial suspended solids breakthrough occurred. This result suggests that in actual practice a chemical conditioning step would be appropriate. The final cake following release of all gravity drainage water was too thin to obtain a sample for determination of moisture content.

TABLE NO. 4. RESULTS OF GRAVITY DRAINAGE
OF CONCENTRATED FOAMATE (Barrel A)

Sample No.	1	2	3	4	5
L (min.)	3	15	30	60	240
Filtrate Vol. (ml)	305	198	150	42	10
Accum. Filtrate Volume (ml)	305	503	653	695	705
pH	7.67	7.65	7.60	7.48	-
SS (mg/l)	500	880	480	284	-
Turbidity (FTU)	96	51	140	130	-
Filtered TOC (mg/l)	22.1	39.6	39.7	42.2	-

Buchner funnel tests: The Buchner funnel test is a laboratory scale measurement of the rate of filtration through commercial filter paper with the aid of a vacuum. The test provides insight into the applicability of filtration-based sludge dewatering processes, particularly vacuum filtration. As noted earlier, the method used in this test has previously been described in the final report on Task No. 2.

Specific resistance tests were conducted on unconditioned foamate from both Barrel A and Barrel B. In each case 200 ml of raw sludge was utilized and a vacuum of 18.8 inches of mercury was employed. Results of this work are summarized in Table 5. The pattern of the filtration curves is indicated in Figures 1 and 2. Because of the nonhomogeneous nature of the reconcentrated foamate, it was not possible to run a Buchner funnel specific resistance test on this material.

The foregoing results again indicate the substantial differences between Barrels A and B. The specific resistance of these foamates appears to be on the order of 1.0×10^{-4} m/kg, a value significantly higher than that previously observed for ferric chloride sludge. Unconditioned ferric chloride sludge had a measured specific resistance of about 0.5×10^{-4} m/kg or about one-half order of magnitude lower than observed for the unconditioned polymer based foamate.

On the basis of these data, it was deemed appropriate to proceed with physical and chemical conditioning studies to enable evaluation of this technique as an aid to filtration-based dewatering of the foamate.

Foamate conditioning experiments: Conditioning of the foamate prior to Buchner funnel specific resistance tests was accomplished by two means. In the first set of experiments the foamate was subjected to freezing and thawing followed by filtration in the manner previously described. The second group of experiments involved the use of selected organic polyelectrolytes as conditioning agents. Both of these methods have previously been utilized in the study of

TABLE NO. 5. RESULTS OF BUCHNER FUNNEL TESTS OF
UNCONDITIONED CONCENTRATE FOAMATE

BARREL A

Test No. 1

Total Suspended Solids: 1.00%

pH: 7.02

Specific Resistance: 7.9×10^{10} m/kg

Test No. 2

Total Suspended Solids: 0.74%

pH: 7.02

Specific Resistance: 8.2×10^{10} m/kg

BARREL B

Test No. 1

Total Suspended Solids: 0.64%

pH: 7.30

Specific Resistance: 3.4×10^{10} m/kg

Test No. 2

Total Suspended Solids: 0.66%

pH: 7.30

Specific Resistance: 4.4×10^{10} m/kg

Figure 1. Specific Resistance Tests of Unconditioned Foamate: Barrel A

Figure 2. Specific Resistance Tests of Unconditioned Foamate: Barrel B

dewatering of the ferric chloride coagulation sludges.

Two freeze-thaw conditioning experiments were conducted. Single samples were taken from Barrels A and B for this purpose. Results of this work are summarized in Table 6. It is evident from the data indicated therein that the freeze-thaw technique was somewhat effective in conditioning of Barrel A foamate, resulting in a decrease in specific resistance from about 8.0×10^{10} m/kg (see Table 5) to the reported level of 2.8×10^{10} m/kg. The test using Barrel B foamate indicated a substantially smaller improvement in specific resistance with a decrease from about 4.0×10^{10} m/kg to 3.0×10^{10} m/kg being noted. The reason for the greater improvement in Barrel A as opposed to Barrel B is not known. Because of the relatively high cost of freezing and thawing, as well as the lack of dramatic improvement noted, further efforts were directed toward use of polymers as chemical conditioning agents.

Two polymers were selected for the polyelectrolyte conditioning experiments. These were Betz 1125L and Magnifloc 835A. Both of these polymers are relatively long-chain anionic polyelectrolytes which have been previously used with success in sludge conditioning applications. In each case, polymer dosage ranged from 0 to 150 mg/l. The polymer was mixed with the foamate in a jar test apparatus for 3 minutes at 75 rpm prior to conducting Buchner funnel specific resistance tests under a vacuum of 18.5 inches of mercury.

The results obtained from the polymer conditioning experiments are summarized in Tables 7 through 9. Table 7 indicates the range of polymer dosages employed and the pH and TOC values of the filtrate. Note that increasing polymer dosages led to increased levels of TOC in the filtrate, indicating the accumulation of unreacted polymer in the filtrate at the higher polymer doses.

TABLE NO. 6. RESULTS OF BUCHNER FUNNEL TESTS OF FREEZE-THAW
CONDITIONED CONCENTRATED FOAMATE

BARREL A

Raw sludge:

Total suspended solids: 0.75%

pH: 7.00

Total solids: 0.83%

Freeze-thaw conditioned sludge:

Filtrate TOC: 39.4 mg/l

Filtrate pH: 7.00

Specific resistance: 2.8×10^{10} m/kg

BARREL B

Raw sludge:

Total suspended solids: 0.62%

pH: 7.27

Total solids: 0.74%

Freeze-thaw conditioned sludge:

Filtrate TOC: 37.5 mg/l

Filtrate pH: 7.40

Specific resistance: 3.0×10^{10} m/kg

TABLE 7. POLYMER DOSAGES WITH CORRESPONDING FILTRATE CHARACTERISTICS
FOR SPECIFIC RESISTANCE TESTS OF POLYMER CONDITIONED FOAMATES

Polymer Dose (mg/l)	<u>BARREL A</u>			
	Betz 1125L		Magnifloc 835A	
	pH	TOC (mg/l)	pH	TOC (mg/l)
0	7.15	36.40	7.20	36.53
10	7.15	37.79	7.30	40.65
30	7.23	41.06	7.20	41.06
60	7.21	94.87	7.10	41.63
100	7.22	159.60	7.11	113.40
150	7.30	--	7.07	138.00

Polymer Dose (mg/l)	<u>BARREL B</u>			
	Betz 1125L		Magnifloc 835A	
	pH	TOC (mg/l)	pH	TOC (mg/l)
0	7.52	39.42	7.55	39.42
10	7.48	86.07	7.55	76.54
30	7.56	81.05	7.62	85.96
60	7.56	85.52	7.58	97.22
100	7.52	93.22	7.61	119.70
150	7.43	102.00	7.50	141.20

Tables 8 and 9 indicate the raw data from the Buchner funnel runs for polymer conditioning studies of foamate from Barrels A and B, respectively. The lack of improvement in the dewatering rate with increasing polymer dose is immediately evident. No increase in filtration rate that could be attributed to polymer conditioning was noted and thus specific resistance values were not calculated.

The lack of favorable results from polymer conditioning is dramatically illustrated in Figure 3 in which filtrate volume versus time curves are plotted for unconditioned, freeze-thaw conditioned and polymer (Betz 1125L) conditioned foamate from Barrel A. In Figure 4 similar curves are presented for Barrel B foamate.

Conclusions

The polymer-based foamate residual study conducted in this phase of the work indicates that two major problems can be anticipated in application of the flotation/foam fractionation process for treatment of TS-1S wastewater. The first concern must be to develop a process in which a reasonably concentrated foamate can be obtained from the primary stage of treatment. It would appear that in order to dewater the foamate in an economically acceptable fashion, an initial solids concentration in the foamate stream of about 1.0 percent solids should be obtained. These levels were not attained in the present study.

A second major problem that must be recognized is that the concentrated foamates studied herein have inferior dewatering properties relative to the previously tested ferric chloride sludges and, in addition, do not respond to the polyelectrolyte conditioning technique employed in this study. In this regard, the polymer-based foamates again differ substantially from the ferric chloride sludges whose dewatering properties have been described in detail in the Task No. 2 report.

TABLE 8. FILTRATION TIMES (IN SEC.) FOR COLLECTION OF STATED VOLUME IN
BUCHNER FUNNEL SPECIFIC RESISTANCE TEST OF POLYMER CONDITIONED FOAMATE
(BARREL A)

Polymer: BETZ 1125L

Polymer Dose (mg/l)	20	25	30	40	50	75	80	100	125	150	160
0	--	39	--	--	108	217	--	351	527	741	828
10	--	52	--	--	233	596	692	--	--	--	--
30	115	170	255	480	783	--	--	--	--	--	--
60	247	426	633	--	--	--	--	--	--	--	--
100	488	--	--	--	--	--	--	--	--	--	--
150	610	--	--	--	--	--	--	--	--	--	--

Polymer: MAGNIFLOC 835A

Polymer Dose (mg/l)	10	20	25	30	40	50	60	75	100	125	150	160
0	--	--	42	--	--	122	--	229	378	574	828	963
10	40	102	142	192	350	508	718	--	--	--	--	--
30	75	214	424	737	--	--	--	--	--	--	--	--
60	152	383	585	786	--	--	--	--	--	--	--	--
100	289	433	593	798	--	--	--	--	--	--	--	--
150	292	588	780	--	--	--	--	--	--	--	--	--

TABLE 9. FILTRATION TIMES (IN SEC.) FOR COLLECTION OF STATED VOLUME IN
BUCHNER FUNNEL SPECIFIC RESISTANCE TEST OF POLYMER CONDITIONED FOAMATE

(BARREL B)

Polymer: BETZ 1125L

Polymer Dose (mg/l)	10	20	25	30	40	50	60	70	75	90	100	110
0	--	--	53	--	--	210	--	--	496	743	905	1105
10	--	--	89	--	--	409	610	840	--	--	--	--
30	65	243	--	559	949	--	--	--	--	--	--	--
60	88	311	--	630	1068	--	--	--	--	--	--	--
100	221	635	--	--	--	--	--	--	--	--	--	--
150	301	696	--	--	--	--	--	--	--	--	--	--

Polymer: MAGNIFLOC 835A

Polymer Dose (mg/l)	10	20	25	30	40	50	60	65	75	100	125
0	--	--	54	--	--	224	--	--	470	837	1325
10	--	--	95	--	--	575	951	1070	--	--	--
30	85	286	--	548	940	--	--	--	--	--	--
60	115	378	--	799	--	--	--	--	--	--	--
100	228	525	711	--	--	--	--	--	--	--	--
150	190	569	832	--	--	--	--	--	--	--	--

Figure 3. Filtrate Volume as a Function of Time
in Buchner Funnel Test of Barrel 'A' Foamate

Figure 4. Filtrate Volume as a Function of Time
in Buchner Funnel Test of Barrel 'B' Foamate

III. LEACHING POTENTIAL OF SLUDGES

Ultimate disposal of dewatered sludges or foamates derived from chemical treatment of TS-1S wastewater will under normal circumstances be in a landfill system. Accordingly, it is important to evaluate the extent to which such a landfill disposal scheme is consistent with sound environmental management practice. To this end, three sludge samples were subjected to a simulated leaching test to determine the anticipated extent of release of selected contaminants in the leaching process. The procedure was repeated three times for each sample.

Experimental Procedure for Leaching Test

The experimental technique chosen by LETC for this phase of the work consists of a 24-hour mixing and extraction procedure at a pH carefully adjusted to 5.0. Following the completion of the extraction phase of the experiment, samples were settled and supernatant was filtered through a pre-filter followed by a 0.45 μ membrane filter under a maximum pressure of 75 psi driven by an inert gas. The details of the procedure designated by LETC as Method "E.P.", are indicated in Appendix A.

Characteristics of Sludges

Three sludges were available for study during this phase of the work. A brief description of each is indicated in the following:

Ferric chloride sludge: This sludge resulted from coagulation of TS-1S wastewater with a ferric chloride dose in the range of 400-500 mg/l. The dewatering properties of this sludge have been extensively described in the Task No. 2 report. The total solids concentration of this sludge was about 2.1 percent. All samples were identical.

Polymer foamate: This material is identical to that described as "concentrated foamate" in Section II of this report. Several foamate samples were utilized. The average solids concentration was about 1.0 percent.

Alum sludge: This sludge was generated for the purpose of utilization in the leachate test by coagulation of TS-1S wastewater with alum at a dose of 1000 mg/l. Coagulation was effected by a rapid mix of 2 minutes at 70 rpm and a slow mix for 30 minutes at 30 rpm. The 20-liter batch unit described in the Task No. 2 report was utilized. A sludge with a solids content of 2.7 percent was obtained. All sludge samples were identical.

Results of Leaching Test

The principal results of the leaching describe the extent of organic matter which is ultimately measured in the filtrate. These results are summarized in Table 10 which gives filtrate COD and TOC for each run. As noted therein, the ferric chloride sludge showed the least tendency to leach organic material, followed by alum sludge with the polymer foamate being the most likely to leach organics. This general result is to be anticipated since the polymer is itself an organic substance and unreacted polymer would exert a measurable COD or TOC. However, it should be noted that all of these values are relatively low and serious environmental impact from these data alone would not be indicated. The nature of the organics present, however, are not known and must represent a further concern.

In addition to the foregoing determination of organic material in the leachate, a full analysis of trace elements in each of the nine samples was conducted by Mr. Thomas Cogswell of the University of Wyoming Research Corporation staff. A Jarrell-Ash Atom Comp Series 1100 Inductively Coupled Argon

TABLE 10. RESULTS OF LEACHING TEST: ORGANIC MATTER IN FILTRATE

	COD mg/l	TOC mg/l
<u>Ferric Chloride Sludge</u>		
Sample No. 1	120.	47.4
2	118.	46.6
3	122.	47.6
Average	120.	47.2
<u>Polymer Foamate</u>		
Sample No. 1	280.	73.3
2	300.	85.4
3	276.	85.1
Average	285.	81.3
<u>Alum Sludge</u>		
Sample No. 1	143.	55.4
2	119.	48.8
3	131.	52.3
Average	131.	52.2

Plasma Unit was used for this purpose. Test conditions employed were:

Generator (RF) power	1.0 KW
Gas Flow	25 L/min codant
	0.65 L/min sample
Sample uptake	1.0 ± 0.1 mL/min
Observation height	16mm above top load coil
Standardization	two point; low=0, high=1ppm

The results of the trace element analysis are given in Appendix B. In reviewing these results, a consistent pattern is evident with relatively few exceptions. Substantial aluminum leaching from alum sludge is immediately evident as would be expected. There is also evidence of marginally increased leaching of arsenic, mercury, and selenium, and to a lesser extent, lead and tin in the alum system, perhaps indicating that the coagulant utilized in the alum experiment was contaminated with these metals. A similar, and possibly

insignificant relative increase was noted for the leaching of nickel and zinc in the ferric chloride system. Leaching of trace heavy metals from the polymer foamate was uniformly low.

Discussion and Conclusions

The primary concern that underlies the leaching study is the potentially adverse environmental impacts associated with land disposal of the residuals generated from treatment of the wastewater under study. In order to assess this problem and to utilize to the extent possible the trace element data generated during the course of the study, a summary comparing average values obtained for some of the more important potential trace metal contaminants is given in Table 11. In addition, the table also lists the current EPA drinking water standard for that metal.

TABLE 11. SUMMARY OF AVERAGE CONCENTRATIONS OF
SELECTED TRACE HEAVY METALS IN LEACHATE AS
COMPARED WITH CURRENT EPA PRIMARY DRINKING
WATER STANDARDS.

Constituent	(all concentrations in mg/l) Avg. Leachate Conc.			EPA D.W. Std.
	FeCl ₃ Sludge	Polymer Foamate	Alum Sludge	
Arsenic	0.0053	0.0063	1.09	0.05
Barium	0.15	0.15	0.10	1.0
Cadmium	0.004	0.003	0.004	0.01
Chromium	0.01	0.007	0.006	0.05
Lead	0.035	0.044	0.152	0.05
Mercury	0.145	0.101	0.812	0.002
Selenium	0.09	0.10	0.39	0.01
Silver	0.003	0.006	0.002	0.05

In examining Table 11, it is immediately evident that, when compared with drinking water standards, leaching of barium, cadmium, chromium, and silver was not significant. Among the other trace metals examined, there was substantial lead leached from alum sludge while the level remained below the drinking water standard for the ferric chloride sludge and polymer foamate systems. A similar result occurred with respect to arsenic, with very substantial quantities being released from alum sludge. In these cases, it is entirely possible that the original major source of arsenic and lead was the coagulant itself as opposed to the wastewater. Contamination of commercial alum with these metals is not uncommon and must be considered in selection of a coagulant for the indicated purpose.

Selenium and mercury were both observed at concentrations well in excess of the drinking water standards in the leachate from all three sludges. For both

TABLE 12. SUMMARY OF COST ESTIMATES FROM TASK NO. 1
STUDY OF FERRIC CHLORIDE COAGULATION OF
TS-1S WASTEWATER

<u>Treatment Scheme</u>	(Cost in \$/1000 gal wastewater)	
	<u>Plant Capacity</u>	
	<u>20 MGD.</u>	<u>100 MGD.</u>
Conventional	\$ 0.13	\$ 0.108
Solids Contact Clarifier	\$ 0.12	\$ 0.065

selenium and mercury, however, the observed concentration in the alum system was significantly higher than for ferric chloride sludge or polymer foamate. The evidence seems to point to two major conclusions. First, it would be logical to assume that there probably were significant quantities of both selenium and mercury in the raw wastewater. These metals were evidently concentrated in the sludge and released during the extraction procedure. Second, it seems evident that the tendency for trace metal release from alum sludge at the pH level of the leachate is greater than that exhibited for ferric chloride sludge or for polymer foamate.

IV. SUMMARY OF ECONOMIC CONSIDERATIONS

The Final Report for Task No. 1 included an economic analysis of the ferric chloride coagulation process for treatment of TS-1S wastewater. Costs were estimated for 20 and 100 mgd facilities for both conventional coagulation, flocculation, and sedimentation processes, as well as for the less expensive upflow solids contact clarifier. In each case, the cost of sludge handling and disposal was not considered. The results of this work are indicated in summary form in Table 12.

The Task No. 1 report defined appropriate dewatering techniques for ferric chloride sludges produced from coagulation of TS-1S wastewater. Based on the results of the Buchner Funnel specific resistance test, it was evident that vacuum filtration would be a particularly attractive means of dewatering this sludge, particularly for treatment plants of the size range contemplated in Table 12.

Vacuum filtration dewatering costs for ferric chloride sludge were estimated using the EPA Manual for Estimating Water Treatment Costs. The same publication was used in the Task No. 1 economic studies. Assuming that a solids loading rate of 1.7 lbs/hr/ft^2 could be obtained in a prototype installation, the cost of vacuum filtration is estimated at about \$0.04 to 0.07 per 1000 gallons of wastewater treated depending on plant capacity. An additional cost for ultimate disposal would also be incurred, but this expense is not possible to estimate.

The above figures clearly indicate that for this type of chemical treatment of TS-1S wastewater a substantial portion of the total expense will be related to sludge dewatering and disposal. This conclusion should be readily evident from consideration of the nature of the primary treatment process. The generation of large volumes of wet sludge is a major problem which leads to the need

for large sludge handling facilities and with it substantial capital as well as operating expense. It is reasonable to assume that thirty to fifty percent of the total cost of treatment will be related to sludge disposal.

The relative lack of success achieved in the dewatering of the polymer foamate residuals does not allow for an estimate of the cost of dewatering these materials. It does seem evident that the development of a process to enable production of a reasonably concentrated foamate prior to dewatering is a priority concern. Until such a process is developed it would appear that, at best, the cost of sludge dewatering in the polymer foamate system would be substantially higher than that estimated for the ferric chloride coagulation process.

APPENDIX A

DETAILED PROCEDURE OF LEACHING TEST METHOD "E.P." AS DEVELOPED BY LETC

METHOD "E.P."

APPARATUS:

1. Agitation Equipment: The agitator will be supplied by the Department of Energy. This equipment was designed, built and tested by the National Bureau of Standards.
2. Filtration Equipment - Millipore #YT30-142HW or Nuclepore Corp., Pleasanton, California 94566, equipped with 1.5 liter reservoir, or an equivalent filter holder.
3. Inert Gas.

REAGENTS:

4. All chemicals shall be of reagent grade or better.
- 4.1 Unless otherwise indicated, reference to water shall be understood to mean distilled or deionized water of A.S.T.M. reagent Type IV.
- 4.2 Nitric acid; all nitric acid shall be distilled or better quality.

HOUSEKEEPING:

5. All glassware and equipment that comes into contact with the sample, except teflon coated, shall be washed before each use.
- 5.1 Wash with a suitable detergent solution.
- 5.2 Rinse twice with tap water.
- 5.3 Rinse twice with distilled water.
- 5.4 Wash with 10% solution of nitric acid (100 ml-dist. nitric acid + 900 ml of dist. water per 1000 ml).
- 5.5 Rinse twice with distilled water.
- 5.6 Teflon equipment shall be double distilled water rinsed between each use.

EXTRACTION PROCEDURE:

6. Add to the container a weight of water equal to 16 times the weight of the solid material in the container.
- 6.1 Close the container and shake to uniformly mix the contents.
- 6.2 Place the container in the agitator so that the top of the container is four (4) inches above the holder and the bottom of the container is four (4) inches below the holder (center mounted). Turn on the agitator and agitate the sample for 5 minutes. Stop the agitator and allow the sample to settle for 1 minute.
- 6.3 Determine and record the pH of the solution by placing the pH probes in the extraction container.
- 6.3.1 The pH meter should be standardized using two buffers: 6.86 and 4.01.
- 6.4 Using a mechanical stirrer, equipped with a teflon stirring rod to mix the solution, adjust the pH to 5.0 ± 0.2 with 0.5N acetic acid. Close the container and continue agitation for 5 minutes, then recheck the pH and adjust it if necessary. Continue this procedure until the pH is 5.0 ± 0.2 , or until .4 ml of acid for each gram of sample has been added. At this point, complete the 24-hour extraction without adding additional acid.
- 6.5 Continue pH adjustments at 15, 30 and 60-minute intervals, moving to the next longer interval if the pH did not have to be adjusted more than 0.5 pH units since the previous adjustment.
- 6.6 Record the time interval, pH and volume of acid added for each addition.
- 6.7 Continue adjustments for a period of not less than 6 hours.
- 6.8 Final pH after a 24-hour period must be within the range 4.9-5.2; unless 4 ml. of acid per gram of solids has already been added.
- 6.8.1 If the conditions of 6.9 are not met, continue pH adjustments at approximately one hour intervals for a period of 4 hours.

FILTRATION PROCEDURE:

7. Remove the leach container from the agitator and allow the sample to settle for 3 minutes, then measure and record the pH.
- 7.1 Place a 0.45 micron membrane filter on the support screen of the filter holder. On top of the membrane (upstream) place a prefilter (Millipore AP15, Nuclepore P040, or equivalent) secure filter holder as directed in the manufacturer's instructions.
- 7.2 Decant all but about 250 ml. of the settled sample into the filter reservoir, pressurize as directed in the manufacturer's instructions, (with inert gas) to not more than 75 psi, and filter until no significant amount of fluid (5 ml) is released during a 10-minute period.
- 7.3 After the liquid flow stops, depressurize and open the top of the reservoir and if any liquid remains in the reservoir pour it into a container. Replace filter pads as in Step 7.1 above and pour the liquid that was left in the reservoir back into the reservoir and resume filtering.
- 7.4 If no liquid remains in the reservoir, replace the filter pads as in 7.1 above. Shake the leach container to mix the sample and liquid and pour the mixture into the reservoir. Pressurize to no more than 75 psi (with inert gas) and filter until no significant amount of fluid (5 ml) is released during a 10-minute period. Repeat Steps 7.3 and 7.4 if necessary.
- 7.5 Determine the pH of the filtrate and adjust its volume, with water, so that it is 20 times that occupied by a quantity of water equal in weight to the initial weight of solid material (e.g. for initial sample weight of 100 grams dilute to 2000 ml).
- 7.6 Adjust the pH to 1.4-2.0 using distilled nitric acid; record the volume of acid used.
- 7.7 Transfer the filtrate to the plastic containers provided and label them.

APPENDIX B

RESULTS OF TRACE ELEMENT ANALYSIS OF LEACHATE FILTRATE

Element	FeCl ₃ -Coagulation			Polymer Foamate			Alum Coagulation		
	#1	#2	#3	#1	#2	#3	#1	#2	#3
Ag	0.008	0.002	0.0006	0.009	0.006	0.004	0.003	0.0001	0.0015
Al	0.37	0.42	0.42	0.016	0.0006	0.017	44.3	38.1	41.7
As	0.020	0.029	0.044	0.042	0.087	0.085	1.16	1.01	1.11
Au	0.018	0.023	0.023	0.015	0.023	0.024	0.021	0.016	0.026
B	1.04	1.23	1.32	1.32	1.26	1.42	1.16	1.26	1.16
Ba	0.12	0.18	0.14	0.15	0.09	0.323	0.10	0.09	0.12
Be	0.0001	0.0002	0.0004	0.0003	0.0001	0.0001	0.0005	0.0003	0.0003
Bi	0.039	0.048	0.062	0.035	0.046	0.053	0.054	0.057	0.064
Ca	21.7	22.1	22.9	22.8	22.2	21.1	32.6	28.6	31.7
Cd	0.003	0.004	0.005	0.003	0.003	0.004	0.004	0.004	0.005
Ce	0.004	0.017	0.024	0.0002	0.008	0.013	0.008	0.009	0.010
Co	0.073	0.090	0.089	0.64	0.03	0.07	0.072	0.048	0.061
Cr	0.005	0.011	0.011	0.005	0.008	0.008	0.006	0.006	0.007
Cu	0.021	0.026	0.026	0.009	0.012	0.007	0.050	0.038	0.045
Fe	0.417	0.596	0.582	0.145	0.533	0.562	0.290	0.246	0.266
Ga	0.0004	0.012	0.015	0.005	0.001	0.009	0.004	0.003	0.007
Hf	0.004	0.015	0.016	0.005	0.012	0.016	0.012	0.010	0.012
Hg	0.776	0.978	0.181	0.148	0.020	0.134	1.052	0.807	0.576
K	13.4	12.9	14.5	19.7	18.1	16.5	13.3	9.4	11.0
La	0.0001	0.0031	0.0038	0.0010	0.0007	0.0017	0.0007	0.0010	0.0011
Li	0.057	0.054	0.058	0.104	0.091	0.089	0.108	0.081	0.095
Mg	8.37	8.86	9.34	11.29	10.90	10.76	9.80	8.66	9.50
Mn	0.843	0.812	0.766	0.558	0.653	0.553	0.923	0.813	1.312
Mo	0.006	0.013	0.014	0.020	0.014	0.014	0.054	0.050	0.055

Element	FeCl ₃ -Coagulation			Polymer Foamate			Alum Coagulation		
	#1	#2	#3	#1	#2	#3	#1	#2	#3
Na	65.5	64.3	70.3	80.5	43.2	45.4	45.4	41.3	42.5
Ni	0.135	0.135	0.135	0.071	0.079	0.083	0.074	0.073	0.078
P	0.397	0.935	0.578	0.669	0.488	0.413	0.318	0.280	0.620
Pb	0.008	0.042	0.055	0.016	0.051	0.064	0.159	0.133	0.165
Pt	0.022	0.038	0.052	0.043	0.042	0.040	0.131	0.116	0.154
Sb	0.053	0.178	0.241	0.115	0.167	0.217	0.586	0.507	0.570
Se	0.089	0.095	0.091	0.089	0.111	0.100	0.396	0.378	0.413
Si	40.4	42.6	44.1	60.9	64.6	63.7	49.8	43.3	46.6
Sn	0.043	0.052	0.061	0.064	0.081	0.084	0.124	0.111	0.117
Sr	0.187	0.138	0.192	0.217	0.231	0.213	0.288	0.248	0.277
Th	0.027	0.043	0.052	0.034	0.041	0.050	0.034	0.0-3	0.039
Ti	0.002	0.0006	0.0005	0.002	0.002	0.001	0.001	0.001	0.001
U	0.186	0.098	0.071	0.261	0.207	0.164	0.232	0.195	0.211
V	0.001	0.004	0.006	0.003	0.004	0.005	0.003	0.003	0.004
W	0.016	0.041	0.052	0.204	0.031	0.047	0.301	0.259	0.284
Y	0.0005	0.0002	0.0004	0.0007	0.0003	0.0001	0.0001	0.0002	0.0002
Zn	0.481	0.742	0.771	0.132	0.109	0.322	0.236	0.391	0.263
Zr	0.005	0.001	0.0003	0.006	0.004	0.002	0.002	0.002	0.002

Note: All values in mg/l.