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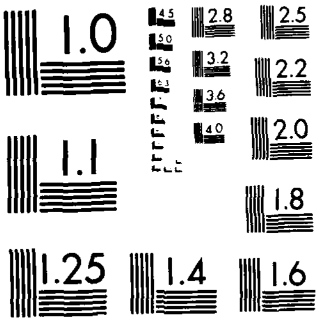
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SD-TR-84-08

STS Hazardous Waste Management Facility
Vandenberg AFB, California

STUDY ON THE TREATMENT OF WASTEWATER GENERATED AT KSC STS OPERATIONS AND PROJECTED EFFECTS ON THE DESIGN OF THE STS HAZARDOUS WASTE MANAGEMENT FACILITY AT VANDENBERG AFB, CALIFORNIA

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OCTOBER 1983

Approved for public release; distribution unlimited.

Prepared For

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PREFACE

The study of the Treatment of Wastewater generated at Kennedy Space Center and its projected effects on the design of the STS Hazardous Waste Management Facility at Vandenberg AFB, California was prepared by Fluor Engineers Inc., Irvine, California.

It describes the procedure used in obtaining data of a similar operation at KSC defining this data in a laboratory analysis and then extrapolating the laboratory data to a commercial design.

This work was initiated in December, 1982 and completed in October, 1983. Mr. Dan Pilson, Headquarters Space Division was the Project Manager.

This report has been reviewed by the office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At the NTIS, it will be available to the general public, including foreign nations.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Space Shuttle launching at Vandenberg AFB is expected to deposit corrosive materials on the launch support facilities. These materials will be washed off, the contaminated wash water collected and treated. The treatment process consists of a precipitation step where the metal cations are removed from the contaminated water. The clarified water is filtered and passed through reverse osmosis membranes where the inorganic salts are reduced to a level satisfactory for the water to be recycled for reuse in a subsequent launch. The solid residue is disposed of at a landfill and the reject brine water is evaporated in a solar

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20. (continued)

pond. This report describes the establishing of the design criteria for the project based on measurement data obtained at Kennedy Space Center and delineates the selected commercially proven technology.

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1.0 EXECUTIVE SUMMARY

Based on extensive testing at KSC on STS-6 and -7 and on historical data and on the analysis presented in this report, we find that:

- Project Book data on wastewaters, adjusted for Vandenberg raw water, are substantially correct, with a few minor exceptions.
- The wastewater treatment plant design is adequate to treat the projected STS VAFB sound suppression water and washdown water.
- The treatment plant unit processes were verified with jar tests.
- The sludge resulting from the treatment process will probably not be hazardous. The design basis will be for a non-hazardous sludge, but with provision for proper handling in the event that it is hazardous.
- There is a possibility of concrete damage in the flame ducts. After first launch at Vandenberg, an assessment should be made to determine the extent, if any, of concrete damage in the flame ducts. If extensive damage is observed, a design should be evaluated for partial neutralization in the ducts following a launch or coating of the concrete.

2.0 PURPOSE

The purpose of the study is to summarize the activities establishing the composition of wastewater generated during Space Transport System (STS) Operations at Vandenberg and to confirm the wastewater treatment process reaction kinetics. To support this objective the study evaluated representative samples of wastewater collected from the first seven launches at Kennedy Space Center (KSC). Comprehensive laboratory tests were conducted for STS-6 and -7 to prove the process design that has been developed to treat the wastewater to a quality suitable for reuse at Space Launch Complex (SLC-6), the Vandenberg launch site.

3.0 BACKGROUND

A new generation of manned space flight began in April 1982. The first Space Transportation System flights have been launched from Kennedy Space Center, Florida, and are conducted by the National Aeronautics and Space Administration (NASA).

In addition to the eastern launch site, a western launch site at Vandenberg Air Force Base, California, is being built to provide launch capability for polar orbiting satellites. The Air Force, which is the Department of Defense executive agency for the Shuttle Program, will have the responsibility for all Space Shuttle Vehicle launches from Vandenberg.

The shuttle rocket motors consist of three Space Shuttle Main Engines (SSMEs) fueled by liquid oxygen and liquid hydrogen, and two Solid Rocket Boosters (SRBs). The major emissions from these engines will be water vapor (main engine emission), carbon monoxide gas (mostly converted to carbon dioxide during afterburning), aluminum oxide particles, and hydrogen chloride gas. Additionally, a great deal of heat will be released. During the entire ignition and lift-off sequence, emitted rocket engine exhausts will be ducted under the launch pad and discharged to the side, whereupon the plumes will rise and merge into what is called a ground cloud. The mechanism causing this rise, and thus inducing the strong convective currents that will lift and transport dust and debris with the cloud, will be the thermal buoyancy of the hot exhaust. It is to be noted that this is a highly localized and short term event.[1]

At KSC, during ignition and lift-off, deluge and sound suppression water is required to cool the launch pad area and minimize acoustic impacts. The waters flow under the launch pad and combine with the rocket motor emissions into the ground cloud. Due to the tremendous velocities and heat created during lift-off, these waters will be in both the liquid and vapor phases. Water continues to flow after shuttle lift-off; this remaining water is collected in two holding ponds.

As one would expect, these waters are extremely acidic due to the hydrogen chloride gas that is scrubbed out. In addition, metals (from the structures) and debris from the ground cloud are also scrubbed out.

The localized effects of the ground cloud cause acid particulates to be deposited in and around the launch pad area. To minimize corrosion from these depositions, launch pad structures are washed down immediately after launch. These washdown waters (highly acidic and containing metals) combine with the residual sound suppression water in the holding ponds. Regulatory requirements of the California Regional Water Quality Control Board do not permit the discharge to grade of these wastewaters. The wastewaters must be treated and either reused or disposed of by an approved method (i.e., land spreading, evaporation, etc.). Alternate approaches to treatment are discussed in other documents.[2]

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[1] SOURCE: FES - January 1978, Space Shuttle Program, Vandenberg AFB, California

[2] SOURCE: Fluor Engineers, Inc. "Process Evaluation Report For Wastewater Treatment and Disposal," December, 1982.

As a first step to designing a wastewater treatment plant at Vandenberg, we obtained test data from KSC to establish the water composition. Design basis for the project was based on projected deluge, sound suppression and washdown requirements for Vandenberg plus data from STS-1 and -2. With the Project Book water composition established, Fluor began work on the Hazardous Waste Management Project in December 1982.

In the early stage of the Hazardous Waste Management Facility Design for SLC-6, we evaluated the process alternatives available for treatment of the hazardous wastewater. The findings were summarized and issued in a report entitled "Process Evaluation Report for Wastewater Treatment and Disposal," December 1982. The evaluations were based upon design criteria specified in the Project Book. This report is a follow-on to that report and expands and refines the design basis for the Hazardous Waste Management Project.

4.0 WATER TEST PROGRAM

During the preliminary design phase of this project, test data from STS-3 and -5 were added to the initial test data; results from these four launches and the wastewater composition issued in the Project Book are presented in Table 4-1.

Fluor's review of the data from these launches revealed that certain data were missing which would be required to verify the design basis established for Vandenberg. Specifically, barium, calcium, selenium, sodium, borate, sulfate and COD were not analyzed in the initial data and are required for design. Second, it was necessary to determine what the water quantity and composition from each source was so a better prediction could be made of the expected washdown water composition at Vandenberg. Finally, water samples were required for testing of the proposed treating plant operations. Water samples from the first five KSC launches were no longer available for jar tests. Consequently, Fluor established a supplemental test program for STS-6 and 7.

4.1 Wastewater Sampling at KSC: The objective of the wastewater sampling program for STS-6 was to obtain samples at specific locations on the launch pad area sufficient to allow a composite wastewater determination to be made which would be representative of the Vandenberg STS wastewater. The systems at KSC which can be quantified and correlated to SLC-6 include sound suppression and washdown water.

To help describe how the sampling program at KSC relates to the conditions at Vandenberg, we have prepared a flow chart depicting water source, composition and quantity for KSC Launch Pad 39A and Vandenberg SLC-6. This is shown in Figure 4-1. The objective was to confirm C_t' and Q_t', the composition and total quantity of wastewater, for the wastewater treatment plant at SLC-6 presented in the Project Book. The approach was to measure these corresponding quantities, at KSC and ratio them to the Vandenberg design.

At KSC the following quantities could be measured:

C_R - Raw water composition

Q_R - Total raw water make-up

C_A - Sound suppression water composition

Q_A - Quantity of sound suppression water recovered per launch

C_B - Washdown water composition

C_t - Composite composition of collected water

Q_t - Composite quantity of collected water

Having these measurements allowed the calculation of washdown quantity, Q_B, by the following material balance equation:

$$Q_B = Q_t - Q_A$$

TABLE 4-1

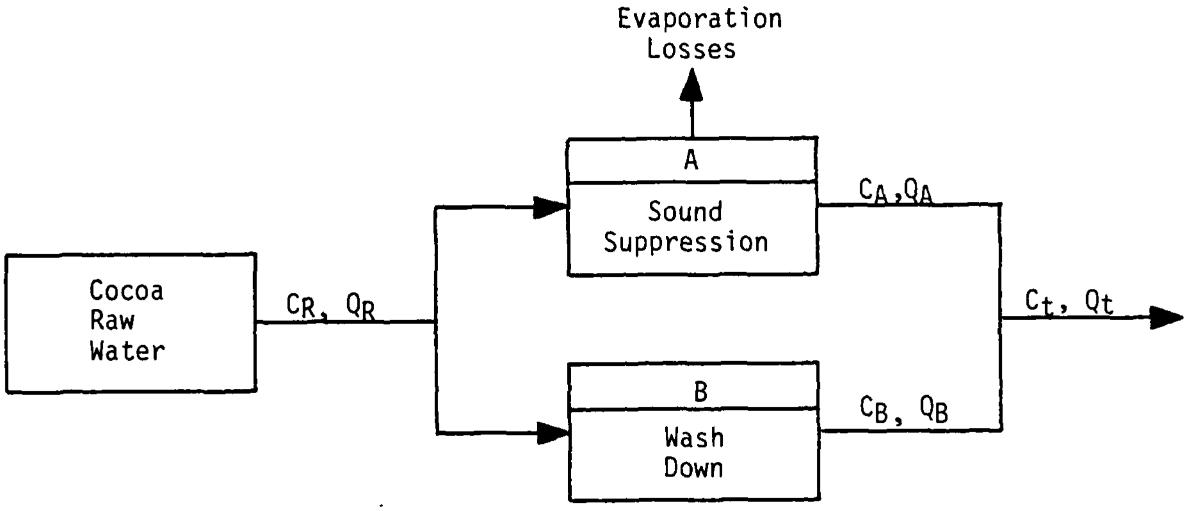
STS-1 THRU 5 WASTEWATER TEST DATA

Parameter	STS-1	STS-2	STS-3	STS-5	Vandenberg Project Book
pH	1.6	1.7	1.8	2.0	1.8-2.5
Aluminum	26.5	29	22	-	52
Barium	-	-	-	-	1
Cadmium	0.12	0.10	1.2	0.09	0.2
Calcium	-	-	-	-	400
Chromium	0.19	0.39	0.5	0.30	0.6
Copper	0.20	0.36	0.09	0.49	0.7
Iron	25	29	12	23.2	-
Lead	0.95	1.1	0.9	0.79	1.4
Magnesium	-	50	37	37	37
Manganese	-	0.61	0.39	0.49	0.7
Nickel	0.54	0.92	0.84	0.48	1.3
Selenium	-	-	-	-	4
Silver	-	0.05	-	-	0.2
Sodium	-	-	-	-	200
Zinc	183	219	107	122	270
Boron	-	-	-	-	10
Chloride	2.2	3250	1769	1162	2820
Nitrate	-	-	1.6	-	-
Phosphate	-	-	2.7	-	-
Silica	-	50	-	50	50
Sulfate	-	-	-	-	20
COD	-	-	-	-	20
TDS	-	-	-	-	3849
Suspended Solids	-	50	50	50	20-320

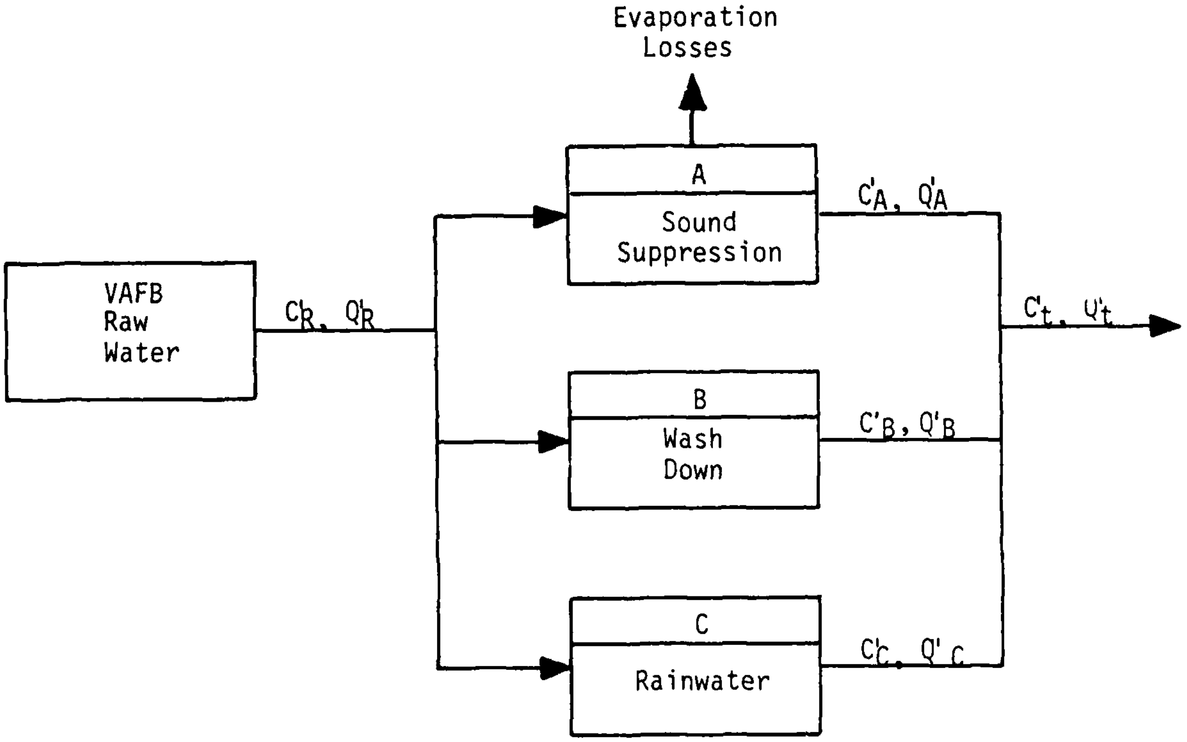
Figure 4-1

Wastewater Source Block Flow Diagram

KSC LP-39A



Vandenberg SLC-6



NOTE: Washdown water includes fixed and manual quantities in both cases.

Data from STS-6 resulted in the following flow quantities obtained from the pond measurements.

Total Water Collected = Q_t = 469,000 Gallons

Sound Suppression Water = Q_A = 358,000 Gallons

Washdown Water Collected = Q_B = 111,000 Gallons

The KSC sound suppression system approximates the SLC-6 system in terms of overall function. The same amount of SRB exhaust will be exposed to the sound suppression water, and the quantities of water used and recovered are estimated to be similar. The sound suppression water is expected to be the most concentrated of the wastewaters, due to its intimate contact with the SRB exhaust. Test data at KSC supports this prediction.

KSC has a minimal amount of fixed washdown which is activated during launch. The quantity of this water is included in the sound suppression quantity in the KSC tests. Moreover, the composition of this deluge water could be determined by obtaining samples of the wastewater around the Launch Mount and Fixed Service Tower. In contrast, the design at SLC-6 will have a significant quantity of fixed spray systems. Approximately 340,000 gallons per launch will be collected during the initial launch and up to 450,000 gallons per launch if the Phase II washdown facility is installed. This wastewater will be the most concentrated washdown wastewater for facilities near the launch mount (near field). Facilities more remote from the launch point (far field) will receive a lesser quantity of contaminants. The Martin Marietta test stand was used to gather samples representative of the far field water samples. Based upon these two points and noting ambient conditions at the time of launch permitted approximating a concentration gradient. The average of these values approximate the fixed washdown wastewater concentration projected for SLC-6.

The third contribution to the composite wastewater is the contribution of the SRB fallout that deposits on structures, launch pad, etc., is washed manually, and is subsequently picked up in the wastewater via the collection system. At KSC this quantity was estimated by observing the difference in pond levels before and after the washdown operation and determining the difference. At Vandenberg this volume is estimated to vary between 250,000 and 400,000 gallons, depending on the wind conditions during launch and the effectiveness of the fixed washdown system. Therefore, the total water to be gathered at SLC-6 is estimated to be approximately one million gallons for the initial design and 1.5 million gallons per launch if the total design is constructed. This includes rainwater which adds to the wastewater volume but is partially offset by reducing the amount of manual washdown required. The rainwater concentration should be more dilute than the other wastewaters collected.

4.2 STS-6 Wastewater Composition: The procedures and mechanics of taking wastewater samples for STS-6 are described in the Appendix, along with the field data obtained. Samples taken by the Air Force for STS-7 follow the same guidelines. The data book prepared for STS-7 is also included in the Appendix.

Figure 4-2 is a schematic of KSC launch pad 39A. The figure depicts the location of the collection points where the primary sampling was conducted, plus the location of the test stand erected by Martin Marietta Corporation, which measured washdown effectiveness for various spray rates.

Table 4-2 lists the wastewater samples that were collected at STS-6. The samples were shipped to OEHL at Brooks AFB where they were analyzed. Table 4-3 lists the corresponding analyses of the samples taken.

To assess the contribution of the contaminants from the potable water used for sound suppression and washdown water, Fluor analyzed the City of Cocoa potable water and compared it to the various wastewaters that were generated during STS-6. This composition is also included in Table 4-3. The City of Cocoa and South Vandenberg potable water compositions are listed in the Appendix.

In addition to the samples indicated, samples were also obtained of residual water and sludge in the bottoms of the two ponds. At KSC the acidic wastewaters are neutralized with regenerant wastes from other Base operations. A resulting sludge has formed over the period launch pad 39A has been operational. The reason for obtaining the samples was to assess the influence the residue might have on the other water samples. The sample results for the residual water and sludge in the ponds are presented in Table 4-4.

Review of the test data for STS-6 results in the following observations:

- The sound suppression water had the lowest pH of all samples; however, the deluge (fixed washdown) was higher in aluminum and chlorides, which are the major fallout constituents from the rocket fuel.
- The deluge water showed higher concentrations of calcium, iron, zinc and silica, as was expected. The calcium and silica reflect possible concrete erosion or leaching, as well as solubilizing of residual sand from sandblasting operations. The iron is from corrosion of the structure, and the zinc is removed from the paint. The deluge water sample was obtained from puddles around the immediate launch pad area and represents a worst condition for each of these constituents.
- Test data from the Martin Marietta test stand indicates a high fall-out from the acid cloud. The increase in trace minerals in the test stand data probably came from the equipment itself. No blank run or flushing water run through the system was obtained. The increase in calcium, magnesium and silica is probably from dust raised during launch which gradually falls back to earth. This dust could be a combination of residual sandblasting sand on the launch support facilities, soil from around the pad, and eroded material from the pad itself. The average of this composition and that of the deluge represent the approximation of the average fixed washdown in the near and far field.
- Composition of the inlet flume sample indicates that the manual washdown rinsed away most of the impurities and its composition was approaching the City of Cocoa water analysis. The manual washdown composition is a function of the quantity of water used. The volume used at KSC for STS-6 was 111,000 gallons, compared to Vandenberg estimates of an average of 310,000 gallons.

Figure 4-2

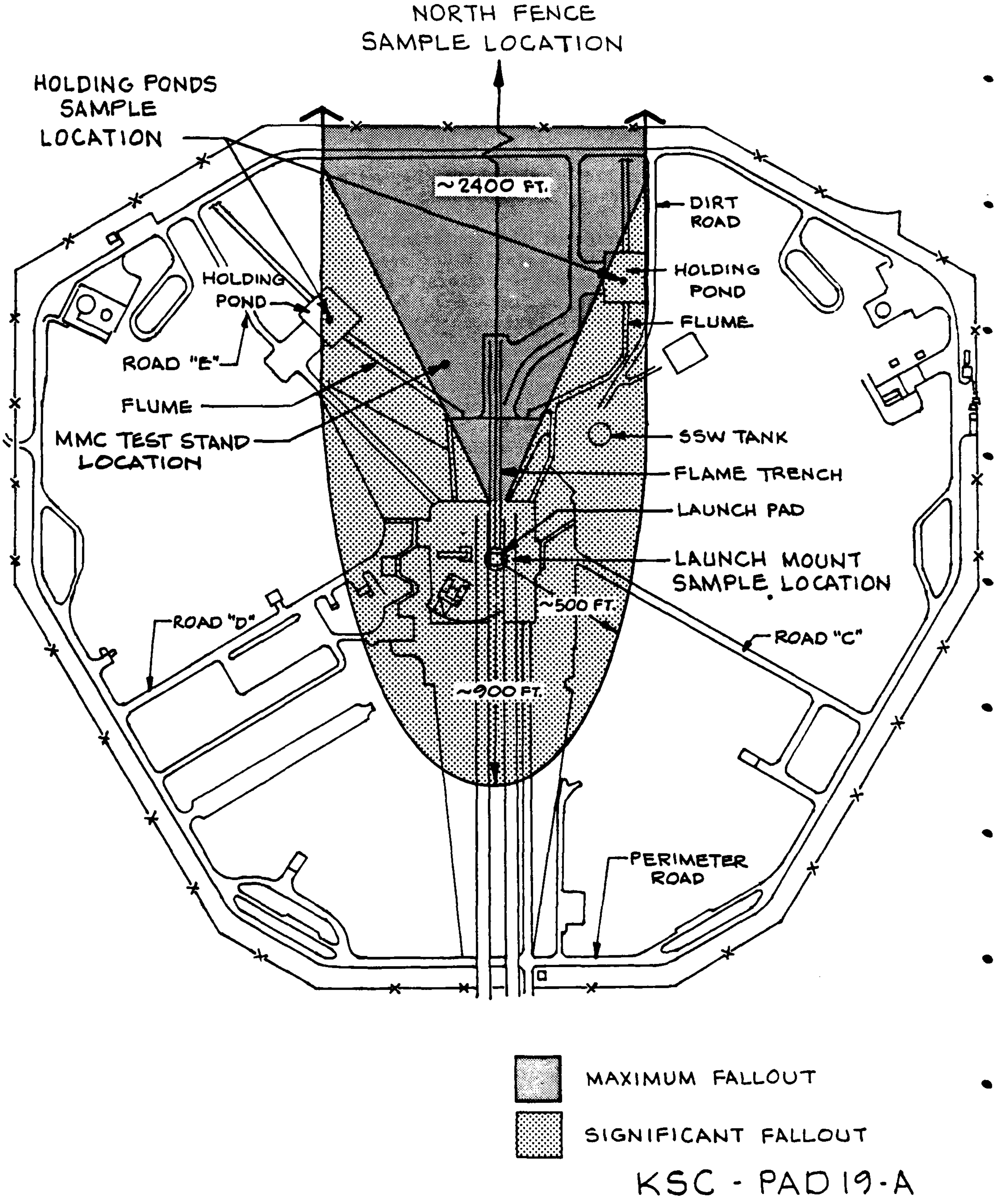

NORTH FENCE SAMPLE LOCATION
HOLDING PONDS SAMPLE LOCATION
~2400 FT.
DIRT ROAD
HOLDING POND
HOLDING POND
FLUME
ROAD "E"
FLUME
MMC TEST STAND LOCATION
SSW TANK
FLAME TRENCH
LAUNCH PAD
LAUNCH MOUNT SAMPLE LOCATION
~500 FT.
ROAD "D"
ROAD "C"
~900 FT.
PERIMETER ROAD
MAXIMUM FALLOUT
SIGNIFICANT FALLOUT
KSC - PAD 19-A

Table 4-2

STS-6 WASTEWATER SAMPLES

SAMPLE NUMBER	DESCRIPTION	LOG BOOK PAGE
GN 830005	NE Pond (Pond A) Launch Day (Sound Suppression Water)	21
GN 830006	NW Pond (Pond B) Launch Day (Sound Suppression Water)	23
GN 830007	Deluge Water Launch Day (Fixed Washdown, Concentrated)	17
GN 830011	Martin Marietta Test Stand 0-10 Min Launch Day (Fixed Washdown, Dilute)	25
GN 830010	NW Pond Washdown Post Launch Inlet Flume (Manual Washdown)	33
GN 830008	NE Pond (A) Post Launch Day (Composite Sample)	35
GN 830009	NW Pond (B) Post Launch Day (Composite Sample)	37

TABLE 4-3

STS-6 WASTEWATER SAMPLE ANALYSES

	KSC Raw Water, C_R	Sound Suppression Water			Deluge Water	MM Test Stand, 0-10 min	NW Pond Inlet Flume	Composite Water		
		NE Pond A	NW Pond B	C_A				NE Pond A	NW Pond B	C_t
SAMPLE NO.	A19409	005	006	AVE.	007	011	010	008	009	AVE.
Parameter										
pH	-	1.6	1.6	1.6	2.6	2.2	7.1	2	3.5	-
Aluminum	-	19	49	35	62	27	0.4	22	16	19
Barium	-	0.6	0.4	0.5	1.3	0.01	0.2	0.5	0.4	0.5
Cadmium	-	0.04	0.06	0.05	0.5	0.02	0.02	0.05	0.06	0.05
Calcium	21	233	170	106	476	87	39	216	126	171
Chromium	-	0.3	0.5	0.4	0.2	2.1	0.05	0.2	0.5	0.4
Copper	-	0.3	1.7	1.0	0.4	0.6	0.05	0.2	1.5	0.9
Iron	6.6	27	23	20	73	53	0.44	27	20	24
Lead	-	0.9	1.6	1.3	0.9	6.6	0.05	0.8	1.3	1.0
Magnesium	8.4	40	18	29	30	14	10	42	20	31
Manganese	-	0.6	0.5	0.6	4.4	1.0	0.08	0.6	0.5	0.5
Nickel	-	0.8	0.9	0.9	1.9	4.1	0.05	0.8	0.8	0.8
Selenium	-	0.002	0.001	0.001	0.01	0.01	0.01	0.01	0.01	0.01
Silver	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sodium	75	218	67	142	101	75	65	217	87	152
Zinc	-	69	71	70	98	64	21	65	72	69
Boron	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Chloride	87	2800	2000	2400	3600	3600	148	2400	1600	2000
Nitrate	-	0.66	0.66	0.66	0.98	0.77	0.58	0.75	0.78	0.77
Phosphate	-	-	-	-	-	-	-	-	-	-
Silica	3.9	65	50	58	202	53	20	65	78	71
Sulfate	96	-	-	-	-	-	-	40	25	33
COD	-	50	18	34	-	-	-	-	-	-

NOTE: All concentrations are in mg/l

TABLE 4-4

PRELAUNCH RESIDUAL WATER AND SLUDGE IN PONDS A & B

	Residual Pond Water			Prelaunch Pond Sludge		Composite Water		
	NW Pond B	NE Pond A		NE Pond A	NW Pond B	NE Pond A	NW Pond B	Ct.
SAMPLE NO.	001	002	AVE.	18724	18723	008	009	AVE.
Parameter								
pH	10.0	9.3	-	-	-	2	3.5	-
Aluminum	0.27	0.29	0.28	67	1147	22	16	19
Barium	0.2	0.2	0.2	-	-	0.5	0.4	0.5
Cadmium	0.01	0.01	0.01	1.5	3.6	0.05	0.06	0.5
Calcium	33	45	39	2360	2350	216	126	171
Chromium	0.05	0.05	0.05	13.5	46.3	0.2	0.5	0.4
Copper	0.02	0.02	0.02	16.7	41.7	0.2	1.5	0.9
Iron	.31	.23	.27	856	2436	27	20	24
Lead	0.05	0.05	0.05	17.3	2.2	0.8	1.3	1.0
Magnesium	7.6	44	26	720	740	42	20	31
Manganese	0.05	0.05	0.05	6.3	12.0	0.6	0.5	0.5
Nickel	0.05	0.05	0.05	11.4	33.5	0.8	0.8	0.8
Selenium	0.01	0.01	0.01	-	-	0.01	0.01	0.01
Silver	0.01	0.01	0.01	1.1	1.1	0.01	0.01	0.01
Sodium	75	316	196	449	127	217	87	152
Zinc	0.54	0.24	0.39	900	1764	65	72	69
Boron	0.5	0.5	0.5	-	-	0.5	0.5	0.5
Chloride	112	800	456	-	-	2400	1600	2000
Nitrate	0.1	0.1	0.1	-	-	0.75	0.78	0.77
Phosphate	-	-	-	-	-	-	-	-
Silica	5.8	5.6	5.7	15	13	65	78	71
Sulfate	-	-	-	-	-	-	-	-
COD	20	35	28	18	34	40	25	33

NOTE: All concentrations are in mg/l

- o The composite analysis shows a decrease in concentration based on the dilution which occurs during the manual washdown. The average treatment plant feed composition should approach this composition if a plant were installed at KSC.

- o The effect the residual water and sludge have on the pond samples can be estimated by comparing the deluge and test stand samples to the sound suppression samples. Most evident is the increase in magnesium and sodium from the residual water. The sludge composition is in agreement directionally with the sound suppression water samples, but its impact on the composition can not be quantified.

Comparison of the STS composite composition with the Project Book is tabulated in Table 4-5. Silica and iron are the only major constituents in the STS-6 analysis that exceed the Project Book values. In the Project Book analysis, iron was not listed, whereas STS-6 has approximately 30 mg/l of iron. This presents no problem to the process chemistry but does add to the amount of sludge produced.

The zinc concentration is 200 mg/l higher in the Project Book analysis and may have resulted from the early STS-1 and 2 launches removing large quantities of paint from the launch pad structures. Inorganic zinc primer was used extensively on the structure. STS-6 had the advantage of acid-resistant coatings having been applied to large areas of the Fixed Service Tower. This may have helped reduce the zinc contamination.

The Project Book specified 320 mg/l of suspended solids in the wastewater. The STS-6 composite had essentially no suspended solids in it by visual observation.

4.3 STS-7 Wastewater Composition: Wastewater samples were taken for STS-7 by NASA and the Air Force and shipped to Fluor Corporation for analysis and jar testing. Fluor contracted the analytical services of Chemical Research Laboratories to perform the analysis and testing of the wastewater samples. The report of the results of their investigation is included in the Appendix.

The STS-7 samples were initially screened for pH, turbidity, and silica content. The samples showed comparable characteristics, as indicated in Table 4-6. Consequently, the samples were proportionately combined into a single composite for analysis and testing purposes. Table 4-7 shows the analysis of the STS-7 wastewater composite presented along with STS-6 data and the SLC-6 Project Book composition. The values are slightly higher than the STS-6 data because the samples are a combination of all samples gathered from the launch, and not necessarily in the ratios representative of the collected composite, as in STS-6. The most significant difference is the increase in zinc concentration of the STS-7 composite over that of STS-6. The Mobile Launch Pad was repainted prior to STS-7, which probably caused the zinc level to increase. The STS-7 value more closely approximates the SLC-6 Project Book.

4.4 Wastewater Comparison, STS-1 through 7: Table 4-8 presents a summary of all composite wastewater sample test results for STS-1 through 7 (exclusive of STS-4, for which Fluor did not receive data) and the Vandenberg SLC-6 Project Book wastewater composition. The data is relatively consistent for all launches for the constituents impacting the plant design. These principal constituents are aluminum,

TABLE 4-5

STS-6 COMPOSITE COMPOSITION COMPARED TO SLC-6 PROJECT BOOK

SAMPLE NO. Parameter	STS-6 Composite Composition, Ct AVE.	Vandenberg Project Book AVE.
pH	-	1.8-2.5
Aluminum	19	52
Barium	0.5	.1
Cadmium	0.5	0.2
Calcium	171	400
Chromium	0.4	0.6
Copper	0.9	0.7
Iron	24	-
Lead	1.0	1.4
Magnesium	31	37
Manganese	0.5	0.7
Nickel	0.8	1.3
Selenium	0.01	4.
Silver	0.01	0.2
Sodium	152	200
Zinc	69	270
Boron	0.5	10
Chloride	2000	2820
Nitrate	0.77	-
Phosphate	-	-
Silica	71	50
Sulfate	-	20
COD	33	Nil
TDS	-	3849
Suspended Solids	-	20-320

NOTE: All concentrations are in mg/l

TABLE 4-6

STS-7 WASTEWATER SAMPLES SCREENING RESULTS

SAMPLE	pH	TURBIDITY (NTU)	Si(SiO_2)
EPLA #1a	1.8	34.	79.
EPLA #1b	1.9	27.	77.
EPLA #2a	1.7	28.	81.
EPLA #2b	1.8	33.	79.
EPLA #3a	1.8	46.	81.
EPLA #3b	1.8	38.	81.
EPLA #4a	1.7	12.	81.
EPLA #4b	1.8	15.	79.
EPLB #1a	1.9	4.2	88.
EPLB #1b	1.9	9.0	88.
EPLB #2a	1.9	4.2	83.
EPLB #2b	1.9	4.2	88.
EPLB #3a	2.0	4.4	88.
EPLB #3b	2.0	6.0	88.
EPLB #4a	2.0	6.4	88.
EPLB #4b	2.0	10.0	86.
LPLA #1a	2.1	2.4	88.
LPLA #1b	2.1	3.0	81.
LPLA #2a	2.1	3.0	81.
LPLA #3a	2.0	6.0	81.
LPLA #3b	2.0	4.1	83.
LPLA #4a	2.0	5.6	81.
LPLA #4b	2.1	3.0	83.
LPLB #1a	1.9	10.2	83.
LPLB #1b	1.9	5.6	83.
LPLB #2a	1.9	13.0	86.
LPLB #3a	1.8	6.4	86.
LPLB #3b	1.8	5.6	86.
LPLB #4a	1.8	--	83.
LPLB #4b	1.8	--	83.
COMPOSITE	2.0	--	88.

TABLE 4-7

STS-6 AND 7 COMPOSITE COMPOSITION COMPARED TO SLC-6 PROJECT BOOK

	STS-6 Composite Composition, Ct	STS-7 Composite Composition, Ct	Vandenberg Project Book
SAMPLE NO. Parameter	AVE.	AVE.	AVE.
pH	2-3.5	2.0	1.8-2.5
Aluminum	19	26	52
Barium	0.5	0.6	1
Cadmium	0.5	0.2	0.2
Calcium	171	173	400
Chromium	0.4	0.3	0.6
Copper	0.9	1.2	0.7
Iron	24	30	-
Lead	1.0	1.4	1.4
Magnesium	31	34	37
Manganese	0.5	0.5	0.7
Nickel	0.8	0.9	1.3
Selenium	0.01	0.2	4.
Silver	0.01	0.01	0.2
Sodium	152	193	200
Zinc	69	206	270
Boron	0.5	-	10
Chloride	2000	1960	2820
Nitrate	0.77	0.6	-
Silica	71	88	50
Sulfate	-	203	20
COD	33	104	Nil
TDS	2540	2360	3849
Suspended Solids	-	57	20-320

NOTES: All concentrations are in mg/l

TABLE 4-8

COMPOSITE WATER COMPOSITIONS FOR STS LAUNCHES

Parameter	STS-1	STS-2	STS-3	STS-5	STS-6	STS-7	Vandenberg Project Book
pH	1.6	1.7	1.8	2.0	2-3.5	2.0	1.8-2.5
Aluminum	26.5	29	22	-	19	26	52
Barium	-	-	-	-	0.5	0.6	1
Cadmium	0.12	0.10	1.2	0.09	0.5	0.2	0.2
Calcium	-	-	-	-	171	173	400
Chromium	0.19	0.39	0.5	0.30	0.4	0.3	0.6
Copper	0.20	0.36	0.09	0.49	0.9	1.2	0.7
Iron	25	29	12	23.2	24	30	-
Lead	0.95	1.1	0.9	0.79	1.0	1.4	1.4
Magnesium	-	50	37	37	31	34	37
Manganese	-	0.61	0.39	0.49	0.5	0.5	0.7
Nickel	0.54	0.92	0.84	0.48	0.8	0.9	1.3
Selenium	-	-	-	-	0.01	0.2	4.
Silver	-	0.05	-	-	0.01	0.01	0.2
Sodium	-	-	-	-	152	193	200
Zinc	183	219	107	122	69	206	270
Boron	-	-	-	-	0.5	-	10
Chloride	2.2	3250	1769	1162	2000	1960	2820
Nitrate	-	-	1.6	-	0.77	0.6	-
Phosphate	-	-	2.7	-	-	-	-
Silica	-	50	-	50	71	88	50
Sulfate	-	-	-	-	-	203	20
COD	-	-	-	-	33	104	Nil
TDS	-	-	-	-	2540	2360	3849
Suspended Solids	-	50	50	50	-	57	20-320

NOTE: All concentrations are in mg/l

calcium, iron, magnesium, sodium, zinc, and chloride. The maximum variation that has been reported from all launches for all species is presented in Table 4-9 along with the Project Book composition for SLC-6.

The comparison indicates that the Vandenberg wastewater composition is generally representative of the maximum contaminant concentration that has been experienced to date at KSC. Ionic balances of the Project Book, STS-6 and 7 wastewater compositions have been included in Table 4-10 for comparison purposes. The deficiency in the cation equivalent is thought to be due to the hydrogen ion concentration, or to organic and inorganic cations not included in the analyses.

The Vandenberg Project Book wastewater composition had been based on KSC launch data from STS-1 and 2. It had not been adjusted for the difference in raw water concentration. Table 4-11 shows the adjusted wastewater composition calculated by taking the difference between the two raw waters and adding it to the wastewater composition in the Project Book. It has been adjusted for calcium, magnesium, chlorides, potassium, silica, sodium, and sulfate.

Figure 4-3 depicts the variation in chemical constituents measured during the first seven launches at KSC previously presented in tabular form in Table 4-9. The adjusted Vandenberg Project Book wastewater composition which is the design point for the wastewater treatment plant is indicated for each constituent.

In determining the design composition for the Vandenberg wastewater from KSC test data, one must finally look at the effect on the composite wastewater composition as a function of the quantity of water used. If the data from STS-6 are used for comparison to the projected Vandenberg conditions, the following sources and corresponding volumes in gallons per launch are obtained:

Water Source	KSC STS-6 Water, Gals.	Vandenberg Water, Gals Package 1	Package 4
Sound Suppression	360,000	350,000	350,000
Fixed Washdown	---	340,000	451,000
Manual Washdown	111,000	150-250,000 *	150-400,000 *
Rainwater	---	195,000	425,000
Expected (W/O Rain)	471,000	940,000	1,201,000
Maximum Expected	---	1,035,000	1,376,000

* Assumes 150,000 gallons used in conjunction with rainfall and 250,000 or 400, 000 gallons used without rainfall.

TABLE 4-9

VARIATION OF IONIC SPECIES FOR STS-1 THROUGH 7

	Minimum	Maximum	Vandenberg Project Book
pH	3.5	1.6	1.8 - 2.5
Aluminum	19	29	52
Barium	0.5	0.6	1
Cadmium	0.09	1.2	0.2
Calcium	171	173	400
Chromium	0.19	0.5	0.6
Copper	0.09	1.2	0.7
Iron	12	30	--
Lead	0.79	1.4	1.4
Magnesium	31	50	37
Manganese	0.39	0.61	0.7
Nickel	0.48	0.92	1.3
Selenium	0.01	0.2	4
Silver	0.01	0.05	0.2
Sodium	152	193	200
Zinc	69	219	270
Boron	0.5	0.5	10
Chloride	1162	3250	2820
Nitrate	0.6	1.6	--
Phosphate	2.7	2.7	--
Silica	50	88	50
Sulfate	20	203	20
COD	33	104	Nil
TDS			3849
Suspended Solids	50	57	20-320

NOTE: All concentrations are in mg/l

TABLE 4-10

STS-6 STS-7 IONIC BALANCE COMPARISON

Parameter	Equivalent Weight	Ion	Ionic Weight	Project Book Analysis	Equivalents		STS-6	Equivalents		STS-7	Equivalents	
					+	-		+	-		+	-
Aluminum	9			52	5.8		70.9	7.88		26	2.9	
Boron	3.6	BO_3	58.8	10		0.17	<0.47		<0.13			
Calcium	20			400	20		184	9.2		173	8.65	
Chromium	17.3			0.6	0.03		0.57	0.03		0.3	0.02	
Chlorine	35.5			2820		79.44	2445		68.87	1960		55.2
Copper	31.8			0.7	0.02		0.87	0.03		1.2	0.04	
Barium	68.7			1	0.01		0.6	0.01		0.6	0.01	
Cadmium	56.2			0.2	--		0.05	--		0.15	--	
Lead	103.6			1.4	0.01		1.75	0.02		1.4	0.01	
Magnesium	12.1			37	3.06		28	2.31		34	2.81	
Manganese	27.5			0.7	0.03		0.87	0.03		0.54	0.02	
Nickel	10.1			1.3	0.13		1.33	0.13		0.85	0.08	
Silica	4.5	S_1O_2	60	50			74			88		
Silver	108			0.2	--		<0.01	--		0.012	--	
Selenium	20			4	0.2		<0.01	--		0.23	0.01	
Sodium	23			200	10		136	5.91		193	8.39	
Zinc	32.7			270	8.26		70.9	2.17		206	6.30	
TOTAL					47.6	79.61		27.72				
Iron	18.6						30.2			30	1.61	
Hydrogen	1											
pH/Hydrogen Ion Concentration							1.8-2.5	13-24		1.9/10	10	
TOTAL CATIONS/ANIONS								40.7	69.0		40.85	55.2

Table 4-11

ADJUSTED PROJECT BOOK WASTEWATER COMPOSITION(1)

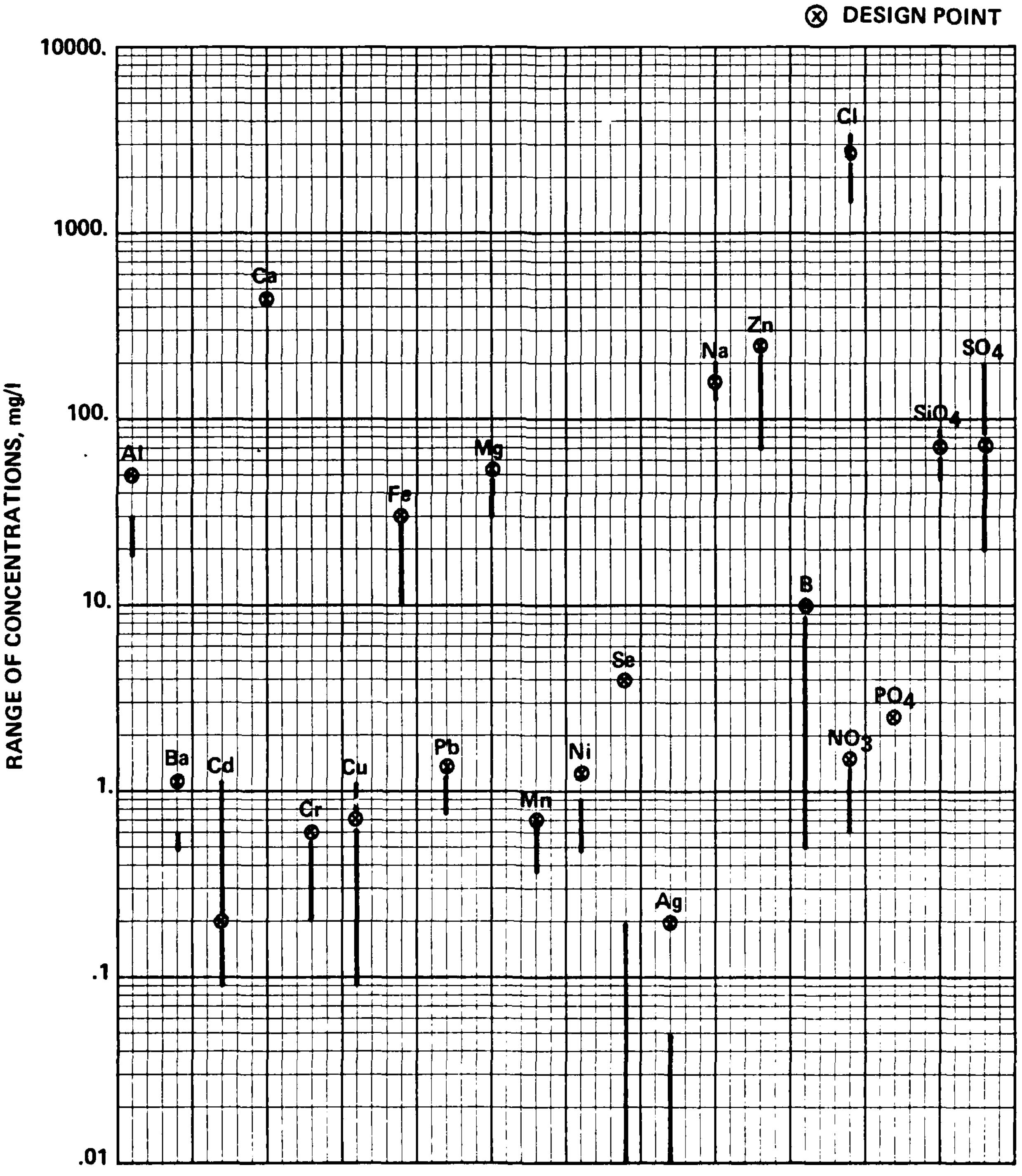
Parameter	Vandenberg Project Book
pH	2-3.3
Aluminum	52
Barium	less than 1.2
Cadmium	0.2
Calcium	465
Chromium	0.6
Copper	0.7
Iron	30
Lead	1.4
Magnesium	57
Manganese	0.7
Nickel	1.3
Potassium	9
Selenium	less than 4
Silver	0.2
Sodium	181
Zinc	270
Boron	10
Chloride	2881
Silica	70
Sulfate	79
COD	Nil
Suspended Solids	20-320

NOTE: All concentrations are in mg/l

(1) Extracted from STS Project Book and modified to account for the difference in constituents between KSC potable water and Vandenberg potable water.

FIGURE 4-3

VANDENBERG DESIGN POINT VERSUS KSC WASTEWATER SAMPLES FROM STS-1 THRU 7



CHEMICAL CONSTITUENTS

From the test data, it is evident that the sound suppression and fixed washdown waters are the most concentrated, the manual washdown more dilute, and the rainwater (by definition) with minimal contamination. From the material balance equations previously developed, the following relationships exist for each of the three cases:

$$471{,}000\ C_t = 360{,}000\ C_A + 111{,}000\ C_B$$

$$1{,}000{,}000\ C'_t = 690{,}000\ C'_A + 250{,}000\ C'_B \text{ (Excludes Rainwater)}$$

$$1{,}500{,}000\ C'_t = 801{,}000\ C'_A + 400{,}000\ C'_B \text{ (Excludes Rainwater)}$$

$$1{,}000{,}000\ C'_t = 690{,}000\ C'_A + 150{,}000\ C'_B + 195{,}000\ C'_R \text{ (Including Rainwater)}$$

$$1{,}500{,}000\ C'_t = 801{,}000\ C'_A + 150{,}000\ C'_B + 526{,}000\ C'_R \text{ (Including Rainwater)}$$

The equations indicate that for Package 1 approximately twice as much water will be collected at SLC-6 as at KSC, and that each of the contributors (sound suppression, fixed washdown, and manual washdown) will be in the same ratio. Therefore the resulting composite concentration will be similar to KSC. For Package 4, the quantity ratio is approximately three to one if the rainwater is excluded. However, if the rainwater is included, a significant dilution effect results and the wastewater composition is overstated in the Project Book. Based on these data, we determined that the treatment plant should be designed for the worst condition recorded at KSC, with an appropriate safety factor. The original Project Book wastewater composition adjusted for the Vandenberg raw water reflects that resulting wastewater composition.

A separate study performed by Fluor indicates that the capital costs are relatively insensitive to small reductions in contaminant concentration, but that operating costs will be reduced. Chemical costs are directly related to contaminant concentrations. RO membrane costs will depend on how completely the metal hydroxides and sulfides are precipitated and removed in the pretreatment process.

5.0 PROCESS ANALYTICAL EVALUATION

To assess the process design described in the process evaluation report and to prove out the chemical reactions, Fluor implemented a jar test program to obtain the following data:

- Chemical consumption requirements to neutralize and precipitate heavy metals and silica.
- Optimization of reaction time, pH, sulfide residual, and slurry recirculation for removal of heavy metals and silica.
- Settling and thickening characteristics of the precipitated solids.
- Sludge dewatering.
- Sludge leachate testing for hazardous metals.

5.1 STS-6 Jar Test Program: The jar tests for STS-6 wastewater were conducted at OEHL Brooks AFB, Texas under the direction of OEHL and Fluor. Tests were based on the composite samples listed in Tables 5-1 and 5-2. The composite sample indicated in Table 5-1 was used for the initial screening tests to determine how the process reacted. This was necessary to conserve sample quantities for the more extensive tests using the Table 5-2 composite sample.

The metal precipitation test optimized the precipitation of aluminum, zinc, and other heavy metals with sodium hydroxide and sodium sulfide. The heavy metals in the washdown water were precipitated as hydroxides, and further reduced in solubility as sulfides. The pH was controlled to avoid formation of aluminates, zincates, and other amphoteric metal complexes. The optimum dosages of sodium hydroxide and sodium sulfide were based on the wastewater composition. The procedures followed are presented in detail in the Appendix.

5.2 STS-6 Jar Test Results: Sodium hydroxide was used to neutralize the hydrochloric acid and to precipitate metallic hydroxides. This was supplemented with sodium sulfide to maximize the precipitation of the heavy metals at a pH which would not cause significant formation of soluble aluminate and zincate ions.

When a soluble sulfide is added to a solution containing heavy metals, the mixture does not indicate any sulfide ion in solution until the metallic sulfides have been precipitated. The presence of sulfide ion can be indicated colorimetrically or with an oxidation-reduction probe (ORP). The laboratory tests used a colorimetric indicator N.N.-Dimethyl-P-Phenylene Diamine Sulfate/Sulfuric acid solution prepared according to the APHA "Standard Methods of Analysis" 1960 issue. The mixture was dark brown, indicating a contaminated reagent, according to the APHA standards. Experimentation with the solution showed that its addition to a sulfide-free water produced a violet color. When sulfide was added, the solution turned yellow. Colorimetric spot tests were used to determine the presence of excess sulfide in the one-liter jar tests. In the 300-ML jar tests, sulfide odor was used as an excess sulfide indicator; however, this was inaccurate, as indicated by the respective sulfide dosages. A cationic polymer was added to enhance floc formation to improve settling and the clarity of the supernatant water.

TABLE 5-1

STS-6 WASTEWATER COMPOSITE
300 ML JAR TESTS

	Post Launch SS Water	Deluge Washdown	Post Launch Composite	300 ML Composite
SAMPLE NO.	830005	830007	830008	
pH	1.6	2.6	2.0	2.2
Aluminum	49	62	22	45
Barium	0.4	1.3	0.5	0.8
Cadmium	0.06	0.05	0.05	0.05
Calcium	106	476	216	266
Chromium	0.5	0.2	0.2	0.3
Copper	1.7	0.4	0.2	0.8
Iron	20	73	27	40
Lead	1.6	0.9	0.8	1.1
Magnesium	17	30	42	30
Manganese	0.5	4.4	0.6	1.9
Nickel	0.9	1.9	0.8	1.2
Selenium	<0.01	<0.01	<0.01	<0.01
Silver	0.01	0.01	0.01	0.01
Sodium	67	101	217	128
Zinc	71	98	65	78
Boron	<0.5	<0.5	<0.5	<0.5
Chloride	2000	3600	2400	2667
Nitrate	0.7	1.0	0.8	0.8
Silica	50	202	65	106
Sulfate	18	40	40	32.7

NOTE: All concentrations are in mg/l

TABLE 5-2

STS-6 WASTEWATER COMPOSITE
1 LITER JAR TESTS

SAMPLE NO. Parameter	0005 (1.75L)	0006 (1.28L)	0007 (0.54L)	0008 (1.36L)	0009 (1.93L)	0011 (0.88L)	Composite (7.74L)
pH	1.6	1.6	2.6	2.0	3.5	2.2	1.6
Aluminum	19	49	62	22	16	27	28
Barium	0.6	0.4	1.3	0.5	0.4	0.9	0.6
Cadmium	0.04	0.06	0.05	0.05	0.06	0.02	0.05
Calcium	233	106	496	216	124	87	184
Chromium	0.3	0.5	0.2	0.2	0.5	2.1	0.6
Copper	6.3	1.7	0.4	0.2	1.5	0.6	0.9
Iron	27	20	73	27	20	53	30
Lead	0.9	1.6	0.9	0.8	1.3	6.6	1.8
Magnesium	40	17	30	42	20	14	28
Manganese	0.6	0.5	4.4	0.6	0.5	1.0	0.9
Nickel	0.8	0.9	1.9	0.8	0.8	4.1	1.3
Selenium	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sodium	218	67	101	217	87	75	136
Zinc	69	71	98	65	72	65	71
Boron	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.47
Chloride	2800	2000	3600	2400	1600	3600	2445
Nitrate	0.7	0.7	1.0	0.8	0.8	0.8	0.7
Silica	65	50	202	65	78	53	74
COD	50	18	40	40	25	85	40

NOTE: All concentrations are in mg/l.

Six successive jar tests were made with 300-ML samples of the composite shown in Table 5-1. The settled sludge was returned to the subsequent test, as described in the jar test procedure. The test data and the sludge settling curves are shown on Figures 5-1 through 5-6.

Four successive one-liter jar tests followed by two 500-ml tests were made with the composite shown in Table 5-2. The settled sludge was returned to the subsequent test, as previously described. The test data and the settling curves are shown on Figures 5-7 through 5-13.

The settled sludge from the first test of each series of tests using the Table 5-1 and 5-2 samples was returned to the second test, and from each sequential test to the following test. Magnesium chloride was added to determine the optimum magnesium dosage to reduce the silica concentration to less than 15 mg/l, which is the maximum concentration limit to be fed to the reverse osmosis unit. However an analysis of the composite wastewater made on May 16 showed only 5 mg/l of silica, compared to 60 mg/l when SiO_2 was analyzed on April 5. It appeared that the pH of about 1.6 caused the formation of silicic acid which polymerized and caused precipitation of the silica. (Ref: "Activated Silica in Wastewater Coagulation" W. J. Weber et al., prepared for EPA PB 232454 June 1974.) The rate of silica reduction in the low-pH washdown water was tabled and studied with samples obtained from the STS-7 launch.

Overall, the tests confirmed our ability to precipitate metals from a cold solution by using sulfides and hydroxide as reaction agents. They also proved to a limited extent the ability to reduce dissolved silica. The results indicated that, without sludge recycle, the lamella-type clarifier design proposed for the treatment process is conservative with a 0.15 gpm/ft^2 design rate. Table 5-3 summarizes the effect of sludge return on the sludge settling rate.

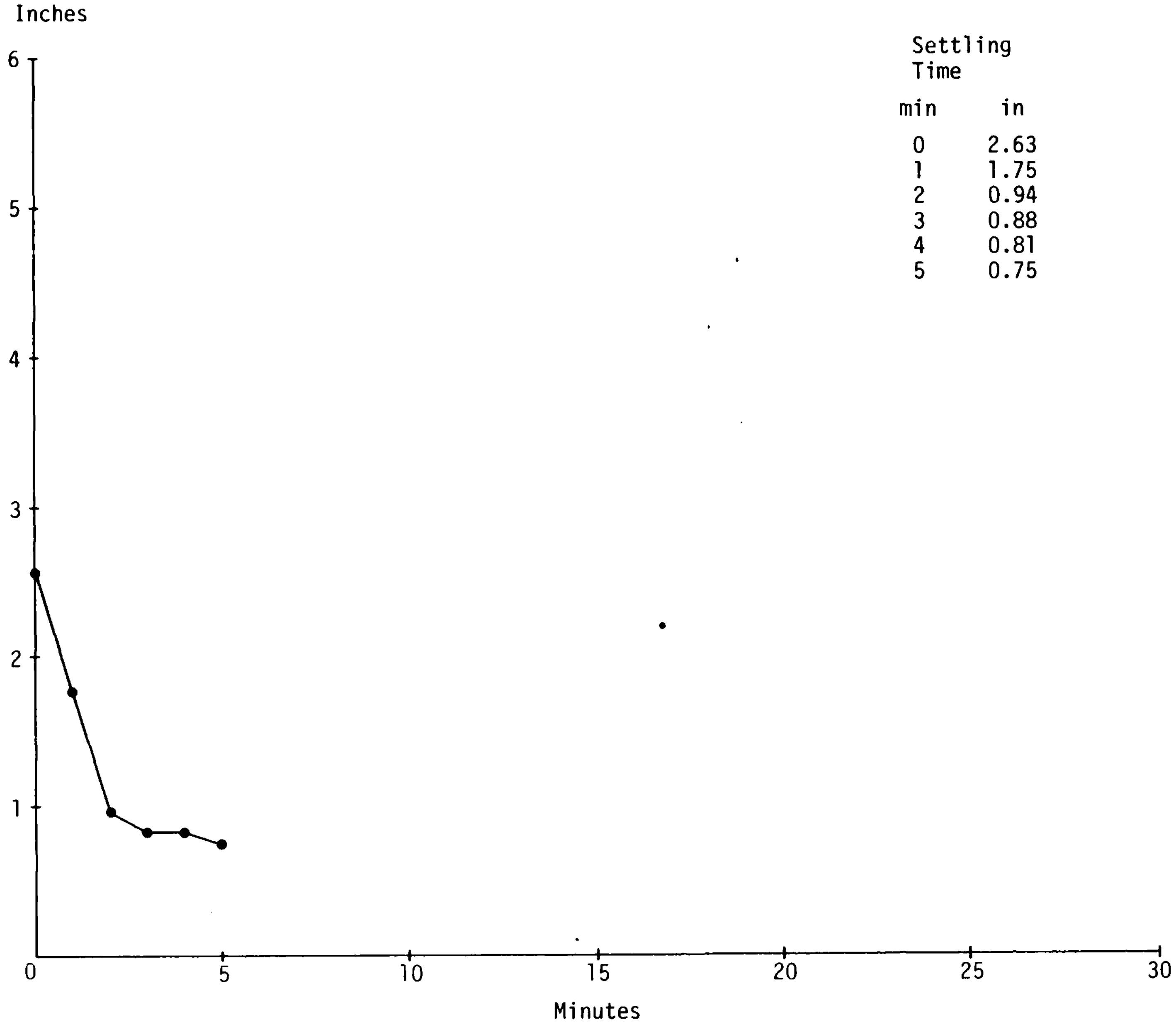
5.3 STS-7 Jar Test Program: Jar tests of wastewater samples from STS-7 were performed by Chemical Research Laboratories under subcontract to Fluor Corporation. The STS-7 test program was a continuation of the tests run for STS-6 wastewater samples. Tests were conducted to determine process considerations, which were identified as follows on items from the STS-6 jar test evaluations:

- The Effect of Temperature on Silica Precipitation - Silica precipitation was monitored by determining silica levels at various time intervals and temperatures.
- The Effect of Sodium Sulfide on Metal Concentration - The effect of sodium sulfide on the metal concentration of the wastewater composite was determined for various pH levels by atomic absorption spectrophotometry. The supernatant from the jar tests was used to determine the unprecipitated metals. The test also generated settling curve data.
- Variations of Treatment - Calcium carbonate was introduced to determine the effect of $CaCO_3$ as a sludge compaction additive. Sodium hydroxide was added to determine if the sulfide additive was necessary.
- Sequestering of Barium - Barium present in the raw water at Vandenberg could present a precipitation problem in the final stage of the RO membrane. It

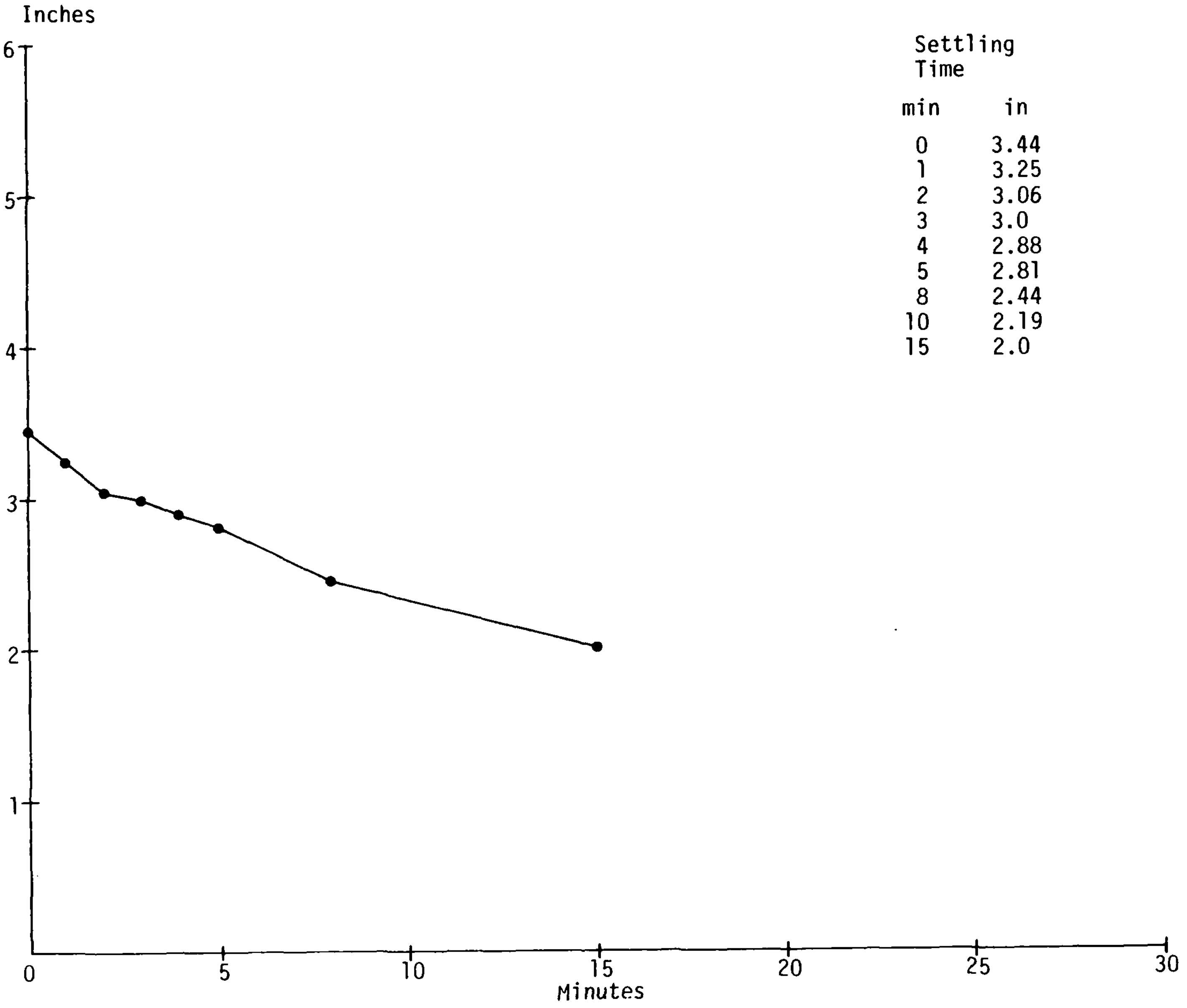
Figure 5-1
STS-6 Test #1
300 ML Composites

TEST #1

Settling Time min	in	$\frac{GPM}{FT^2}$
0	2.63	
1	1.75	0.55
2	0.94	0.50
3	0.88	0.04
4	0.81	0.04
5	0.75	0.04



TEST #2



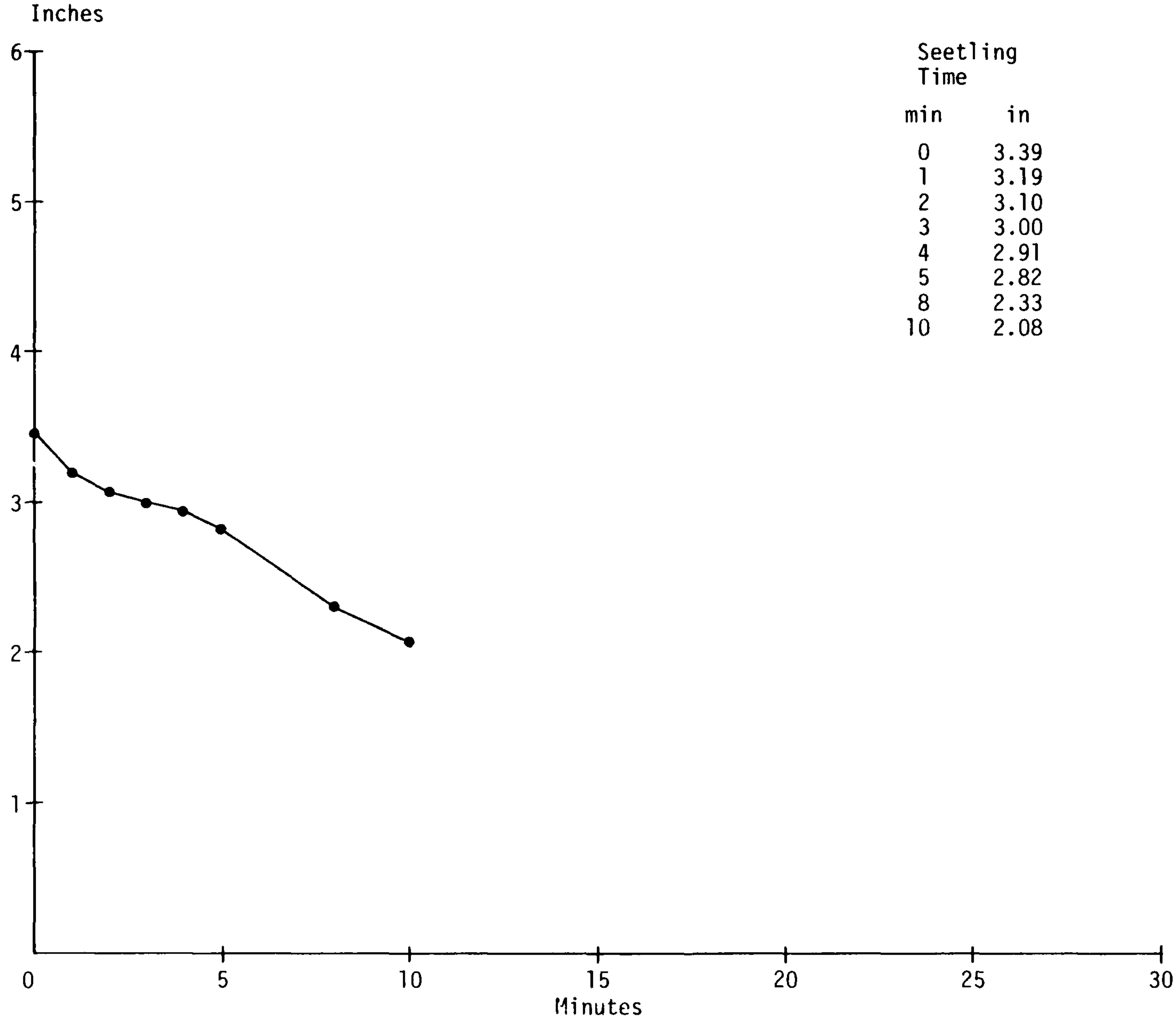
Settling Time min	in	$\frac{GPM}{FT^2}$
0	3.44	
1	3.25	0.12
2	3.06	0.12
3	3.0	0.04
4	2.88	0.12
5	2.81	0.04
8	2.44	0.08
10	2.19	0.08
15	2.0	0.02

Figure 5-2

STS-6 Test #2

300 ML Composites

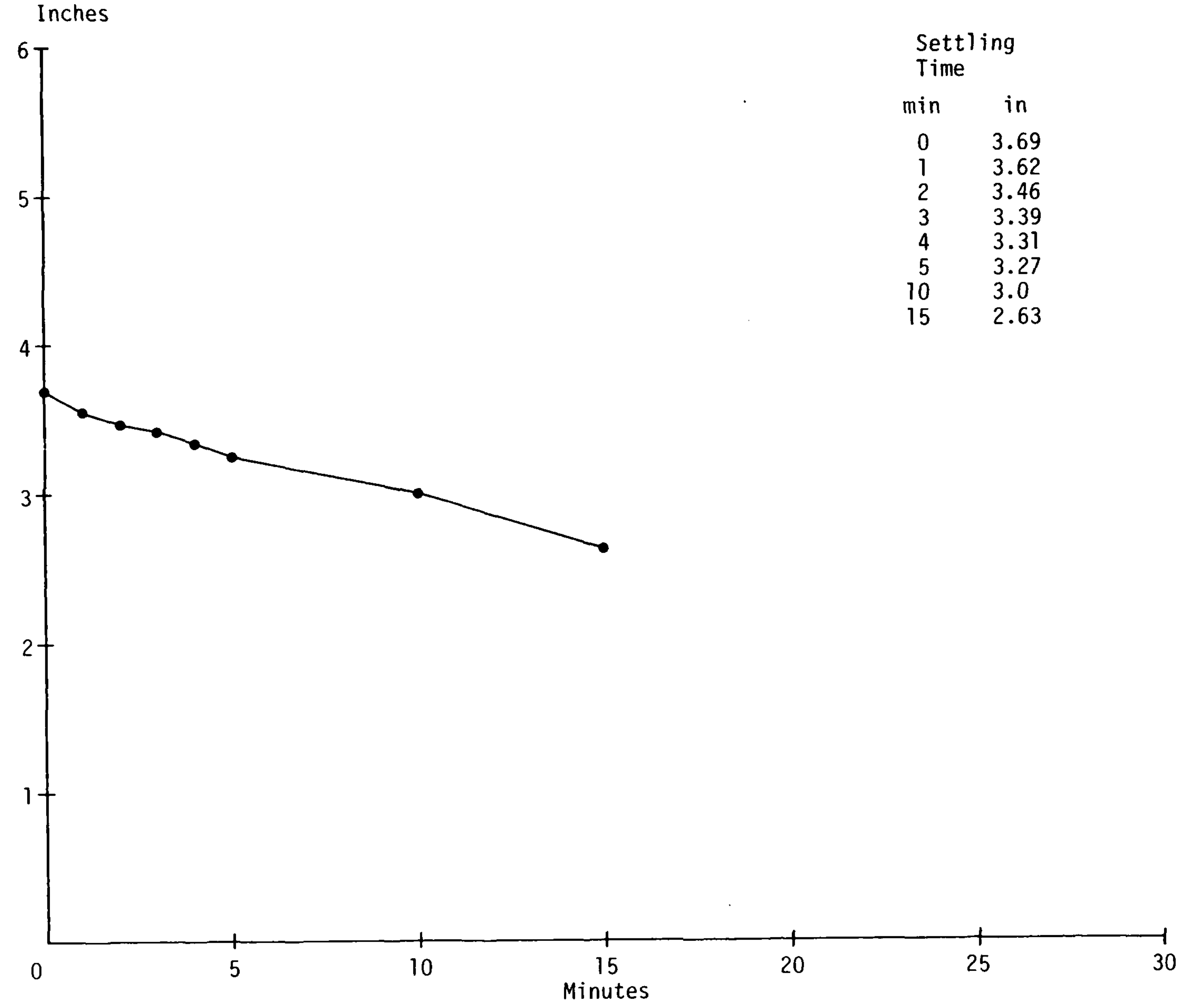
TEST #3



Seetling Time		GPM
min	in	
0	3.39	
1	3.19	0.13
2	3.10	0.06
3	3.00	0.06
4	2.91	0.06
5	2.82	0.06
8	2.33	0.10
10	2.08	0.08

Figure 5-3
STS-6 Test #3
300 ML Composites

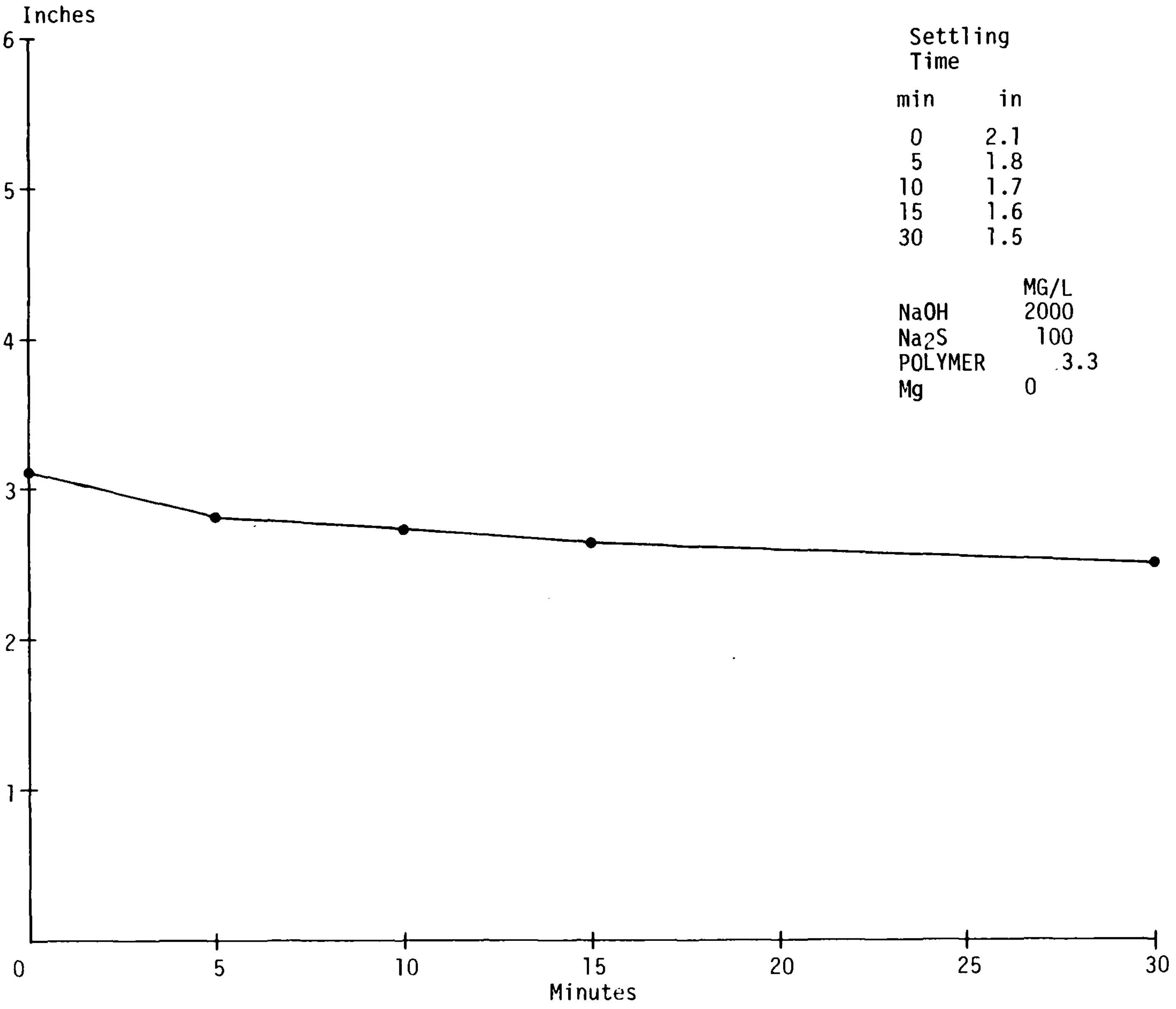
TEST #4



Settling Time min	in	$\frac{GPM}{FT^2}$
0	3.69	
1	3.62	0.04
2	3.46	0.10
3	3.39	0.04
4	3.31	0.05
5	3.27	0.02
10	3.0	0.03
15	2.63	0.05

Figure 5-4
STS-6 Test #4
300 ML Composites

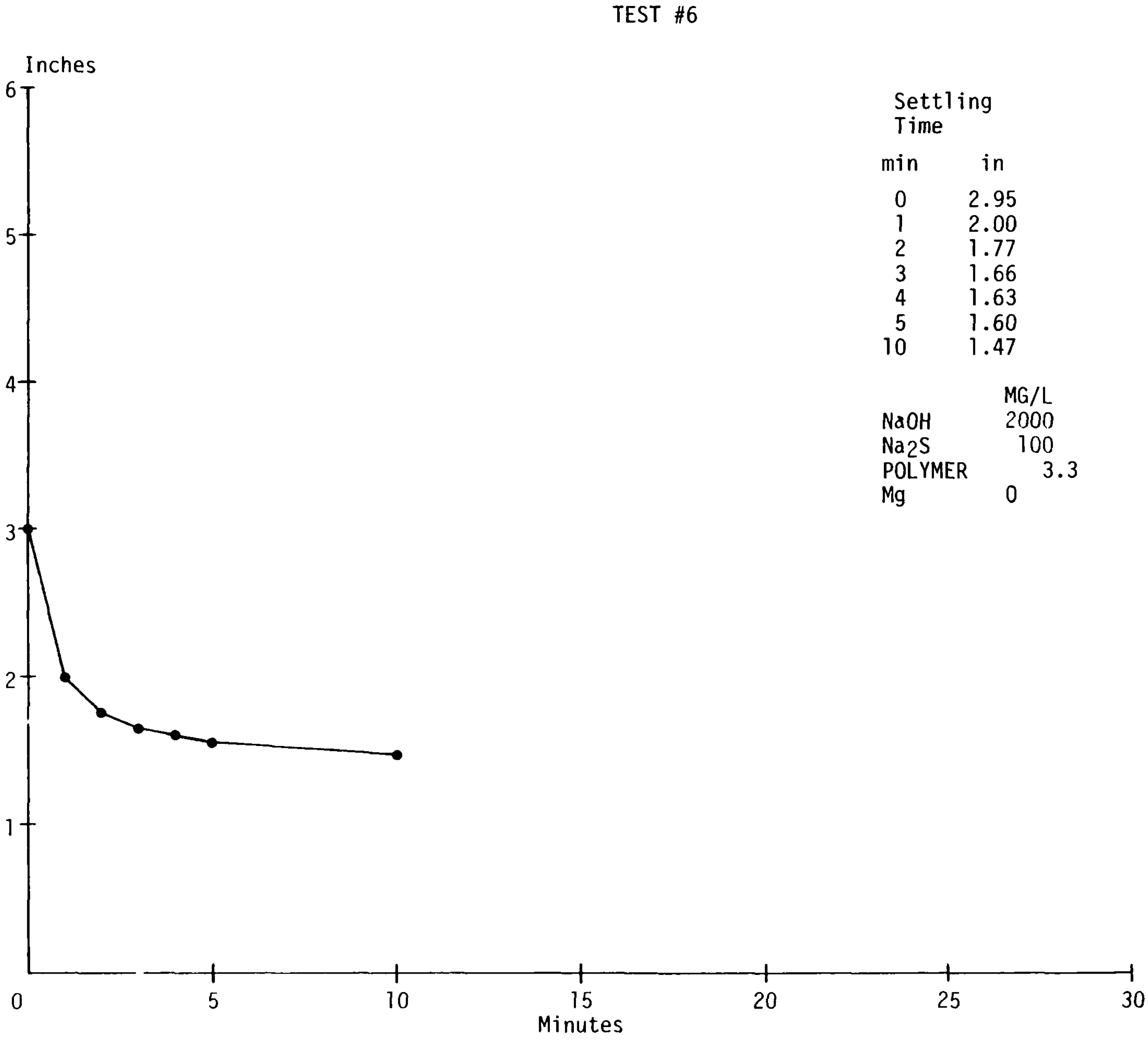
TEST #5



Settling Time min	in	$\frac{GPM}{FT^2}$
0	2.1	
5	1.8	0.04
10	1.7	0.01
15	1.6	0.01
30	1.5	0.004

	MG/L
NaOH	2000
Na_2S	100
POLYMER	3.3
Mg	0

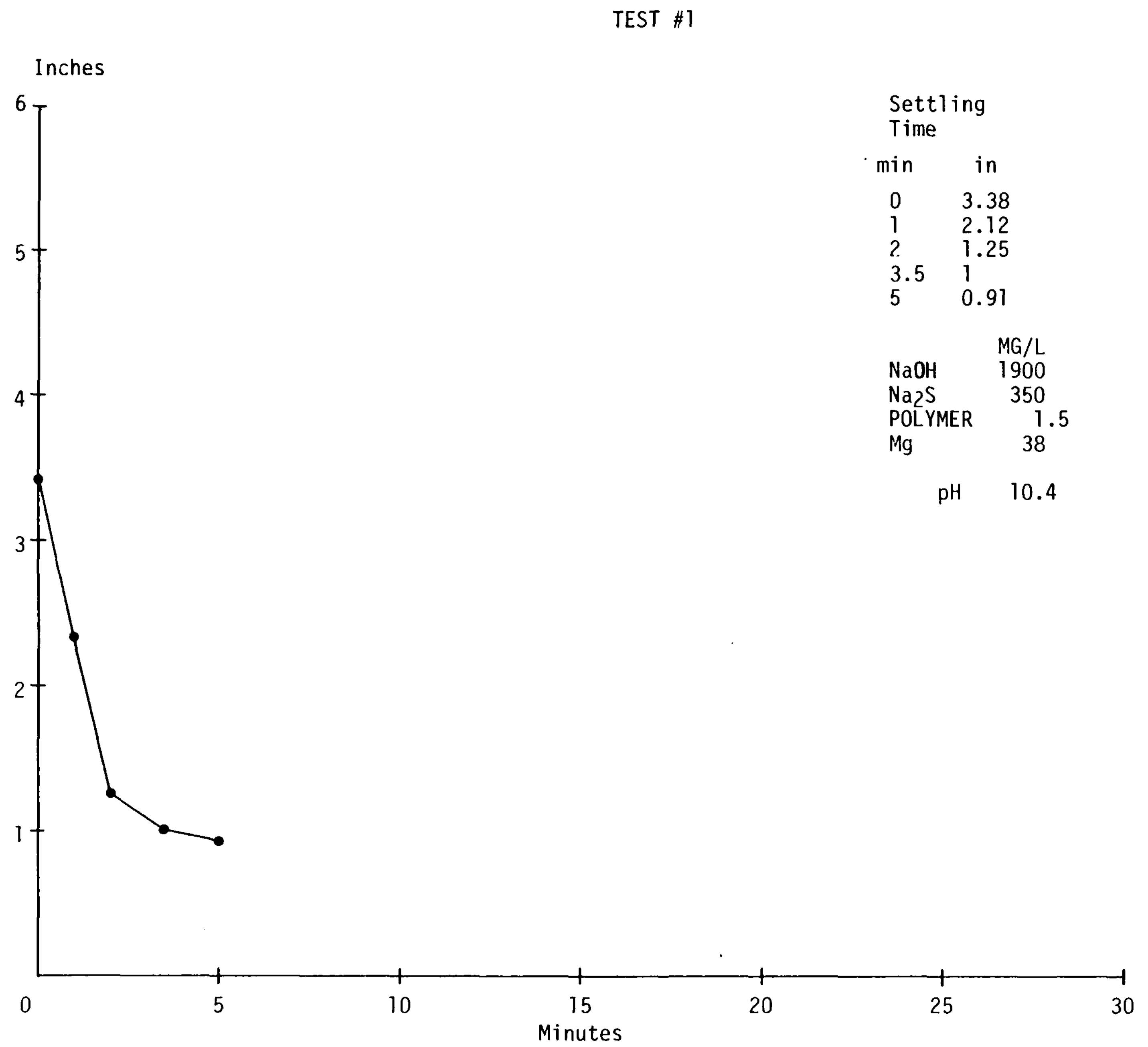
Figure 5-5
STS-6 Test #5
300 ML Composites
in 2 Liter Beaker



Settling Time min	in	$\frac{GPM}{FT^2}$
0	2.95	
1	2.00	0.59
2	1.77	0.14
3	1.66	0.07
4	1.63	0.02
5	1.60	0.02
10	1.47	0.02

	MG/L
NaOH	2000
Na_2S	100
POLYMER	3.3
Mg	0

Figure 5-6
STS-6 Test #6
300 ML Composites


TEST #1

Settling Time min	in	$\frac{GPM}{FT^2}$
0	3.38	
1	2.12	0.79
2	1.25	0.54
3.5	1	0.10
5	0.91	0.04

	MG/L
NaOH	1900
Na_2S	350
POLYMER	1.5
Mg	38

pH 10.4

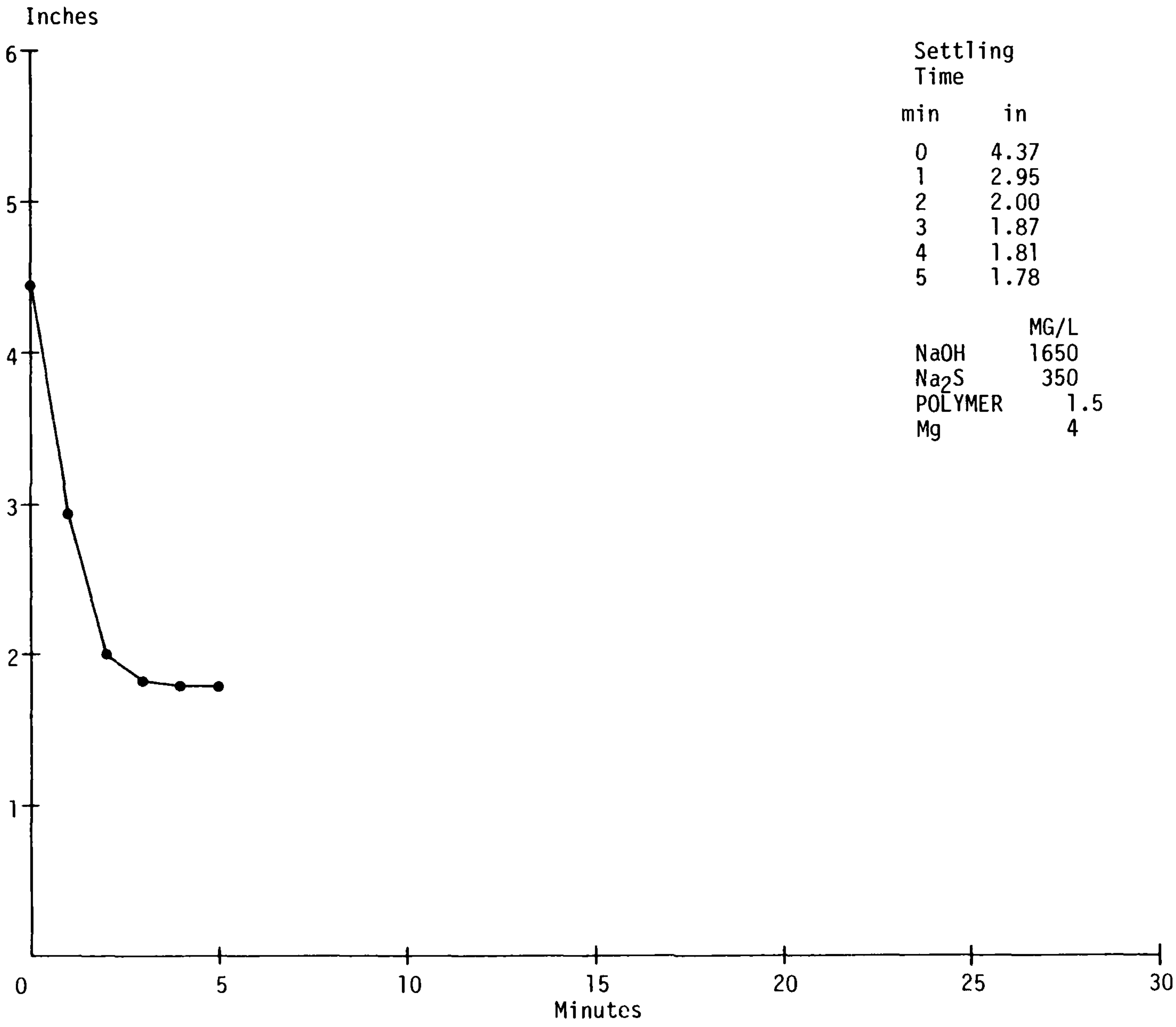
Figure 5-7
STS-6 Test #1
1 Liter Composites

Figure 5-8

STS-6 Test #2

1 Liter ML Composite

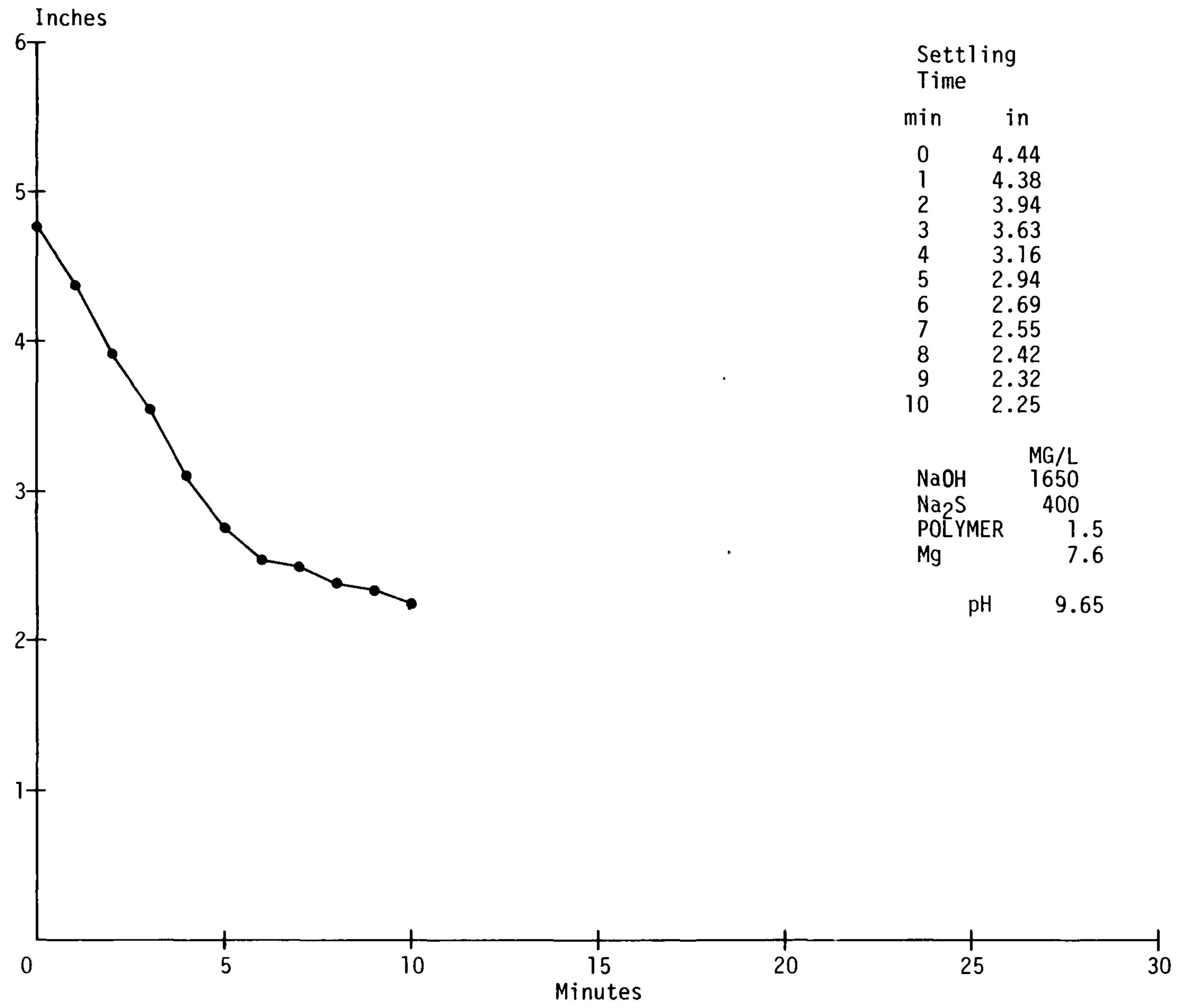
TEST #2



Settling Time min	in	$\frac{GPM}{FT^2}$
0	4.37	
1	2.95	0.89
2	2.00	0.53
3	1.87	0.14
4	1.81	0.04
5	1.78	0.02

	MG/L
NaOH	1650
Na_2S	350
POLYMER	1.5
Mg	4

TEST #3



Settling Time min	in	$\frac{GPM}{FT^2}$
0	4.44	
1	4.38	0.04
2	3.94	0.27
3	3.63	0.19
4	3.16	0.29
5	2.94	0.14
6	2.69	0.14
7	2.55	0.09
8	2.42	0.08
9	2.32	0.06
10	2.25	0.04

	MG/L
NaOH	1650
Na_2S	400
POLYMER	1.5
Mg	7.6

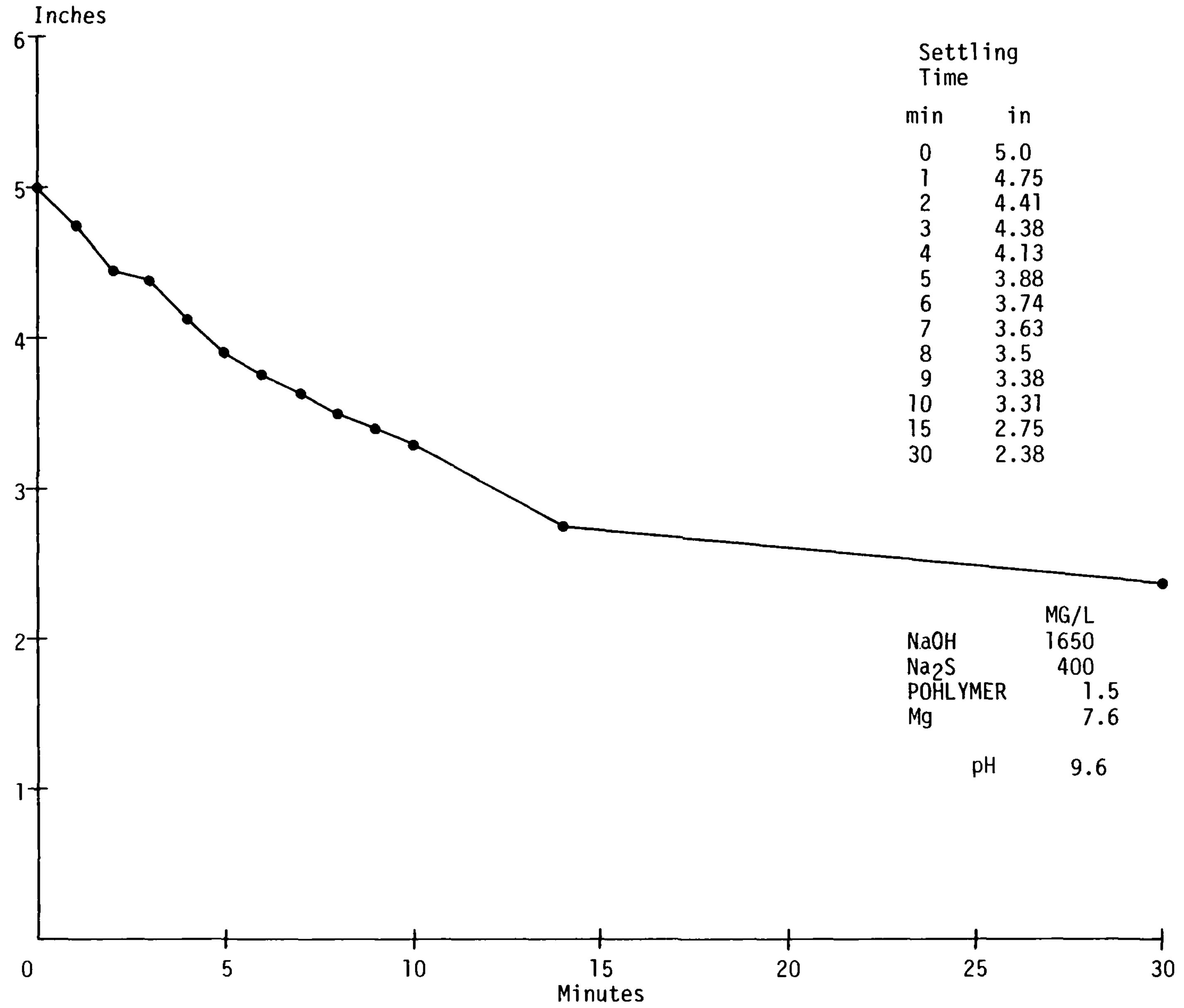
pH	9.65

Figure 5-9

STS-6 Test #3

1 Liter Composites

TEST #4



Settling Time min	in	$\frac{GPM}{FT^2}$
0	5.0	
1	4.75	0.16
2	4.41	0.21
3	4.38	0.02
4	4.13	0.16
5	3.88	0.16
6	3.74	0.09
7	3.63	0.07
8	3.5	0.08
9	3.38	0.07
10	3.31	0.04
15	2.75	
30	2.38	

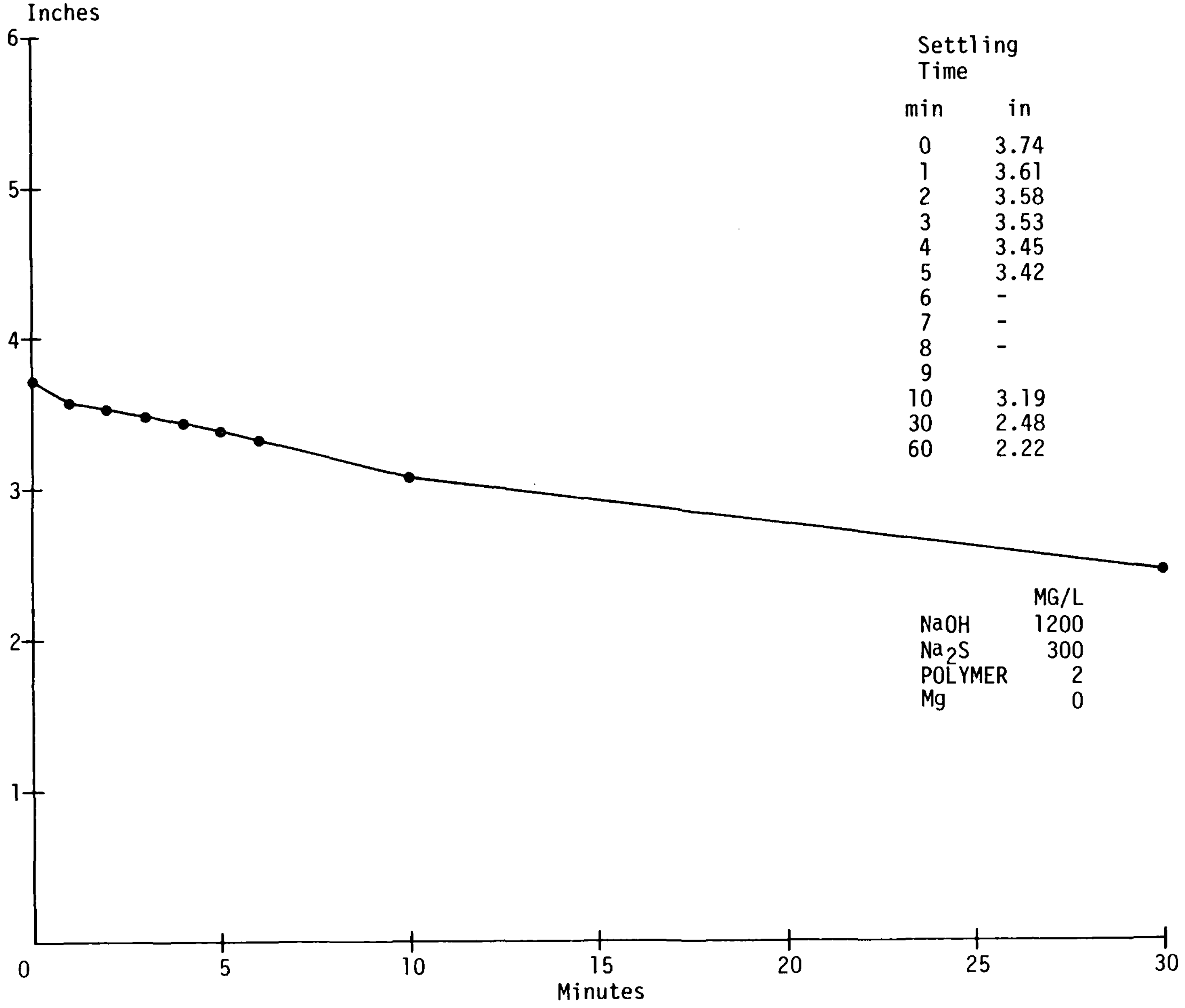
	MG/L
NaOH	1650
Na_2S	400
POHLYMER	1.5
Mg	7.6
pH	9.6

Figure 5-10

STS-6 Test #4

1 Liter Composites

TEST #5



Settling Time min	in	$\frac{GPM}{FT^2}$
0	3.74	
1	3.61	0.08
2	3.58	0.02
3	3.53	0.03
4	3.45	0.05
5	3.42	0.02
6	-	
7	-	
8	-	
9		
10	3.19	
30	2.48	
60	2.22	

	MG/L
NaOH	1200
Na_2S	300
POLYMER	2
Mg	0

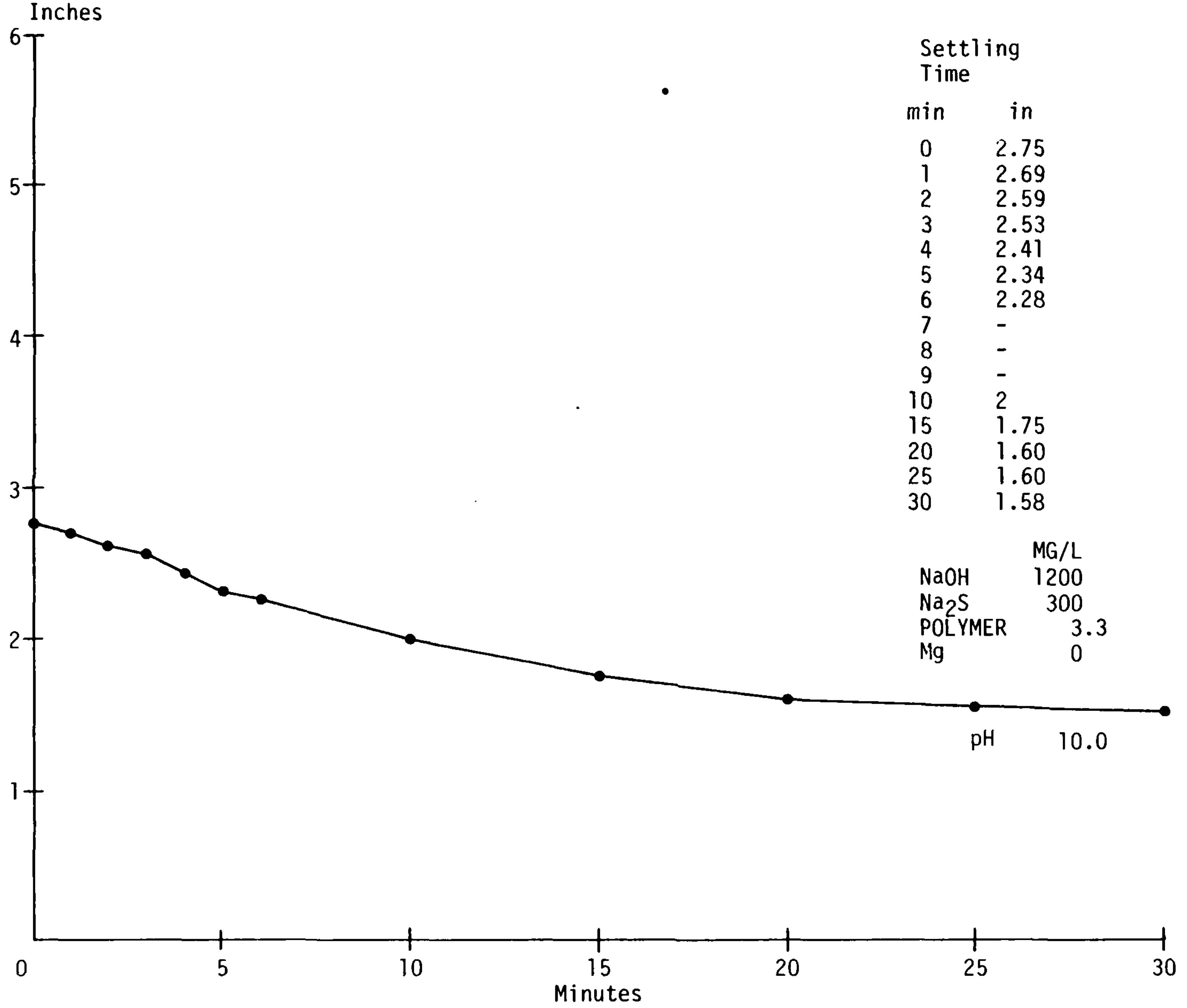
Figure 5-11

STS-6 Test #5

1 Liter Composites

Figure 5-12
STS-6 Test #6
500 ML Composites

TEST #6



Settling Time min	in	GPM/FT^2
0	2.75	
1	2.69	0.04
2	2.59	0.06
3	2.53	0.04
4	2.41	0.07
5	2.34	0.04
6	2.28	0.04
7	-	
8	-	
9	-	
10	2	
15	1.75	
20	1.60	
25	1.60	
30	1.58	

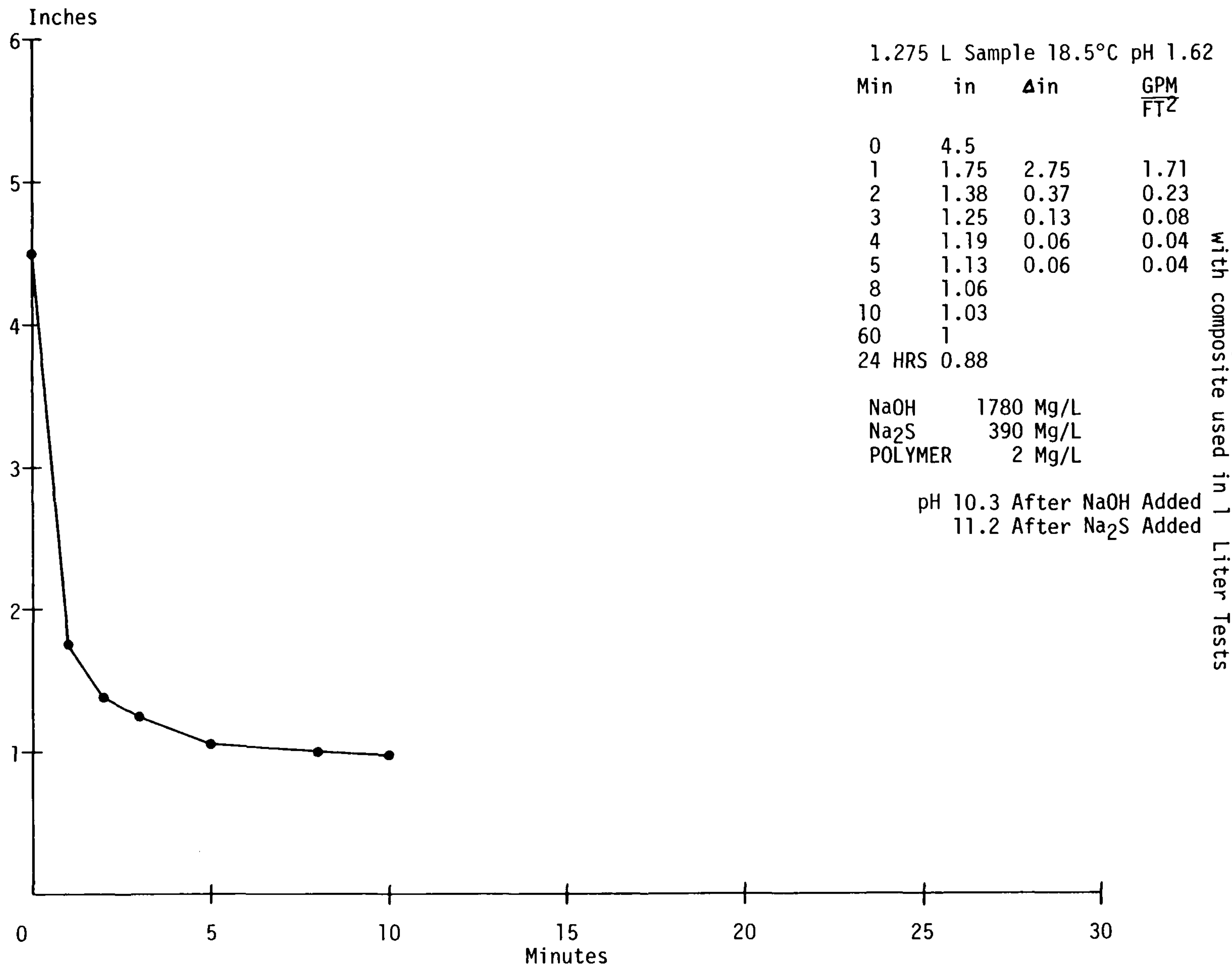
	MG/L
NaOH	1200
Na_2S	300
POLYMER	3.3
Mg	0

pH 10.0

Figure 5-13

STS-6

Test run by LT Dave Gibson - OEHL Lab
with composite used in 1 Liter Tests



1.275 L Sample 18.5°C pH 1.62

Min	in	Δin	$\frac{GPM}{FT^2}$
0	4.5		
1	1.75	2.75	1.71
2	1.38	0.37	0.23
3	1.25	0.13	0.08
4	1.19	0.06	0.04
5	1.13	0.06	0.04
8	1.06		
10	1.03		
60	1		
24 HRS	0.88		

NaOH	1780 Mg/L
Na_2S	390 Mg/L
POLYMER	2 Mg/L

pH 10.3 After NaOH Added
11.2 After Na_2S Added

TABLE 5-3

STS-6 SUMMARY OF MAXIMUM SETTLING RATES AND THE EFFECT OF SLUDGE RECYCLE

1 LITER COMPOSITE SAMPLES

TEST	VOLUME OF SLUDGE RECYCLED	MINUTES TO BREAK IN SETTLING RATE	INCHES SETTLED	GPM/FT^2
1	0X	3.5	2.38	0.42
2	1X	3	2.5	0.52
3	2X	5	2.09	0.26
4	3X	15	2.25	0.09
5	6X	10	0.55	0.03
6	12X	10	0.75	0.05
		300 MILLILITER COMPOSITE SAMPLES		
1	0X	2	1.69	0.53
2	1X	8	1	0.08
3	2X	10	1.31	0.11
4	3X	15	1.06	0.04

was proposed to control this potential problem by sequestering the barium to keep it in solution. Tests performed on the Vandenberg raw water indicate this to be effective. Test results are presented in the Appendix.

- Sludge Production and Dewatering - Sludge produced from each of the treatment studies was combined and allowed to settle for an additional 24 hours. The supernatant was then decanted and the remaining sludge evaluated for dewatering by centrifugation.
- Moisture Determination - The sludge produced from the treatment studies was filtered through a nominal 0.45-micron glass fiber filter and the sludge cake volume determined. A portion of the sludge was used for moisture determination and two other portions were used for Resources Conservation and Recovery Act (RCRA) and California Assessment Manual for hazardous wastes (CAM) evaluation.
- Relative Corrosion of Wastewater on Concrete - Concrete specimens (Type II Portland cement) were immersed in the composite wastewater sample under both quiescent and dynamic conditions to determine the corrosivity of the fluid.

The procedures followed and the results obtained by the Jar test simulations are presented in the Technical Report by Chemical Research Laboratories in the Appendix.

5.4 STS-7 Jar Test Results: The STS-7 jar tests confirmed the viability of heavy metal removal, via sodium sulfide precipitation, to levels that meet drinking water standards. The significant test results included the following:

- Precipitation and separation of the heavy metals was not affected by the high COD of the wastewater.
- A test made using sodium hydroxide without sodium sulfide for precipitation showed no significant change in heavy metal removal.
- The silica content of the wastewater did not change within the time frame of the test program.
- Silica was reduced from 88 mg/l to the range 3.6 to 9.6 mg/l by co-precipitation with the heavy metals present in the raw waste, and without slurry recirculation. The addition of calcium carbonate did not increase the sludge settling or compaction rates.
- The precipitated solids settled rapidly in 30 minutes, and concentrated from 2100 ml to 270 ml volume in one hour and from 0.663 gm/l to 4.96 gm/l density, as shown on Figure 5-14. The concentration increased to 6.96 gm/l in 24 hours. After 100 hours settling the concentration had increased only to 7.72 gm/l.

STS-7 Settling Rate of Precipitated Solids

Time HRS	Sludge
0	0.663
1	4.96
2	5.45
4	5.79
6	6.04
8	6.17
24	6.96
32	6.96
52	7.11
96	7.72

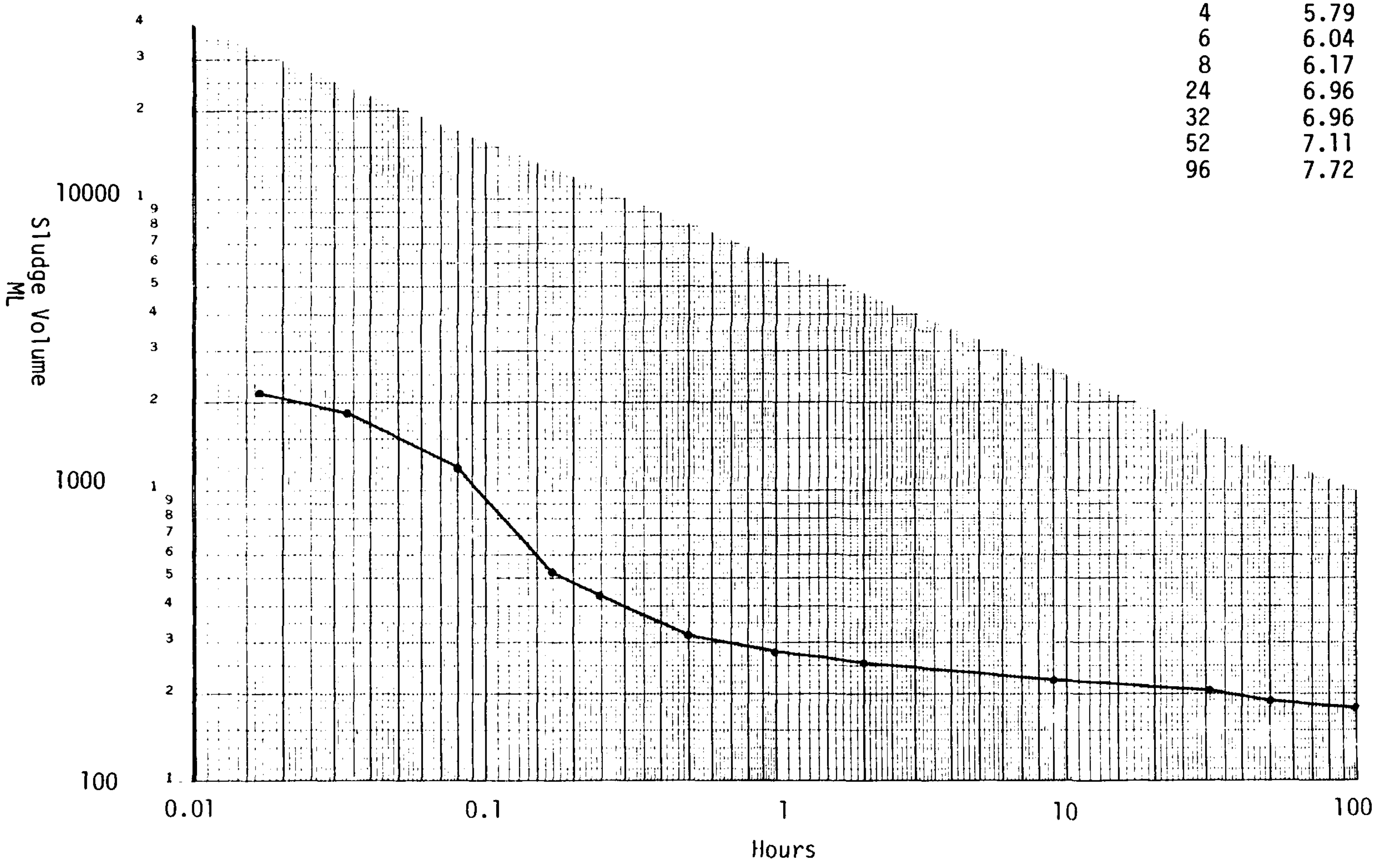


Figure 5-14
Sludge Volume
ML

5.5 Sludge Evaluation:

Sludge Dewatering: Sludge dewatering tests were made with the jar test sludges from STS-6 and STS-7. Methods employed consisted of vacuum filtration and centrifugation.

Vacuum filtration was carried out with a filter flask, Buechner Funnel, and filter paper. Filtration was rapid. Even without filter aid a dry filter cake was formed in both of the tests. These tests indicate that the filter cake produced in a filter press, operating with a pressure differential of 225 PSI, should comply with the EPA Test for Standing Water.

The centrifugation test for sludge dewatering indicated that at compaction levels of 2624 g and 4101 g, both were inefficient and inadequate. A conventional lab centrifuge was used for the test, and sludge compaction was measured at increasing time intervals.

Hazardous Classification: Sludge samples from STS-7 were subjected to numerous analyses as required by RCRA and proposed regulations of CAM. The sludge passed all leachate tests under the CAM and RCRA procedures with the exception of the test for zinc under the CAM Procedure.

6.0 PROCESS DESIGN

Based on the results of the test data, Fluor developed the following process design for the wastewater treatment plant at Vandenberg.

6.1 Design Basis: Basis of design for the wastewater treatment process includes the following:

- Wastewater design feed rate is 150 gpm.
- Total wastewater generated, exclusive of contaminated stormwater, is 1.5 million gallons per launch.
- Total stormwater subject to containment and treatment during first hour after launch is 227,330 gallons per launch.
- Mean evaporation rate is 40 inches/year.
- Mean rainfall rate is 15 inches/year.
- Discharge of effluents to surrounding areas shall be in accordance with current environmental regulations.
- Intermittent operation is based on five launches per year.
- Stormwater entering collection system during non-launch periods shall be routed to offsite storm drainage system.
- Contaminated stormwater collected during launch will be shared between two launches for evaporation purposes. Stormwater evaporated between launches will be approximately 114,000 gallons.

6.1.1 Wastewater Composition: The influent wastewater composition used for the process design is shown below. It is based on data extracted from the STS Project Book and modified to account for the difference in constituents between KSC potable water and Vandenberg potable water.

Contaminant	Concentration, mg/l
pH	2-3.3
Aluminum	52
Barium	less than 1.2
Cadmium	0.2
Calcium	465
Chromium	0.6
Copper	0.7
Iron	30
Lead	1.4
Magnesium	57
Manganese	0.7
Nickel	1.3
Potassium	9
Selenium	less than 4
Silver	0.2

Contaminant	Concentration, mg/l
Sodium	181
Zinc	270
Boron	10
Chloride	2881
Silica	70
Sulfate	79
C.O.D.	Nil
Suspended Solids	20-320

6.1.2 Treated Wastewater Composition:

Contaminant	Concentration mg/l
Calcium	116.1
Magnesium	0.5
Sodium	201.0
Chloride	720.3
Sulfate	24.0
Silica	1.6
Potassium	2.3

6.1.3 RO Analyses: Based upon 80% permeate and 20% reject hydraulic split and 80% ionic rejection, the following are the expected results associated with the heavy metals "in" and "out" of the RO unit.

	RO FEED	RO PERMEATE	RO REJECT
	DESIGN (mg/l)	DESIGN (mg/l)	DESIGN (mg/l)
Aluminum	1.5	0.4	6.0
Chromium	1.0	0.25	4.0
Copper	1.0	0.25	4.0
Barium	1.0	0.25	4.0
Cadmium	1.0	0.25	4.0
Lead	1.0	0.25	4.0
Nickel	1.0	0.25	4.0
Silver	1.0	0.25	4.0
Selenium	1.0	0.25	4.0
Zinc	1.0	0.25	4.0
Iron	1.0	0.25	4.0

6.2 Process Description: The wastewater treatment plant includes the following unit operations:

a. Neutralization & Precipitation:

- o Acid neutralization
- o Precipitation of metals
- o Adsorption of silica
- o Clarification

b. Filtration and Reverse Osmosis:

- Granular media filtration
- Cartridge filtration
- Reverse osmosis

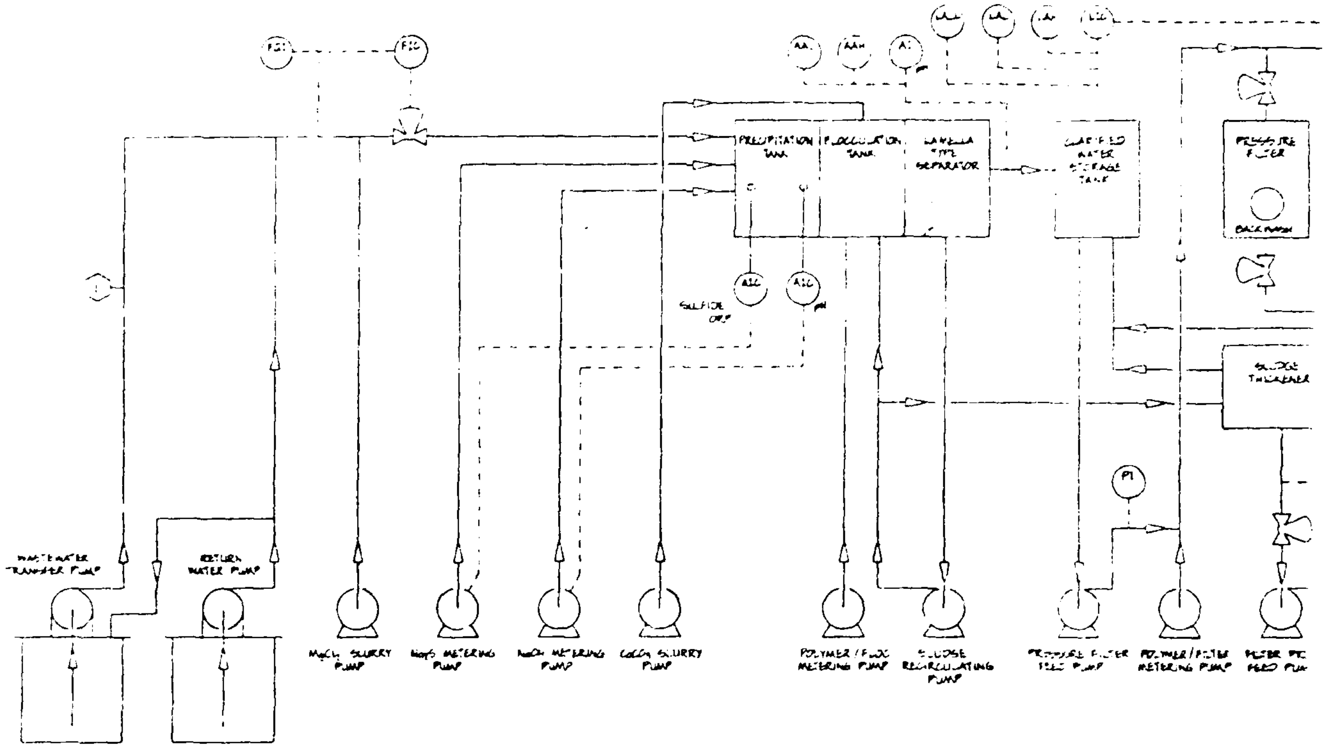
c. Sludge Handling & Disposal:

- Sludge thickening
- Sludge filtration
- Sludge containerization

d. Solar Evaporation:

- Evaporation ponds

The overall process flow and material balance is shown on drawing 80-M-550 and will be referenced in the following discussion.



MATERIAL BALANCE

STREAM / COMPONENTS	CHEMICAL ADDITIVES	① WASTEWATER	② FILTERED WATER	③ FILTER CAKE	④ RO REJECT	⑤ RO PERMEATE
ALUMINUM, ppm		[illegible]	[illegible]		[illegible]	0.88
[illegible], ppm		5.6	0.4		[illegible]	[illegible]
CADMIUM, ppm		0.15	[illegible]		0.08	0.005
CALCIUM, ppm		[illegible].6	[illegible]		[illegible]	43.[illegible]
[illegible], ppm		0.3	0.01		[illegible]	[illegible]
IRON, ppm		30.0	[illegible]		0.4	[illegible]
LEAD, ppm		1.4	[illegible]		[illegible]	[illegible]
MAGNESIUM, ppm		54.0	[illegible]		8.0	0.5[illegible]
SILVER, ppm		[illegible]	0.006		[illegible]	[illegible]
[illegible], ppm		[illegible]	[illegible]		[illegible]	[illegible]
[illegible], ppm		[illegible]	0		[illegible]	0.0
CHLORIDE, ppm		[illegible]	[illegible]		[illegible]	490
[illegible], ppm		0.69	[illegible]		[illegible]	[illegible]
[illegible], ppm		[illegible]	[illegible]		[illegible]	[illegible]
SILICA, ppm		88.0	8.[illegible]	[illegible]	[illegible]	[illegible]
SULFATE, ppm		203.0	[illegible]		650.0	55.[illegible]
TOTAL DISSOLVED SOLIDS, lb		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]				[illegible]		
[illegible]				[illegible]		
[illegible]				[illegible]		
[illegible]				[illegible]		
[illegible]				[illegible]		
[illegible]				[illegible]		
[illegible]				[illegible]		
Z[illegible]				[illegible]		
[illegible]		[illegible]		[illegible]		
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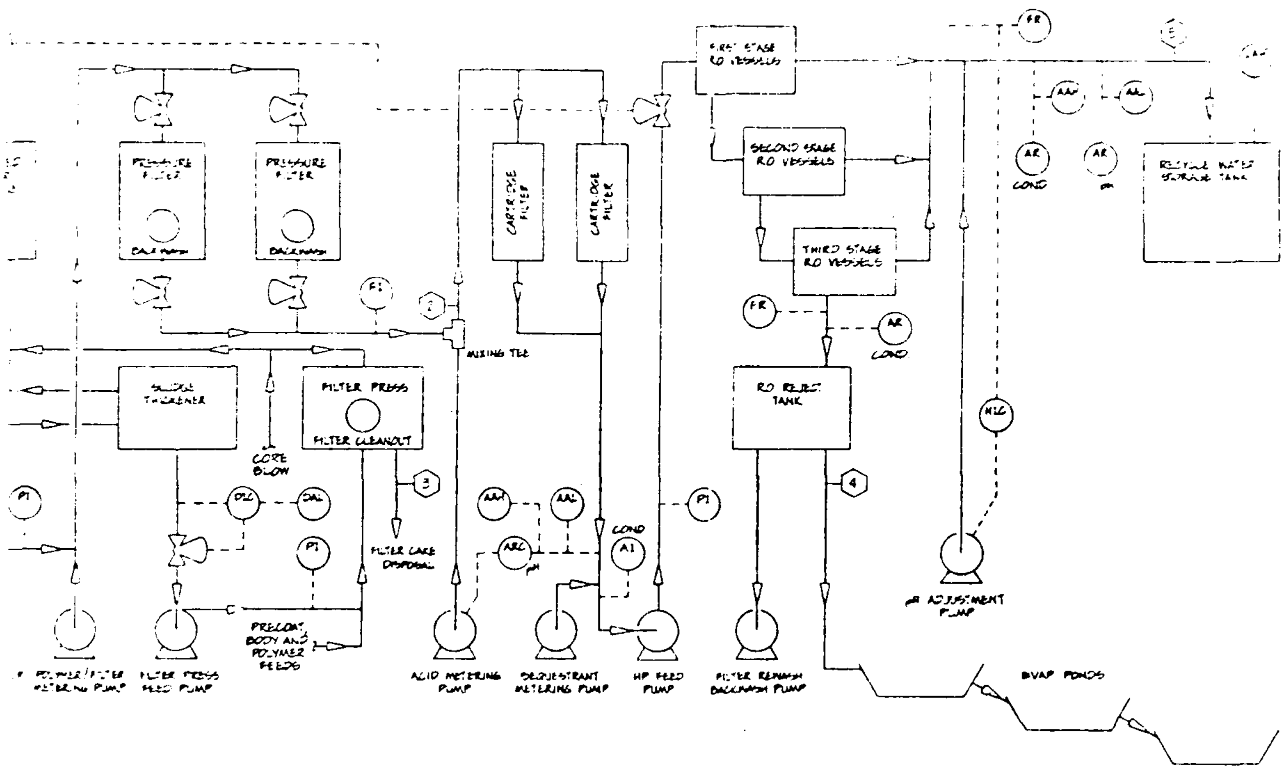

NOTES

1. ALL TEMPERATURES, PRESSURES, FLOW QUANTITIES AND COMPOSITIONS ARE FOR PROCESS DESIGN PURPOSES ONLY AND NO GUARANTEE IS EXPRESSED OR IMPLIED.
2. MATERIAL BALANCE IS BASED ON 1,000,000 GALLONS OF WASTEWATER AND DATA FROM STS-7 ANALYSIS

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JOB NO 836604

DEPARTMENT OF THE ARMY
SACRAMENTO DISTRICT CORPS OF ENGINEERS
SACRAMENTO, CALIFORNIA

R. K. GEERY
BERTRAN
R. K. GEERY

STS HAZARDOUS WASTE, VANDENBERG AFB CA
WASHDOWN FACILITY PROJECT PACKAGE ONE
PROCESS FLOW DIAGRAM
WASTEWATER TREATMENT PLANT

221-25-642

6.2.1 Neutralization and Precipitation: The first stage of wastewater treatment is neutralization of the hydrochloric acid in the wastewater combined with precipitation of the heavy metals as hydroxides and sulfides. The optimum pH for treatment and the residual sulfide concentration will be selected to minimize the concentration of the metals remaining in solution. The precipitation of hydroxides and sulfides is necessary because of the amphoteric properties of aluminum, zinc, and iron.

Silica removal is necessary for optimum permeate recovery in the reverse osmosis system. Silica will be coprecipitated with magnesium hydroxide and other metal hydroxides. A solution feeder for magnesium chloride is included so that the magnesium concentration can be increased if necessary to limit the final silica concentration (to less than 15 mg/l as SiO_2) in the feed to the reverse osmosis system.

A reaction/precipitation tank with a retention time of 30 minutes is included to maximize precipitation. This tank has a slow speed agitator, and a polymer will be added to enhance floc formation. Sludge from the final clarifier will be recycled to improve floc formation and also to aid in silica removal.

Solids separation will take place in a lamella type clarifier which has inclined plates on which the precipitated solids settle. The inclination angle is set so that the settled solids will slide down into the sludge hopper below the lamella plates. The sludge is pumped into a thickener to maximize the sludge solids concentration before the sludge is dewatered in a filter press.

6.2.2 Filtration and Reverse Osmosis: The lamella clarifier supernatant flows by gravity into a surge tank and is then pumped through granular media filters and cartridge filters to remove suspended solids and thus minimize the potential fouling of the reverse osmosis membranes.

The pH of the filtered wastewater is adjusted with sulfuric acid, and a sequesterant is added to avoid the deposition of solids on the RO membranes.

The wastewater is then boosted to the RO operating pressure of 450 psi. A three-stage reverse osmosis unit is provided to complete the final dissolved solids reduction of the wastewater. The RO permeate and reject flow rates are adjusted and monitored with conductivity sensors to maintain the total dissolved solids level at approximately 1100 mg/l in the permeate. The reject from the first RO stage passes to the second stage, and the second stage reject is passed to the third stage. The flow rates are adjusted so precipitation on the third set of RO units is avoided or kept to a minimum by avoiding an excessive TDS level in the reject from the third stage.

The permeates are combined and the pH is increased with sodium hydroxide to the Langelier saturation index non scaling point. This avoids corrosion and scale formation in the recycle system. The reject brine from the third stage of the R/O unit flows to the evaporation ponds for disposal.

A composite analysis of STS-7 wastewater before and after treatment and the projected analysis of the RO permeate after pH adjustment is shown on drawing 80-M-550.

6.2.3 Sludge Production and Disposal: The precipitation of metals by sodium hydroxide and sodium sulfide produces a mixture of metal sulfides and hydroxides. In addition, silica will be adsorbed by the metal hydroxides and the suspended solids which do not settle in the exhaust duct will flocculate and be removed in the lamella clarifier. Approximately eight hours of settling time is provided in the clarifier, plus 20 hours settling time in the thickener, to clarify this suspension. The settling and thickening characteristics of STS-7 sludge are shown on Figure 5-14.

Table 6-1 summarizes the approximate sludge production from STS-1, -2, -3 and -5 launches.

Table 6-2 presents the sludge quantities per million gallons of wastewater volume projected for Vandenberg assuming STS-7 water composition, and the corresponding modified Project Book composition. Based on STS-7 launch data, 10 tons of sludge per launch are estimated to be produced, predicated on the rainwater composition approximating the manual washdown composition. If the rainwater is more dilute than the manual washdown composition, the produced sludge will be less.

Figure 6-1 presents a graphical depection of the sludge produced by source for Vandenberg. The values are based on KSC measurements adjusted for Vandenberg raw water. The graph reflects where the major source of sludge originates and suggests where the greatest variations in quantity may exist. The sludge resulting from the raw water should remain relatively constant. It represents about 10% of the total sludge produced.

The sludge produced from the SRB exhaust is projected to be 15% of the total sludge. This quantity will depend premarily on the amount of sound suppression water recovered, the scrubbing efficiency of the fixed washdown sprays and the fallout on the launch pad area that will be contained in the wastewater collection system.

Sludge produced because of steel corrosion is 5%. The quantily could increase because of the greater amount of steel structures at Vandenberg. However, a high quality coating system is being applied at Vandenberg which could reduce the sludge produced from this source.

The sludge resulting from paint absorption is projected to contribute 37% of the total sludge. At Vandenberg a three-coat paint system is being applied which should reduce the zinc level in the wastewater.

The last main contributor to the sludge is the concrete which comprises 13% of the total sludge. This quantity could increase because of the quantity of exposed concrete and the geometry of the flame ducts at Vandenberg compared to KSC.

The other 20% of the sludge results from additives (diatomite and polymer) to accomplish the sludge formation. If the other sludge sources vary, this quantity will vary in direct proportion.

The interesting aspect of this analysis is that only about 20% of the sludge is primary sludge associated with the launch exhaust. About 80% can be classified as secondary sludge production which is a result of the particular environment in which the vehicle is launched.

We assumed that suspended solids will not exceed 50 mg/l in the collected wastewater in the exhaust ducts. The zinc concentration was unexpectedly high in samples tested from STS-1 thru -7. This is believed to be due to removal during launch of the inorganic zinc coatings used on the structures at the pad, and the zinc being picked up by the wastewater. The zinc is dissolved by the hydrochloric acid.

The thickened sludge will be dewatered in a plate and frame filter press with an operating pressure of 225 psig. This is required to produce a filter cake which will pass the EPA Standing Water Test specification. The filter cake will then be containerized and transported to the Casmelia Resources Sanitary Land Fill, as illustrated and described in the Appendix.

If the filter cake passes the RCRA and proposed CAM leachate tests and is classified as a non-hazardous sludge, it can be hauled to the dump site in large bulk containers and dumped into an open pit. However, there is a potential for the sulfides to be converted to sulfates by biological action with potential leaching. If the leachate does not comply with RCRA and CAM metal concentration limits, the sludge will then be classified as a hazardous sludge. This classification requires the sludge to be transported and disposed of in non-corrosive and sealed containers. Provision is made in the design for containerizing the sludge for either classification. This decision was based upon analysis of sludge from STS-7 which did not pass the CAM leachate test for zinc concentration. It is believed that with the improved paint system at Vandenberg the zinc load will be significantly reduced so that the produced sludge will meet proposed CAM requirements. Until actual sludges can be evaluated from the first launch at Vandenberg, the design will incorporate the ability to dispose of either type of sludge. It is probable the produced sludge at Vandenberg will meet the required standards. Tables 6-3 and 6-4 list the STS-7 sludge analysis compared to the RCRA and proposed CAM standards.

6.2.4 Solar Evaporation: The most economical method of reducing the TDS of the wastewater to an acceptable level for reuse, is through reverse osmosis. Associated with this operation is the requirement to concentrate (as much as economically possible) the dissolved salts removed from the wastewater before they are discharged to the evaporation process. Based upon an economic trade-off between the stages required for RO and methods available for final evaporation of the reject brine, a three-stage RO unit and solar evaporation ponds were selected. The three-stage RO process will recover 80 percent of the feed. The 20 percent brine reject is sent to three evaporation ponds with a total surface area of 15 acres. The ponds have a high density polypropylene liner to prevent brine from leaching into the groundwater system and to comply with California EPA regulations.

TABLE 6-1

THEORETICAL CALCULATIONS OF SLUDGE PRODUCED FROM STS LAUNCHES

	STS 1 MG/L	STS 2 MG/L	STS 3 MG/L	STS 5 MG/L
$Al(OH)_3$	76.56	83.78	44.44	53.4
CdS	0.15	0.13	0.15	0.12
$Cr(OH)_3$	0.38	0.77	0.99	0.59
CuS	0.30	0.54	0.14	0.74
$Fe(OH)_3$	47.77	55.41	22.93	44.33
NiS	0.83	1.42	1.30	0.74
PbS	1.1	1.27	1.04	0.91
TiO_2	0.82			
ZnS	273	327	160	182
SiO_2		50	50	50
$Ca_3(PO_4)_2$		31.33	4.41	
$Mn(OH)_2$		0.99	0.63	0.79
AgS		0.06		
$Mg(OH)_2$		121	89.42	89.42
Suspended Solids		50	50	50
TOTAL	401	724	426	473
LBS/10^6GAL	3409	6154	3621	4021
LBS/$1.376x10^6$GAL	4690	8468	4983	5532

TABLE 6-2

SLUDGE PRODUCTION

	SLUDGE QUANTITY PER MILLION GALLONS OF WASTEWATER, LBS	
CONSTITUENT	STS-7 LAUNCH	VANDENBERG (MODIFIED)*
$AL(OH)_3$	626	1251
CdS	2	2
$Cr(OH)_3$	5	12
$Fe(OH)_3$	478	478
PbS	13	13
$Mg(OH)_2$	684	1147
SeS_2	4	60
ZnS	2556	3350
SiO_2	666	539
Suspended Solids	475	417
Diatomite	1693	1691
Polymer	117	117
Total Dissolved Solids	7319	9077
Water in Cake	13127	17234
TDS in Water	46	60
Total	20,492	26,371

* Vandenberg Project Book Composition modified to account for the difference in dissolved solids between KSC potable water and Vandenberg potable water.

TABLE 6-3

STS-7 SLUDGE COMPOSITION COMPARED TO RCRA

CONSTITUENT	STS-7	RCRA
Arsenic	0.020	5.0
Barium	ND (1.0)	100.0
Cadmium	ND (0.1)	1.0
Chromium	ND (0.1)	5.0
Lead	ND (0.1)	5.0
Mercury	ND (.01)	0.2
Selenium	0.015	1.0
Silver	ND (0.1)	5.0

NOTE: All concentrations in ppm.

TABLE 6-4

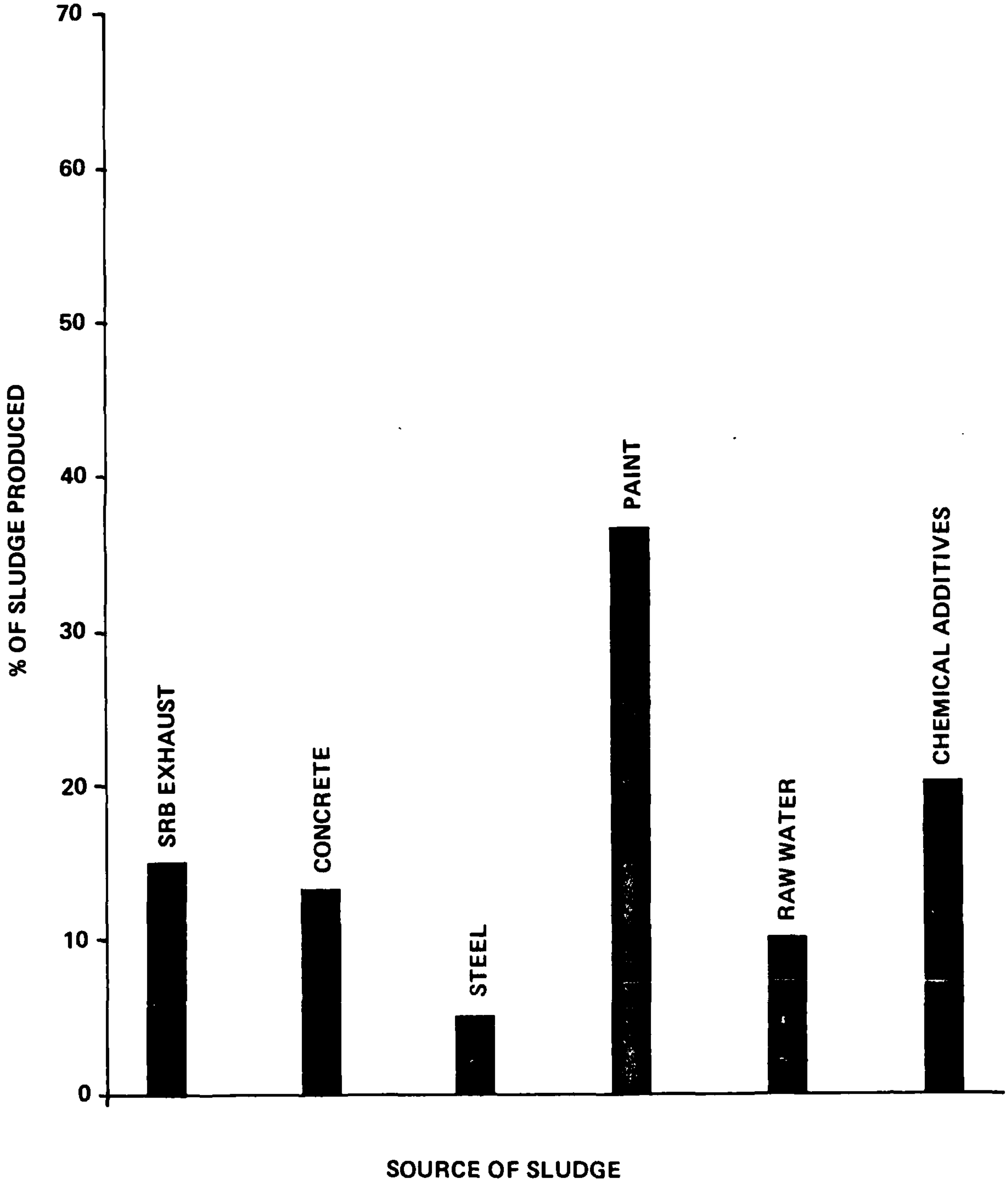
STS-7 SLUDGE COMPOSITION COMPARED TO CAM

CONSTITUENT	STS-7	STLC	TTLC
Antimony	0.7	100	500
Arsenic	0.14	5.	500
Barium	2.0	100	10,000
Beryllium	ND(0.1)	7.5	75.
Cadmium	ND(0.1)	1.	100.
Chromium	4.6	5.	500.
Cobalt	0.36	80.	8,000.
Copper	ND(0.1)	2.5	250.
Lead	1.1	5.	1,000.
Mercury	ND(0.01)	0.2	20.
Molybdenum	ND(1.)	350.	3,500
Nickel	9.7	20.	2,000
Selenium	0.80	1.	100
Silver	ND(0.1)	5.	500
Thallium	0.7	7.	700
Vanadium	1.4	24.	2,400
Zinc	1600.	25.	2,500

NOTE: All concentrations in ppm.

FIGURE 6-1

SOURCE OF SLUDGE PRODUCED AT VANDENBERG



7.0 EVALUATION OF VANDENBERG DESIGN BASIS

The analytical work conducted on wastewater samples form STS-6 and STS-7 have provided results that confirm the process developed by Fluor is a viable design for removing heavy metals down to the required levels. The following subsections will address the impact of the test results on the design criteria developed originally for the project.

7.1 Wastewater Composition: The major constituents of the wastewater which have a significant impact on the treatment plant design criteria include the hydrogen ion concentration (pH) and the concentration of metals in the wastewater.

The wide swings of the wastewater pH from low to high levels impacts the materials of construction and process chemistry. At low pH levels, the hydrochloric acid can cause rapid disintegration of concrete; this has structural design implications with respect to the exhaust duct system.

At higher wastewater pH levels than those recorded at KSC STS operations the magnesium oxide would be ineffective for neutralization and the formation of soluble magnesium ions to aid in silica removal after a first stage of neutralization. It was therefore decided to provide for feeding magnesium chloride instead of magnesium oxide to aid in silica removal.

The concentration of metal ions in the wastewater will have a major effect upon the sludge disposal system. The metals will be precipitated as hydroxides or sulfides. After thickening and dewatering by compression at 225 PSIG, the filter cake must be subjected to leachate tests as specified by RCRA and by the State of California. If the filter cake leachate does not exceed RCRA or proposed CAM standards, the cake can be hauled in a lined and covered dumpster to a sanitary land fill and discharged into open pits. If the RCRA or proposed CAM Standards are exceeded for even one ion, the sludge must be packed into corrosion resistant drums, sealed and hauled to a sanitary land fill where the drums are deposited. A small scale test with filter cake from STS-7 passed all of the tests except the proposed CAM test for zinc. The Vandenberg facility will therefore be designed to load filter cake into dumpsters or into drums, depending upon the results of the leachate tests after each launch.

Aluminum, iron, magnesium and manganese will be precipitated as hydroxides. Tests with wastewater from STS-7 have indicated that precipitation of the mixed hydroxides reduced the silica from 88 mg/l to about 8.0 mg/l without supplementary magnesium feed or sludge recirculation. However a magnesium chloride feeder is included in the design, as well as a sludge pump to recycle underflow from the lamella clarifier, if either or both are necessary to maintain the silica concentration at less than 15 mg/l in the feed to the reverse osmosis units.

The optimum pH and sulfide residuals will be maintained to minimize the residual metal concentrations in the treated water. Because of the amphoteric characteristics of aluminum, iron, and zinc ions, it will be necessary to adjust the hydroxide and sulfide ion concentrations to achieve the lowest soluble metal ion concentrations in the treated wastewater.

The barium ion concentration cannot be reduced appreciably by precipitation. Sulfuric acid and a sequesterant will be fed ahead of the reverse osmosis units to inhibit barium precipitation, especially in the third stage of the RO units. However, the membranes will require periodic cleaning if the system is to operate with a maximum dissolved solids concentration in the reject water.

Reverse osmosis, with three-stage membranes, will be used to reduce the calcium, sodium, and chloride concentrations in the RO product water, together with most of the residual concentrations of the metal ions and silica remaining after precipitation and filtration.

The reverse osmosis product water will have a pH of about 6.8. The addition of 11 mg/l of NaOH (138 lbs/launch) will raise the pH to about 9.4. The Langelier pH saturation is 9.4, so the saturation index will be +0.17. This will minimize corrosion in the recycle water system.

7.2 Equipment Design Considerations

7.2.1 Chemical Addition: The first stage neutralization tank was eliminated because the wastewater composition did not indicate that the pH will be low enough to consistently dissolve magnesium oxide.

A solution feeder for magnesium chloride will be included for the precipitation of additional magnesium hydroxide, if it is required for silica removal.

A dry feeder for calcium carbonate has been included in the system design to increase the density of the metal hydroxides and sulfides to aid in sludge dewatering.

7.2.2 Sludge Flocculation: Jar tests with washdown water from the STS-6 launch demonstrated that sludge recirculation in excess of one concentration reduced the free settling rate of the sludge dramatically. There was not enough of the STS-7 wastewater to permit an extensive evaluation of the effects of slurry recirculation on silica removal. However, the jar test data indicate that slurry recirculation may not be necessary, so the size of the flocculation tank was reduced to one-half of the initial volume, with only one flocculator in the unit.

7.2.3 Sludge Disposal: Based upon the STS-7 sludge classification tests, there is the possibility that the sludge produced after first launch at Vandenberg will not pass the leachate tests for hazardous metals. As a precautionary measure, the sludge handling system will be designed to (a) handle the bulk disposal of sludge in large reusable truck containers (if classified non-hazardous), (b) load hazardous classified sludge into non-returnable sealed drums.

The option of either disposal method will require a conveyor system and loading chute to route the sludge to the bulk container or to individual drums. This is a manual operation requiring an operator to operate the filter press during the cleaning cycle and to load out the sludge.

8.0 EFFECTS OF WASTEWATER ON CONCRETE

Low pH water and metal chlorides will cause deterioration of concrete, according to the Portland Cement Association. The rate of deterioration will depend upon the pH and the metal chloride concentration. Other factors are the type of cement, the aggregate, the ratio of cement-to-aggregate-to-water, and the curing time before use. Protective treatment is recommended in the Portland Cement Association Bulletin which is included in the Appendix.

The Chemical Research Laboratory made a study of the rate of corrosion of concrete in untreated wastewater from the STS-7 launch. Type 2 Portland Cement tabs weighing between 16 and 17 grams were immersed in 55 ml wastewater samples having a pH of 2.0. One of the samples was agitated continuously during the test. The pH changes with time are listed in Table 8-1.

It is assumed that the lower pH values after immersion of the tab in the agitated samples was due to carbon dioxide being scrubbed from the sample before it could react with the hydroxide ion leached from the concentrate. In a wastewater sample with a pH of 2.0, the hydrogen ion concentration is 0.01 grams/liter. A 55-ml sample would have 0.55 milligrams of hydrogen ion. A 16-gram concrete tab would probably have at least 100 mg of hydroxide ion which would dissolve, depending upon the curing time and the formation of calcium carbonate. The loss of weight of the concrete tabs was between 310 and 330 milligrams during the tests.

There has been very little corrosion of the concrete side walls observed in the two holding ponds at KSC. This can be attributed to the following factors:

- The side walls appear to be coated with algae or bacterial growths which would act as a protective coating against corrosion.
- The ponds each have about 1,740 ft^2 of surface which would be in contact with the wastewater, based upon a three-foot water depth. If it is assumed that pond turbulence during filling and due to wind action and/or convection currents would cause wall contact with the water within two feet of the wall, the annular volume of exposed water would be about 25,700 gallons in each pond.
- At a pH of 1.5, the hydrogen concentration is 30 mg/l, or 6.42 lbs/25,700 gal. This would amount to 0.0037 lbs/ft^2 per launch. It is unlikely that, based upon these conditions, there would be appreciable corrosion after six launches.

The use of the ponds for the collection of spent cation and anion exchange regenerants and their effects on the pond walls cannot be evaluated, although it is apparent that they have not caused any significant damage to the concrete. Conversely, their neutralizing effect helped minimize concrete corrosion. However, the design of the wastewater collection and storage system at Vandenberg could introduce other concrete corrosion problems. The geometry of the flame duct will expose more concrete to contact with the acid wastewater. The return water sump will also have contact with acid water. It might be necessary to add sodium hydroxide to the flame duct sump immediately after the launch and to inject air into the flame duct sump for mixing. If it were possible to increase the pH to about 4.0 as soon as possible after washdown operations, corrosion to concrete would be minimized.

TABLE 8-1

PH CHANGES FROM IMMERSION OF TYPE 2 PORTLAND CEMENT TABS IN STS-7 WASTEWATER

CONTACT TIME (HOURS)	TAB IMMERSION WITH MIXING	TAB IMMERSION WITHOUT MIXING
0	2.0	2.0
6	5.0	4.4
24	7.2	10.1
36	8.2	10.3
48	8.2	10.3
72	8.2	10.6
	Second Immersion	
0	2.0	2.0
6	6.0	8.0

9.0 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions: Analyses of the wastewater from STS-1 through -7 have shown appreciable variations in some of the ionic constituents. However, the analyses showed only minor deviations from the scope analysis in Project Book SDYV0098 which was used for the design of the wastewater treatment plant.

The recommended wastewater treatment, which includes neutralization and precipitation, filtration, desalination by reverse osmosis, and pH adjustment, will produce a treated wastewater suitable for reuse as sound suppression makeup and washdown water at SLC-6.

A leachate test with sludge produced from treatment of STS-7 wastewater has indicated that the zinc concentration of the leachate would classify the sludge as hazardous according to proposed California standards. This could make it necessary to pack the filter cake in lined, sealed drums for disposal at a sanitary land fill.

The washdown water has a pH low enough to cause serious corrosion of concrete, although this has not been demonstrated appreciably on the pond walls at the KSC. Concrete corrosion at Vandenberg could be more serious in the flame ducts because of their geometric configuration, and in the return water sump because of the greater amount of acid water in contact with the concrete walls and base.

9.2 Recommendations: Although laboratory tests indicate a possibility for concrete damage in the flame ducts, very little indication of concrete corrosion exists at KSC. It is recommended that an assessment be made after first launch at Vandenberg to determine the extent of corrosion. If extensive damage is observed, the concrete could be coated or partial neutralization of the sound suppression and deluge water immediately after the launch should be evaluated. Sodium hydroxide could be pumped into the flame duct sump, with air mixing provided, both with timer control, to increase the pH of the water to about 4.0 before treatment.

The process treatment developed by Fluor is a viable method of handling the wastewater produced from STS operations. The wastewater scope analysis specified in the Vandenberg Hazardous Waste Management facility Project Book, adjusted for Vandenberg raw water, is representative of the wastewater that has occurred for STS-1 through -7 at KSC.

Arrangements should be made with a laboratory in the Los Angeles area to conduct RCRA and CAM leachate tests with the sludge filter cake as soon after launch as a representative sample of filter cake is available. Treatment could be delayed for the three days that would be required for the leachate tests. If the filter cake does not produce a hazardous leachate, there would be an appreciable cost saving by hauling the filter cake to a sanitary land fill in dumpsters.

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APPENDIX I

WASTEWATER SAMPLING PROCEDURES FOR STS-6 & 7

SAMPLING METHODS

a. Background Samples: A one-liter sample was taken of the sound suppression water supply prior to launch. In addition, the holding ponds which receive water from the launch were inspected and emptied to the lowest level. Any residual material in the ponds was sampled to obtain a composite of the background contribution. This consisted of both liquid and solid materials.

b. Pre-Launch Sampling System Placement:

- The primary means of obtaining a representative sample of the sound suppression and deluge water was to sample the ponds immediately after launch. Through the use of a dip stick sampler, a pond sample profile was developed as a function of depth and coordinate location. From the data, a representative sample of the pond contents was generated.

- The fixed washdown samples from the Fixed Service Tower deluge system were obtained from the launch mount perimeter ditch.

- The north perimeter fence, north of the flame trench, was the location for sampling sound suppression and deluge water during launch. Several containers were spaced in the area of maximum deluge.

- The Martin Marietta washdown water test stand was equipped with a collection pan to gather samples during launch.

c. Post Launch Sampling Procedures:

- Immediately after launch and as soon as access could be gained to the launch pad, samples of the holding ponds, launch mount perimeter trench, fixed service structure area, Martin Marietta test stand, and north perimeter fence were taken. Any other areas where wastewater was accumulated were sampled. The priority was to obtain undisturbed those samples which were subject to dilution from systems activated after launch, such as rectification of the sound suppression system, testing of fire suppression systems, etc.

- After the post launch sampling activities were completed, preparation was made to obtain samples of the holding ponds and around the structures during the manual washdown process. Holding pond depths prior to manual washdown were marked on the sidewalks with measuring tapes.

- During the interim period, samples of the solid residue were collected at various locations around the launch complex. These were to assist in assessing the relative values of each of the constituents in the wastewater.

d. Sample Mechanics

- The volume of all samples taken was normally one liter.

- Each sample taken was identified on a sample map of the launch complex and noted in a log book. Temperature, pH, time from launch and date, commodity, sample number, and sample ID were recorded on the sample and in the log book.

- The samples were preserved in clean containers using tight locking type caps and water proof labels marked with indelible ink.

- Sampling of the holding ponds was done by using a sample dip stick which had the depth of submergence marked at six-inch intervals. By taking samples at various pond depths and blending them, a representative sample of the pond contents was obtained. It was important to develop a pond sample map prior to sampling to ensure sufficient samples were taken, due to potential for incomplete mixing in the pond.

e. Samples Gathered

- Ponds prior to launch - four-liter composite samples of each pond unless ponds were previously emptied.

- Ponds after launch - prior to manual washdown - four-liter composite samples of each pond.

- Ponds after launch and after manual washdown was completed - four-liter composite samples of each pond.

- Sample of sound suppression water at fence - one-liter sample.

- Samples of puddled areas - one-liter sample each.

- Sample of washdown waters in area of LM and AT - one-liter sample of each.

- Sample of washdown water at test stand - two-liter sample.

- Sample of solid residue - 250 ml bucket samples from LM, AT, and surrounding pad area.

APPENDIX II

STS-6 WASTEWATER SAMPLE DATA BOOK

WASTEWATER SAMPLE COLLECTION PROGRAM FOR STS-6 KSC, FLORIDA

DATA BOOK

VOLUME I

FLUOR ENGINEERS, INC.

TABLE OF CONTENTS

SECTION PAGE

SECTION 1.0

PRELAUNCH ASSESSMENT OF LAUNCH PAD

1.1 METHODIGALLY

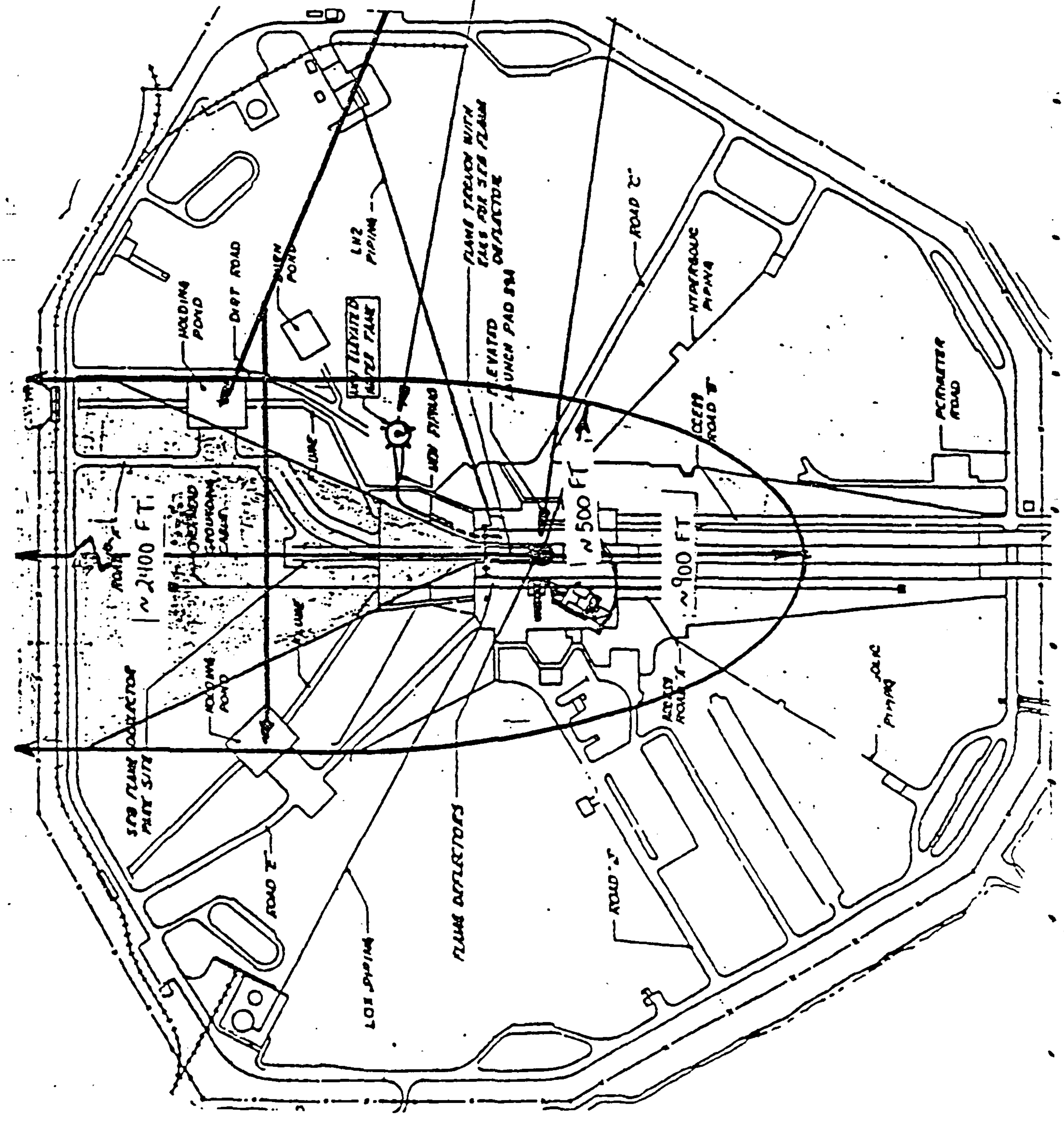
The Prelaunch Assessment Sampling procedure consists of a) checking the conditions of the holding ponds to ensure they are empty prior to launch b) measurement of the holding ponds to allow determination of the volume of wastewater collected in the post launch periods c) obtaining a sample of the sound suppression water supply for background water analysis d) placement of sample containers along the north perimeter fence to collect sound suppression water during launch.

The basic approach is to characterise the holding ponds wastewater as much as possible. This is accomplished by prelaunch inspection & taking samples of any liquid or solid wastes in the ponds prior to launch: by analysis of the holding ponds prelaunch condition then the impact of the launch wastewater can be quantified.

The amount of prelaunch samples taken of the ponds (if req'd) are to be of sufficient quantity to allow an analysis to be made of each pond contents, as indicated in Appendix B.

This is also required for the sound suppression supply water.

SOUND SUPPRESSION WATER TK WATER



1.2 METEOROLOGY

DATE —
WIND DIRECTION & VELOCITY —
TEMPERATURE —
PRECIPITATION —

1.3 SOUND SUPPRESSION SUPPLY WATER SAMPLE

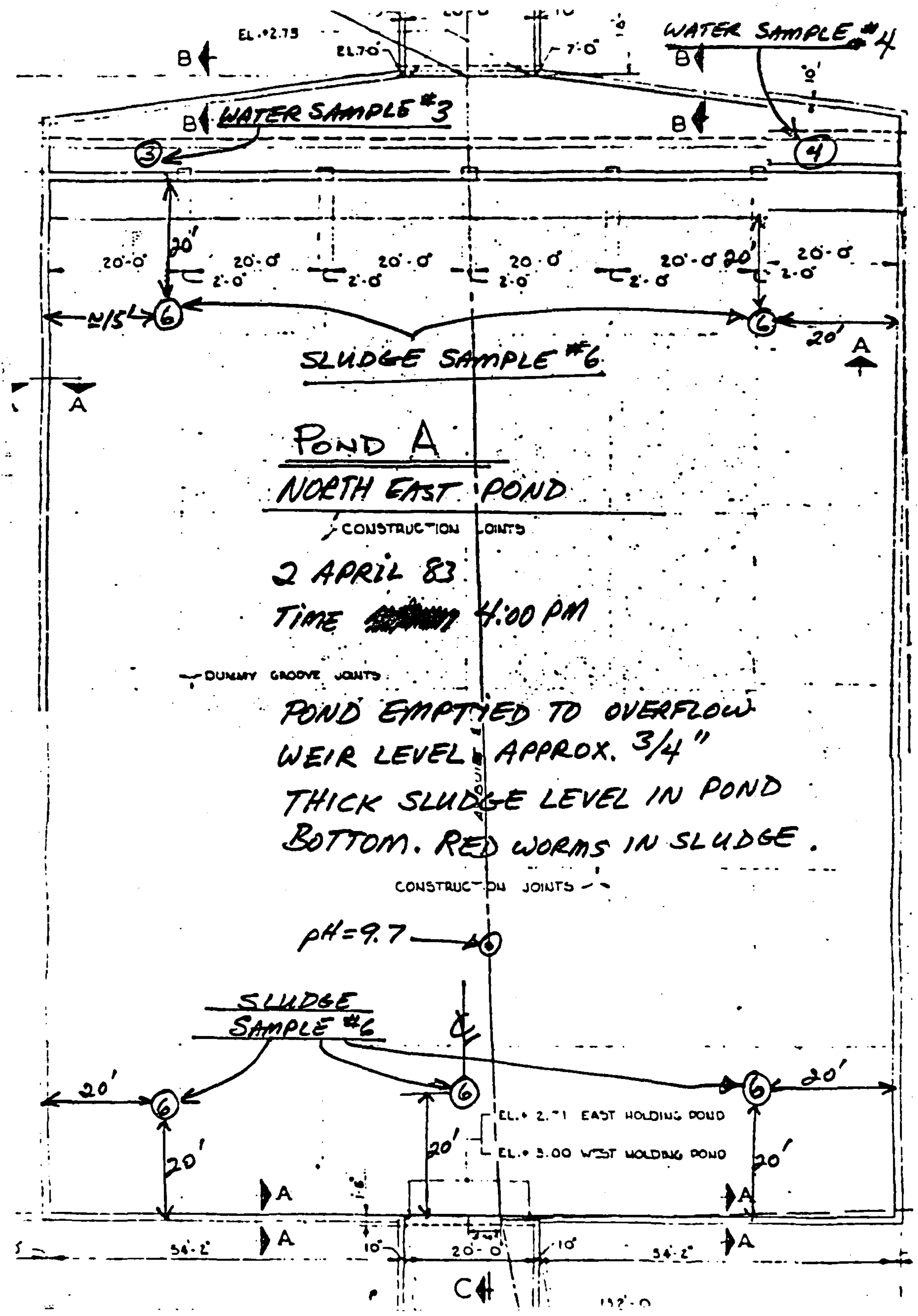
— NO SAMPLE REQUIRED —

OBTAIN A 4 LITER SAMPLE OF SOUND SUPPRESSION SUPPLY WATER AT THE SOUND SUPPRESSION TANK. RECORD ON SAMPLES & IN LOG BOOK FOLLOWING DATA;

SAMPLE ID(1) —
DATE —
COMODITY —
TIME —
PH —
QUANITY —

(1) SAMPLE ID IS REFERENCED TO SAMPLE MAP ON PAGE 2

Not NECESSARY — Previous SAMPLE WAS TAKEN From Fire System. It provides the information needed for this requirement.



POND A

NORTH EAST POND

2 APRIL 83

TIME 4:00 PM

POND EMPTIED TO OVERFLOW WEIR LEVEL. APPROX. 3/4" THICK SLUDGE LEVEL IN POND BOTTOM. RED WORMS IN SLUDGE.

pH=9.7

1.4 HOLDING PONDS ASSESSMENT

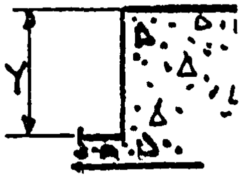
POND A (SEE SAMPLE MAP PAGE 4)

a) POND CONCRETE CONDITION ASSESSMENT
(PICTURES RECOMMENDED)

- 3/4" sludge in bottom of pond sometimes covered by shallow water pH = 9.7, Live Red worms in sludge
- Concrete in Good Condition where it could be seen. Some etching, but not very much. ~~(sludge~~
- (Sludge depth varied, shallower near inlet flumes)

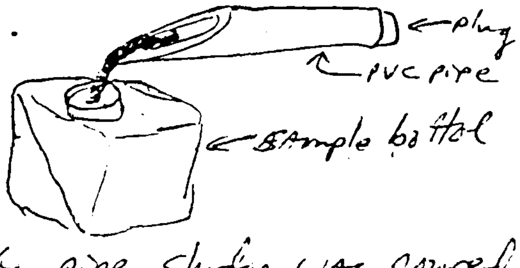
b) POND VOLUME MEASUREMENT

Top level LENGTH ____
WIDTH ____
AREA ____
BOTTOM LEVEL LENGTH ____
WIDTH ____
AREA ____
SIDE WALL DEPTH (L) ____
SIDE WALL SLOPE ____
VERTICAL DEPTH (Y) ____ 6'-3"



METHOD OF COLLECTION

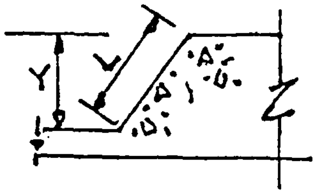
Sample scooped with Angle cut section of ≈ 3" pvc pipe with plug.



from the pipe, sludge WAS poured into the mouth of the sample bottel

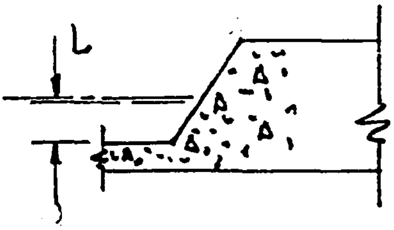
OVERFLOW WEIR

SIDE WALL DEPTH (L) — NA
SLOPE — NA
VERTICAL DEPTH (Y) — 2'-0"



c) Prelaunch Water Level Referenced To Side Wall Depth (L);

Water Level (L) — 0"
Time — 4:00 PM
Date — 2 APRIL '83



d) Pond Prelaunch Solid Residual Assessment
Overall Assessment Description;

Pond empty, approx. 3/4" sludge over entire pond. Build up over many launches w/ no history of pond being washed / cleaned out.

<u>Sample</u>

Solid Residual Sample, Take 4, 250 ML Samples around perimeter of pond to obtain a 1 liter representative sample. Record following data in log & on sample container;

Sample ID(1) 0004 6# (labeled on duct tape)
Date / Time — 2 APRIL 83 4:00 PM
Color — DARK BROWN/BLACK
Characteristic — About 15% WATER ON TOP. RED WORMS IN SAMPLE (alive). Composite Sample from 5 points

e) POND PRELAUNCH RESIDUAL WASTEWATER ASSESSMENT

REFERING TO POND A sample MAP ON PAGE 4 TAKE 4 ONE LITER SAMPLES AND RECORD DATA IN LOG & ON CONTAINERS AS FOLLOWS;

Sample 1

SAMPLE ID 0002 3# (labelid on duct tape)
COMODITY ——
DATE / TIME —— 2 April 83, 1600
pH —— 9.3
COLOR —— CLEAR
QUANTITY —— 1 Qt.
TEMP —— 13.6°C
method —— sample bottol submerged by hand

Sample 2

SAMPLE ID 0002 4# (labelid on duct tape)
method — sample bottol submerged by hand
COMODITY ——
DATE / TIME —— 2 April 83, 1600
pH —— 9.3
COLOR —— CLEAR
QUANTITY —— 1 Qt.
TEMP —— 13.6°C

~~**Sample 3**~~

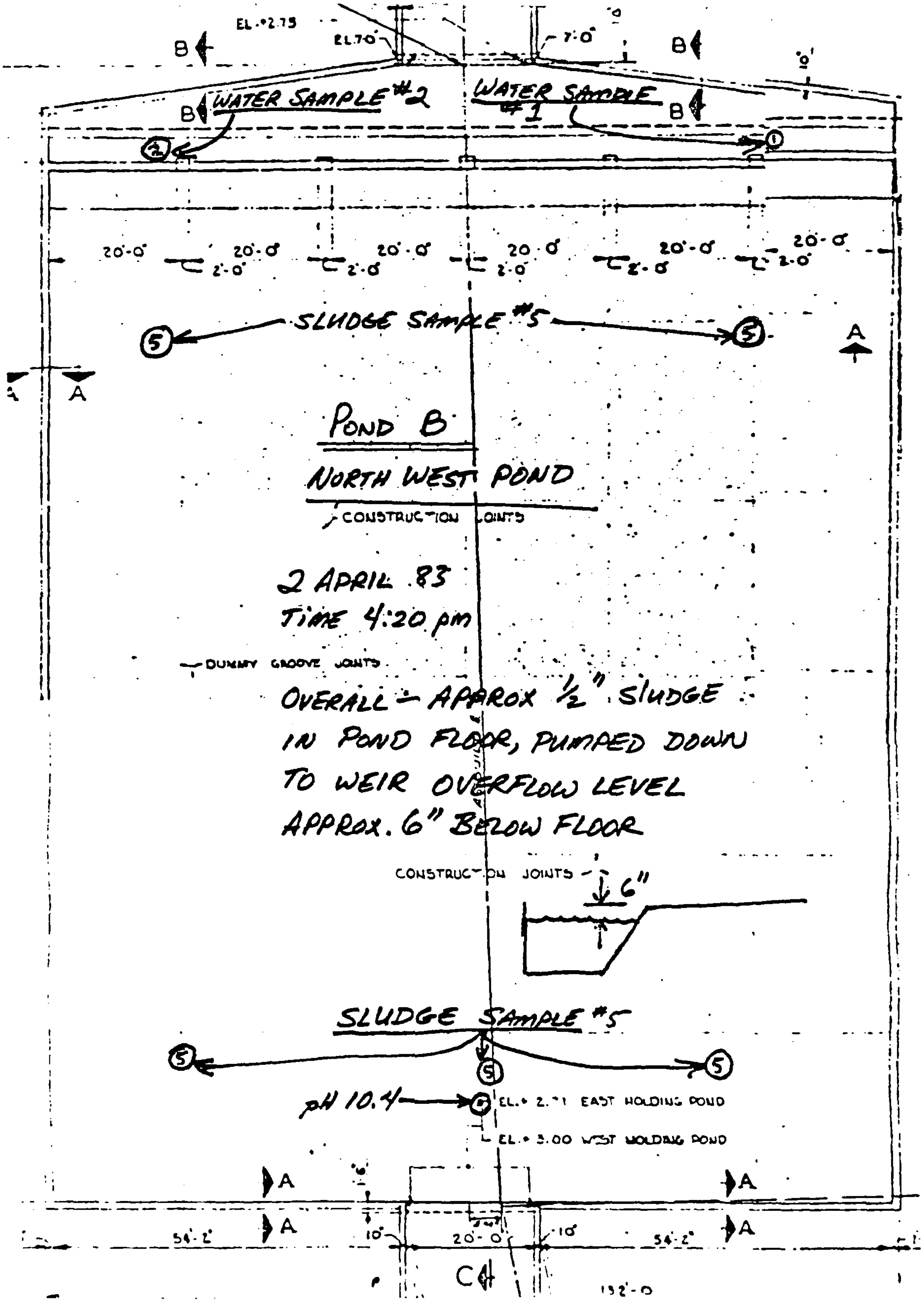
~~SAMPLE ID ——~~
~~COMODITY ——~~
~~DATE / TIME ——~~
~~pH ——~~
~~COLOR ——~~
~~QUANTITY ——~~

~~**Sample 4**~~

~~SAMPLE ID ——~~
~~COMODITY ——~~
~~DATE / TIME ——~~
~~pH ——~~
~~COLOR ——~~
~~QUANTITY ——~~

NOTE: Bird observed WALKING IN POND.

000 2 analyzed as a composite sample



POND B

NORTH WEST POND

2 APRIL 83
TIME 4:20 pm

OVERALL – APPROX ½" SLUDGE IN POND FLOOR, PUMPED DOWN TO WEIR OVERFLOW LEVEL APPROX. 6" BELOW FLOOR

a) POND CONCRETE CONDITION ASSESSMENT
(PICTURES RECOMMENDED)

- Little visable damage, some etching
- MANY more chunks of ROCK in pond, but not apparently from the pond or flume itself.

b) POND VOLUME MEASUREMENT

TOP LEVEL LENGTH —
" " WIDTH —
" " AREA —

BOTTOM LEVEL LENGTH —
" " WIDTH —
" " AREA —

SIDE WALL DEPTH (L) —
SLOPE —
VERTICAL DEPTH (Y) —

OVERFLOW WEIR
SIDE WALL DEPTH (L) —
SLOPE —

POND PRELAUNCH Residual Wastewater

SLUDGE.

Sample I.D. Number 0003 #5 (labeled on duct tape)
Date/Time ________ 2 April 83, 1615
Color ________ Dark Brow/BLACK
CHARACTERISTICS ________ Composite from 5 points in pond
Approx. 15% WATER
Live Red worms in sample
Method of collection — Same as for sample ID #6 pg. 6

WATER

Sample ID Number 0001 #1 (labeled on tape duct tape)
DATE/TIME ________ 2 April 83, 1615
pH ________ 10
Temperature ________ 13.6°C
color ________ Clear
Quantity ________ 1 Qt.
Method of Sampling ________ bottol submerged by hand

Sample I.D. Number 0001 #2 (labeled on duct tape)
Date/Time ________ 2 April 83, 1615
pH ________ 10
Temperature ________ 13.6°C
Color ________ Clear
Quality ________ 1 Qt.
Method of Sampling ________ bottol submerged by hand

0001 analyzed as a composite sample

SECTION 2.0

EARLY POST LAUNCH ASSESSMENT

2.1 METHODOLOGY

The early post launch sampling procedure consists of a) obtaining samples of wastewater at the launch mount perimeter trench and the vincanty of the fixed service tower b) measurement of the holding ponds liquid level c) obtaining samples of the holding ponds prior to manual washdown d) obtaining samples at the north perimeter fence e) obtaining samples at the Martin Marretta test stand f) obtaining exhaust cloud solid residue samples

The basic approach to post launch pond sampling is to obtain representative samples of each pond & maintain them separately inorder to access the contribution of the background condition of each pond prior to launch. It is important to obtain samples as soon as possible after launch inorder to obtain representative samples of the sound suppression & deluge wastewater.

Also after launch, samples of wastewater around the mobil launch platform and the fixed service tower are important to obtain inorder to characterize the contribution of washdown water from the spray systems during launch.

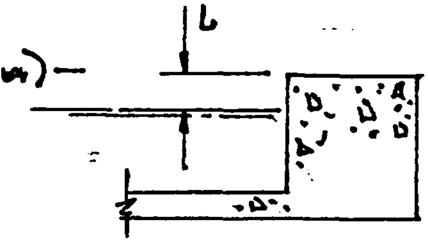
Date — 4 Apr '83
Time — 1700
pH —
color — yellowish-green
Quantity — 20 ml

2.5 Holding Ponds Assessment

<u>Pond A</u> (See Sample map Page)

a) Pond Volume Measurement. Measure water level referenced to top edge of pond wall;

86.7, 87.5, 88.7 cm (actual depth at 3 sites) Water level (L inches) —
Time — 1900
Date — 4 Apr 83



Note; comment is to be made if wastewater has overflowed the pond

b) Early Post launch Wastewater Samples

Refer to Pond A Sample map on page . Take eight one liter samples as indicated (2 liters @ each location) & Record following data;

<u>Sample 1</u>
Sample ID 0005 /
[illegible]

Date ——— 4 Apr 83
Time ——— 1900
pH ——— 1.6
Color ——— cloudy
Quantity ——— 2 L

Sample 2

Sample ID. 0005 — 2
Commodity —
Date ——— 4 Apr 83
Time ——— 1900
pH ——— 1.6
Color ——— cloudy
Quantity ——— 2 L

Sample 3

Sample ID 0005 — 3
Commodity —
Date ——— 4 Apr 83
Time ——— 1900
pH ——— 1.6
Color ——— cloudy
Quantity — 2L

Sample 4

Sample ID 0005 — 4
Commodity ——
Date ——— 4 Apr 83
Time ——— 1900
pH ——— 1.6
Color ——— cloudy
Quantity —— 2L

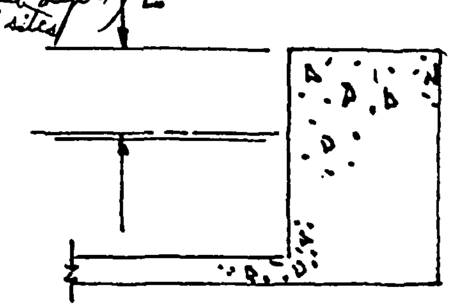
0005 analyzed as a composite sample

Pond B (See Sample Map)

a) Pond Volume Measurement. Measure water level referenced to top edge of pond wall:

123.5, 104.5, 104.5 cm (actual depth at 3 sites) L

Water level (L, inches) ——
Time ——— 1900
Date ——— 4 Apr 83



c) EARLY POST LAUNCH SAMPLES
REFER TO POND B SAMPLE MAP ON PAGE .
TAKE EIGHT, ONE LITER SAMPLES AS INDICATED
(2 LITERS @ EACH LOCATION) & RECORD DAT

Sample 1#

Sample ID 0006 5
COMMODITY —
DATE / TIME — 4 Apr 83/1930
pH — 1.6
COLOR — cloudy
QUANITY — 2L

Sample 2#

Sample ID 0006 6
COMMODITY —
Date/Time — 4 Apr 83/1930
pH — 1.7
COLOR — cloudy
QUANTITY — 2L

Sample 3#

Sample ID 0006 7
COMMODITY —
DATE / TIME — 4 Apr 83/1930
pH — 1.6
COLOR — cloudy
QUANTITY — 2L

Sample 4#

Sample ID 0006 8
COMMODITY —
Date / Time — 4 Apr 83/1930
pH — 1.6
COLOR — cloudy
QUANTITY — 2L

0006 analyzed as composite sample

2.6 Martin Marietta Test Stand Sample

a) obtain 4 liter sample & record following Data;

Sample ID 0011 /0012

Commodity ———

Date / Time ——— 4 Apr 83 / 1330

pH ——— 2.2 / 1.6 (measured 14 Apr 1510)

Color ——— slightly cloudy / greenish tint

Quantity ——— 2L / 1L

2.7 Exhaust Cloud Solid Residue Samples

obtain solid residue (aluminum oxide) at the Fixed Service Tower & MLP. Identify each sample location on sample map page & description of metal surface location. Pictures would be beinficial and should be attached to log in space provided below;

ALUMIUM OXIDE SOLID Sample NO. 1*

Sample ID 0194 (M1)
COMMODITY
DATE / TIME 4 Apr 83
COLOR grey
QUANTITY ~~100 mg~~ ~ 2 cc

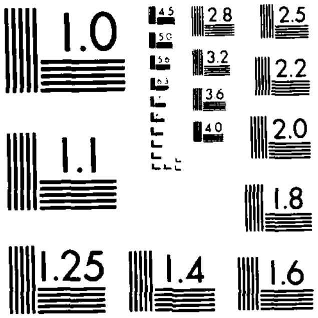
ALUMIUM OXIDE Solid Sample NO. 3*

Sample ID 0195 (M2)
COMMODITY
DATE / TIME 4 Apr 83
COLOR grey on bottom; greenish yellow on top
QUANTITY ~ 2cc

SECTION 3.0

LATE POST LAUNCH ASSESSMENT

AD-A144 420   STUDY ON THE TREATMENT OF WASTEWATER GENERATED AT KSC   2/4
(KENNEDY SPACE CENT..(U) FLUOR ENGINEERS INC IRVINE CA
ADVANCED TECHNOLOGY DIV OCT 83 SD-TR-84-08
UNCLASSIFIED   DACA05-83-C-0028   F/G 13/2   NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

3.1 Methodology

The late Post launch sampling program is Designed To provide a Representative sample of the Manual washdown contribution to the overall wastewater composition. The primary area of concern is the holding ponds for obtaining the samples. The procedure described in the following is a duplicate of the Early post launch procedure. The key point is that samples will be segregated from each pond.

3.2 meterology

Date —
Wind direction & velocity —
Temperature ———
precipitation ———

3.3 Fixed Service tower & MLP Samples

A representative sample of manual washdown wastewater is required from the Fixed Service Tower & MLP. The samples are to be Taken as washdown water falls from the structures. Locate samples taken on sample Map on page .

Sample

Sample ID ——— sample not collected (washdown occurred at night)
Commodity ———
Date / TIME ———
pH ———
COLOR ———

3.4 HOLDING PONDS INLET FLUME Sample

TO ASSESS THE IMPACT OF WASHDOWN WATER PICKING UP CONTAMINANTS FROM THE CONCRETE AREAS OF THE LAUNCH PAD, SAMPLES ARE TO BE TAKEN IN THE INLET FLUME OF THE HOLDING PONDS DURING MANUAL WASHDOWN. FOLLOWING DATA IS TO BE TAKEN ON THE SAMPLE;

INLET FLUME WASHDOWN WATER Sample
(REFER TO Sample MAP ON PAGE)

Sample ID 0010
DATE / TIME —— 5 Apr 83
pH —— 7.1 (measured 14 Apr 1500)
QUANTITY —— 4 L

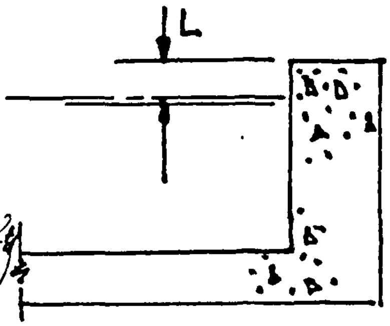
3.5 HOLDING PONDS ASSESSMENT

POND A (SEE Sample MAP PAGE)

a) POND VOLUME AFTER MANUAL WASHDOWN. WATER LEVEL TO BE MEASURED BY REFERENCE TO TOP OF POND WALL;

36 5/8", 37" 37½" (actual depth) at 3 sites WATER LEVEL (L, INCHES) ——
TIME —— 1530
DATE —— 5 Apr 83

(this is a slight volume increase from previous day - probably due to the evening washdown. No washdown water currently flowing into pond.



b) Later Post launch Wastewater Samples
Refer to Pond A Sample map page
. Take eight one liter samples
As indicated (2 liters @ each location) &
record the following Data ;

Sample 1#

COMMODITY —— #
Sample ID 0008 (11) (NE corner)
Date / Time —— 5 Apr 83 / 1530
pH —— 2.3
QUANTITY —— 2L
Temperature —— 29.1°C

Sample 2#

Sample ID 0008 (12)
COMMODITY ——
Date / Time —— 5 Apr 83 / 1530
pH —— 1.8 (NW corner)
QUANTITY —— 2L
Temperature — 29.5°C

Sample 3#

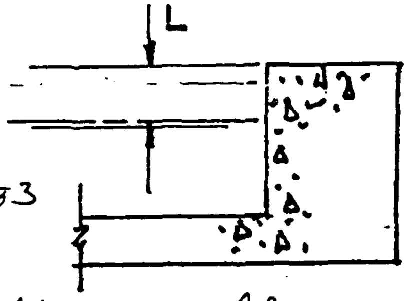
Sample ID 0008 (13) (W side)
COMMODITY ——
Date / Time —— 5 Apr 83 / 1530
pH —— 2.2
QUANTITY —— 2L
Temperature — 29.3°C

Sample 4#

Sample ID 0008 (14) (S side)
COMMODITY ——
Date / Time —— 5 Apr 83 / 1530
pH —— —
QUANTITY —— 2L

0008 analyzed as composite sample

a) POND VOLUME AFTER WASHDOWN. MEASURE POND WATER LEVEL REFERENCED TO TOP OF POND WALL;



WATER LEVEL

46 3/8", 47 1/8", 41 3/4" (L, INCHES) ——
(actual depth)
at 3 sides

TIME ——— 5 Apr 83

DATE ——— 1552

Water level was about 1/2" from top due to steady flow of washdown water. Pond had not yet overflowed.

b) LATE POST LAUNCH WASTEWATER SAMPLES REFER TO POND B SAMPLE MAP PAGE. TAKE EIGHT ONE LITER SAMPLES (2 @ EACH LOCATION) & RECORD DATA;

Sample 1#

SAMPLE ID 0009 (15) (NE corner)

COMMODITY ——

TIME / DATE —— 5 Apr 83 / 1552

pH —— 3.9

QUANTITY —— 2L

Temperature —— 28.6°C

Sample 2#

SAMPLE ID 0009 (16) (NW corner)

COMMODITY ——

TIME / DATE —— 5 Apr 83 / 1552

pH ——— 3.0

QUANTITY —— 2L

Temperature —— 28.0°C

Sample 3#

SAMPLE ID 0009 (17) (W side)

COMMODITY ——

TIME / DATE — 5 Apr 83 / 1552

pH —— 3.7

QUANTITY —— 2L

Temperature — 28.2°C

Sample 4#

SAMPLE ID 0009 (18) (S side)

COMMODITY ——

TIME / DATE — 5 Apr 83 / 1552

pH —— ——

QUANTITY —— 2L

APPENDIX III

STS-7 WASTEWATER SAMPLE DATA BOOK

VANDENBERG STS PROJECT
Vandenberg AFB, California

FLUOR ENGINEERS, INC.

STS-7 WASTEWATER SAMPLING DATA BOOK

This data book has been prepared by Fluor Engineers, Inc. to assist the Air Force and NASA in the obtaining of representative wastewater samples at KSC Launch Complex 39A, during the STS-7 launch operation. The intent of the STS-7 sample program is to provide additional data to confirm the wastewater composition to be used for the Vandenberg STS Hazardous Wastewater Treatment Plant Design.

DATA BOOK

TABLE OF CONTENTS

SECTION 1

PRELAUNCH ASSESSMENT

The STS-7 prelaunch wastewater sampling program has two areas of concern. The first area is the measurement of the Northeast and Northwest Holding Ponds at LC 39A, in order to determine how much wastewater were in the ponds prior to the launch. The second area is the obtaining of wastewater samples in both ponds prior to launch to provide a datum from which to evaluate the launch contribution to the pond contents.

Referring to the holding pond sample maps, take 2 one liter samples from opposite sides of each pond, and record the data in the log and on the sample containers as follows;

A. Pond A-Northeast Pond

Sample 1	Sample 2
Sample I.D. - Prelaunch #1	Sample I.D. - Prelaunch #2
Date/Time	Date/Time
pH	pH
Temp. °F	Temp. °F
Method of Sampling	Method of Sampling

B. Pond B-Northwest Pond

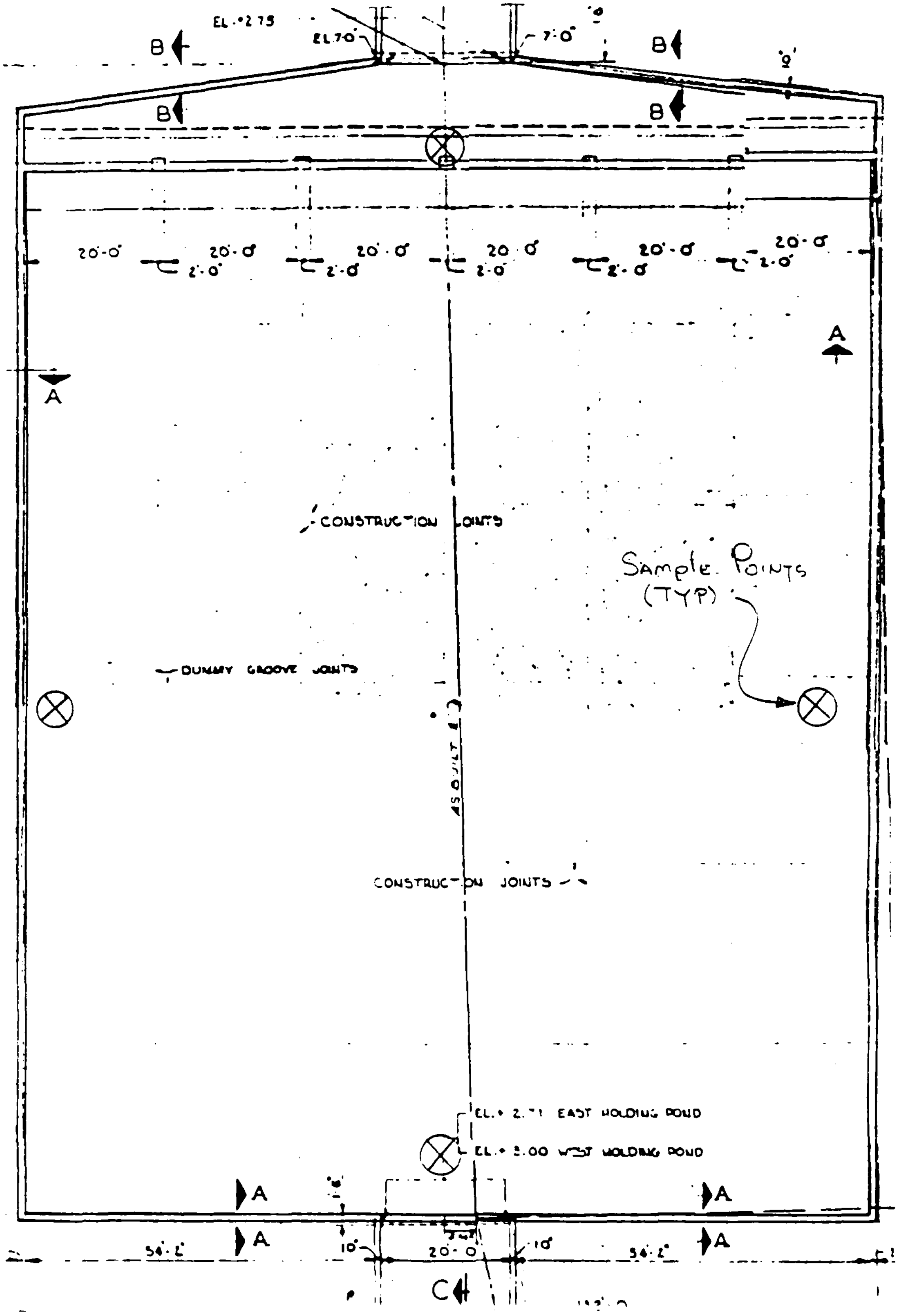
Sample 1	Sample 2
Sample I.D. - Prelaunch #3	Sample I.D. - Prelaunch #4
Date	Date
Time	Time
pH	pH
Temp.°F	Temp. °F
Method of Sampling	Method of Sampling

The depth of the wastewater in each pond prior to launch should be measured and by using the pond sample map dimensions, the volume of wastewater can be computed. Record the wastewater depth for each pond as follows;

Pond A Wastewater depth - ______ inches
Pond B Wastewater depth - ______ inches

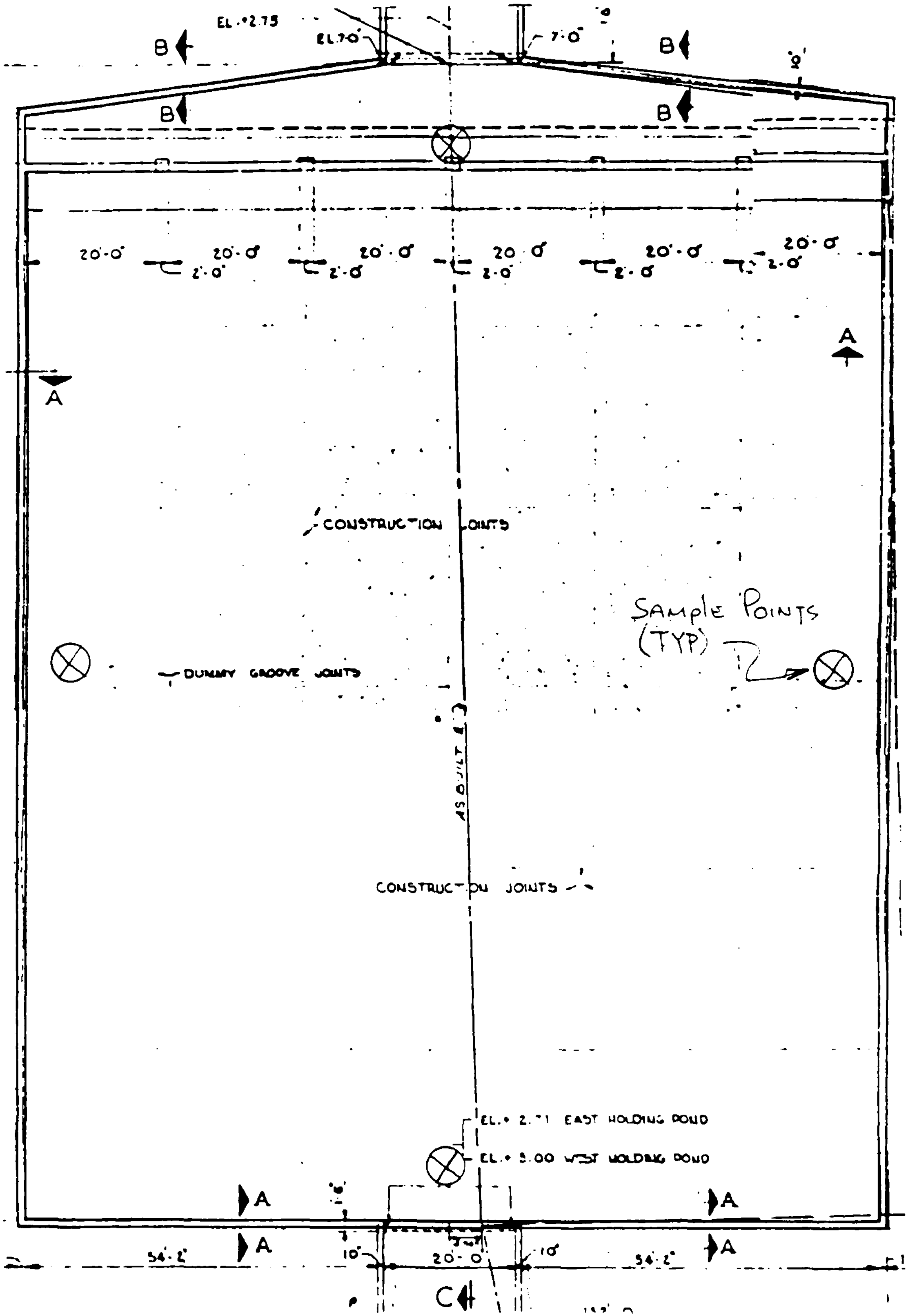
SAMPLE MAP

HOLDING POND A



SAMPLE MAP

HOLDING POND B



SECTION 2

EARLY POST LAUNCH ASSESSMENT

The early post launch sampling procedure consists of obtaining samples of the holding pond wastewaters prior to manual washdown. The basic approach is to obtain representative samples of each pond and maintain them separately in order to access the contribution of the background condition of each pond prior to launch. It is important to obtain as soon as possible after launch in order to obtain representative samples of the sound suppression and deluge wastewater. Also after launch, samples of wastewater around the Mobile Launch Platform and the Fixed Service Tower are important to obtain in order to characterize the contribution of washdown water from the spray systems during launch. If possible, samples should be taken at 5 minute intervals during the washdown for field pH measurement.

Washdown Sample	pH
1 Min	
5 Min	
10 Min	

Referring to the holding pond sample maps, take 4 two liter samples from opposite sides of each pond and record the data in the log and on the sample containers as follows;

A. Pond A - Northeast Pond

Sample No.	1.	2.	3.	4.
Date	7-18	7-18	7-18	7-18
Time	1143	1148	1149	1153
Sample ID(1)	EPLA #1	EPLA #2	EPLA #3	EPLA #4
pH	1.67	1.67	1.65	1.68
Quantity	2L.	2L.	2L.	2L.

B. Pond B - Northwest Pond

Sample No.	1.	2.	3.	4.
Date	7-18	7-18	7-18	7-18
Time	1129	1129	1130	1132
Sample ID(2)	EPLB #1	EPLB #2	EPLB #3	EPLB #4
pH	1.68	1.92	1.92	1.91
Quantity	2L.	2L.	2L.	2L.

(1) EPLA - Early Post Launch Pond A

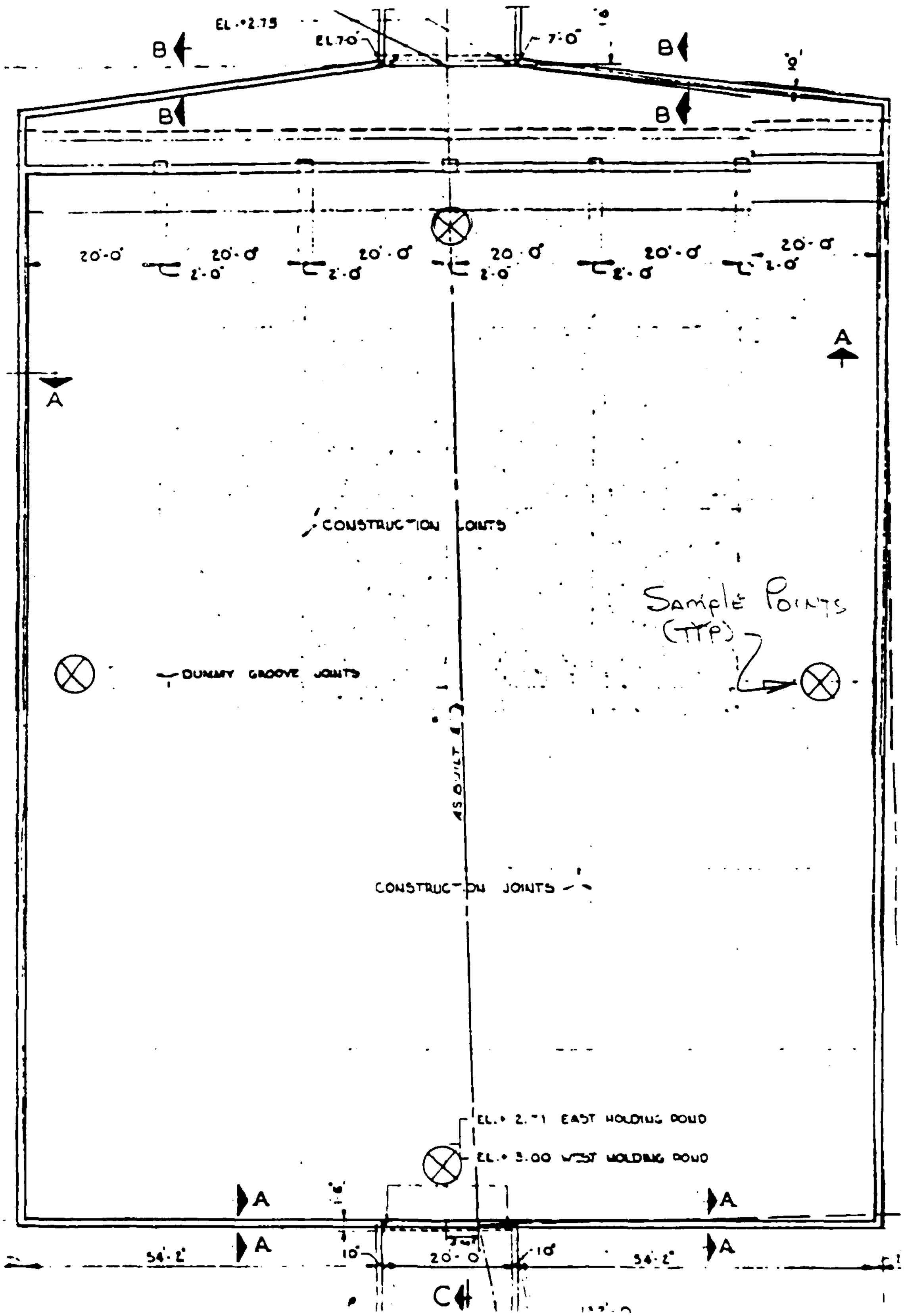
(2) EPLB - Early Post Launch Pond B

As discussed in Section 1, the wastewater depth in each pond should be obtained before any manual washdown activities. Rain on any other activity that contributes to the wastewater volume should be noted.

Pond A Wastewater depth - 11 inches
Pond B Wastewater depth - 9 inches

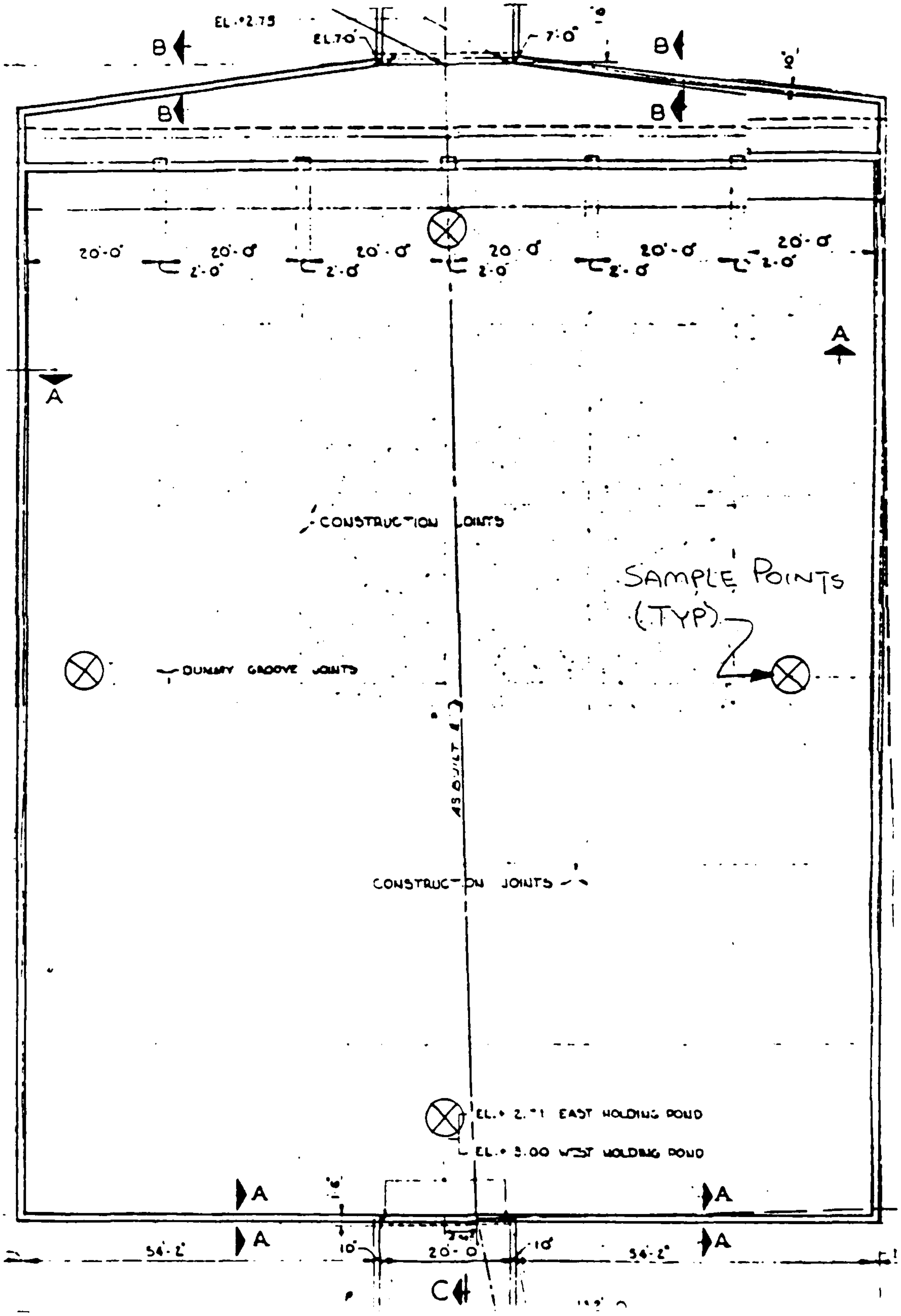
SAMPLE MAP

HOLDING POND A



SAMPLE MAP

HOLDING POND B



SECTION 3

LATE POST LAUNCH ASSESSMENT

The late post launch sampling program is designed to provide a representative sample of the manual washdown contribution to the overall wastewater composition. The primary area of concern is the holding ponds for obtaining the samples. The procedure described in the following is a duplicate of the early post launch procedure. The key point is that samples will be segregated from each pond to allow an evaluation to be made on each pond separately.

Referring to the holding pond sample maps take 4 two liter samples from opposite sides of each pond and record the data in the log and on the sample containers as follows;

A. Pond A - Northwest Pond

Sample No.	1.	2.	3.	4.
Date				
Time				
Sample ID(1)	LPLA #1	LPLA #2	LPLA #3	LPLA #4
pH				
Quantity	2L.	2L.	2L.	2L.

B. Pond B - Northwest Pond

Sample No.	1.	2.	3.	4.
Date				
Time				
Sample ID(2)	LPLB #1	LPLB #2	LPLB #3	LPLB #4
pH				
Quantity	2L.	2L.	2L.	2L.

(1) LPLA - Late Post Launch Pond A

(2) LPLB - Late Post Launch Pond B

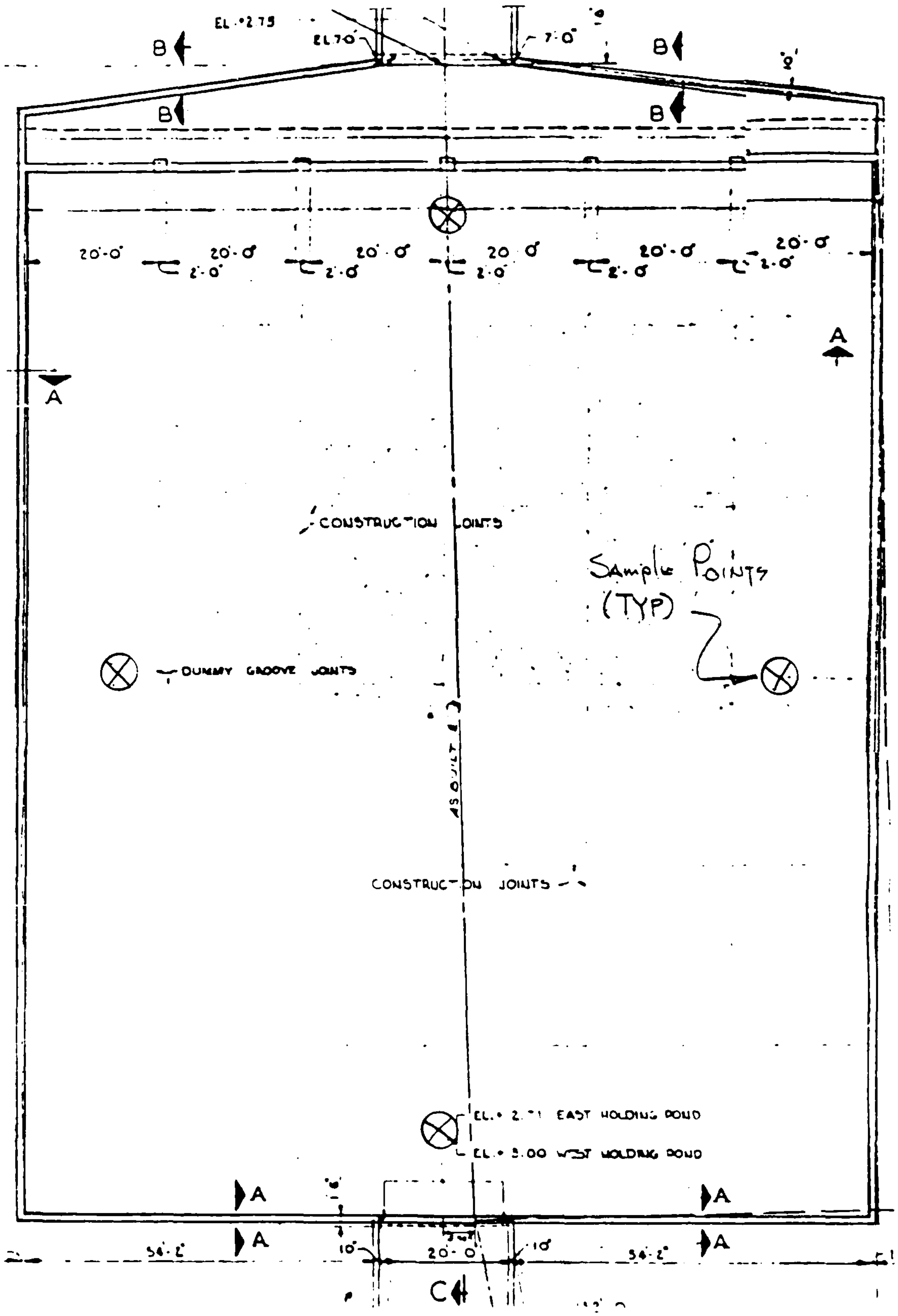
The wastewater depth in each pond should now be obtained and recorded in the following. Any significant climatic or launch recertification conditions should also be recorded.

Pond A -Wastewater Depth - _______ inches

Pond B -Wastewater Depth - _______ inches

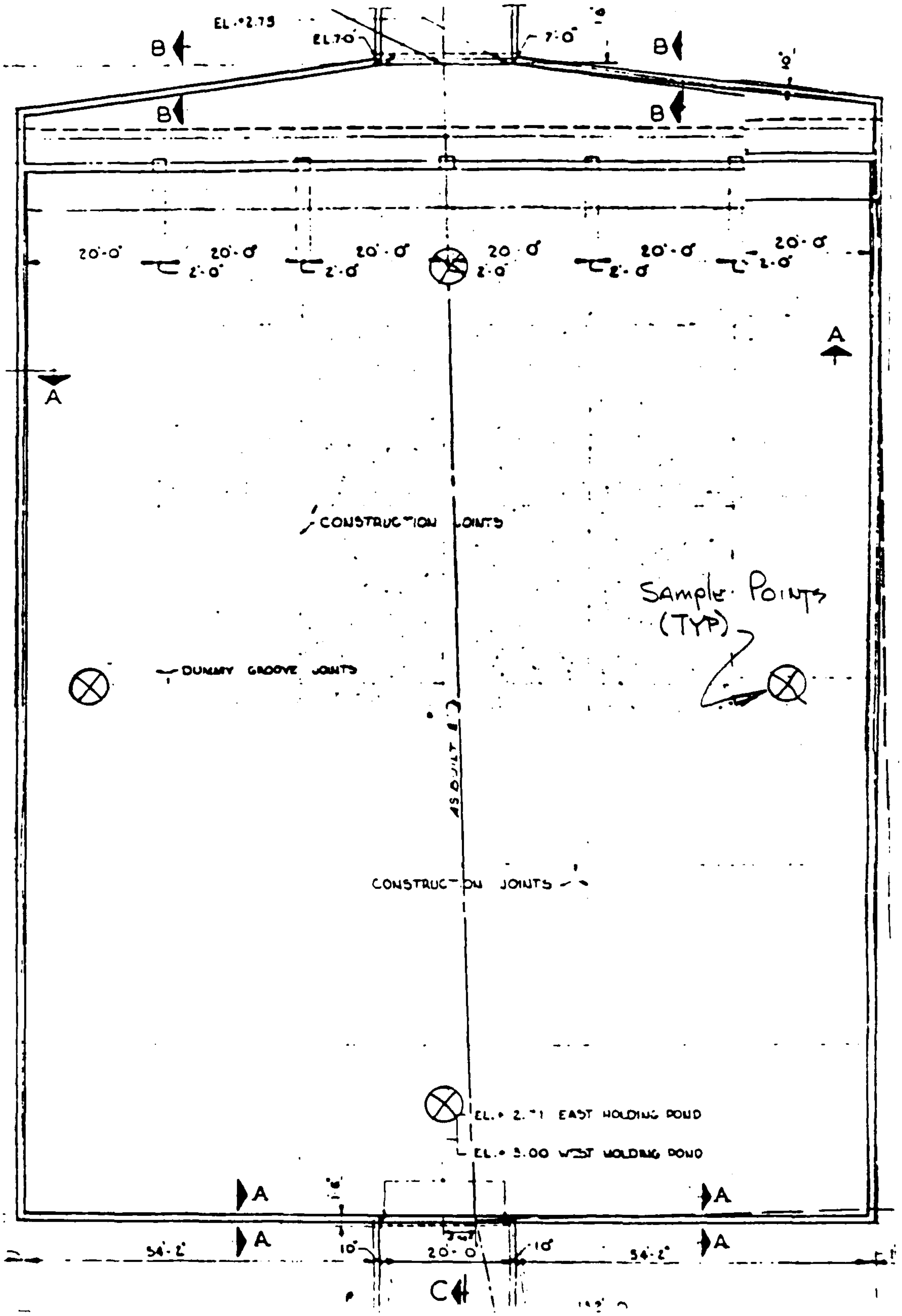
SAMPLE MAP

HOLDING POND A



SAMPLE MAP

HOLDING POND B



SECTION 4

SAMPLE SHIPPING INSTRUCTIONS

All sample containers should be securely sealed to prevent leakage. The samples should be packed with sufficient padding to prevent damage during air freight shipment. Call Delta Airlines, Orlando, Fla, Phone 305-855-3643 to pick up the packaged samples. Ship via air freight collect to:

CHEMICAL RESEARCH LABORATORIES
11100 ARTESIA BLVD.
CERRITOS, CA 90701
ATTN: EDGAR P. CABALLERO

Notify E. G. Kominek, Fluor Engineers, 714-966-5861, when shipment is made and shipping labels are attached.

APPENDIX IV

KSC AND VANDENBERG POTABLE WATER ANALYSIS

ANALYTICAL CRL SERVICES
CHEMICAL RESEARCH LABORATORIES

11100 ARTESIA BLVD.
CERRITOS, CA 90701
(213) 924-0780

RECEIVED
MAR 5 1983
ATD CONTRACTS DEPT

LABORATORY REPORT

From: Fluor Engineers, Inc. (ATD)
2801 Kelvin Avenue
Irvine, CA 92714

Attn: Mr. E. G. Kominek

Analysis No. A19409
Sampling Date
Date Sample Rec'd. 2/11/83

NATURE OF SAMPLE Water from Kennedy Space Center LC 39 A

PARAMETERS	RESULTS, in mg/l
Barium	*ND(0.08)
Strontium	0.1
Calcium	21.
Magnesium	8.4
Potassium	2.3
Sodium	75.
Iron	6.6
Manganese	*ND(0.1)
Bicarbonate	54.
Sulfate	96.
Chloride	87.
Fluoride	0.96
Borate	0.60
Silica	3.9

*Not Detected (Below indicated limit of concentration).

ANALYST

REVIEWED & APPROVED
CHEMICAL RESEARCH LABORATORIES Date 3/14/83

CHEMICAL RESEARCH LABORATORIES

11100 ARTESIA BLVD.
CERRITOS, CA 90701 (213) 924-0780

AMENDED

LABORATORY REPORT

From: Fluor Engineers, Inc. (ATD)
2801 Kelvin Avenue
Irvine, California 92714

ATTN: Mr. Edward G. Kominek

Analysis No. A18248 - A18249
Sampling Date 1/04/83
Date Sample Rec'd. 1/05/83

NATURE OF SAMPLE Well #1 & Well #30 from Vandenberg AFB

CATIONS	A18248 Well #1 RESULTS(mg/l)	A18249 Well #30 RESULTS (mg/l)
Barium (as Ba)	0.28	0.34
Calcium (as Ca)	63.	110.
Iron (as Fe)	0.35	0.30
Magnesium (as Mg)	24.	35.
Manganese (as Mn)	*ND(0.1)	*ND(0.1)
Potassium (as K)	3.5	5.0
Silica (as Si)	20.	28.
Strontium (as Sr)	0.5	0.6
Sodium (as Na)	73.	60.
ANIONS		
Bicarbonate (as HCO_3)	180.	230.
Borate (as BO_3)	1.2	1.3
Chloride (as Cl)	140.	180.
Fluoride (as F)	0.62	0.54
Sulfate (as SO_4)	59.	98.
**pH	7.43 units	7.74 units
**Flow	450. gpm	500 gpm

**pH and Flow taken by client.
*Not Detected (Below indicated limit of concentration).

ANALYST

Ron Romualdo
REVIEWED & APPROVED
CHEMICAL RESEARCH LABORATORIES Date 1-20-83

CHEMICAL RESEARCH LABORATORIES

11100 ARTESIA BLVD.
CERRITOS, CA 90701 (213) 924-0780

LABORATORY REPORT

From: Fluor Engineers, Inc. (ATD)
2801 Kelvin Avenue
Irvine, CA 92714

Attn: Mr. E. G. Kominek

Analysis No. A19409A
Sampling Date
Date Sample Rec'd. 2/11/83

NATURE OF SAMPLE Vandenberg Water Sample

A water sample from Vandenberg AFB was used to determine the effectiveness of a sequestering agent on Barium under fivefold sample concentration conditions. The results are as follows:

Concentration	Barium (mg/l) Well No. 1	Barium (mg/l) Well No. 2
Control	0.20	0.20
3 ppm	0.10	0.10
10 ppm	0.10	0.10

BC
ANALYST

REVIEWED & APPROVED
CHEMICAL RESEARCH LABORATORIES Date 3/14/83

APPENDIX V

JAR TEST PROCEDURE FOR STS-7
WASTEWATER SAMPLES

JAR TEST PROCEDURE

Step #1: Determine solubility curves for aluminum and zinc ions vs. pH by the addition of sodium hydroxide.

Step #2: To a new sample add sodium hydroxide to the optimum pH for $Al(OH)_3$ precipitation as developed in Step 1. Then slowly add Na_2S. The sulfide ion will further precipitate remaining heavy metals from solution. Allow 10 minutes mixing to ensure complete reactions. When the sulfide concentration, preferably measured by an ORP sensor, increases perceptibly, this is an indication that the metal sulfide precipitation has been maximized. Measure and record pH, aluminum ion and sulfide ion concentrations. It is anticipated that the sulfide ion concentration should not exceed about 0.2 mg/l.

Step #3: If the aluminum ion concentration has increased from Step 1 because of aluminate ion formation at the higher pH, repeat Step 2, adding NaOH to a pH of only 8.0. Then add Na_2S as described in Step 2 and measure pH, aluminum and sulfide ion concentrations. It may be necessary to repeat the procedure (by reducing the pH to less than 8.0 in Step 2 before repeating Step 3) to keep the pH low enough to avoid aluminate formation.

Step #4: After optimizing the NaOH and Na_2S dosages as described in Step 3, filter the sample and analyze for all heavy metals and silica. If the filtrate is not clear due to colloidal substances, 5 mg/l of a polymer should be added as a coagulant aid and filter aid.

If the silica concentration is less than 15 mg/l, further chemical treatment for SiO_2 reduction as discussed in the next section is not necessary.

Silica Removal: The purpose of this test is to determine the treatment necessary to reduce the SiO_2 in the treated water to less than 15 mg/l. This might be accomplished by coprecipitation of the heavy metals and magnesium in the raw waste.

If necessary, additional magnesium (as the oxide or chloride) will be added if increasing the reaction time or slurry concentration isn't sufficient. Silica removal is accomplished by adsorption/coprecipitation of ion hydroxide of magnesium hydroxide. It is possible that the magnesium and other heavy metals precipitated may reduce the silica to the desired level without the addition of magnesium. If this does not occur, it may be necessary to add 1.8 mg of magnesium per mg of silica removed.

Critical variables which influence the silica removal efficiency are:

Reaction time
Slurry concentration
Magnesium - heavy metals precipitated

Step #1: If the SiO_2 concentration is more than 15 mg/l, increasing the slurry concentration to one percent by weight should accomplish this reduction. Preparing a one percent slurry concentration in the jar tests can be accomplished as follows:

a. Assume that one liter samples will be used.

b. Add NaOH and Na_2S to precipitate metals as discussed earlier, and add 5-10 mg/l of polymer for effective settling.

c. Note settling rate of precipitated solids in inches per minute for 10 minutes, but continue settling for 30 minutes.

d. Decant supernatant water.

e. The weight of precipitated solids is calculated so that the weight of solids recirculated with each test will be indicated by the number of tests with sludge returned.

f. Based upon the scope analysis, there will be about 1,000 mg/l of precipitated and suspended solids. With one liter samples used, 10 returns of settled sludge will approximate one percent slurry, based upon the raw waste volume treated.

g. The settling rate of the slurry should be measured after each test and the settling time continued until the sludge volume is substantially constant over a five minute period.

h. Record the temperature at which the jar tests are run. Settling velocities vary inversely with kinematic viscosity, which is related to temperature.

Relationship of Kinematic Viscosity to Water Temperature

Temperature		Kinematic Viscosity, v
°C	°F	$(10)^{-5}$ ft^2/Sec
0	32	1.792
5	41	1.519
10	50	1.310
15	59	1.146
20	68	1.011
30	86	0.804

The difference between the temperature at which jar test are run and the anticipated minimum plant operating temperature must be factored into the plant design separation rate. If lab is 20°C and plant may be 10°C, the lab settling rate should be multiplied by 1.011/1.310.

Sludge Settling: All of the accumulated sludge should be saved for a sludge thickening test. The accumulated sludge should be mixed and tested to determine the percent in weight of the settled sludge. The sludge should then be diluted to one percent by weight with supernatant water and settled in a graduated cylinder, preferably 1,000 ml capacity. The graduate should be filled in the morning so that hourly sludge volumes can be noted during the day. The sample should be allowed to settle for 24 hours, with the sludge by volume and by weight being determined.

The weight percent of each of the following hazardous metals in the thickened sludge should be determined.

Barium
Cadmium
Chromium
Lead
Selenium
Silver

The sludge should then be vacuum filtered, using a Buchner Funnel with a diatomite precoat. A sample of the filter cake should be weighed and dried to determine the percent moisture of the filter cake. Another sample of the cake should be tested for free moisture in accordance with the EPA Free Liquid Test.

> "Use 500 micron paint filter, put 100 grams of filter cake in funnel for five minutes. If one drop of water comes through, the filter cake does not meet the EPA standard."

The weight percent of each of the hazardous metals previously listed should also be determined in the filter cake, based upon the filter cake weight before drying.

APPENDIX VI

CHEMICAL RESEARCH LABORATORIES REPORT STS-7

ANALYTICAL CRL SERVICES
CHEMICAL RESEARCH LABORATORIES

RECEIVED
JUL 19 1983
ATD CONTRACTS DEPT.

TECHNICAL REPORT FOR FLUOR CONSTRUCTORS, INC.
EVALUATION OF TREATMENT FOR HEAVY METAL REMOVAL
JULY 12, 1983

ATTN: MR. ED KOMINEK x 5861

11100 ARTESIA BOULEVARD CERRITOS, CALIFORNIA 90701 • (213)924-0780

ANALYTICAL
CRL
SERVICES
CHEMICAL RESEARCH LABORATORIES

July 12, 1983

Fluor Constructors, Inc.
3333 Michelson Dr.
Irvine, CA 92730

RE: Evaluation of treatment for heavy metal removal

ATTN: Mr. Ed Kominek

Gentlemen:

We at Chemical Research Laboratories, Inc. are pleased to submit our final report on the treatment study for heavy metal removal from the Space Shuttle Launch, Kennedy Space Center.

This report includes all pertinent laboratory details.

It has been a pleasure working with you and we look forward to serving your company again.

Respectfully submitted,

Edgar P. Caballero

EPC/ca

cc: Mr. Jack Buckameir

11100 ARTESIA BOULEVARD CERRITOS CALIFORNIA 90701 • (213)924-0780

TECHNICAL REPORT FOR FLUOR CONSTRUCTORS, INC.
Evaluation of Treatment for Heavy Metal Removal
July 12, 1983

EXECUTIVE SUMMARY

Chemical Research Laboratories, Inc. conducted a study of the treatment used to remove heavy metals from waste effluent generated at the space shuttle launch, Kennedy Space Center. This study concludes that sodium sulfide is an effective treatment when maintained at a pH of 10.5. Moreover, heavy metals are removed to levels which meet drinking water standards. The sludge produced from the treatment is relatively stable and meets RCRA requirements for declassification as a potential hazardous waste, but does not meet CAM declassification requirements. CAM requirements are not achieved due to the solubility of zinc sulfide at pH 4.

The corrosivity of the composite water is significant and may require neutralization to reduce corrosion of concrete ponds. Additionally, dewatering studies indicate that centrifugation may not be adequate for economical handling and sludge disposal.

TECHNICAL REPORT FOR FLUOR CONSTRUCTORS, INC.
Evaluation of Treatment for Heavy Metal Removal
July 12, 1983

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Technical Report

List of Tables

List of Figures

TECHNICAL REPORT FOR FLUOR CONSTRUCTORS, INC.
Evaluation of Treatment for Heavy Metal Removal
July 12, 1983

EVALUATION OF TREATMENT FOR HEAVY METAL REMOVAL

INTRODUCTION

Fluor Constructors, Inc. is currently under contract to design a treatment system to process the wastewater from the Space Shuttle Launch at Kennedy Space Center. Upon rocket engine ignition, a deluge of water is delivered into the fire pit as cooling fluid. The vapors, gases and fuel combustion by-products are washed into concrete basins and detained for subsequent treatment.

The purpose of this investigation is to determine the most effective physicochemical conditions for the removal of heavy metals. Chemical Research Laboratories, under sub-contract to Fluor, has characterized the composite sample (Table I) and subsequently performed treatment studies to determine the efficacy of heavy metal removal by sodium sulfide at pH levels between 9 and 11. Additional investigations were performed to determine the unaided precipitation of silica at various temperatures as well as to determine corrosive properties of the launch effluent on concrete (Type II Portland cement).

Subordinate studies have also been performed to determine the effect of calcium carbonate on sludge compaction and the possibility of centrifugation as a mode of sludge dewatering.

METHODOLOGY

The various testing procedures employed to determine the effectiveness of treatment were: settling rate tests, chemical analysis of metal constituents and their respective concentrations, and E.P. toxicity. Settling rate was determined by the Jar test technique over 72 - 96 hour periods. Chemical analysis incorporated a wide range of lab tests including: pH, turbidity, demand analysis, heavy metals, solids, and nutrients.

The method of study for each of the evaluations is listed below:

1. SAMPLE CHARACTERIZATION

   The initial 32 samples were received and individually evaluated for pH, turbidity and silica. The samples were then composited and fully characterized (Table II).

2. THE EFFECT OF TEMPERATURE ON SILICA PRECIPITATION

   To determine the effect of temperature on silica precipitation, two aliquots were taken from the composite: One was placed at 34 ° F and the other at 75 ° F. Silica precipitation was monitored by determining silica levels at various time intervals.

3. THE EFFECT OF SODIUM SULFIDE ON METAL CONCENTRATION

   The effect of sodium sulfide on the metal concentration of the composite was determined for various pH levels by atomic absorption spectrophotometry. The supernatant from the Jar tests was used to determine the unprecipitated metals. The treatment also generated data for the settling curves.

4. VARIATIONS OF TREATMENT

   Treatment #4 received 300 mg/l of calcium carbonate ($CaCO_3$) to determine the effect of $CaCO_3$ as a sludge compaction additive.

   Only sodium hydroxide was added to treatment #6 to determine if the sulfide additive was necessary.

5. SLUDGE PRODUCTION AND DEWATERING

Sludge produced from each of each of the six treatment studies was combined and allowed to settle for an additional 24 hours. The supernatant was then decanted and the remaining sludge was evaluated for dewatering by centrifugation.

6. MOISTURE DETERMINATION

The sludge produced from the six treatment studies was filtered through a nominal 0.45 micron glass fiber filter and the sludge cake volume was determined (Table III). A portion of the sludge was used for moisture determination and two other portions were used for RCRA and CAM evaluation.

7. RELATIVE CORROSION OF EFFLUENT ON CONCRETE

Concrete specimens(Type II Portland cement) were immersed in the composite sample under quiescent and dynamic conditions to determine the corrosivity of the fluid.

EQUIPMENT

Nonstandard equipment used in these testing procedures includes: atomic absorption, centrifuge, and a specially devised mixing apparatus to insure continuous mixing at a prescribed rate without simultaneously contaminating the test solution. The mixing device is illustrated in figure 1.

RESULTS

The thirty-two samples received from Kennedy Space Center were chemically evaluated for pH, turbidity, and silica content and exhibited comparable characteristics. Thus, they were proportionately combined into a single composite. Table I shows the results of the tested parameters.

The results of unaided silica precipitaiton (Table IV) indicate that neither time nor temperature have any effect on precipitating silica at pH 2.0. This determination was conducted at 75° F and 34° F.

The effect of alkaline pH and sodium sulfide acting synergistically, was investigated for its impact on settling rate and heavy metal removal. The results of this investigation are represented in figures 2 - 7. Upon settling completion, heavy metal analyses were performed on the supernatant from the Jar tests. The results of heavy metals remaining in the supernatant are shown in Table V and are plotted as pH vs. metal concentration in figures 8 - 18. The following conditions are variations in the treatment studies:

1. Treatment #4 contained an additional 300 mg/l of $CaCO_3$ as a compaction additive.
2. Treatment #6 contained only sodium hydroxide for pH control—no sodium sulfide was added.

The addition of the $CaCO_3$ produced no appreciable increase in compaction nor any significant improvement in settling rate. The compaction, settling rate, and heavy metal removal of the sodium hydroxide treatment was comparable to those with sodium sulfide addition.

The centrifugation test for dewatering indicated that sludge compaction at 2624 g and 4101 g is both inefficient and inadequate. A conventional lab centrifuge was used for this test and sludge compaction was measured at increasing time intervals.

The possibility of classifying the produced sludge as non-hazardous was tested by subjecting the sludge to numerous analyses as required by RCRA and CAM. Results from these tests are listed in Tables VI and VII, respectively. It was found that the leachate under RCRA tests falls within non-hazardous guidelines. However, the leachate maintained excessive zinc levels under the CAM procedure and cannot be classified as non-hazardous.

The concrete (Type II Portland cement) was determined to have comparable corrosion rates from both the quiescent and dynamic conditions. The quiescent exposure exhibited 1.94% corrosion and the dynamic exposure exhibited 1.98% corrosion. The samples for these tests weighed approximately 16 grams and were immersed in approximately 60 cc of composite fluid.

The settling rates for samples of the composite treated with increasing sodium hydroxide and sodium sulfide were correlated with various pH's. However, none of these samples showed additional settling due to increases in the additives.

DISCUSSION

Based on analytical results, it appears that effective treatment of composited discharge from rocket launches can be achieved through the use of controlled pH at levels of 10 and through the addition of sodium sulfide for heavy metal precipitation. Although sodium hydroxide alone will precipitate the heavy metals, the addition of sodium sulfide forms the relatively insoluble metal sulfide at pH levels below 7 with the exception of zinc. The metal hydroxides are relatively soluble with changes in pH to levels below 7.

The levels of magnesium and calcium naturally present in the wastewater sample aid in the removal of silica at pH levels above 9, therefore no additional treatment is required for silica. Although the compaction of produced sludge is significant (Table X), it results in excessive bulk. Additionally, centrifugation of sludge does not yield adequate compaction. The disposal of this sludge may represent a considerable problem due to its quantity alone. The toxicity of the leachate from the sludge meets RCRA requirements but does not pass CAM requirements due to the solubility of zinc sulfide at pH 4 and must be handled independently.

The corrosivity of the composite is significant, but it appears that quiescent contact is less detrimental than dynamic contact: This is suggested by the formation of a $CaCO_3$ layer in the quiescent sample as contact time increases.

RECOMMENDATIONS

Since zinc instability in the sludge is the only impediment to State classification as non hazardous waste, Chemical Research Laboratories recommends a study to investigate the stabilization characteristics of the zinc. Eligibility for CAM classification as a non hazardous waste would assuredly prove less costly than available disposal techniques.

Sludge handling costs may also be minimized through modification of the existing process possible through compaction or filtration techniques.

Finally, improved corrosion inhibition can be achieved through monitored acid neutralization. Based on a monitored flow, the controlled sample would be maintained neutral by the addition of caustic whenever pH exceeded 7.

Table I

Chemical Analysis of Composite Sample

(A23991 - A24022)

PARAMETERS	RESULTS, mg/l
Aluminum, Total	26.
Barium, Total	0.600
Cadmium, Total	0.150
Calcium, Total	173.
Chemical Oxygen Demand	104.
Chloride	1960.
Chromium, Total	0.300
Copper, Total	1.2
Iron, Total	30.
Lead, Total	1.400
Magnesium, Total	34.
Manganese, Total	0.59
Nickel, Total	0.85
Nitrogen (N-NO$_3$)	0.59
Selenium, Total	0.23
Silicon, Total (as SiO$_2$)	88.
Silver, Total	0.012
Sodium, Total	193.
Suspended Solids	57.
Total Dissolved Solids	2360.
Zinc, Total	206.
Sulfate (as SO$_4$)	203.
Phosphate (as PO$_4$)	0.7

Table II

Results of Individual Sample Screening

SAMPLE	pH	TURBIDITY (NTU)	Si(SiO_2)
EPLA #1a	1.8	34.	79.
EPLA #1b	1.9	27.	77.
EPLA #2a	1.7	28.	81.
EPLA #2b	1.8	33.	79.
EPLA #3a	1.8	46.	81.
EPLA #3b	1.8	38.	81.
EPLA #4a	1.7	12.	81.
EPLA #4b	1.8	15.	79.
EPLB #1a	1.9	4.2	88.
EPLB #1b	1.9	9.0	88.
EPLB #2a	1.9	4.2	83.
EPLB #2b	1.9	4.2	88.
EPLB #3a	2.0	4.4	88.
EPLB #3b	2.0	6.0	88.
EPLB #4a	2.0	6.4	88.
EPLB #4b	2.0	10.0	86.
LPLA #1a	2.1	2.4	88.
LPLA #1b	2.1	3.0	81.
LPLA #2a	2.1	3.0	81.
LPLA #2b	2.1	3.0	81.
LPLA #3a	2.0	6.0	81.
LPLA #3b	2.0	4.1	83.
LPLA #4a	2.0	5.6	81.
LPLA #4b	2.1	3.0	83.
LPLA #1a	1.9	10.2	83.
LPLA #1b	1.9	5.6	83.
LPLA #2a	1.9	13.0	86.
LPLA #2b	1.8	6.4	86.
LPLB #3a	1.8	6.8	86.
LPLB #3b	1.8	5.6	86.
LPLB #4a	1.8	—	83.
LPLB #4b	1.8	—	83.
COMPOSITE	2.0	—	88.

Table III

Physical Characterization of Sludge

The sludge produced from the six treatment studies was allowed to settle for 7 days and subsequently filtered through a nominal 0.45 micron glass fiber filter. The cake produced was evaluated for volume and moisture content. Results are as follows:

PARAMETER	RESULTS
Sludge Volume	25.5 cm^3
Moisture Content	89.3 %

Table IV

The Effect of Time and Temperature on Silica Precipitation

Evaluation performed on the precipitate of silicates at 75°F and 34°F vs. Time. The results are as follows:

TIME (hours)	SILICA CONC. AT 75°F (mg/l)	SILICA CONC. AT °F (mg/l)
0	41	——
24	39	——
48	39	——
72	39	——
96	39	39
120	39	39
144	39	39
168	39	39
192	39	39

Table V

Heavy Metals Present After Treatment

PARAMETER	TREAT #1			TREAT #2			TREAT #3			TREAT #4			TREAT #5			TREAT #6		
	METAL	pH	$S^=$RES	METAL	pH	$S^=$RES.	METAL	pH	$S^=$RES.	METAL	pH	$S^=$RES.	METAL	pH	$S^=$RES.	METAL	pH	$S^=$R
Aluminum	700.	10.2	53.	1100.	9.2	0.89	3500.	11.0	0.15	1100.	10.1	3.	——	10.6	.35	——	10.4	*
Barium	400.	"	"	400.	"	"	400.	"	"	400.	"	"	400.	"	"	400.	"	*
Cadmium	18.	"	"	12.	"	"	14.	"	"	18.	"	"	16.	"	"	20.	"	*
Chromium	10.	"	"	8.	"	"	6.	"	"	ND(2.)	"	"	ND(2.)	"	"	ND(2.)	"	*
Iron	ND(100.)	"	"	ND(100.)	"	"	ND(100.)	"	"	ND(100.)	"	"	——	"	"	——	"	*
Lead	ND(20.)	"	"	20.	"	"	20.	"	"	40.	"	"	40.	"	"	25.	"	*
Magnesium	10,800	"	"	23,000	"	"	200.	"	"	11,000.	"	"	——	"	"	——	"	*
Mercury	ND(10.)	"	"	ND(10.)	"	"	ND(10.)	"	"	ND(10.)	"	"	ND(10.)	"	"	ND(10.)	"	*
Nickel	42.	"	"	47.	"	"	35.	"	"	42.	"	"	47.	"	"	40.	"	*
Selenium	118.	"	"	119.	"	"	226.	"	"	181.	"	"	181.	"	"	198.	"	*
Silicon (as SiO_2)	7500.	"	"	3640.	"	"	9640.	"	"	5790.	"	"	——	"	"	——	"	*
Silver	6.	"	"	6.	"	"	6.	"	"	6.	"	"	6.	"	"	4.	"	*
Zinc	ND(100.)	"	"	ND(100.)	"	"	110.	"	"	130.	"	"	——	"	"	——	"	*

NOTE: METAL = Concentration in ppb, $S^=$RES. = sulfide residual in mg/1, Treatment #4 included 300 mg/1 $CaCO_3$

*No sulfide residual in treatment #6 since sodium sulfide was not introduced in this test.

Table VI

Analysis of Sludge According to RCRA

The composite wastewater was subjected to treatment evaluation with sodium hydroxide and sodium sulfide. The sludge produced from a total of six studies was composited and subsequently analyzed in accordance with the procedures set forth in the Federal Register of Monday May 19, 1980. The results are as follows:

PARAMETER	RCRA MAX. CONC. (ppm)	RESULTS(ppm)
Arsenic	5.0	0.020
Barium	100.0	ND(1.)
Cadmium	1.0	ND(0.1)
Chromium	5.0	ND(0.1)
Lead	5.0	ND(0.1)
Mercury	0.2	ND(0.010
Selenium	1.0	0.015
Silver	5.0	ND(0.1)

Table VII

Analysis of Sludge According to CAM

The composite wastewater was subjected to treatment evaluation with sodium hydroxide and sodium sulfide. The sludge produced from a total of six studies was composited and subsequently analyzed in accordance with the guidelines set forth under the "Procedures for Evaluating Wastes," part 3 section 6669 of the California Assessment Manual (CAM) for Hazardous Wastes, January 19, 1982. The results are as follows:

PARAMETERS	STLC (ppm)	TTLC (ppm)	RESULTS (ppm)
Antimony, Total	100.	500.	0.7
Arsenic, Total	5.	500.	0.14
Barium, Total	100.	10,000.	2.0
Beryllium, Total	7.5	75.	ND(0.1)
Cadmium, Total	1.	100.	ND(0.1)
Chromium, Total	5.	500.	4.6
Cobalt, Total	80.	8,000.	0.36
Copper, Total	2.5	250.	ND(0.1)
Lead, Total	5.	1,000.	1.1
Mercury, Total	0.2	20.	ND(0.010)
Molybdenum, Total	350.	3,500.	ND(1.)
Nickel, Total	20.	2,000.	9.7
Selenium, Total	1.0	100.	0.80
Silver, Total	5.0	500.	ND(0.1)
Thallium, Total	7.0	700.	0.7
Vanadium, Total	24.	2,400.	1.4
Zinc, Total	25.	2,500.	1,600.

Table VIII

Relative Corrosivity Under Quiescent and Dynamic Conditions

Concrete samples containing Type II Portland cement (normal weight) were evaluated for corrosion within an acid environment which was provided by the Fluor sample (composite). These samples were examined under both quiescent and dynamic conditions.

SAMPLE	% CORROSION
QUIESCENT	1.94
DYNAMIC	1.98

Table IX

Relative Dissolution of Concrete by Constituent

PARAMETER	QUIESCENT RESULTS, ppm	DYNAMIC RESULTS, ppm
Aluminum	<0.2	<0.2
Calcium	670.	1050.
Magnesium	0.4	44.
Silica	4.	6.

Table X

Compaction by Centrifugation

The sludge from the six treatment studies was allowed to settle for 24 hours and subsequently evaluated for compaction by centrifugation at 2624 g and 4101 g. The results are as follows:

2624 g		4101 g	
COMPACTION	TIME	COMPACTION	TIME
33% cake	1 min	31% cake	1 min
26% cake	3 min	28% cake	3 min
25% cake	6 min	26% cake	6 min
25% cake	9 min	25% cake	9 min

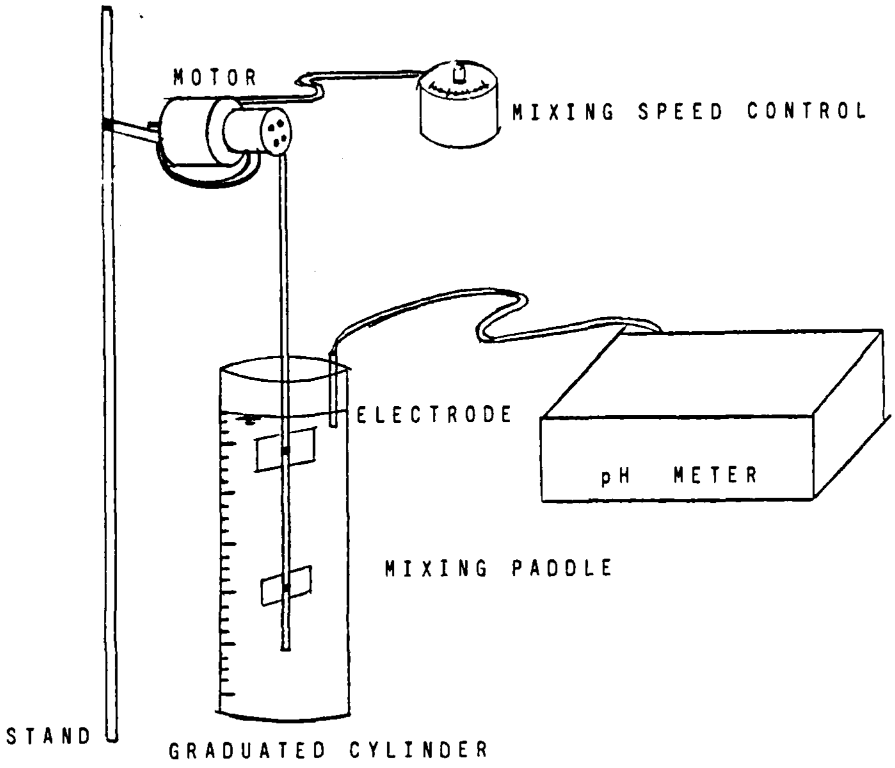

Fig. 1 EXPERIMENTAL SET-UP

SCALE:	**APPROVED BY:**	**DRAWN BY**
DATE: July 12,83		**REVISED**

TECHNICAL REPORT FOR FLUOR CONSTRUCTORS, INC.

Evaluation of Treatment for Heavy Metal Removal

DRAWING NUMBER

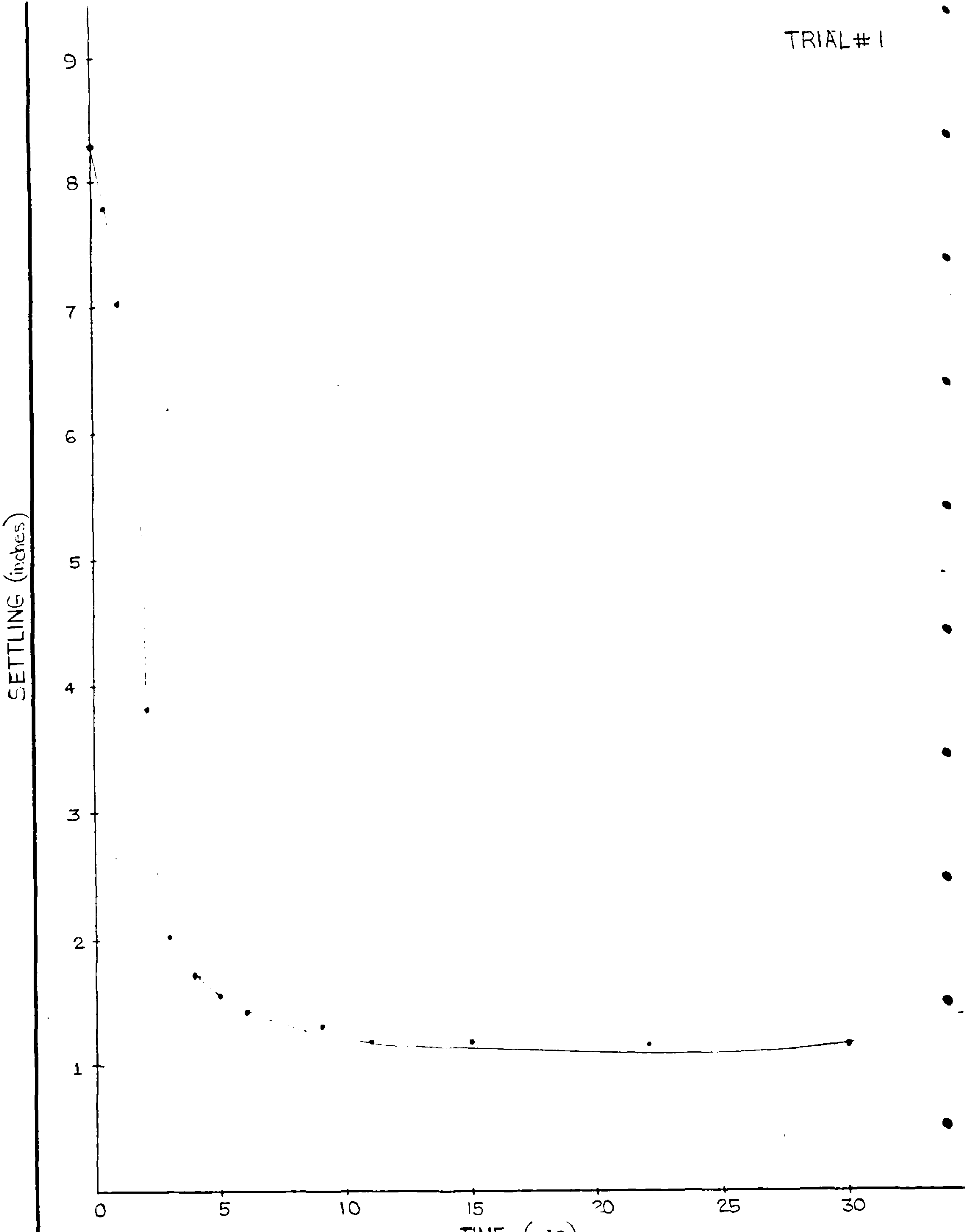

Fig. 2 SETTLING vs. TIME

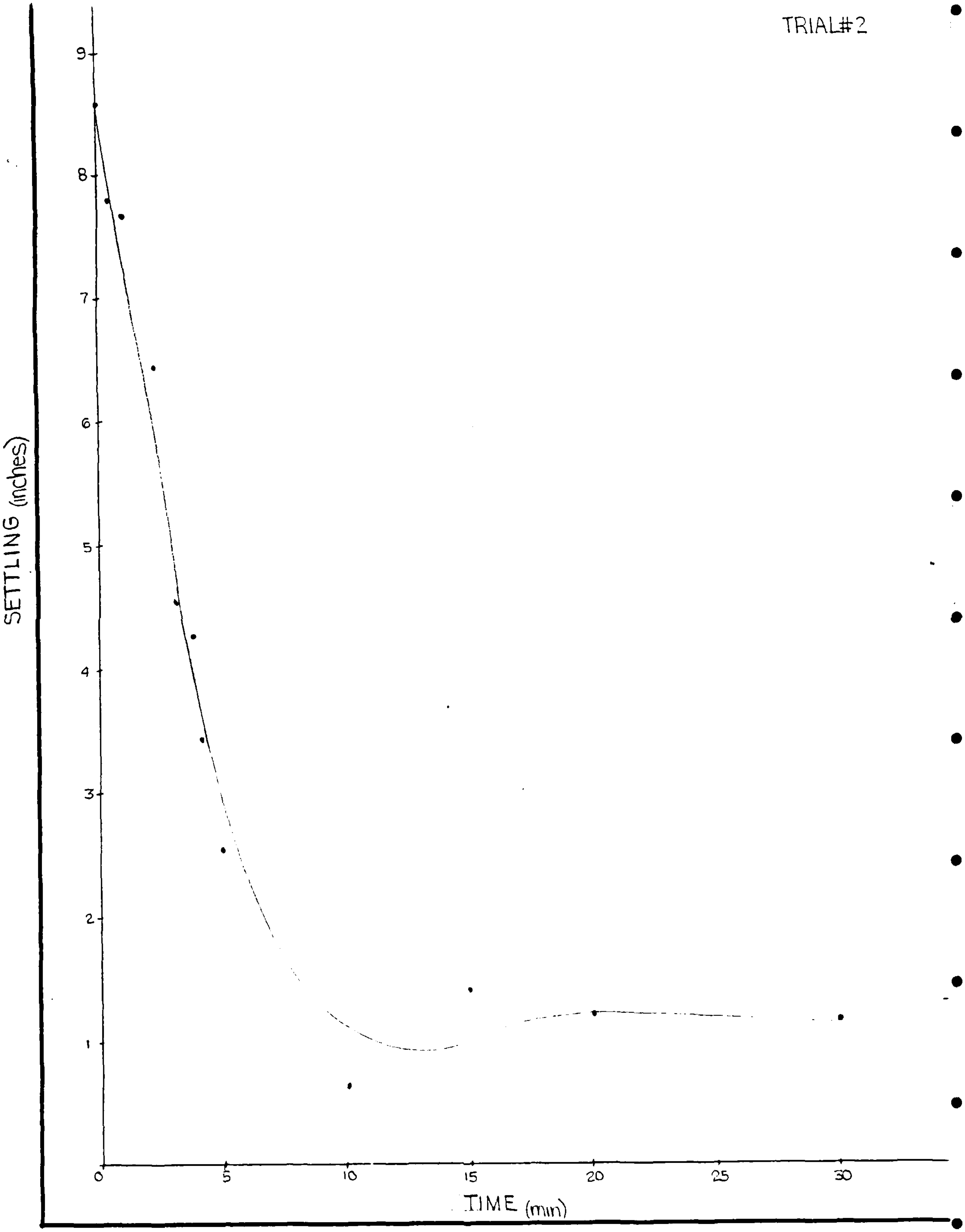

Fig. 3 SETTLING vs. TIME

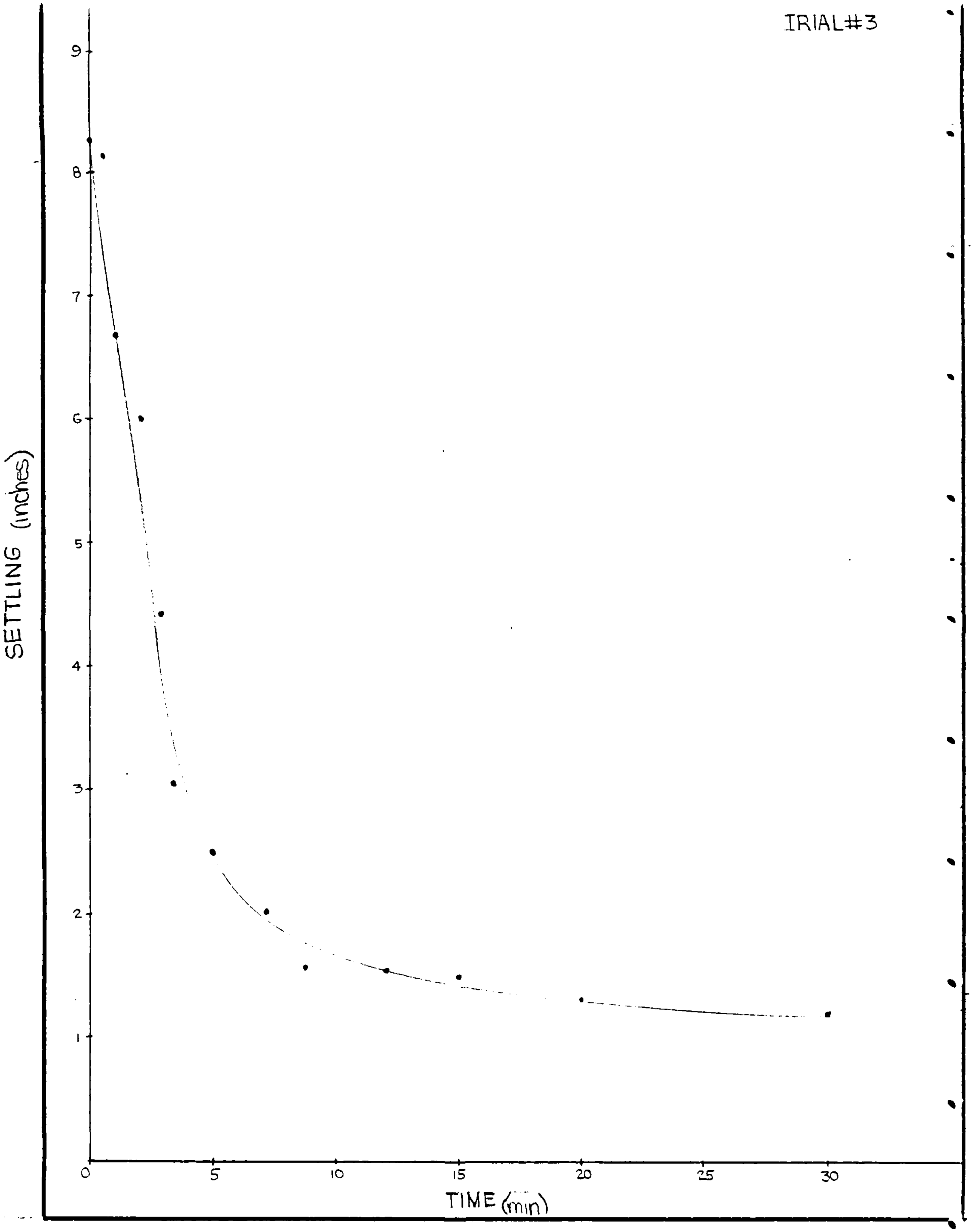

Fig 4 SETTLING vs TIME

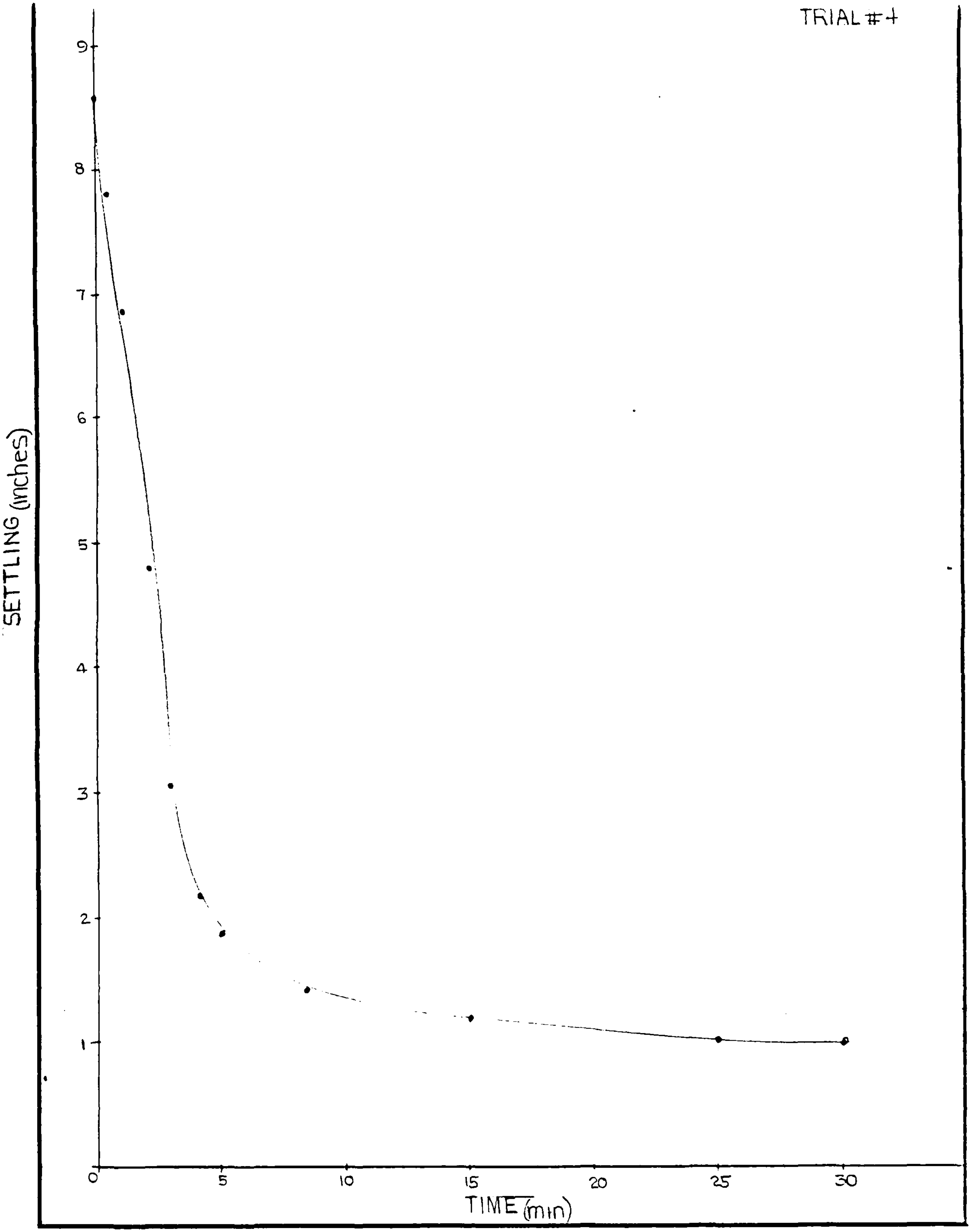

Fig. 5 SETTLING vs. TIME

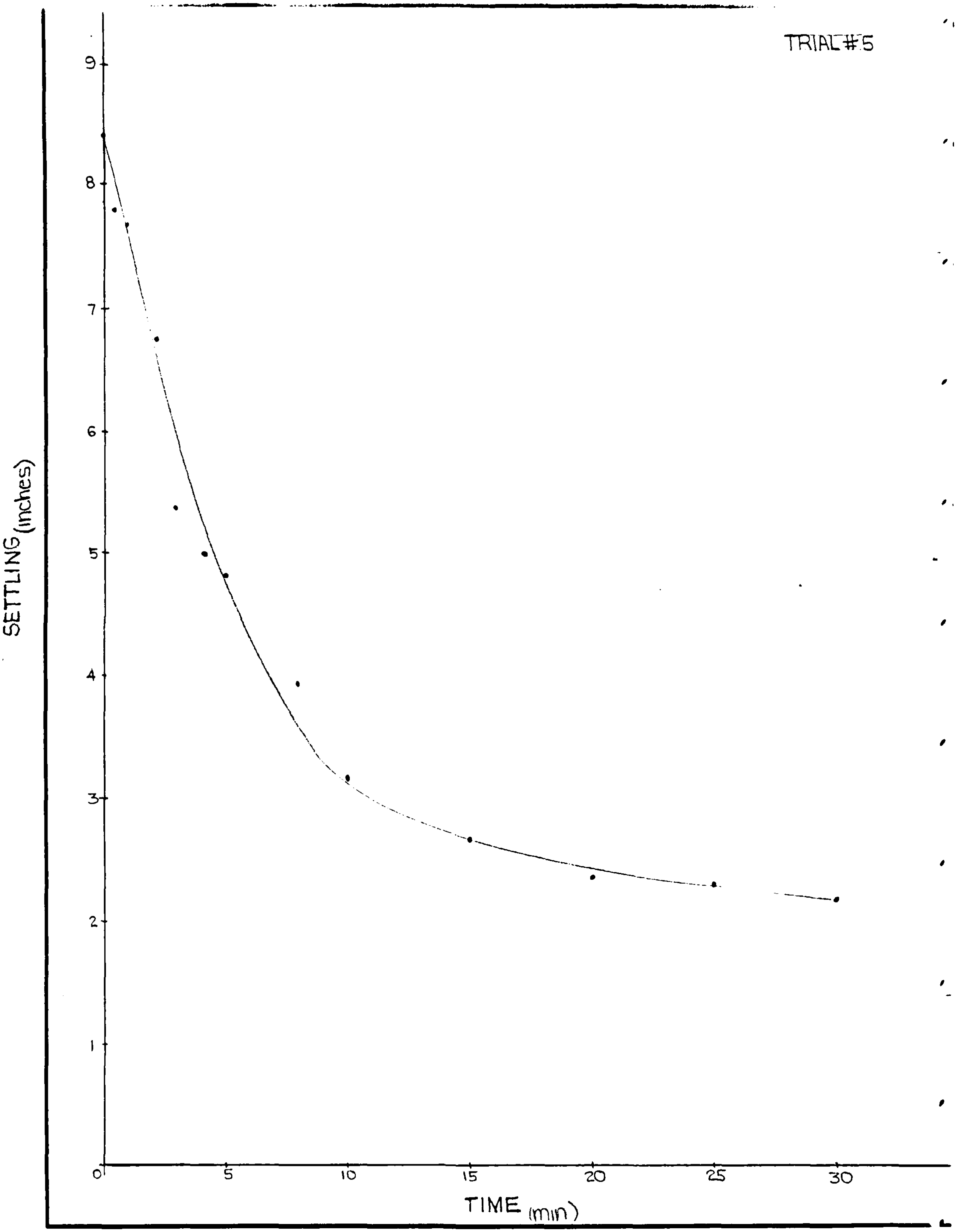

Fig. 6 SETTLING vs. TIME

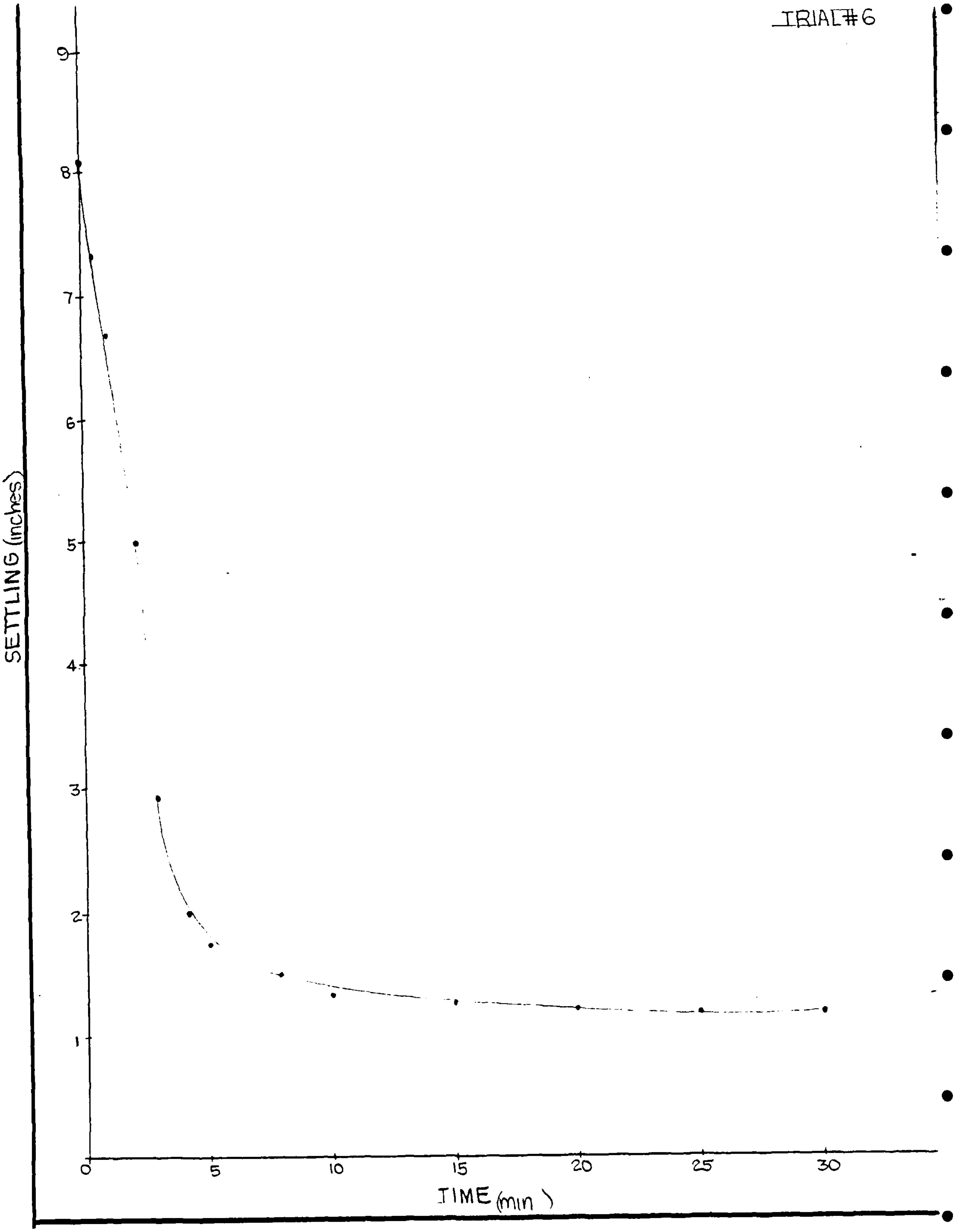

Fig. 7 SETTLING vs. TIME

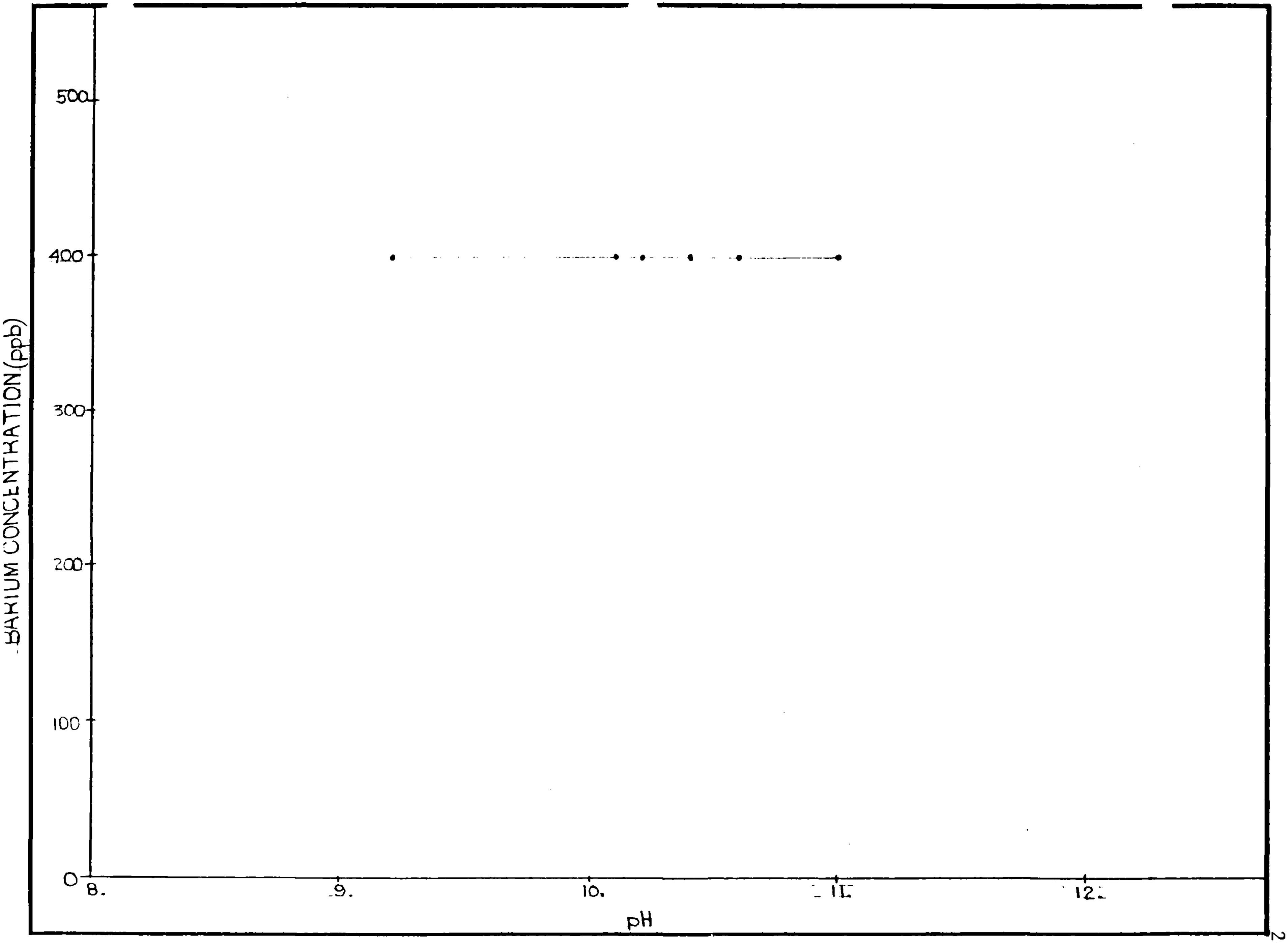

Fig. 8 BARIUM CONCENTRATION vs. pH

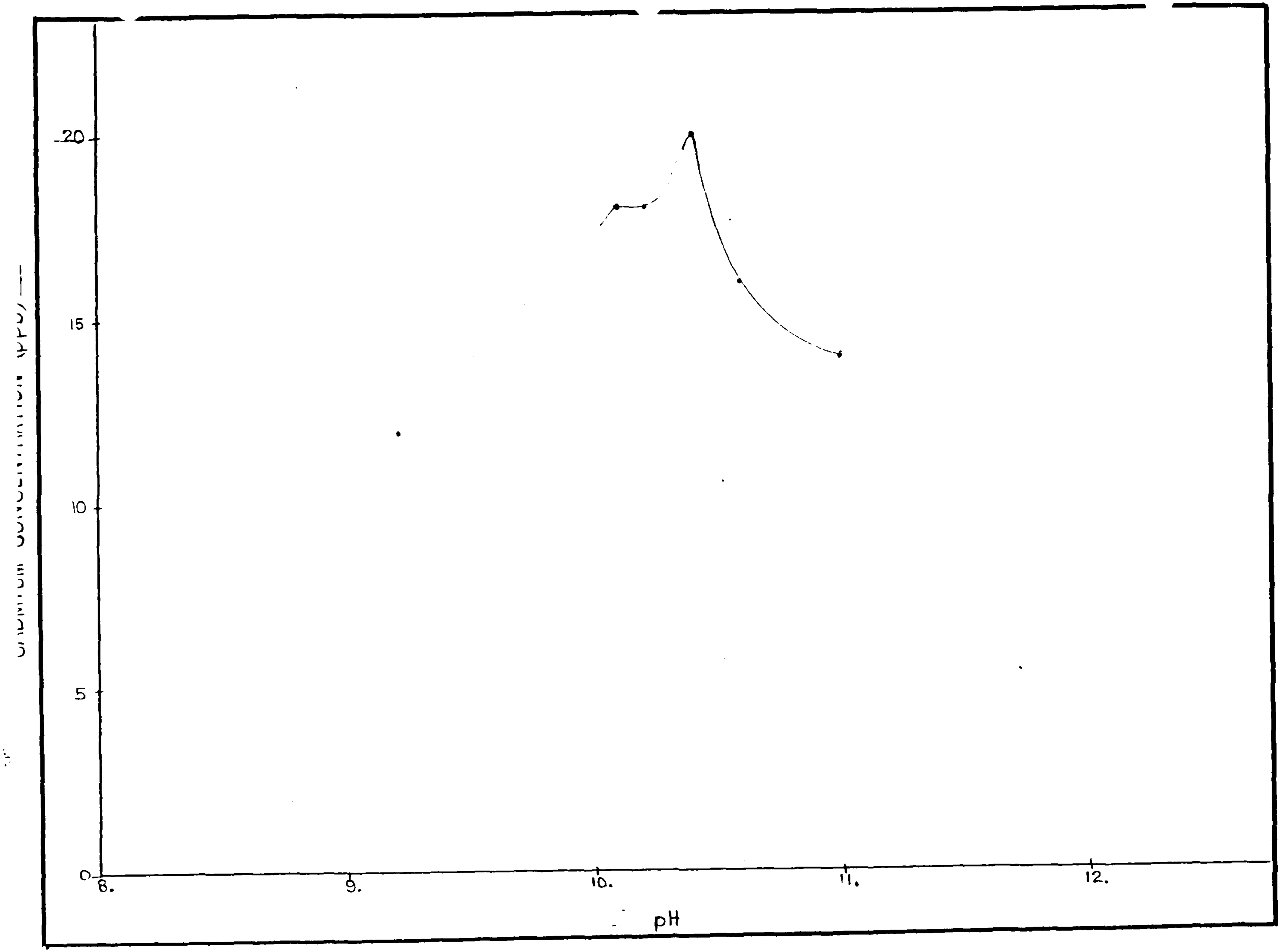

Fig.9 CADMIUM CONCENTRATION vs. pH

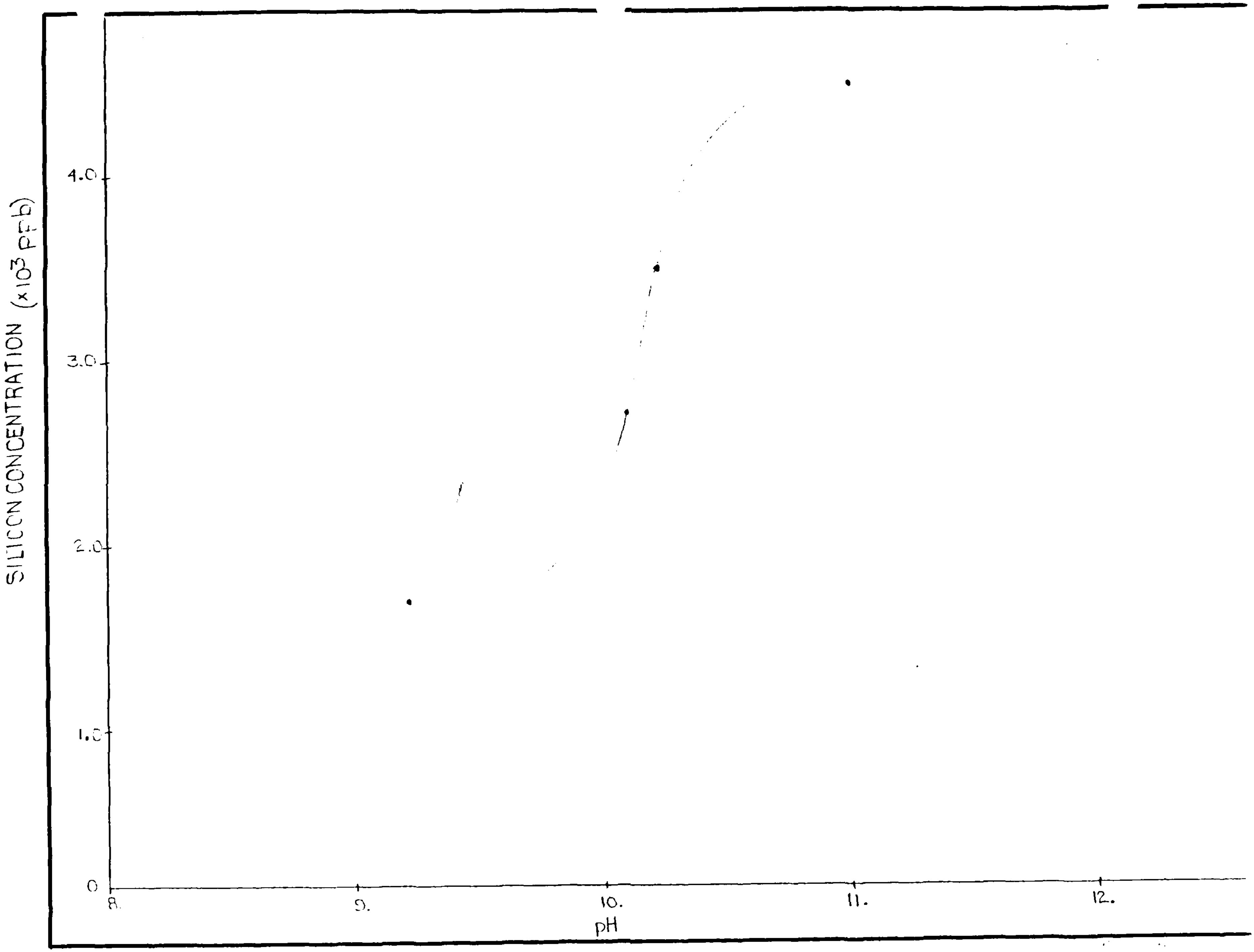

Fig. 10 SILICON CONCENTRATION vs. pH

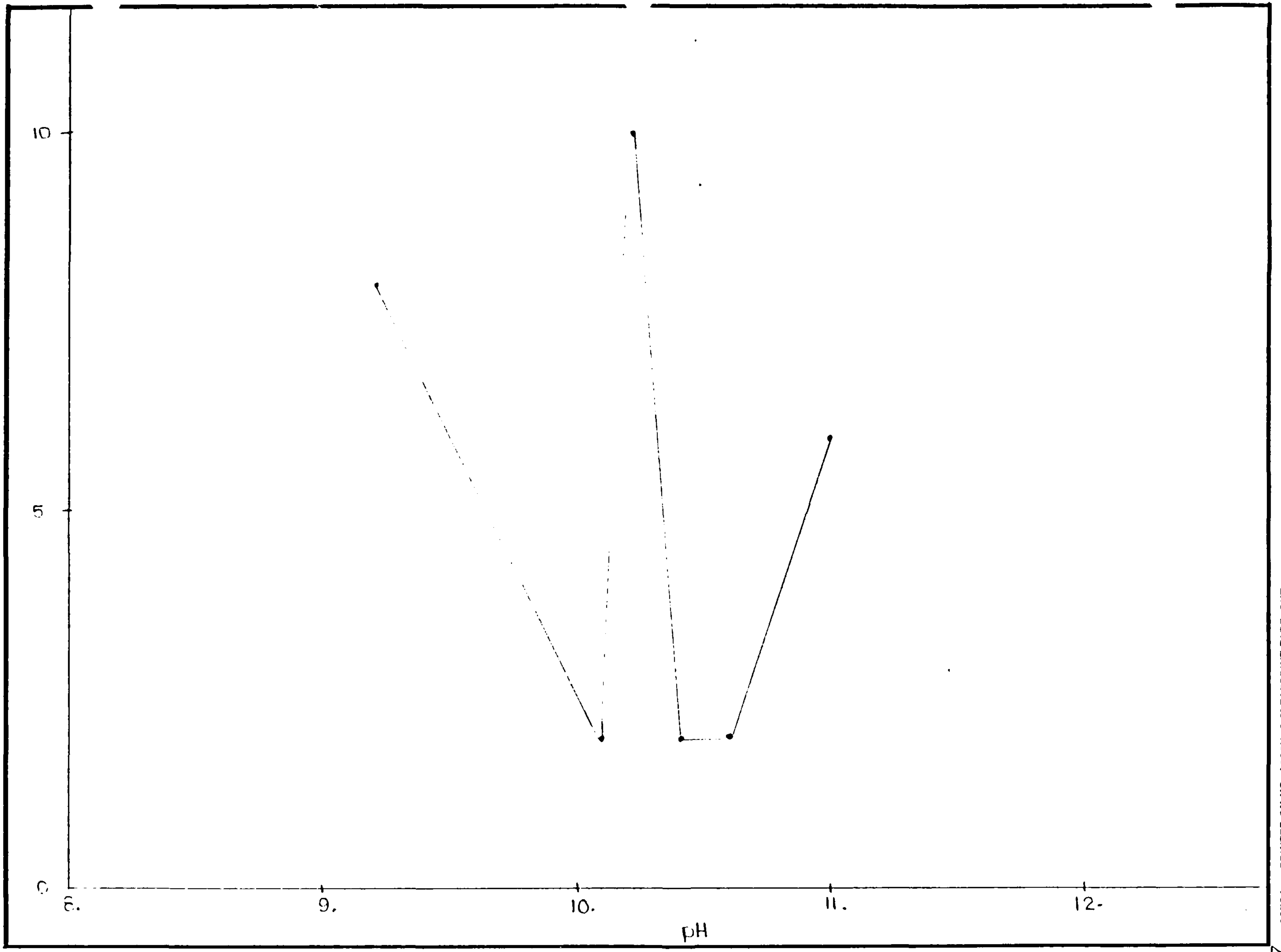

Fig. 11 CHROME CONCENTRATION vs.. pH

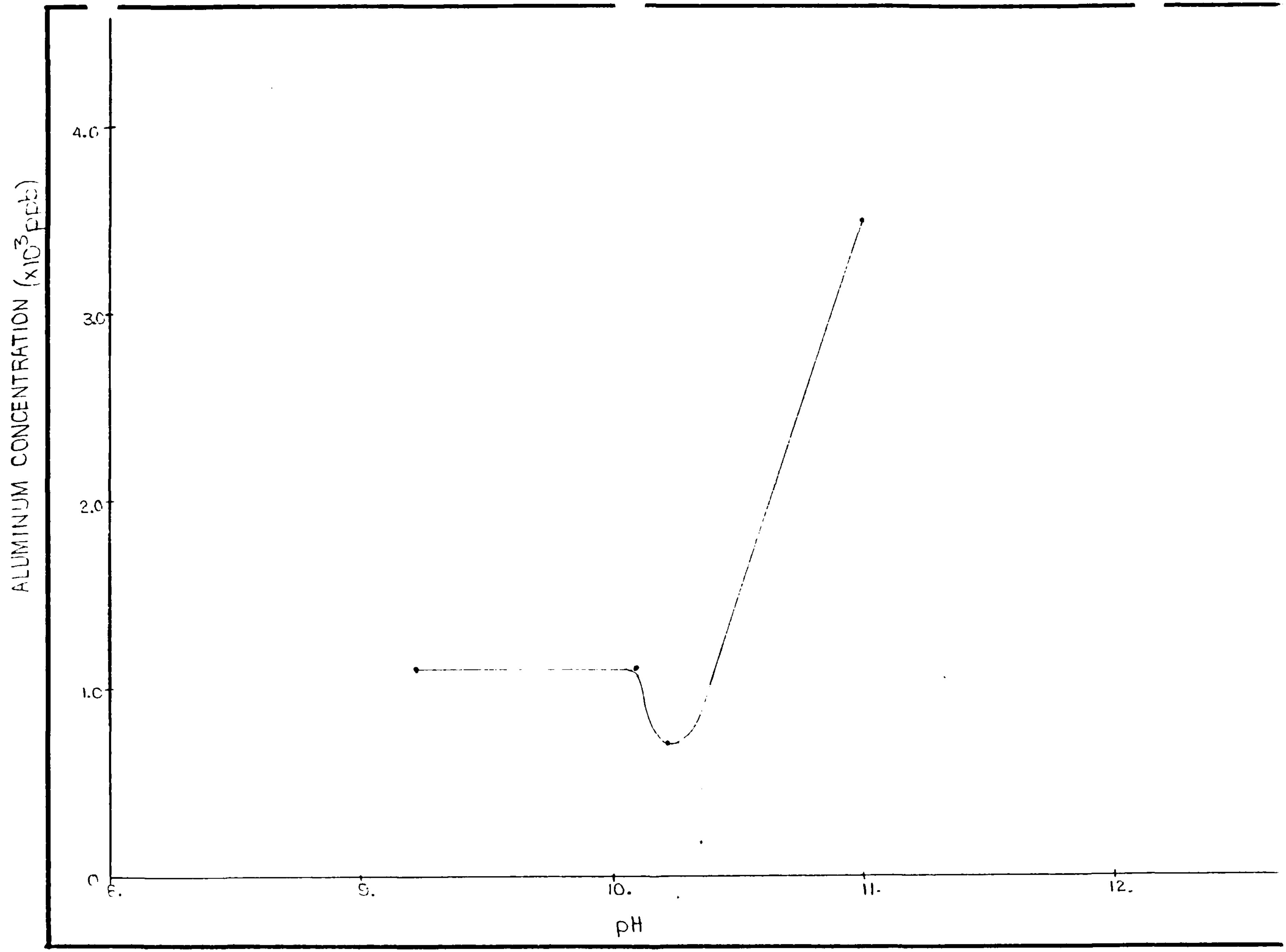

Fig. 12 ALUMINUM CONCENTRATION vs. pH

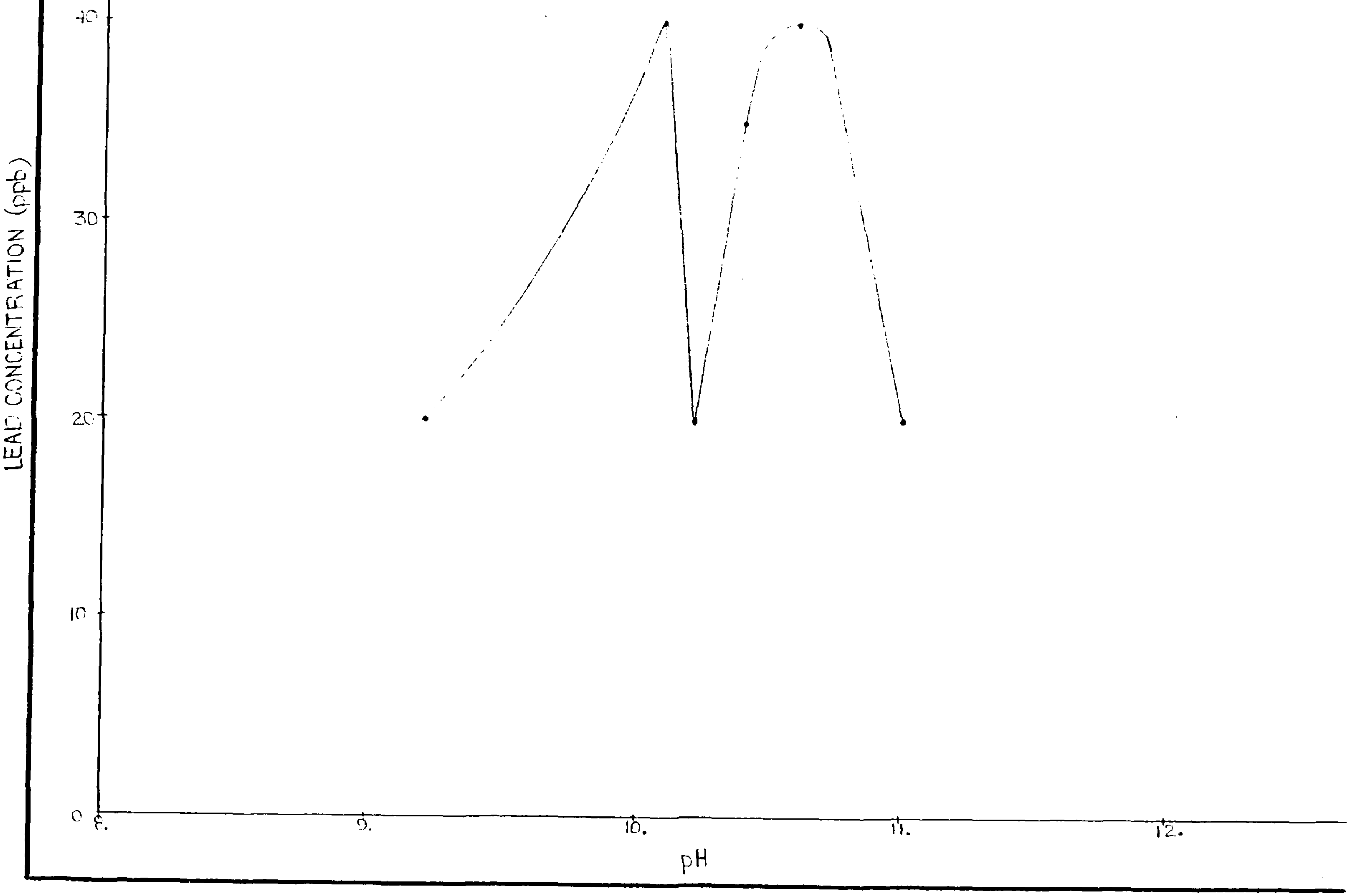

Fig. 13 LEAD CONCENTRATION vs. pH

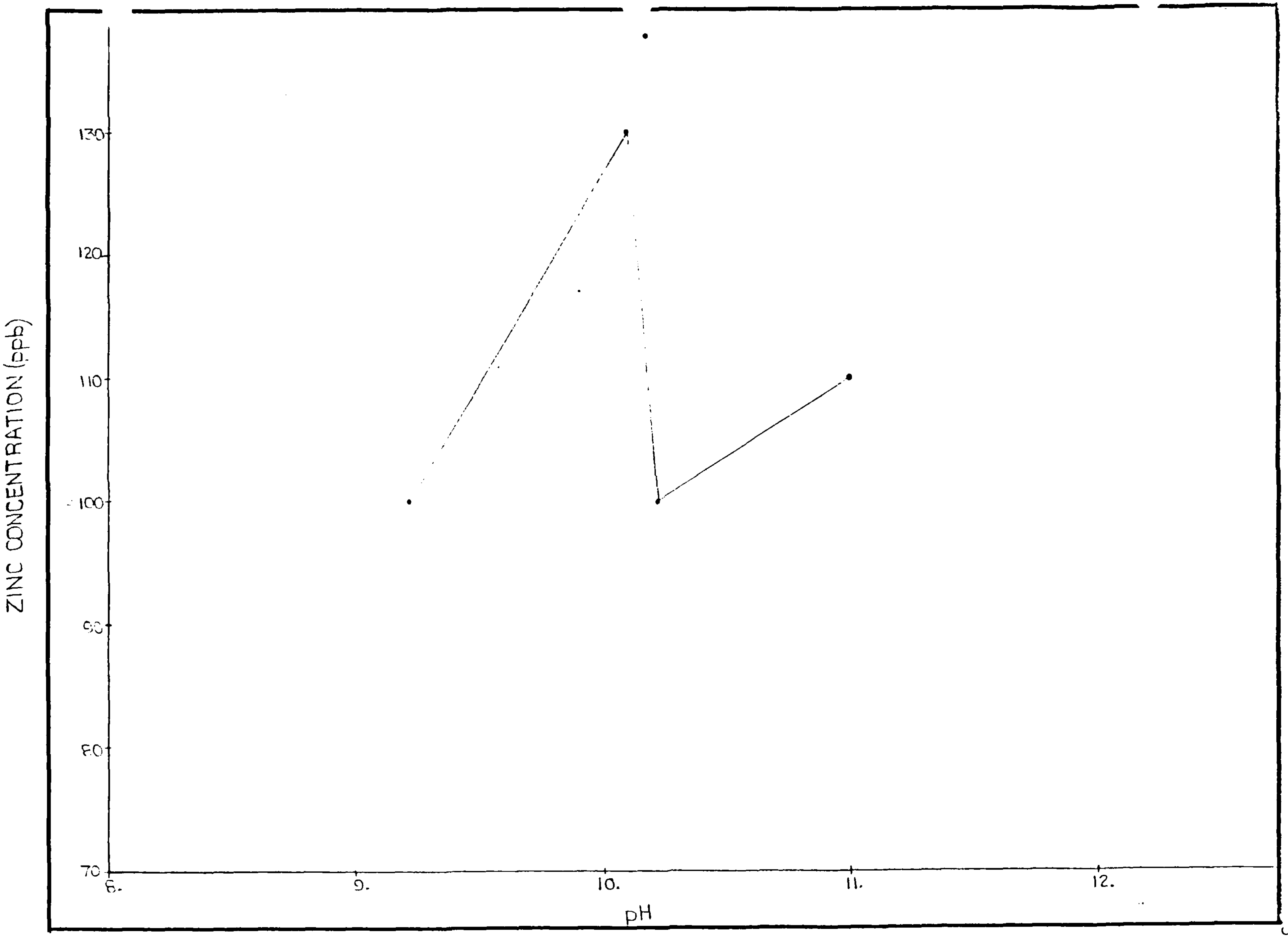

Fig. 14 ZINC CONCENTRATION vs. pH

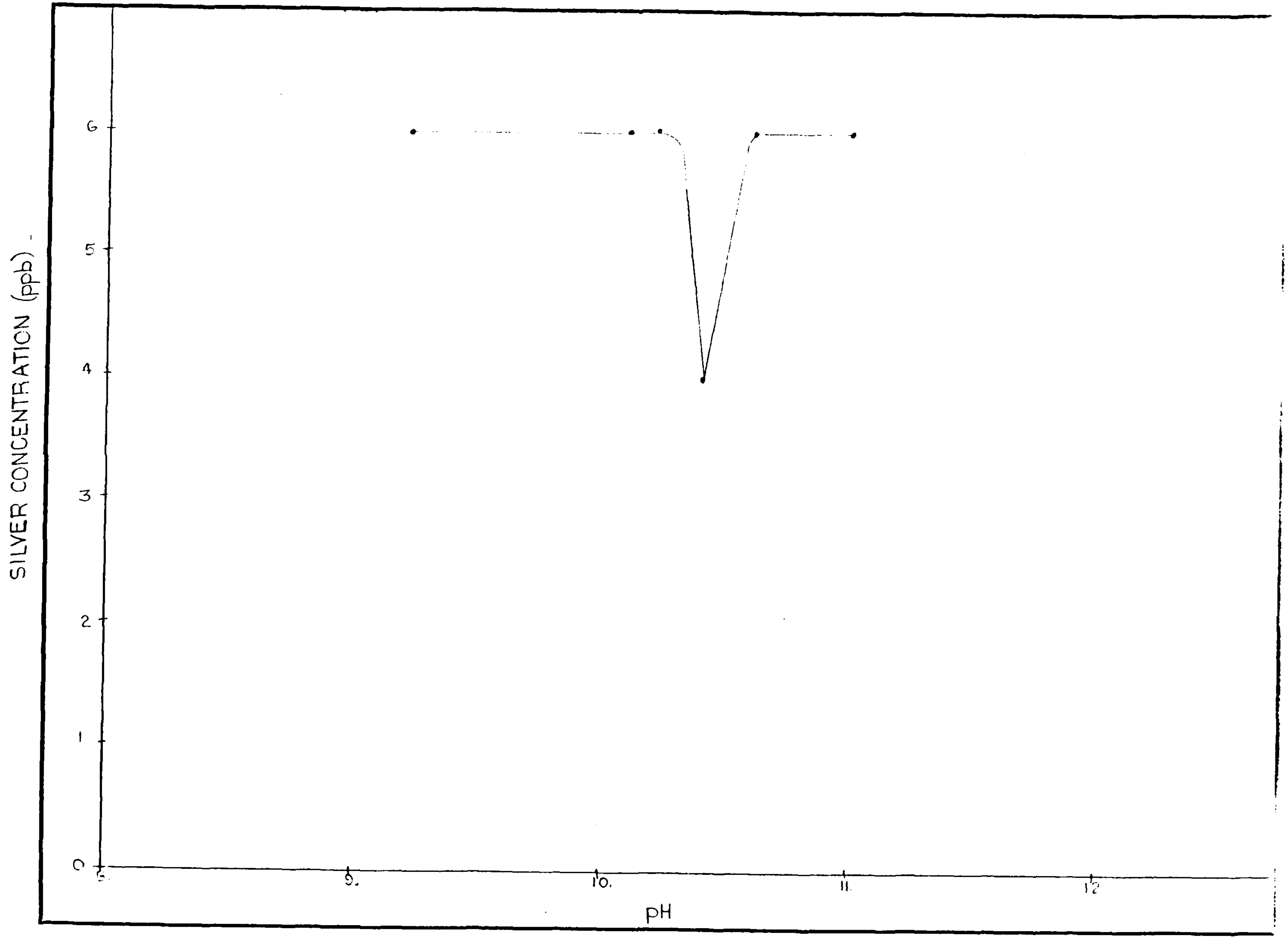

Fig. 15 SILVER CONCENTRATION vs. pH

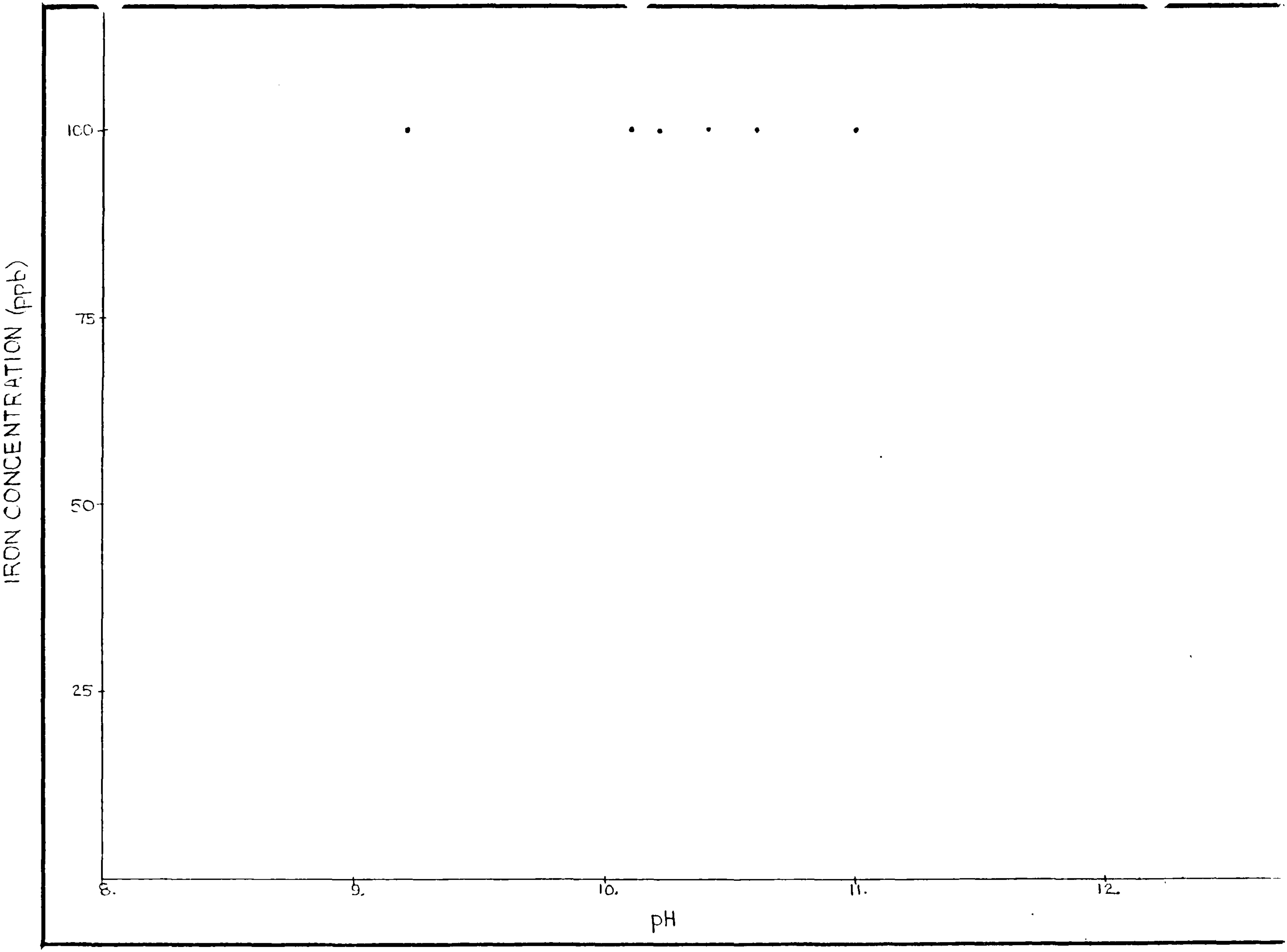

Fig. 16 IRON CONCENTRATION vs pH

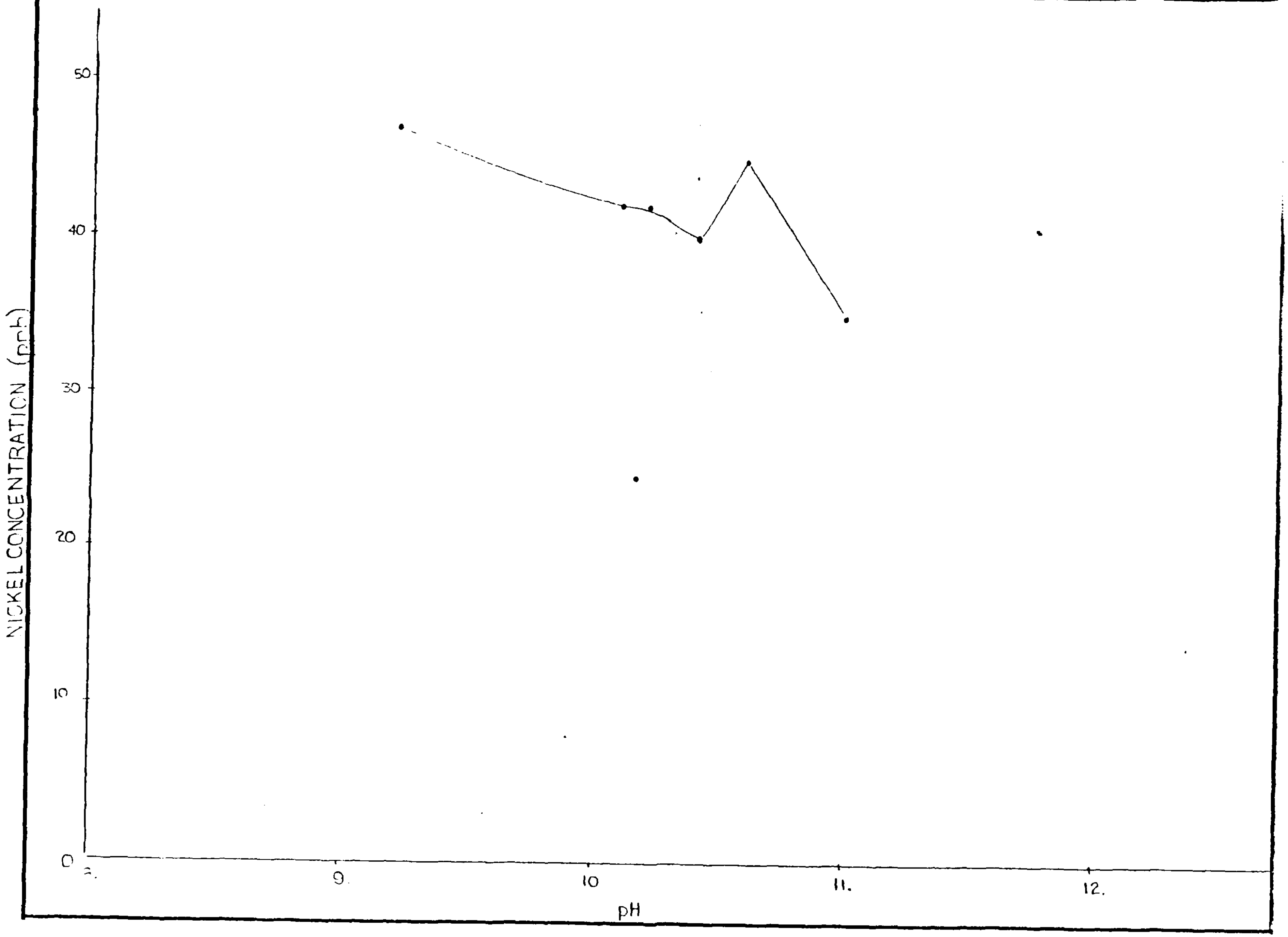

Fig. 17 NICKEL CONCENTRATION vs. pH

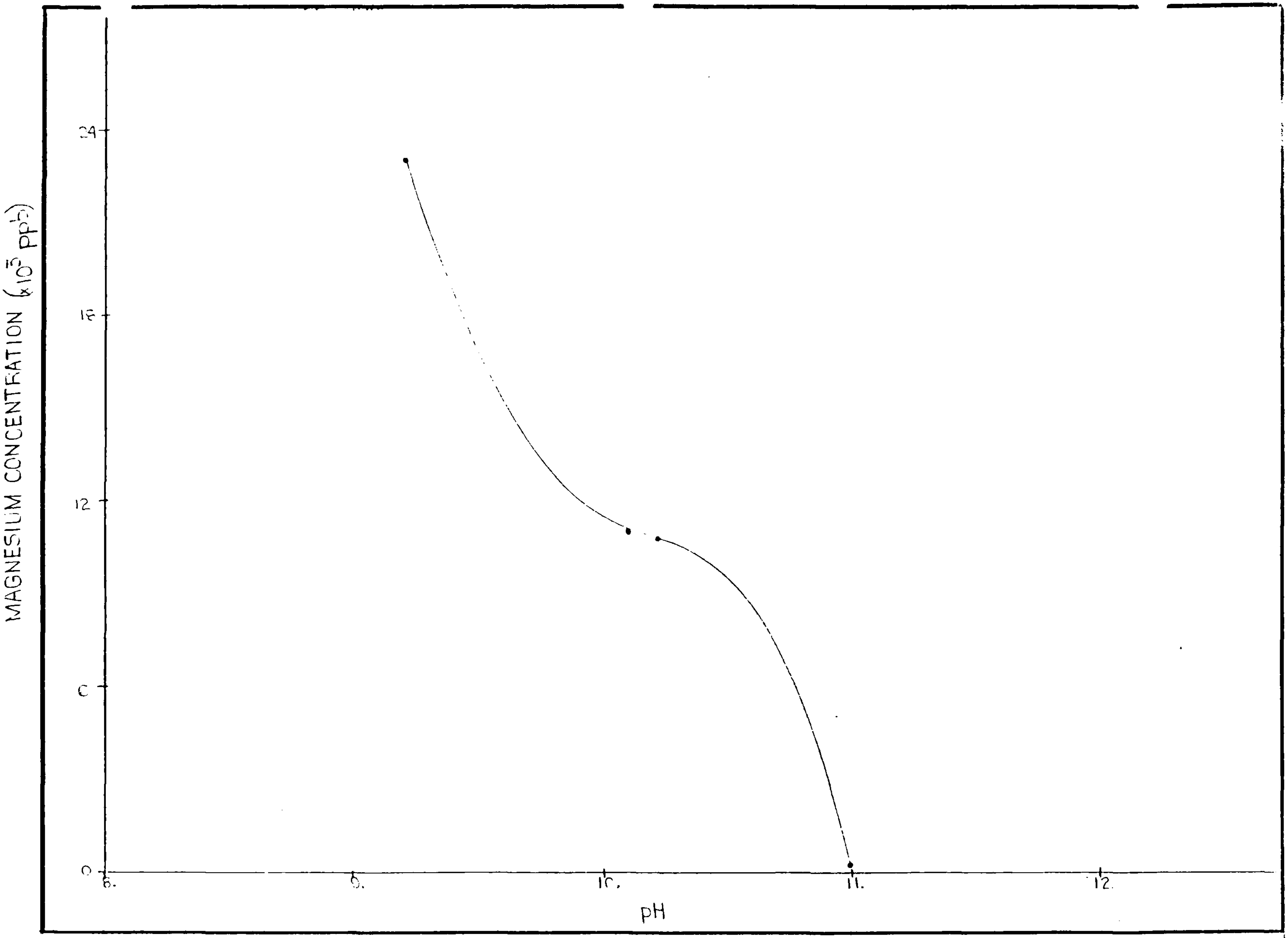

Fig. 18 MAGNESIUM CONCENTRATION vs. pH

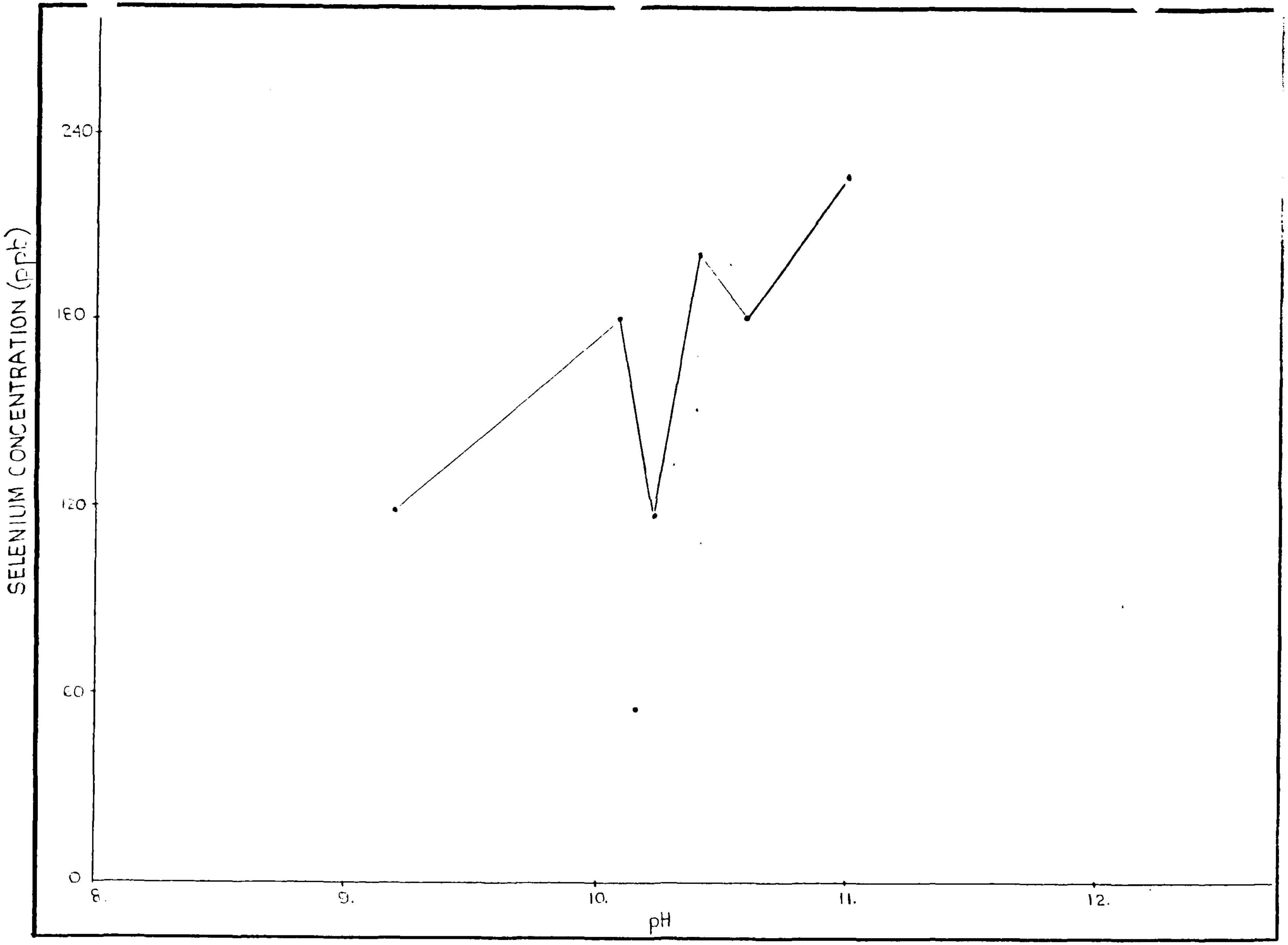

Fig. 19 SELENIUM CONCENTRATION vs. pH

PEM
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Du Pont Company / Polymer Products Dept. / Permasep* Products / Wilmington, DE 19898

BULLETIN 305

SPECIAL APPLICATIONS OF B-9 "PERMASEP" PERMEATORS

TABLE OF CONTENTS

A. INTRODUCTION

This section presents information on B-9 performance in special applications which generally use process and waste streams rather than natural waters. The data do not cover all the uses in which B-9 permeators have been employed. Pilot testing is recommended on all special situations to determine such factors as chemical compatibility, separation performance and fouling potential. Long-term system performance guarantees for special applications are available on the basis of the data obtained from pilot tests.

B. GENERAL CONSIDERATIONS

Several factors must be considered before using permeators on special applications. The concentration of the stream is important. As a general rule, the osmotic pressure of the brine stream should not exceed about 1,400 kPa (200 psi). Thus, B-9 permeators are usually not applicable for streams that are highly concentrated.

The constituents in the feed stream must be chemically compatible with the fiber as well as the other materials of construction in the permeator. If the feed contains strong oxidizing agents, e.g., Cl_2, O_3, or $KMnO_4$, they must be removed.

Since permeators are plastic mechanical devices and thereby subject to dimensional changes with time, they should be used with caution in medical or surgical applications. Permeators may not provide bacteria or pyrogen-free performance.

C. INDUSTRIAL APPLICATIONS

1. DEIONIZED WATER STREAMS

Permeators have been used to remove colloidal material, organics, and pyrogens from deionized water streams. For this application, the pH of the system must be carefully controlled. For normal applications, i.e., salt present in feedwater, the lower pH limit for the permeator is 4.0 for continuous operation. However, for deionized water with less than 10 mg/ℓ TDS (as ion), the pH of the feed, brine, and product streams must be $\geqslant 7.0$. The best approach to prevent fiber degradation is to adjust the feed pH to > 7.5 using base, e.g., NaOH, KOH, or NH_4OH. Proper in-line instrumentation must be used to accurately measure the pH.

2. ELECTROPAINTING

Many B-9 systems are purifying rinse water from electropainting lines. Typically the feed stream has a pH of 9 to 10 and its constituents include:

- Polyacrylic resin (~11 percent solids)
- Isopropyl alcohol (~2 percent)
- Butyl Cellusolve® (~2.5 percent)
- Methanol (~0.3 percent)
- Acetone (~0.2 percent)
- Triethylamine (~1.7 percent)

Both the brine and permeate are recycled back to the painting lines. Plants which operate at a low conversion (7.5 percent) have given excellent performance for over two years. Based on conductivity, these systems have rejections of about 95 percent.

3. NICKEL PLATING

B-9 permeators are being used for the closed-cycle recovery of nickel salts from the rinse of nickel plating operations. Both the product and brine are recycled back to the plating bath. The product water is used for rinsing while the brine is added back to the plating bath. Using a brine-staged system (3 stages), conversions of up to 95 percent have been obtained with removal of 92 percent of the nickel from the feed stream. The pH of the feed stream is usually 4.5. The data in Table I, B-9 Separation Performance on Nickel

TABLE I
B-9 SEPARATION PERFORMANCE* ON NICKEL PLATING RECOVERY

Ion	Concentration in Feed (mg/ℓ as ion)	Concentration in Product (mg/ℓ as ion)	% Rejection
Ni^{++}	4,610	230	95.0
$SO_4^{=}$	3,924	53	98.6
Cl^-	2,580	270	89.5

*Feed pressure = 2,760 kPa (400 psig); feed temperature = 12°C; conversion - 75%.

[illegible]

Plating Recovery, show the separation performance of a system operating at 75 percent conversion.

D. SEPARATION PERFORMANCE FROM LABORATORY AND FIELD TESTS

1. ORGANIC ACIDS AND THEIR SODIUM SALTS

Separation data for dilute solutions of organic acids and their sodium salts are given in Table II, Separation of Organic Acids and their Salts by B-9 Permeators.

As the pH is increased, a rapid increase in rejection occurs where formation of the salt form occurs (Figure 1, Effect of pH on Rejection of Organic Acids). The difference between rejection of the acid form and the salt form is particularly dramatic for acids with a low dissociation constant, e.g., phenol or acids with low molecular weights, e.g., formic and acetic acid.

The data in Table II also show the effect of molecular weight of organic acids on rejection. The relationships between molecular weight and rejection for three straight-chain acids is shown in Figure 2, Effect of Molecular Weight on Rejection of Organic Acids. Molecular weight "cut off" for 90 percent rejection of the acid form appears to be approximately 120 to 130 for this series.

The effect of molecular size on rejection of organic acids can be seen by comparing the data in Table II.

TABLE II
SEPARATION OF ORGANIC ACIDS AND THEIR SALTS BY B-9 PERMEATORS*

Compounds	Molecular Weight	Dissociation Constant	Feed Concentration (mg/ℓ)	Feed pH	Percent Rejection
Formic Acid HCOOH	46	1.77×10^{-4}	500	3.2	50
Sodium Formate	68	—	740	6.9	94
Acetic Acid CH_3COOH	60	1.75×10^{-5}	500	3.7	40
Sodium Acetate	82	—	680	8.1	98
n-Butyric Acid $CH_3CH_2CH_2COOH$	88	1.51×10^{-5}	500–2,000	2.8–4.2	70
Sodium Butyrate	110	—	2,500	7.0	98
Phenol C_6H_5OH	94	1.28×10^{-10}	500–2,000	7.0–9.0	55
Sodium Phenolate	116	—	2,500	10.7	95
Pivalic Acid $(CH_3)_3C—COOH$	102	8.91×10^{-6}	500–2,000	4.0	98
Sodium Pivalate	124	—	2,400	8.1	99
n-Caproic Acid $CH_3(CH_2)_4COOH$	116	1.32×10^{-5}	500	4.2	87
Sodium Caproate	138	—	600	7.8	99
Benzoic Acid C_6H_5COOH	122	6.32×10^{-5}	500	3.7	83
Sodium Benzoate	144	—	590	8.1	99
Oxalic Acid HOOC—COOH	90	K_1 6.5×10^{-2} K_2 6.1×10^{-5}	500–2,000	2.2	94
Di-Sodium Oxalate	134	—	2,980	6.7	98
Adipic Acid $HOOC(CH_2)_4COOH$	146	K_1 3.7×10^{-5} K_2 3.87×10^{-5}	500–2,000	2.7–4.3	95
Di-Sodium Adipate	190	—	2,600	5.6–10	99

*Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 20°C; conversion = 75%.

2. CARBOHYDRATES AND GLYCOLS

Rejection data obtained for carbohydrates are given in Table III, Separation of Carbohydrates and Glycols by B-9 Permeators. Excellent rejection was obtained for dilute solutions of saccharides and glycols with molecular weight 100. As shown in Figure 3, Effect of Molecular Weight on Rejection for Carbohydrates and Glycols, a sharp break in the rejection curve occurs at a molecular weight of approximately 100. This molecular weight "cut-off" is consistent with that for other small, neutral, linear organic compounds.

3. ALCOHOLS

Rejection data for alcohols obtained with B-9 permeators are given in Table IV, Separation of Alcohols by B-9 Permeators. For straight-chain alcohols, rejection increases with molecular weight up to about 70% rejection (Figure 4, Effect of Molecular Weight on Rejection for Straight-Chain Alcohols). Straight-chain alcohols with molecular weight > 102 were not investigated because of their low water solubility.

The effect of branching on rejection can be seen in Table V, Effect of Branching on Rejection of Alcohols.

Figure 1. Effect of pH on Rejection of Organic Acids

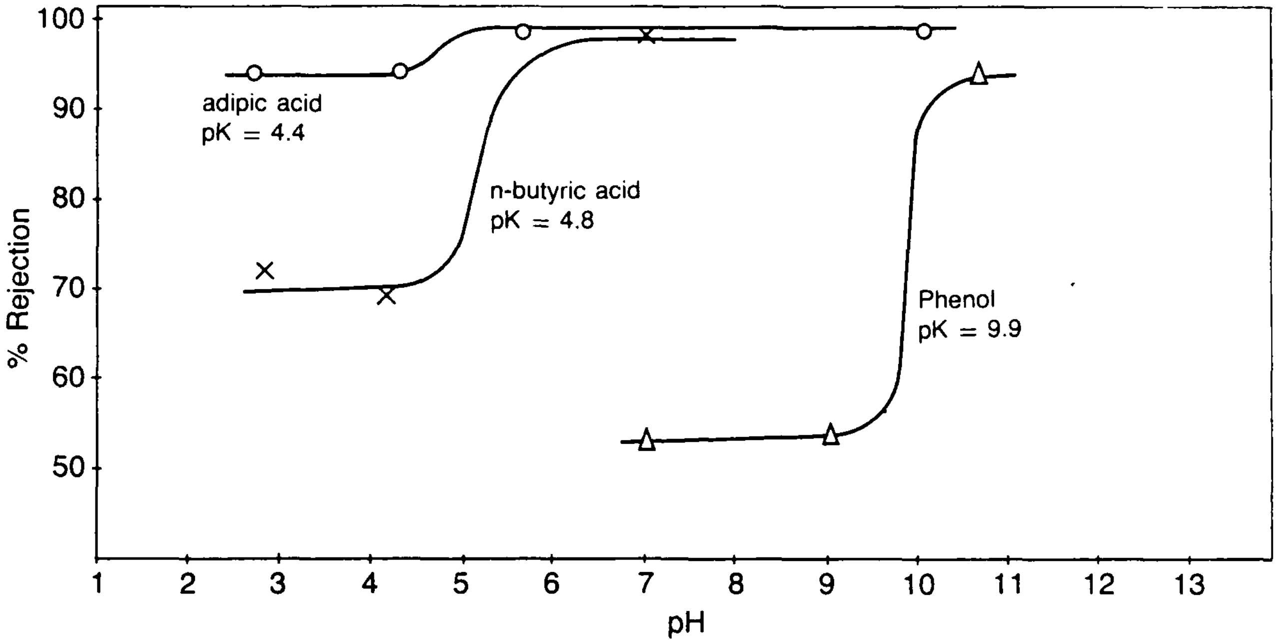


Figure 2. Effect of Molecular Weight on Rejection of Organic Acids

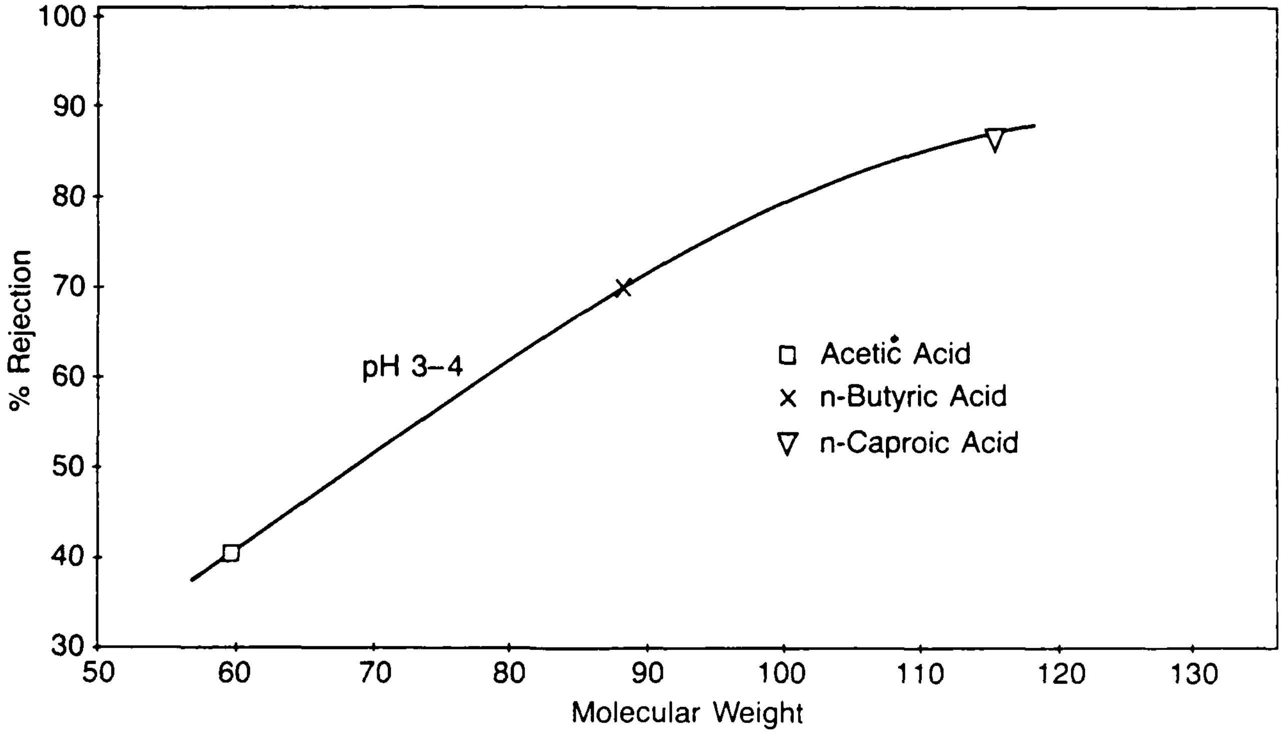


TABLE III
SEPARATION OF CARBOHYDRATES AND GLYCOLS BY B-9 PERMEATORS[a]

Compound	Molecular Weight	Feed Concentration (mg/l)	Percent Rejection[b]
Raffinose $C_{18}H_{32}O_{16}$ Trisaccharide	504	2,000	99.4
Sucrose $C_{12}H_{22}O_{11}$ Disaccharide	342	500–2,000	99.8
Sorbitol $C_6H_{14}O_6$ 6-c polyol	182	2,000	99.6
Glucose $C_6H_{12}O_6$ Monosaccharide	180	500–2,000	99.0
Arabinose $C_5H_{10}O_5$ 5-c sugar	150	2,000	98.9
Glycerol $CH_2OH\text{-}CHOH\text{-}CH_2OH$ 3-c polyol	92	500–2,000	90.0
Ethylene Glycol $CH_2OH\text{-}CH_2OH$ 2-c polyol	62	2,000	28.0

[a] Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 20°C; conversion = 75%.

[b] Rejection based on total organic carbon analyses.

Figure 3. Effect of Molecular Weight on Rejection for Carbohydrates and Glycols

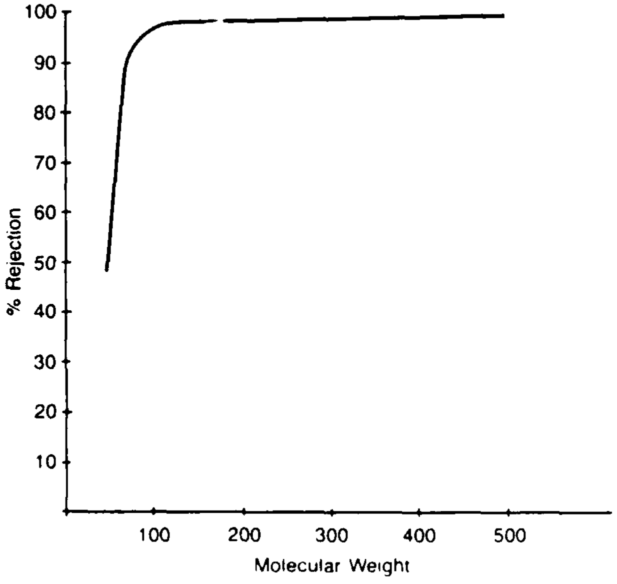


Figure 4. Effect of Molecular Weight on Rejection for Straight Chain Alcohols

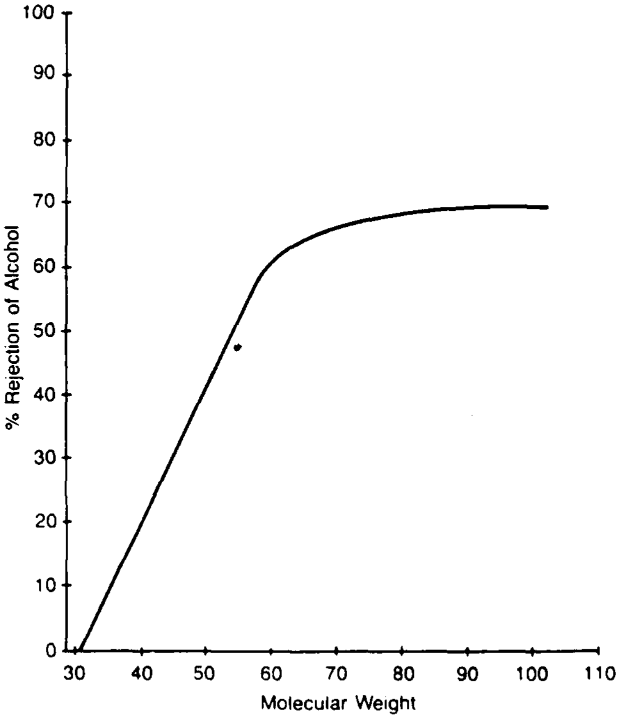


TABLE IV
SEPARATION OF ALCOHOLS BY B-9 PERMEATORS*

Alcohol	Molecular Weight	Feed Concentration (mg/ℓ)	Percent Rejection
Methyl CH_3OH	32	500–2,000	0
Ethyl CH_3CH_2OH	46	500–2,000	28
n-Propyl $CH_3CH_2CH_2OH$	60	500–2,000	62
n-Butyl $CH_3(CH_2)_2CH_2OH$	74	500–2,000	65
n-Amyl $CH_3(CH_2)_3CH_2OH$	88	500–2,000	68
n-Hexyl $CH_3(CH_2)_4CH_2OH$	102	500	68
iso-Propyl	60	500–2,000	75
iso-Butyl $(CH_3)_2CHCH_2OH$	74	500–2,000	95
iso-Amyl $(CH_3)_2CHCH_2CH_2OH$	88	500	90
sec-Butyl $CH_3CH_2CHOHCH_3$	74	2,000	77
t-Butyl $(CH_3)_3COH$	74	500–2,000	96

*Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 20°C; conversion = 75%.

TABLE V
EFFECT OF BRANCHING ON REJECTION OF ALCOHOLS*

Alcohol	Molecular Weight	% Rejection
n-Butyl $CH_3(CH_2)_2CH_2OH$	74	65
sec-Butyl $CH_3CH_2CHOHCH_2$	74	77
iso-Butyl $(CH_3)_2CHCH_2OH$	74	95
t-Butyl $(CH_3)_3COH$	74	96

*Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 20°C; conversion = 75%.

Steric effects (branching) appear to be more important with respect to rejection than molecular weight. This can be seen from Table V as well as from Table IV.

4. PHENOLS

Separation data for substituted phenols from dilute solution is shown in Table VI, Rejection of Substituted Phenols. Both molecular weight and size affect the rejection of phenols. However, the most important factor in regard to phenol rejection is pH. Thus, when the pH was increased with sodium hydroxide to form the sodium salts, the rejection increased significantly (Table VI).

5. AMMONIUM AND NITRATE IONS

Separation data for dilute solutions of ammonium and nitrate ions are given in Table VII, Separation of Ammonium and Nitrate Ions.

For the test conditions used, rejection of nitrate ion appears to be essentially independent of feed pH. Similarly, ammonium ion rejection is independent of feed pH for acidic or neutral feeds. A higher passage of ammonium ion would be expected for basic conditions because NH_3 would form. Thus, acidic conditions are recommended for the maximum rejection of ammonium ion.

6. BORIC ACID AND ITS SODIUM SALT

Separation data for a 300 mg/ℓ H_3BO_3 solution are shown in Figure 5, Borate Rejection by B-9 Permeators. As the pH increases and salt formation occurs, the rejection increases dramatically.

7. ACID MINE DRAINAGE

Field tests have been performed using B-9 permeators to purify acid mine drainage. The data which was obtained is given in Table VIII, B-9 Performance on Acid Mine Drainage. Excellent rejection was obtained over the test period (1,667 hours) at a pH of 3.4. High levels of Fe^{++}, Mn^{++}, and Al^{+++} were present in the feed stream. The feed pH was below the Guideline minimum pH of 4.0 for continuous operation.

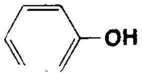
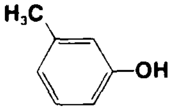
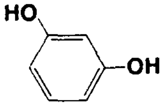
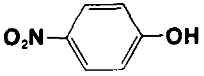
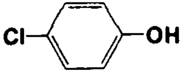
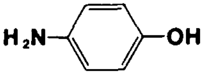
8. HEAVY METALS

Various laboratory and field data show excellent rejection of heavy metals by B-9 permeators. Although the feed pH and exact form of the metal ions can influence the rejection, the separation data given in Table IX, Rejection of Trace Metals by B-9 Permeators, can be used as a guide for trace metal rejection.

9. RADIOACTIVE CONTAMINANTS

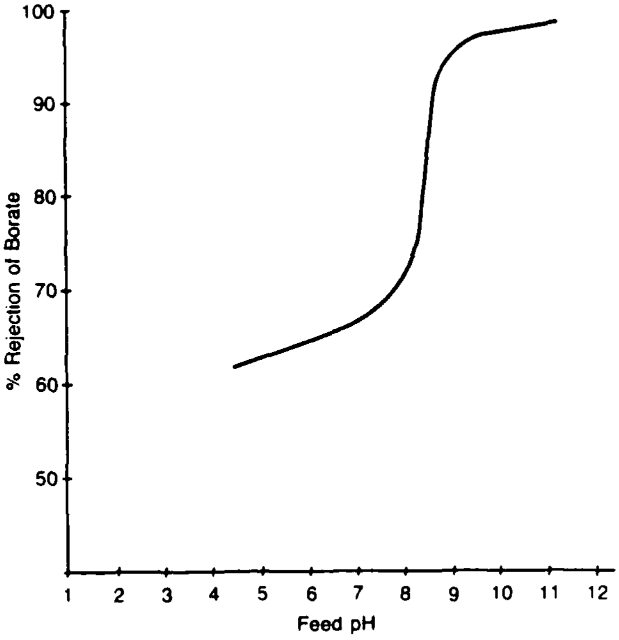
Field data show excellent rejection of radioactive materials when present in trace amounts in the feed water. For example, Ra-226 is rejected by about 96 percent. Since dissolved ionic radioactive ions behave the same as the non-radioactive ion, rejections for any radioactive ion can be estimated from the rejection of corresponding non-radioactive ion.

TABLE VI
REJECTION OF SUBSTITUTED PHENOLS[a,b]

Phenols	Molecular Weight	Dissociation Constant	Feed pH	Percent Rejection
Phenol 	94	1.28×10^{-10}	7–9 11	55 95
m-Cresol 	108	9.8×10^{-11}	7 11	74 94
Resorcinol 	110	1.55×10^{-10}	4–7 10	63 85
p-Nitrophenol 	139	6.5×10^{-8}	6	56
p-Chlorophenol 	128	7.0×10^{-10}	7	51
p-Aminophenol 	109	—	7	84

[a] Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 20°C; conversion = 75%.
[b] All feed concentrations were 2,000 mg/ℓ.

Figure 5. Borate Rejection by B-9 Permeators



Test conditions used were: feed pressure = 2760 kPa (400 psig) feed temperature = 20°C and conversion = 75%

Feed pH adjusted with NaOH

TABLE VII
SEPARATION OF AMMONIUM AND NITRATE IONS[a]

Ion[b]	Feed pH	Percent Rejection
NO_3^-	7.0	80
NO_3^-	9.2	84
NO_3^-	11.1	86
NH_4^+	6.9	85
NH_4^+	5.3	85
NH_4^+	3.2	84

[a] Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 20°C; conversion = 75%.
[b] For NO_3^- test, 1,500 mg/ℓ NO_3^- (added as $NaNO_3$) was the feed concentration and the pH was adjusted with NaOH. For NH_4^+ test, 500 mg/ℓ NH_4^+ (added as NH_4NO_3) was the feed concentration and the pH was adjusted with HCl.

TABLE VIII
B-9 PERFORMANCE[a] ON ACID MINE DRAINAGE

Ion	Feed Concentration (mg/ℓ as ion)	% Rejection
Ca^{++}	111	99.3
Mg^{++}	83	99.2
Fe^{++}	70	99.1
Mn^{++}	14	99.1
Al^{+++}	8	97.4
$SO_4^{=}$	774	99.6
SiO_2	11	92.5
TDS	1,319	98.1
pH	3.4	—

[a] **Test conditions used were: Feed pressure = 2,760 kPa (400 psig); feed temperature = 12.5°C; conversion = 75%; brine-staged plant (2:1).**

TABLE IX
REJECTION[a] OF TRACE METALS BY B-9 PERMEATORS

Metal	% Rejection[b]
As^{+3}	~60
As^{+5}	>95
Ba^{++}	>95
Cd^{++}	>95
Cr^{+6}	>95
Cu^{++}	>95
Se^{+4}	>95
Se^{+6}	>95
Zn^{+2}	>90

[a] **Test conditions used were: For dilute solutions feed pressure = 2,760 kPa (400 psig); feed temperature = 25°C; conversion = 75%.**

[b] **Rejection may vary with pH and exact ion form. Use rejections as a guide only.**

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1. Otten, G., *American Laboratory*, July 1972.
2. Mattair, R., and Kellar, J. B., "Closed Loop Recovery of Nickel Plating Rinse", paper presented at the 75th National Meeting American Institute of Chemical Engineers, Detroit, Michigan, June 4, 1973.
3. "Reverse Osmosis Demineralization of Acid Mine Drainage", U.S. EPA Program No. 14010 FQR, March 1972.
4. Donnelly, R. G., Goldsmith, R. L., et al., Plating 61, 432 (1974) (B-9 for Plating Bath Applications).
5. Goldsmith, R. L., et al., Paper presented at American Electroplaters' Soc., 61st Annual Conference, Chicago 1974, "RO Treatment of Copper Cyanide Rinse Water."

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This treatment is used to prevent formation of calcium carbonate films on zeolites and other ion-exchange materials. It is simpler and requires less constant supervision than recarbonation and is, therefore, well adapted to small public water-supply systems. Its main disadvantage is the hazard of handling sulfuric acid.

Cold Lime-Barium Treatment. This process is restricted to industrial uses and should not be employed for the treatment of drinking water because barium is a poison, even in small amounts, when taken internally. The treatment has very limited application. It is uneconomical because of the relatively high cost of barium salts, which is several times the cost of soda ash.

Barium is an efficient reagent for removal of noncarbonate hardness in the form of calcium and magnesium sulfates. The reactions which occur when barium carbonate is added to water containing such noncarbonate hardness are as follows:

$$\underset{\substack{\text{Calcium sulfate}\\ \text{(soluble)}}}{CaSO_4} + \underset{\substack{\text{Barium carbonate}\\ \text{(soluble)}}}{BaCO_3} \rightarrow \underset{\substack{\text{Barium sulfate}\\ \text{(insoluble)}}}{BaSO_4} + \underset{\substack{\text{Calcium carbonate}\\ \text{(insoluble)}}}{CaCO_3}$$

$$\underset{\substack{\text{Magnesium sulfate}\\ \text{(soluble)}}}{MgSO_4} + \underset{\substack{\text{Hydrated lime}\\ \text{(soluble)}}}{Ca(OH)_2} + \underset{\substack{\text{Barium carbonate}\\ \text{(soluble)}}}{BaCO_3} \rightarrow \underset{\substack{\text{Barium sulfate}\\ \text{(insoluble)}}}{BaSO_4} + \underset{\substack{\text{Calcium carbonate}\\ \text{(insoluble)}}}{CaCO_3} + \underset{\substack{\text{Magnesium hydrate}\\ \text{(insoluble)}}}{Mg(OH)_2}$$

For each part per million of sulfate noncarbonate hardness, expressed as calcium carbonate, there is required 1.97 ppm of barium carbonate, or 0.017 lb per 1,000 gal of water treated. This dosage does not include a slight excess required to insure complete reaction.

This process is not practical for removing sodium sulfate, since an equivalent amount of soda ash remains in the water as a result of the reaction:

$$\underset{\substack{\text{Sodium}\\ \text{sulfate}}}{Na_2SO_4} + \underset{\substack{\text{Barium}\\ \text{carbonate}}}{BaCO_3} \rightarrow \underset{\substack{\text{Barium}\\ \text{sulfate}}}{BaSO_4} + \underset{\substack{\text{Sodium}\\ \text{carbonate}}}{Na_2CO_3}$$

By this reaction, the alkalinity of the water and also the total dissolved solids are increased.

Cold Lime-Zeolite Softening. This type of softening has a number of modifications and has been fairly extensively employed in recent years for conditioning boiler feedwater. The process consists in the reduction of the carbonate hardness by the addition of hydrated lime and, usually, a coagulant to speed up settling of insoluble calcium carbonate formed. The effluent is then discharged to zeolite softeners, where complete softening takes place. It is customary to filter the pretreated water before it is applied to the zeolite units, but in some cases filters are omitted. The omission of filters is practical if the residual calcium carbonate floc carried by the water is dissolved by recarbonation effected by bubbling carbon dioxide gas through the water or by the addition of sulfuric or hydrochloric acid. Sulfur dioxide, generated by burning sulfur, can also be used for this purpose. Where this gas is employed, it is preferable to put it into solution in water, thereby forming sulfurous acid. The reaction is:

$$\underset{\text{Sulfur dioxide}}{SO_2} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Sulfurous acid}}{H_2SO_3}$$

SILICA REMOVAL

Silica can be removed from water by precipitation methods which may accompany clarification or cold- or hot-process softening, the latter being more efficient.* Most of the precipitates formed in the softening or clarification of water will adsorb some silica, especially compounds of alkaline-earth and metallic elements. Of these, calcium carbonate is least effective, and freshly formed hydroxides of iron, magnesium, and aluminum are most effective. Only ferric and magnesium compounds have been employed commercially to an appreciable extent. One investigator used ammonium zincate and sodium hydroxide in laboratory studies[15] but concluded that the ammonia made the process unsuitable for boiler-feedwater purification. Aluminum hydroxide, precipitated from sodium aluminate at a pH of 8.3 to 8.7, was found by Lindsay and Ryznar[16] to reduce silica from over 6 ppm to less than 2 ppm, but the dosage required was excessive. Subsequently, the Alhydro process of preparing aluminum hydroxide electrolytically from an aluminum anode was proposed for silica-removal treatment.[17] Behrman and Gustafson[18] experimented with hydrogen zeolite treated water, prepared in such a manner as to minimize sulfuric and hydrochloric acid while emphasizing carbonic acid. This water was passed through a magnetite bed and then softened with lime and soda ash, which reduced the silica to 2 to 4 ppm from a range of 20 to 61 ppm. Two other early papers discussing the fundamentals of the magnesium process are those by Tiger[19] and by Betz, Noll, and Maguire.[20]

Processes for removing silica by ferric and magnesium oxides have certain similarities and contrasts that should be noted before discussing the two methods separately:

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* Silica removal by ion exchange is discussed in Chap. 8.

1. As silica is reduced in concentration, the efficiency of the process falls off sharply, and increasingly larger quantities of ferric or magnesium hydroxide are required for each additional part per million of silica removed.

2. There is an optimum pH range for each process, and temperature affects their efficiency.

3. For a series of experiments carried out at constant temperature, if the silica removed per unit of reagent is plotted against residual silica on a double logarithmic scale, the graph is a straight line which conforms to a Freundlich adsorption isotherm. This shows that removal occurs by adsorption.[*]

4. The degree of hydration of the oxide used for silica removal is a controlling factor in its effectiveness for silica removal. Ferric hydroxide forms hydrous ferric oxide and then dehydrates in the absence of water:

$$\underset{\substack{\text{Ferric}\\\text{hydroxide}}}{2\text{Fe(OH)}_3} \rightleftharpoons \underset{\substack{\text{Hydrous}\\\text{ferric oxide}}}{\text{Fe}_2\text{O}_3{\cdot}x\text{H}_2\text{O}} \rightleftharpoons \underset{\substack{\text{Anhydrous}\\\text{ferric oxide}}}{\text{Fe}_2\text{O}_3}$$

Magnesium oxide combines with water to form magnesium hydroxide:

$$\underset{\substack{\text{Magnesium}\\\text{oxide}}}{\text{MgO}} + \underset{\text{Water}}{\text{H}_2\text{O}} \xrightleftharpoons{\text{slow}} \underset{\substack{\text{Magnesium}\\\text{hydroxide}}}{\text{Mg(OH)}_2}$$

In contrast to calcium oxide, which hydrates rapidly with evolution of heat, magnesium oxide hydrates very slowly. In all silica-removal investigations so far published, it has been found that the adsorption occurs on the hydrated form of the removal agent and that hydroxides precipitated *in situ* are far more effective than externally prepared oxides. However, prolonged contact with sludge which is not saturated with silica may effect some further removal.

5. The adsorption reactions are rapid and occur in much less time than the detention periods usually provided in water softening.

Silica Removal by Ferric Hydroxide. The commercial types of ferric sulfate marketed as coagulants are generally used in the process and precipitated with caustic soda or lime. The latter produces calcium sulfate, increasing the noncarbonate hardness of the water. The optimum pH value is about 9.0. For waters containing less than 10 ppm of silica, the dosage of ferric sulfate required is 15 to 20 ppm for each part per million of silica removed.[22] At higher silica concentrations, the dosage of ferric sulfate for each part per million of silica removed may be as low as 10 ppm. The lower limit attainable is about 2 ppm of silica, but this varies with different waters. In contrast to adsorption by magnesium hydroxide, efficiency decreases as the temperature rises; hence, this method is best suited to cold-process softening. The treatment is well adapted to waters which require clarification and color removal and where final zeolite softening is used. In one plant, color is removed in a first-stage clarification tank at a low pH, and silica is then removed in a second tank in which the pH is raised by means of caustic soda. The ferric hydroxide process for silica removal has the disadvantage of raising the sulfate content of the water, but, nevertheless, there are specific applications in which it has advantages over the magnesium process.

Silica Removal by Magnesium Compounds. The removal of silica by magnesium is much less efficient and flexible in cold-process softening than in hot-process softening, which is discussed in Chap. 7. At 50°F, the removal of each part per million of silica in excess of 15 ppm requires the precipitation of about 30 ppm of magnesium hardness, and this low efficiency falls off rapidly as the silica is reduced below this level. At 70°F, the ratio is 1 ppm silica removal for about 6 or 7 ppm magnesium hardness removal, and the efficiency increases rapidly as the temperature is raised further. It is apparent that cold-process treatment should not be relied on as a method of silica reduction unless temperate conditions can be assured. Sometimes this can be done by first using the water for cooling to pick up waste heat.

In a few cases, the natural magnesium hardness of the raw water may produce sufficient silica removal when excess lime treatment is applied, but often additional magnesium is needed. This can be supplied from several sources: soluble magnesium sulfate, dolomitic lime, or magnesium oxide.

Magnesium sulfate is of doubtful merit in the relatively inefficient cold-process for removing silica because of cost and the increase in the sulfate content of the water.

Magnesium oxide is available as a compound prepared for water treatment or as an ingredient of hydrated dolomitic lime, whose composition is generally in a ratio of 32 per cent MgO to 62 per cent Ca(OH)_2. If magnesium oxide is added to cold water in an environment of high pH, it will not dissolve. Since the calcium hydroxide of dolomitic lime provides a high pH rapidly, the associated magnesium oxide remains inert.

To bring magnesium oxide into solution, it is necessary that the pH be lower than that which prevails for the precipitation of magnesium hydroxide, and this requires a separate dissolving tank. The bicarbonate alkalinity or the free carbon dioxide of the raw water will dissolve magnesium oxide according to the following reactions:

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[*] Nordell[4] considers that magnesium removes silica as magnesium silicate, although conceding conformity of the data to the Freundlich isotherm.

S.T. Powell

$$\underset{\substack{\text{Magnesium}\\\text{oxide}}}{MgO} + \underset{\substack{\text{Calcium}\\\text{bicarbonate}}}{Ca(HCO_3)_2} \rightarrow \underset{\substack{\text{Magnesium}\\\text{carbonate}}}{MgCO_3} + \underset{\substack{\text{Calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

$$\underset{\substack{\text{Magnesium}\\\text{oxide}}}{MgO} + \underset{\substack{\text{Carbonic}\\\text{acid}}}{H_2CO_3} \rightarrow \underset{\substack{\text{Magnesium}\\\text{carbonate}}}{MgCO_3} + \underset{\text{Water}}{H_2O}$$

If the natural water will not dissolve sufficient magnesium to give the necessary silica reduction, carbon dioxide must be added from a generator or available stack gases. The dissolver should preferably provide about 1 hr of detention.

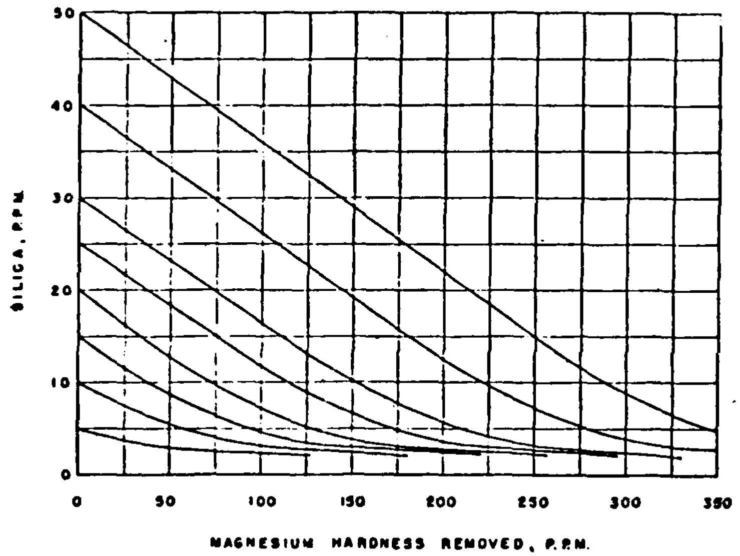

Fig. 9. Silica removed by precipitation of magnesium at 70°F.

Magnesium oxide prepared from calcined magnesite or other special sources can be added directly to raw water in the dissolver and will react in 20 or 30 min. Dolomitic lime cannot be so applied. It is added directly to the softening tank, where it serves to enrich the magnesium content of the sludge that settles in the concentrator zone. Part of this sludge is then recirculated to the dissolver, and the remainder is diverted to waste to keep removing as much silica as comes in with the raw water.

Tiger[19] observed that silica-adsorption powers were exhibited by undissolved magnesium oxide and magnesium-containing sludge, although to a lesser extent than freshly precipitated ionic magnesium. In practical operation, the efficacy of all these forms is utilized, even when no magnesium-dissolving compartment is provided. This is accomplished by utilizing a rapid-flow treatment tank, designed for retention and recirculation of a considerable amount of sludge. Detention time of at least 90 min is specified to take maximum advantage of the silica-removal power of the precipitates.

It is impossible to make precise predictions of the amount of ionic magnesium which must be precipitated from any water supply to produce a specific silica residual. However, experiments by the investigators cited and observations in many plants are reflected in the curves of Fig. 9 for ionic magnesium. For instance, if the silica concentration is 30 ppm, the precipitation of 150 ppm of magnesium hardness will reduce silica in direct proportion down to about 10 ppm. Beyond that, the curve flattens out and has been terminated at 2 ppm because results in that range may vary widely, depending on recirculation and other factors. For design purposes, these curves may be used to evaluate the adequacy of the magnesium hardness of the raw water and the order of magnitude of necessary magnesium additions.

EQUIPMENT FOR COLD-PROCESS SOFTENING

Cold-process softening plants may be broadly classified as *intermittent* or *continuous*. Current practice is dominated by the latter type.

Intermittent Softening Systems. The first precipitation softeners used in this country were of this type and were installed by the Southern Pacific Company at Port Los Angeles about December, 1896. This plant was designed by Howard Stillman. Subsequently, such equipment found wide favor particularly with the railroads for wayside water treatment. Batch softening systems have given good service for years in many boiler plants during the development of modern boiler-feedwater purification methods.

Intermittent softening systems include two or more reaction and settling tanks with chemical feeders, usually gravity filters, and softened water storage. The settled water is withdrawn through a swing-pipe skimmer supported by a float.* The units are operated on a definite fill-and-draw cycle. The dosage of lime, soda ash, and coagulant is calculated and weighed out in advance. These chemicals are added to each tank as it is filled with water, and the initial excess of chemicals during the filling is favorable to low hardness. The water is mixed by motor-driven paddles, and the insoluble salts are then allowed to precipitate while the water remains quiescent. During all this period, softened water is drawn from another tank in which the cycle of filling, treatment, and settling has previously been completed. The system must include enough tanks to permit adequate settling period, usually 4 to 8 hr. After each tank is emptied, precipitated sludge is flushed out, and cycle is repeated

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* See Fig. 3, Chap. 2.

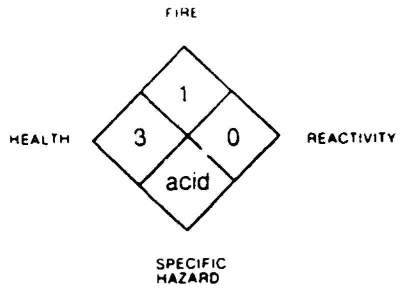
Material safety data

Sodium Sulfide 60% Flake

McKESSON CHEMICAL CO.
1[illegible]02 INDUSTRIAL DRIVE
TUSTIN, CALIFORNIA 92680
PHONE—832-7330

NFPA Designation 704

HAZARD RATING
4 = EXTREME
3 = HIGH
2 = MODERATE
1 = SLIGHT
0 = INSIGNIFICANT



Emergency telephone **(209) 524-1461**

Product Information	**Synonyms**	Sodium Sulfide Hydrated, Sodium Sulphide, Sodium Sulfuret
	Shipping name	**DOT** Corrosive Solid, NOS (Sodium Sulfide)
		IATA Corrosive Solid, NOS
		IMCO Sodium Sulfide, hydrated
	Formula	$Na_2S \cdot XH_2O$ (x averages 3)
	Chemical Family	Sulfide

	Material or component greater than 1%	**%**	**CAS #**	**Hazard Class**
Ingredients	Sodium Sulfide equivalent	60	1313-82-2	Flammable Solid, Corrosive
	Water	36	7731-18-5	Not Classified
	Sodium Hydrosulfide	3	16721-80-5	Flammable Solid, Corrosive
	Sodium Thiosulfate	1	7772-98-7	Not Classified

Physical data	**Melting point**	92° C (198° F)	**Specific Gravity (H_2O = 1)**	1.8
	Boiling point	176° C (349° F)	**Solubility in H_2O, % by WT**	@10° C (50° F), 28
	Vapor pressure @100° C,	7.1 kPa (53mmHg)	**% Volatiles by Volume**	non-volatile
	Vapor Density (Air - 1)	non-volatile	**Evaporation rate (butyl acetate = 1)**	non-volatile
	Room temperature: appearance & state	yellow flakes	**pH (as is)**	NA
	Odor	rotten-egg	**pH (10% solution)**	13.5

Fire, explosion and reactivity data	**Flash point**	Nonflammable	**Flammable Limits (air)**	**Upper** NA
	Autoignition temp.	NA		**Lower** NA
	Extinguishing media	☒ **Water** ☐ **Water Fog** ☐ **CO_2** ☒ **Dry Chemical** ☐ **Other** ______		
	Special fire fighting procedures	Wear self-contained breathing apparatus		
	Degree of fire and explosion hazard	May evolve highly flammable and toxic hydrogen sulfide gas. Highly toxic sulfur dioxide gas may be present.		
	☒ **Stable**	☐ **Unstable**	**Hazardous Polymerization**	☐ **May Occur** X **Will Not Occur**
	Conditions to Avoid	Contact with acids and oxidizing agents.		
	Major contaminates that may contribute to instability	None		
	Incompatibility	With acids, water less than pH 8.0, oxidizers.		
	Hazardous decomposition products	Contact with acid will liberate the poisonous gas, hydrogen sulfide. Sulfur dioxide may be evolved when oxidized or heated.		

*NA—Not Applicable

Health hazard information

	Route	Hazard classification NIOSH 1974 Pb-246698	Source	Date
Routes of exposure	**Inhalation**	No Data. Hazard is suspected low since the physical form is flake. Dusts, if inhaled, can be hazardous.		
	Skin contact	Highly corrosive	FMC	4/77
	Skin absorption	Moderate to highly toxic	FMC	1/82
	Eye contact	Highly corrosive	FMC	4/77
	Ingestion	Moderately hazardous	FMC	4/77

Effects of Overexposure	**Acute exposure**	Sodium Sulfide is corrosive to the eyes and skin and can be poisonous if swallowed or absorbed through the skin.
	Chronic exposure	No Data

Emergency and first aid procedures	**Eyes**	Immediately flush with large amounts of water for at least 15 minutes. Do not use oils or ointments. See an ophthalmologist if irritation persists.
	Skin	Immediately wash skin thoroughly with water and continue for 15-20 minutes. Do not apply salves or ointments to contacted skin surfaces.
	Inhalation	Remove to fresh air. If breathing shallow or difficult call a physician and treat for possible hydrogen sulfide poisoning.
	Ingestion	If swallowed and victim is conscious, have victim drink water or milk.
	Decontamination procedures	Remove contaminated clothing Wash with large amounts of soap and water

Notes to physician

In severe poisoning treat with amyl nitrite and sodium nitrite as for cyanide poisoning, but omit sodium thiosulfate injection. This therapy has had no clinical trials in sulfide poisoning, but is effective in animals.

Atropine sulfate (0.0006 gm intramuscularly) may contribute some symptomatic relief.

Conjunctivitis may be relieved by the instillation of 1 drop of olive oil in each eye and sometimes by 3 to 4 drops of epinephrine solution (1:1000) at frequent intervals (e.g., 5 minutes). Occasionally local anesthetics and hot or cold compresses are necessary to control the pain.

Antibiotics at the first hint of pulmonary infection.

Ref. Gosselin, RE, et al. *Clinical Toxicology of Commercial Products*. 4th ed. Baltimore: [illegible] 1976.

Special protection information	**Ventilation requirements**	Exhaust fan or hood if dust or harmful vapors present.
	Recommended personal protective equipment:	Appropriate eye and skin protection.
	Respiratory (Specify conditions)	Approved toxic dust respirator or if necessary, use NIOSH certified self-contained breathing apparatus.
	Eyes	Monogoggles and/or full face mask.
	Gloves	Liquid proof rubber or neoprene.
	Special clothing and equipment	Safety showers in work area. Rubber footwear, polyester or acrylic full cover clothing

Precautionary statement	**Danger** Causes severe burns to skin and eye. Harmful if swallowed or inhaled. Harmful if absorbed through the skin. Contact with acid releases toxic hydrogen sulfide gas. Do not get in eyes, on skin, on clothing.	Avoid breathing (dust, vapor). Keep container closed. Use with adequate ventilation. Wash thoroughly after handling Wear chemical goggles and impervious gloves.

Storage and handling	Protect against physical damage. Separate from acids, and oxidizing materials. Keep away from high heat. In areas where hazardous levels of hydrogen sulfide might be generated, it is recommended that a continuous monitoring hydrogen sulfide gas detection and alarm system be installed. Do not store in zinc, aluminum or copper containers.

Disposal, spill or leak procedures	**Aquatic toxicity classification** **NIOSH RTECS No. 79-100**	Moderately toxic	**Source** **Date** 1963 Water Quality Criteria McKee, JE,Wolf, HW Calif. State Water Quality Control Board
	Procedure for release or spill Recover in dry form for reuse or disposal. Use proper protective gear for dust and skin and eyes. Do not flush to sewer or streams.		
	Waste disposal method Do not flush to sewer or surface waters. Sodium Sulfide, if discarded for disposal, is a hazardous waste by RCRA regulations Subpart C. Part 261.23 (reactivity). It is recommended that material first be considered for recycle or reuse. Material for disposal should be drummed, labeled, handled and transported according to regulations in a permitted hazardous waste management facility.		
	Neutralizing chemicals Solution will oxidize by aeration or hydrogen peroxide to sulfate, thiosulfate and carbonate		

Transporation data	**Chemtrec Emergency Telephone: (800) 424-9300**	
	Proper shipping name	Corrosive Solid, NOS
	DOT classification	Corrosive Material
	DOT labels	Corrosive
	DOT marking	Corrosive Solid, NOS (Sodium Sulfide, 60% Flake)
	DOT placard	Corrosive
	UN number	1759
	Hazardous substance/RQ	None
	49 STCC number	4936545
	Emergency accident precautions and procedures	Keep people away. Use protective breathing apparatus. Do not flush to sewers or streams.
	Precautions to be taken in transportation	Do not carry acids or liquid oxidants. Solid oxidants must be separated by physical barrier.
	CMA chemcard number	None
	Type packages	Metal drum or plastic bag.

Additional regulatory concerns	**Material is reported in EPA TSCA inventory list** ☒ **Yes** ☐ **No**

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FMC Corporation Industrial Chemical Group 2000 Market Street Philadelphia, Pennsylvania 19103

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Date of issue	Supersedes
4/82	

SILICA REDUCTION BY COLD LIME SOFTENING
REVERSE OSMOSIS PRETREATMENT LABORATORY STUDY

Prepared for

AUG 20 1980

Southwestern Public Service
Tolk Station, Texas

Technical Service No. 9280-131
Job No. A111D17197

Prepared by

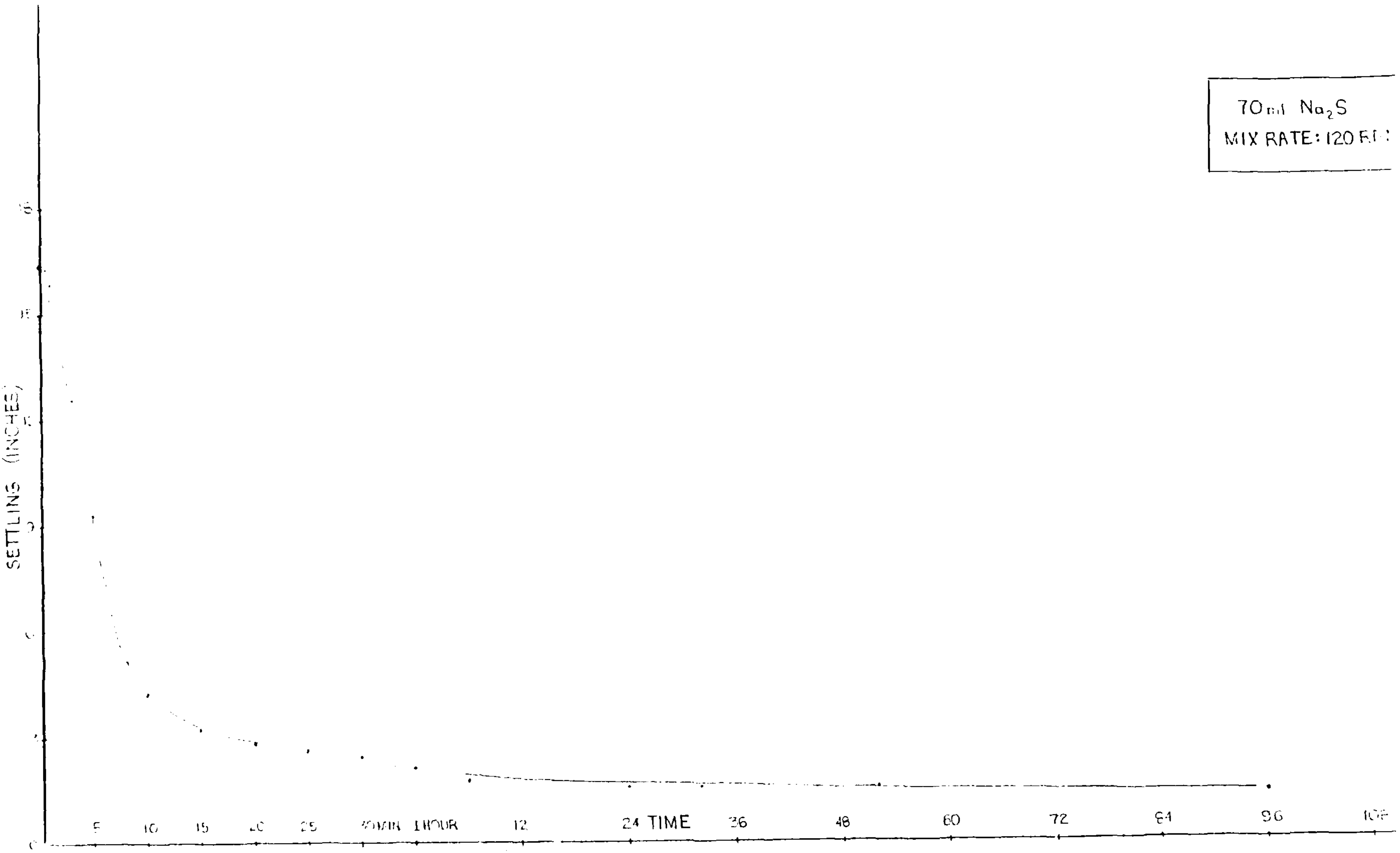
Nancy J. Lemmo
Technical Service Chemist
The Permutit Company, Inc.

February 26, 1980

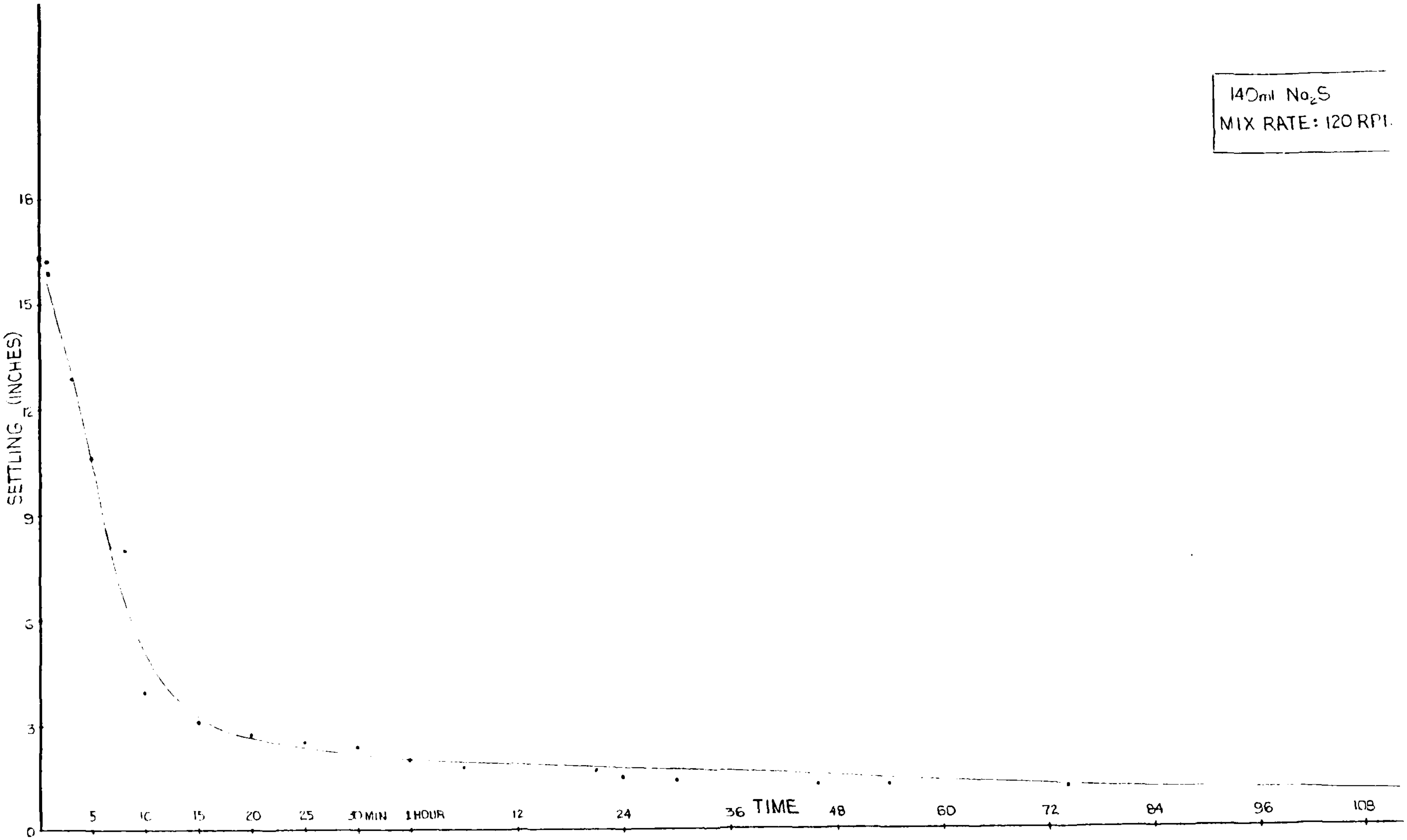
TECHNICAL REPORT FOR FLUOR CONSTRUCTORS, INC.
Evaluation of Treatment For Heavy Metal Removal
July 12, 1983

APPENDIX

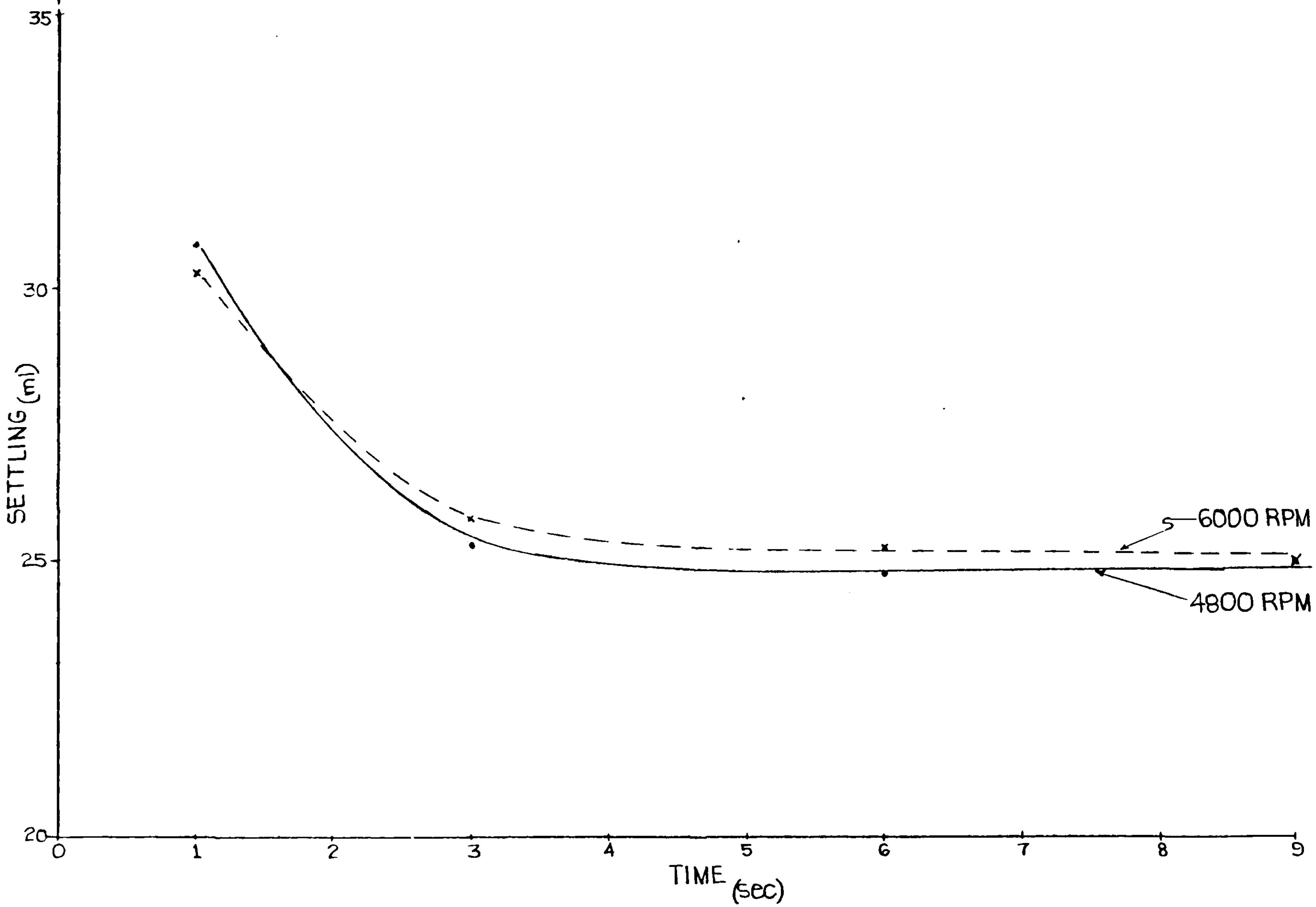
Technical
Report



SETTLING RATE OF SAMPLE OVER PROLONGED PERIOD



SETTLING RATE OF SAMPLE (WITH EXCESS Na_2S) OVER PROLONGED PERIOD



SETTLING vs. TIME

CENTRIFUGATION GRAPH

CONCRETE CONSTITUENTS

Portland cements are primarily composed of four principal constituents which are as follow:

1. Tricalcium silicate
2. Dicalcium silicate
3. Tricalcium aluminate
4. Tetracalcium aluminoferrite

The concrete samples used to compare relative corrosivity of Fluor's sample contained Type II (low sulfate) Portland cement and contained no admixtures. The following information on the concrete samples was provided by the supplier:

1. Compressive strength (f'_c) = 3000 psi
2. Portland cement content: 6 sacks/cu yd P.C.
3. Maximum size of coarse aggregate= 1 inch
4. Average size of aggregate = 3/8 inch
5. Slump of Portland cement concrete = 5 inches

APPENDIX VII

CONCRETE INFORMATION BULLETIN

ENVIRONMENTAL DEPT.

Effect of Various Substances on Concrete and Protective Treatments, Where Required

Quality concrete must be assumed in any discussion of the effect of various substances on concrete and protective treatments. In general, achievement of adequate strength and sufficiently low permeability to withstand many exposures indefinitely requires proper proportioning, placing, and curing. Certain fundamental principles by which the quality of concrete can be controlled are well established:

- *Low water-cement ratio*—not to exceed 0.49.
- *Minimum cement content*—564 lb. (6 U.S. bags) per cubic yard.
- *Suitable cement type*—such as portland cement low in tricalcium aluminate, C3A, to reduce or prevent attack by some chemicals that react with C3A, notably sulfates.
- *Adequate air entrainment*—the amount dependent on maximum aggregate size.
- *Suitable workability*—avoiding mixes so harsh and stiff that honeycomb occurs, and those so fluid that water rises to the surface. Slump should be not more than 3 in.
- *Thorough mixing*—until all concrete is uniform in appearance, with all materials evenly distributed.
- *Proper placing and consolidation*—filling all corners and angles of forms without segregation of materials. Where possible, construction joints should be avoided.
- *Adequate curing*—supplying additional moisture to the concrete during the early hardening period or by covering with water-retaining materials (rapid evaporation of moisture from the concrete surface soon after it is placed may cause plastic shrinkage cracking). *Do not use curing compounds on surfaces that are to receive protective treatment.* Concrete should be kept moist and above 50 deg. F. for at least the first week; however, longer curing times usually increase resistance to corrosive substances. Concrete should not be subjected to hydrostatic pressure during this period.

Design Considerations

Whenever concrete is to be coated for corrosion protection, the forms should be coated with materials that will remain on the forms when they are stripped. Hence, forms coated with form oils or waxes should not be used against surfaces to be coated. Curing membranes may be weakly bonded to the concrete and may in turn develop little or no bond to coatings applied over them. If form oils, waxes, or curing membranes are present, they should be removed by acid washing, sandblasting, scarifying, or other such processes.

Where spillage of corrosive substances is likely to occur, the floor should slope to drains approximately 1/8 to 1/4 in. per linear foot to facilitate washing down of the floor. The slope required depends on the distance between drains and the corrosive substance involved.

Many solutions that have no chemical effect on concrete, such as brines and salts, may crystallize upon drying. It is especially important that concrete subject to alternate wetting and drying of such solutions be impervious. When free water in concrete is saturated with salts, the salts crystallize in the concrete near the surface during the process of drying and this crystallization may exert sufficient pressure to cause scaling. Structures exposed to brine solutions and having a free surface of evaporation should therefore be provided with a protective treatment on the side exposed to the solution.

In addition, movement of salts into the concrete may result in corrosion of reinforcing steel. The corrosion reactions form compounds that cause expansion and disruption of the concrete. Significant corrosion of steel in reinforced concrete will occur if both of the following conditions are met: (1) sufficient oxygen is available, and (2) the normally passive state of steel in concrete is impaired.

Porous concrete or surface cracks permit the penetration of oxygen to the reinforcement. Steel is normally passive because a protective oxide film is formed and maintained on it by the high concentration of hydrogen ions (pH) in the water solution in concrete. This protective film may be impaired by: (1) sufficient lowering of the pH value, as by reaction of carbon dioxide from the air or other sources, or (2) a sufficient concentration of chloride ions in solution. High cement content in high-quality impermeable concrete provides protection against corrosion of reinforcement by producing a high pH value and limiting exposure to the air.

It is important that sufficient concrete coverage be provided for reinforcement where the surface is to be exposed to corrosive substances. Metal chairs for support of

Portland Cement Association
December 1968

GENERAL INFORMATION

reinforcement should not extend to the concrete surface. Deep recesses in the concrete should be provided for form ties, and they should be carefully filled and pointed with mortar.

Acids attack concrete by dissolving both hydrated and unhydrated cement compounds as well as calcareous aggregate. In certain acid waters it may be impossible to apply an adequate protective treatment to the concrete, and the use of a "sacrificial" calcareous aggregate should be considered. Replacement of siliceous aggregate by limestone or dolomite having the equivalent of a calcium oxide concentration of at least 50 percent will aid in neutralizing the acid. The acid will attack the entire exposed surface more uniformly, reducing the rate of attack on the paste and preventing loss of aggregate particles at the surface. The use of calcareous aggregate will also retard expansion resulting from sulfate attack caused by some acid solutions.

The rate of attack on concrete may be directly related to the activity of the aggressive chemical. Solutions of high concentration are generally more corrosive than those of low concentration–but with some, the reverse is true. The rate of attack may sometimes be affected by the solubility of the reaction products of the particular concrete in the corrosive solution. Lowering of the hydrogen ion concentration generally causes more rapid attack in the concrete. Also, high temperatures usually accelerate any possible attack and thus better protection is required than for normal temperatures.

Surface Preparation

Proper preparation of the concrete surface and good workmanship are essential for the successful application of any protective treatment. Concrete should normally be well cured (28 days to six months, depending on service conditions and coatings used) and dry before the protective coatings are applied. Moisture in the concrete may cause excessive internal vapor pressure that can result in the treatment's blistering and peeling.

Precautions should be taken to eliminate objectionable voids in the surface that may cause pinholes in the coating. Good vibration and placing techniques will reduce the number of these surface imperfections. The surface should be smoothed immediately after removal of forms by applying grout or mortar, or by grinding the surface and then working a grout into it.

It is important to have a firm base free of grease, oil, efflorescence, laitance, dirt, and loose particles. The best method of cleaning the concrete surface depends on job conditions.

Removal of chemical contaminants must be accomplished before any other surface cleaning, such as acid-etching or sandblasting, takes place. Grease and oil may be removed with a 10 percent solution of caustic soda or trisodium phosphate, or with steam that incorporates an alkaline detergent. The surface should then be flushed thoroughly with fresh water until a neutral reaction to litmus paper is obtained.

Efflorescence and laitance can be removed by light sandblasting or by washing the surface with a 5 to 10 percent solution of hydrochloric acid. The surface should be dampened with water before the acid treatment and thoroughly flushed with clean water afterward to remove all acid. Complete removal of acid may be assured by washing the surface with a 10 percent solution of ammonia water or potassium hydroxide, followed either by rinsing with water or by allowing the surface to weather for at least one month.

Dirt and dust may be removed by air-blowing, brushing with stiff fiber or wire brush, hosing, or scrubbing. For extremely dirty surfaces, steam-cleaning or wet or dry sandblasting may be used.

Concrete cast against forms is sometimes so smooth as to make adhesion of protective coatings very difficult to obtain. Such surfaces should be acid-etched, sandblasted lightly, or ground with silicon carbide stones to provide a slightly roughened surface.

Choosing the Treatment

Protective treatments for concrete are available for almost any degree of protection required. The coatings vary so widely in composition and performance that no one material will serve best for all conditions.

Every coating is formulated to render a certain performance under specified conditions. Its quality is not determined solely by the merits of any one raw material since minor variations in formulation can make very substantial changes in performance. Coating performance also depends upon the surface preparation, method and quality of coating application, conditions during application, and film thickness. Any general discussion of chemical resistance and other properties of coatings must assume optimum formulation and proper use. The producers of the various coatings can provide valuable information on the merits of their products for a particular use and on the proper and safe procedure for application. Many coatings contain solvents that are fire, explosion, or toxic hazards.

Many protective materials (thermoplastics) soften at elevated temperatures and may even melt or become ineffective. Various grades of coatings are available for use over a fairly wide temperature range. Where flavor or odor is important, the U.S. Food and Drug Administration or the Canadian Food and Drug Directorate should be consulted regarding materials for use with food ingredients.

The coating thickness required depends on: (1) the exposure, whether continuous or intermittent; (2) the resistance of the material to the chemicals involved; and (3) the ability to form a continuous, pinhole-free surface. As a rule, thin coatings are not as durable as heavier coatings and hence are less suitable where there is considerable abrasion.

The more common protective treatments are indicated in the tables (starting on page 7), the numbers and letters corresponding to the descriptions given here. For most substances, several treatments are suggested. They will provide sufficient protection in most cases.

The information in the tables is only a guide for determining when to consider various coatings for chemical resistance. Where more specific information is required, particularly to determine whether protection is required for large installations, small mortar prisms representative of the concrete to be used can be immersed in the corrosive liquid and evaluated as to resistance.* Where continuous service over long periods is desirable, it may be more economical to use the more positive means of protection rather than a treatment of lower first cost that may be less permanent.

Protective Treatments

1. **Magnesium fluosilicate or zinc fluosilicate**: The treatment consists generally of three applications. Either of the fluosilicates may be used separately, but a mixture of 20 percent zinc and 80 percent magnesium appears to give the best results. For the first application, 1 lb. of the fluosilicate crystals should be dissolved in 1 gal. of water; about 2 lb. of crystals per gallon of water are used for subsequent applications.

The solution may be applied efficiently with large brushes for vertical surfaces and mops for horizontal areas. The surfaces should be allowed to dry between applications (about three or four hours are generally required for absorption, reaction, and drying). Care should be taken to brush and wash the surface with water shortly after the last application has dried to remove incrusted salts; otherwise white stains may be formed.

Treatment with fluosilicates reduces dusting and hardens the surface by chemical action. It increases resistance to attack from some substances but does not prevent such attack. With poor-quality concrete, the treatment is not effective.

Concrete surfaces to be treated with fluosilicates should not contain integral water-repellent agents because these compounds will prevent penetration of the solution. Hardeners should not be used when paints are to be applied because they result in poor adhesion of many coatings. Also, the hardened surfaces are difficult to etch properly.

2. **Sodium silicate (commonly called water glass)**: Commercial sodium silicate is about a 40 percent solution. It is quite viscous and must be diluted with water to secure penetration, the amount of dilution depending on the quality of the silicate and permeability of the concrete. Silicate of about 42.5 deg. Baumé gravity diluted in proportions of 1 gal. with 4 gal. of water makes a good solution. Two or three coats should be used. For tanks and similar structures, progressively stronger solutions are often used for the succeeding coats.

Each coat should be allowed to *dry thoroughly* before the next one is applied. On horizontal surfaces it may be liberally poured on and then spread evenly with mops, brooms, or brushes. Scrubbing each coat with stiff fiber brushes or scrubbing machines and water *after it has hardened* will assist penetration of the succeeding application. The treatment increases resistance to attack from some substances but does not prevent such attack.

3. **Drying oils**: Two or three coats of linseed, tung (China wood), or soybean oils may be used as a protective treatment. Boiled linseed oil dries faster than the raw oil and is the most commonly used.

The concrete should be well cured and at least 14 days old before the first application. If this is not possible, the concrete should be neutralized by applying a solution consisting of 3 oz. of zinc chloride and 5 oz. of orthophosphoric acid (85 percent phosphoric acid) per gallon of water. Brushed on the concrete, the solution should be allowed to dry for 48 hours and then any crystals that have formed on the surface should be removed by light brushing. This solution should not be used on prestressed concrete. Sometimes a magnesium fluosilicate treatment is also applied to harden the surface before the oil treatment.

The oil treatment may be applied with mops, brushes, or spray and the excess removed with a squeegee before the oil gets tacky. It is not necessary to build up a heavy surface coating as penetration of the oil into the surface is desirable. Diluting the oil with turpentine or kerosene up to a mixture of equal parts gives better penetration for the first coat; subsequent coatings may be diluted less. Careful heating of the oil to 150 deg. F. or so and hot application to a warm surface are also helpful in securing better penetration. Each coat must dry thoroughly for at least 24 hours before the next application. Drying oils tend to darken the concrete.

4. **Coumarone-indene**: Available in grades from dark brown to colorless, this synthetic resin is soluble in xylol and similar hydrocarbon solvents and should be powdered to aid dissolving. A solution consisting of about 6 lb. of coumarone-indene per gallon of xylol with ½ pint of boiled linseed oil makes a good coating. Two or more coats should be applied to fairly dry concrete. The coatings have a tendency to yellow on exposure to sunlight but this yellowing does not seem to affect the protective properties.

5. **Styrene-butadiene**: Styrene-butadiene copolymer resins are supplied in various medium-strength solvents, some faster drying than others. Three coats are generally recommended, with the first coat thinned for better penetration. Twenty-four hours should elapse between coats, and a delay of 7 days is necessary for thorough drying before the coated surface is placed in service. These coatings tend to yellow under the influence of sunlight.

Decorative styrene-butadiene coatings are widely marketed as latex paints. They are usually not satisfactory for protection against chemical attack because latex paints generally do not form sufficiently impermeable films.

6. **Chlorinated rubber**: This treatment consists of a trowel-applied or sprayed coat of heavy consistency mastic up to 1/8 in. thick, or multiple coats brushed or sprayed on to a thickness of up to 10 mils. A minimum of 5 mils is recommended for chemical exposure. A single brush coat will vary from about 1 to 2 mils, depending on consistency, while a single spray coat usually varies from 0.7 to 1.0 mils.

In general, concrete should age for two months before treatment. The concrete may be damp but not wet, as excessive moisture may prevent adequate bond. It is usually necessary to thin the first coat, using only the producer's recommended thinner (other thinners may be incompatible). A coating dries tack-free in an hour, but a 48-hour delay is recommended between coats.

This treatment is odorless, tasteless, and nontoxic. Its

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*William H. Kuenning, ***Resistance of Portland Cement Mortar to Chemical Attack–A Progress Report***, Bulletin 204, Research and Development Laboratories, Portland Cement Association.

strong solvents, however, may lift and destroy previously painted and aged coatings of oil or alkyd base.

7. **Chlorosulfonated polyethylene (Hypalon):** Four coats of about 2 mils each and an appropriate primer are normally recommended to eliminate pinholes. Thinning is not usually required, but to reduce viscosity for spray application the producer's recommended thinner should be used up to a limit of 10 percent. Each coat dries dust-free within 10 to 20 minutes and the treatment cures completely in 30 days at 70 deg. F. and 50 percent relative humidity. A fill coat of grout or mortar is required as the paint film will not bridge voids in the concrete surface. Moisture on the surface may prevent good adhesion.

These coatings are high in material cost and require trained applicators. They are not used where less expensive coatings are adequate.

8. **Vinyls:** Of the vinyls available, polyvinyl chloride, polyvinyl chloride-acetate, and polyvinylidene chloride are the ones used extensively in corrosion control. The resins are soluble only in strong solvents. Due to the high viscosity of the resins, only solutions of low solids content can be made and multiple coats are therefore required for adequate film thickness. Vinyls should generally be applied to dry surfaces by spray as their fast drying (30 minutes) makes brush application difficult.

Vinyl chloride coatings make good top coatings for vinyl chloride-acetate and others, but they themselves do not adhere well directly to concrete. Polyvinyl acetate latex copolymers are widely available as decorative coatings but, like other latexes, they are usually inferior to the solvent-system coatings for chemical resistance.

9. ***Bituminous paints, mastics, and enamels:*** Asphalt or coal tar coatings may be applied cold (paints and mastics in cutback or emulsion form) or hot (mastics and enamels). Two coats are usually applied to surface-dry concrete: a thin priming coat to ensure bond and a thicker finish coat. The priming solution is of thin brushing consistency and should be applied so as to cover the surface completely; any uncoated spots should be touched up. When the primer has dried to a tacky state, it is ready for the finish coat. Multiple coats should be applied at right angles to each other to secure continuity and avoid pinholes.

Emulsions are slower drying, more permeable, and less protective than the other coatings. Cutbacks and emulsions, if not completely cured, can impart odor or flavor to materials with which they are in contact. The producer's recommendations on service and application temperatures should be strictly observed.

Bituminous mastics may be applied cold or heated until fluid. Cold mastics are cutbacks or emulsions containing finely powdered siliceous mineral fillers, asbestos fibers, or bitumen-coated fabrics to form a very thick, pasty, fibrous mass. This mass increases the coating's resistance to flowing and sagging at elevated temperatures and to abrasion. Thin mastic layers, about 1/32 in. thick, are troweled on and allowed to dry until the required thickness has been obtained. Hot mastics usually consist of about 15 percent asphaltic binder, 20 percent powdered filler, and the remainder sand, graded up to ¼-in. maximum size. They should be poured and troweled into place in layers 1 in. or more in thickness.

Enamels should be melted, stirred, and carefully heated until they reach the required application temperature. If an enamel is heated above the producer's recommended temperature, it should be discarded. If application is delayed, the pot temperature should not be allowed to exceed 375 deg. F. When fluid, it should be applied quickly over tacky cutback primer as it sets and hardens rapidly.

10. **Polyester:** These resin coatings are two- or three-part systems consisting of polyester, peroxide catalyst, and possibly a promoter. The amount of catalyst must be carefully controlled because it affects the rate of hardening. The catalyst and promoter are mixed separately into the polyester. Fillers, glass fabrics, or fibers used to reduce shrinkage and coefficient of expansion compensate for brittleness of resin and increase strength.

Coatings with 2- to 3-hour pot life generally cure in 24 to 36 hours at 75 deg. F. Shorter cure times require reduced pot life because of high heats of reaction. Coatings are sensitive to changes in temperature and humidity during the curing period. Some coatings can be applied to damp surfaces and at temperatures as low as 50 deg. F. The alkali resistance of some polyesters is limited. It is recommended that trained applicators apply the coatings.

11. **Urethane:** These coatings may be one- or two-part systems. There are two types of the one-part system: moisture-cured and oil-modified. The coatings that cure by reacting with moisture in the air must be used on dry surfaces to prevent blistering during the curing period. Oil-modified coatings dry by air oxidation and generally have the lowest chemical resistance of the urethane coatings.

Two types of the two-part system are also available: catalyzed and polyol-cured. Catalyzed coatings have limited pot life after mixing and cure rapidly. For polyol-cured coatings, the mixture is well stirred and allowed to stand for about ½ hour before use; it should have a pot life of about 8 hours. Polyol-cured coatings are the most chemically resistant of the urethane coatings but require the greatest care in application.

All urethane coatings are easily applied by brush, spray, or roller. For immersion service in water and aqueous solutions, it may be necessary to use a primer and the urethane producer should be consulted. Satisfactory cure rates will be attained at relative humidities of 30 to 90 percent and temperatures between 50 and 100 deg. F. Lower temperatures will retard rate of cure.

The principal disadvantages of urethane coatings are the very careful surface preparation needed to ensure adhesion and the difficulty in recoating unless the coating is sanded. Multiple coats should be used and an inert filler added if air voids are present on the concrete surfaces (the coatings are unable to span air voids).

12. **Epoxy:** These coatings are generally a two-package system consisting of epoxy resin–which may be formulated with flexibilizers, extenders, diluents, and fillers–and a curing agent. The coating properties are dependent on the type and amount of curing agent used. The common curing

AD-A144 420 STUDY ON THE TREATMENT OF WASTEWATER GENERATED AT KSC 3/4
(KENNEDY SPACE CENT..(U) FLUOR ENGINEERS INC IRVINE CA
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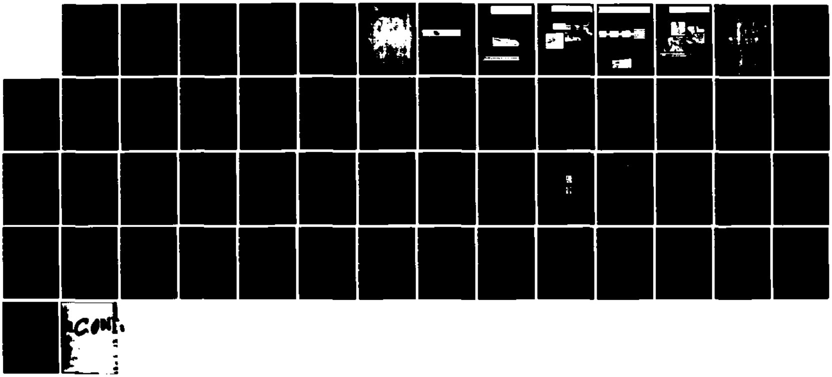
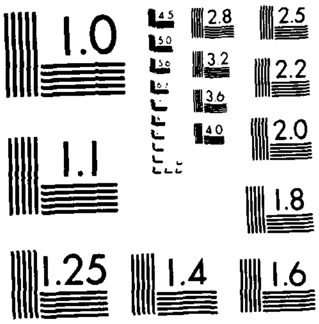
UNCLASSIFIED DACA05-83-C-0028 F/G 13/2 NL




1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

agents suitable for room temperature curing are amines, polyamines, amine adducts, polyamides, polysulfides, and tertiary amines.

The single-package coatings are epoxy esters that are generally inferior to the two-package epoxies in chemical resistance. They require an alkali-resistant primer and are not recommended for immersion service. Some epoxy formulations are 100 percent solids and others are solution coatings. The formulator's recommendations should be followed in selecting the system for desired protection.

It is also desirable to follow the formulator's recommendations for the best application procedures, temperatures, and allowable working life. Generally, three coats must be applied to eliminate pinholes; glass flake to bridge the pinholes may also be used. Contact with epoxy resins or hardeners can cause skin irritation or allergic reactions, and proper protection is necessary.

Epoxy liners may be formed with reinforcement such as woven fabrics, mats, or chopped glass fiber. For example, on concrete that may undergo thermal movements, an isolation layer of two-component polysulfide joint sealant of the self-leveling type is troweled over the surface to form a 1/32-in.-thick layer of synthetic rubber. As soon as the rubber has cured, the epoxy coating is applied with a roller to a film thickness of 9 or 10 mils. Then fiber glass cloth is spread over the wet epoxy coating and pressed into it. A second epoxy coating is applied immediately to embed the fiber glass.

13. **Neoprene**: These coatings may be one- or two-part systems. The one-part system is used as a thinner film than *the two-part and generally has a lower chemical resistance.* It cures slowly at room temperature and some curing agents may limit its shelf life. The two-part system may require a holding period between mixing and application.

Application of either system should not begin for at least 10 days after removal of the forms to allow evaporation of water from the concrete. Some coatings require primers while others are designed to be self-priming. Adhesion is often improved by application of a diluted first coat to increase penetration of the surface. Each coat should be sufficiently solvent-dry before the next application; however, if it becomes too fully cured, it may swell and lose adhesion. Three coats of 2 to 3 mils each are normally recommended to eliminate the possibility of pinholes. For immersion service, minimum dry thickness should be 20 mils.

14. **Polysulfide**: These coatings may be one- or two-part systems. They do not harden with age and they remain rubbery over a broad temperature range. Thick coats of 20 to 25 mils can be applied at one time. For the one-part system, atmospheric moisture serves as the curing agent; when humidities are low, curing can be hastened by spraying with a fine water mist. The two-part system usually has a pot life of 30 to 45 minutes and becomes tack-free overnight.

15. **Coal tar-epoxy**: Coal tar-epoxy coatings are classified in three main types according to epoxy resin content: high-resin coatings for dry thicknesses of 15 mils; medium-resin coatings for integral linings of concrete pipe; and low-resin coatings for building nonsagging barriers up to 40 mils thick. The first type requires a special primer and its thickness is achieved in two coats. The other types do not require primers and may be applied in a single coat, but they require relatively long cure time. Some coal tar-epoxy resin coatings are catalytically cured–with a hardener, or with both hardener and catalyst.

Coal tar-epoxy coatings are a two-package system. A combination of coal tar, filler, solvent, and epoxy resin may be in one package and the curing agent (commonly amines, polyamines, amine adducts, polyamides, or tertiary amines) in the other. These two packages are usually mixed in a ratio of 20:1 or 10:1, but the ratio may be lower. The coal tar, filler, solvent, and curing agent may also be blended together to make up one package and the epoxy resin kept separate for the other package. These two packages are generally mixed in a ratio of 3:1. The packages must be proportioned correctly to secure proper cure and chemical resistance. Storage life of the blends can vary from six months to two years, depending on formulation.

It is important that the two packages be thoroughly mixed, and power agitation is strongly recommended. Mixing small quantities is not recommended. Insufficient mixing will be revealed only after the coating has cured. For some coatings, a ½-hour waiting period between mixing and application is desired. Pot life is generally 3 to 4 hours at 70 deg. F., but it may vary from several minutes to 8 hours, depending on solvent content and formulation.

Coal tar-epoxy coatings should not be applied at temperatures below 50 deg. F. or when danger exists of their becoming wet within 24 hours of application. Spray applications generally result in better coverage. However, the sides of a short, stiff bristle brush or a long nap roller may be used. The second coat should be applied within 48 hours to prevent adhesion problems between coats. These coatings should not be put into service until a minimum of 5 days' curing time has been allowed.

16. **Chemical-resistant masonry units and mortars**: Three basic types of chemical-resistant masonry units are available: Type H brick, generally fire-clay; Type L brick, generally shale; and carbon and graphite brick, intended for use where additional chemical resistance is required. Types H and L brick should conform to Standard Specifications for Chemical-Resistant Masonry Units (ASTM C279).

Brick thickness generally varies from 1¼ to 3¾ in., depending upon severity of service. Brick surfaces should be scored or wire-cut (matt texture). The brick must, of course, be laid in mortar that is also resistant against the substance to which they are to be exposed.

The chemical resistance of mortars may be evaluated by Standard Method of Test for Chemical Resistance of Mortars (ASTM C267). The more commonly used chemical-resistant mortars *may also be used alone*, without masonry units, to form thick coatings–usually applied by trowel. These mortars are:

a. **Asphaltic and bituminous mortars**–supplied for use over a limited range of low temperatures. Some are sand-filled and some are not. They may be applied either as mastics that depend upon evaporation of solvent or as hot-melt compounds.

b. **Epoxy resin mortars**—two- or three-part systems with either amine or polyamide curing agents, they should conform to Standard Specifications for Chemical-Resistant Resin Mortars (ASTM C395) or Specification for Resin Chemical-Resistant Grouts (ASTM C658). For their use, see the Recommended Practice for Use of Chemical-Resistant Resin Mortars (ASTM C399).

c. **Furan resin mortars**—should conform to ASTM C395 or C658. They require a primer to ensure satisfactory adhesion to concrete. For their use, see ASTM C399.

d. **Hydraulic cement mortars**—for their use, see the Recommended Practice for Use of Hydraulic Cement Mortars in Chemical-Resistant Masonry (ASTM C398).

e. **Phenolic resin mortars**—should conform to ASTM C395. For their use, see ASTM C399.

f. **Polyester resin mortars**—should conform to ASTM C395. They are limited in resistance to strong chemicals but will withstand mildly oxidizing solutions such as bleaches. For their use, see ASTM C399.

g. **Silicate mortars**—should conform to Standard Specifications for Chemically Setting Silicate and Silica Chemical-Resistant Mortars (ASTM C466). For their use, see the Recommended Practice for Use of Chemically Setting Chemical-Resistant Silicate and Silica Mortars (ASTM C397).

h. **Sulfur mortars**—should conform to Standard Specifications for Chemical-Resistant Sulfur Mortar (ASTM C287). For their use, see the Recommended Practice for Use of Chemical-Resistant Sulfur Mortars (ASTM C386).

A bed of mortar and an impervious membrane lining are usually placed between the masonry lining and concrete. Rubber and vinyl sheets or properly primed and hot-applied 3/8-in.-thick asphaltic materials, both plain and glass-cloth-reinforced, are preferred for the membrane lining, depending on the corrosive substance. The primer should conform to Standard Specifications for Primer for Use with Asphalt in Dampproofing and Waterproofing (ASTM D41), except that the asphalt content should be not less than 35 percent by weight. Floor slabs that are to receive a masonry lining should have a smooth wood-float finish. A slab having a steel-trowel finish may be too smooth for adhesion of the asphaltic membrane.

17. **Sheet rubber**: Soft natural and synthetic rubber sheets 1/8 to 1/2 in. thick may be cemented to concrete with special adhesives. Sometimes two layers of soft rubber are used as a base, with a single layer of hard rubber over them.

Chemical-resistant synthetics available as sheeting are neoprene, polyvinylidene chloride-acrylonitrile, plasticized polyvinyl chloride, polyisobutylene, butyl, nitrile, polysulfide, and chlorosulfonated polyethylene rubbers.

18. **Resin sheets**: Synthetic resins, particularly polyester, epoxy, and polyvinyl chloride, are available as sheet materials. *These sheets are not referred to in the tables but may be used wherever comparable resin coatings are recommended.* Frequently glass-fiber-reinforced, they may be cemented to concrete with special adhesives.

19. **Lead sheet**: In the United States, lead sheet used for chemical resistance is called "chemical lead." The sheets should be as large as possible (to minimize the number of joints) but not too heavy to handle—up to 8x20 ft. for the thinnest. Thicknesses range from 1/64 to 1/2 in. Lead may be cemented to concrete with an asphaltic paint. Each sheet should be overlapped and the seam welded by conventional lead-burning techniques. If the lead is to be subjected to high temperatures, it may be covered with chemical-resistant masonry to reduce thermal stresses.

20. **Glass**: Two types have been used for corrosion resistance: high-silica glass and borosilicate glass. Borosilicate glass, the more alkali-resistant material, is recommended because alkalies in concrete may cause glass etching. Glass may be cemented to the concrete. Thermal shock is often a cause of failure in glass-lined structures.

Guide for the Selection of Protective Treatments

Adapted from report of American Concrete Institute Committee 515, "Guide for the Protection of Concrete Against Chemical Attack by Means of Coatings and Other Corrosion-Resistant Materials," ACI *Proceedings*, Vol. 63, December 1966, pages 1305-1391. Footnotes appear at the end of each table.

ACIDS

Material	Effect on concrete	Protective treatments
Acetic		
< 10%	Slow disintegration	1, 2, 9, 10, 12, 14, 16 (b, c, e, f, g, h)
30%	Slow disintegration	9, 10, 14, 16 (c, e, f, g)
100% (glacial)	Slow disintegration	9, 16 (e, g)
Acid waters (pH of 6.5 or less)	Slow disintegration.* Natural acid waters may erode surface mortar but then action usually stops	1, 2, 3, 6, 8, 9, 10, 11, 12, 13, 16 (b, c, e, f, g, h), 17
Arsenious	None	
Boric	Negligible effect	2, 6, 7, 8, 9, 10, 12, 13, 15, 16 (b, c, e, f, g, h), 17, 19
Butyric	Slow disintegration	3, 4, 8, 9, 10, 12, 16 (b, c, e, f)
Carbolic	Slow disintegration	1, 2, 16 (c, e, g), 17
Carbonic (soda water)	0.9 to 3 ppm of carbon dioxide dissolved in natural waters disintegrates concrete slowly	2, 3, 4, 8, 9, 10, 12, 13, 15, 16 (b, c, e, f, h), 17
Chromic:		
5%	None*	2, 6, 7, 8, 9, 10, 16 (f, g, h), 19
50%	None*	16 (g), 19
Formic:		
10%	Slow disintegration	2, 5, 6, 7, 12, 13, 16 (b, c, e, g), 17
90%	Slow disintegration	2, 7, 13, 16 (c, e, g), 17
Humic	Slow disintegration possible, depending on humus material	1, 2, 3, 9, 12, 15, 16 (b, c, e)
Hydrochloric:		
10%	Rapid disintegration, including steel	2, 5, 6, 7, 8, 9, 10, 12, 14, 16 (b, c, e, f, g, h), 17, 19, 20
37%	Rapid disintegration, including steel	5, 6, 8, 9, 10, 16 (c, e, f, g, h)
Hydrofluoric:		
10%	Rapid disintegration, including steel	5, 6, 7, 8, 9, 12, 16 (carbon and graphite brick; b, c, e, h), 17
75%	Rapid disintegration, including steel	16 (carbon and graphite brick; e, h), 17
Hypochlorous, 10%	Slow disintegration	5, 8, 9, 10, 16 (f, g)
Lactic, 5%	Slow disintegration	3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 15, 16 (b, c, e, f, g, h), 17
Nitric:		
2%	Rapid disintegration	6, 8, 9, 10, 13, 16 (f, g, h), 20
40%	Rapid disintegration	8, 16 (g)
Oleic, 100%	None	
Oxalic	No disintegration. It protects concrete against acetic acid, carbon dioxide, and salt water. POISONOUS, it must not be used on concrete in contact with food or drinking water.	
Perchloric, 10%	Disintegration	8, 10, 16 (e, f, g, h)
Phosphoric		
10%	Slow disintegration	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 (b, c, e, f, g, h), 17, 19
85%	Slow disintegration	1, 2, 3, 5, 7, 8, 9, 10, 13, 14, 15, 16 (c, e, f, g, h), 17, 19
Stearic	Rapid disintegration	5, 6, 8, 9, 10, 11, 12, 13, 15, 16 (b, c, e, f, g, h), 17
Sulfuric.		
10%	*Rapid disintegration*	5, 6, 7, 8, 9, 10, 12, 13, 14, 15, 16 (b, c, e, f, g, h), 17, 19, 20
110% (oleum)	Disintegration	16 (g), 19
Sulfurous	*Rapid disintegration*	6, 7, 9, 11, 12, 13, 16 (b, c, e, h), 19, 20
Tannic	Slow disintegration	1, 2, 3, 6, 7, 8, 9, 11, 12, 13, 16 (b, c, e, g), 17
Tartaric, solution	None. See wine under "Miscellaneous."	

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*In porous or cracked concrete, it attacks steel. Steel corrosion may cause concrete to spall.

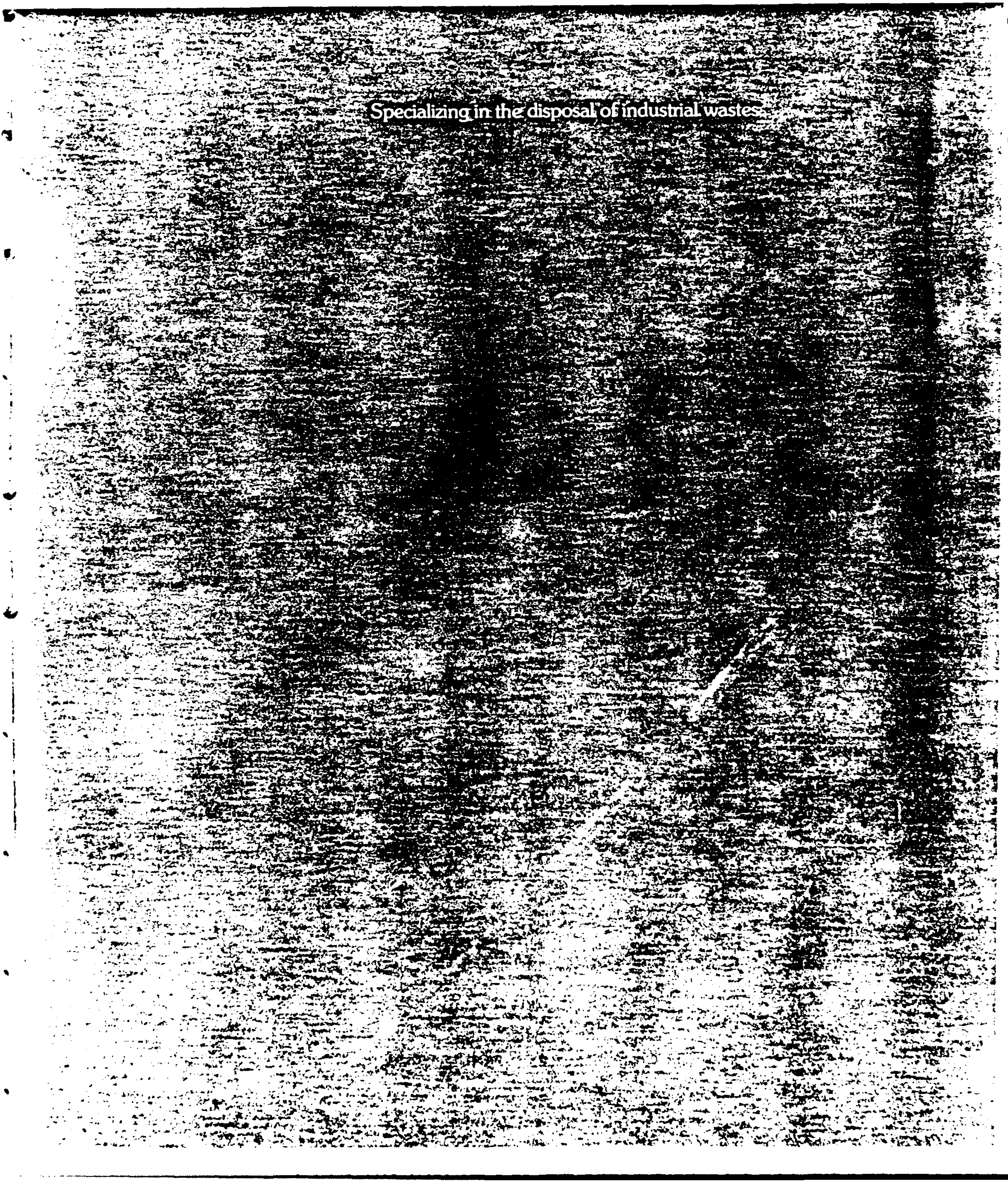
SALTS AND ALKALIES (SOLUTIONS)*

Material	Effect on concrete	Protective treatments
Bicarbonate:		
Ammonium Sodium	None	
Bisulfate:		
Ammonium** Sodium	*Disintegration*	5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 (b, c, e, f, h), 17
Bisulfite:		
Sodium	Disintegration	5, 6, 7, 8, 9, 10, 12, 13, 16 (b, c, e, f, h), 17
Calcium (sulfite solution)	Rapid disintegration	7, 8, 9, 10, 12, 13, 16 (b, c, e, f, h), 17
Bromide, sodium	Slow disintegration	1, 2, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 16 (b, c, e, f, h), 17
Carbonate:		
Ammonium Potassium Sodium	None	
Chlorate, sodium	Slow disintegration	1, 4, 6, 7, 8, 9, 10, 16 (f, g, h), 17, 19
Chloride:		
Calcium† Potassium Sodium† Strontium	None, unless concrete is alternately wet and dry *with the solution***	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 15, 16 (b, c, e, f, g, h), 17
Ammonium Copper Ferric (iron) Ferrous Magnesium Mercuric Mercurous Zinc	Slow disintegration**	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 15, 16 (b, c, e, f, g, h), 17
Aluminum	Rapid disintegration**	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 15, 16 (b, c, e, f, h), 17
Chromate, sodium	None	
Cyanide:		
Ammonium Potassium Sodium	Slow disintegration	7, 8, 9, 12, 13, 16 (b, c), 17

APPENDIX VIII

CASMELIA RESOURCES SANITARY LANDFILL

Casmalia
Resource
Management



Specializing in the disposal of industrial wastes.

Our site is a permitted, full service waste disposal facility located in Northern Santa Barbara County. Locally owned and operated, we have been in the business of providing responsible waste management to communities and industry since 1972.

Why is our site ideally suited for hazardous waste disposal?

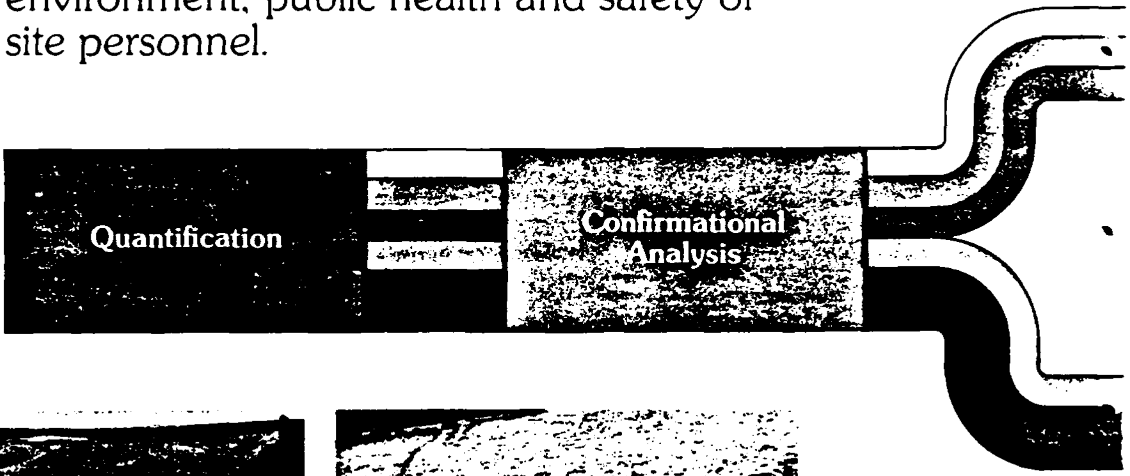
It is located in an area known for its unsurpassed geological integrity. Site selection was based on the availability of impermeable formations underlying the site, the lack of groundwater and its remoteness from populated areas. The operational area is surrounded by an extensive company owned buffer zone of 4,300 acres.

What types of waste do we handle?

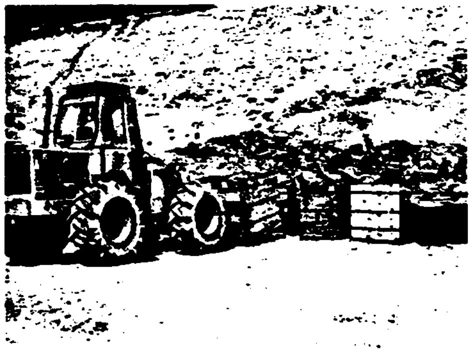
A wide spectrum of chemical, industrial and municipal waste is expertly handled by a qualified technical staff. Waste can be identified in an on-site analytical laboratory insuring compatible segregation.

What disposal techniques are employed?

Our methods of disposal meet federal, state and local regulations as well as reflecting a concern for the natural environment, public health and safety of site personnel.



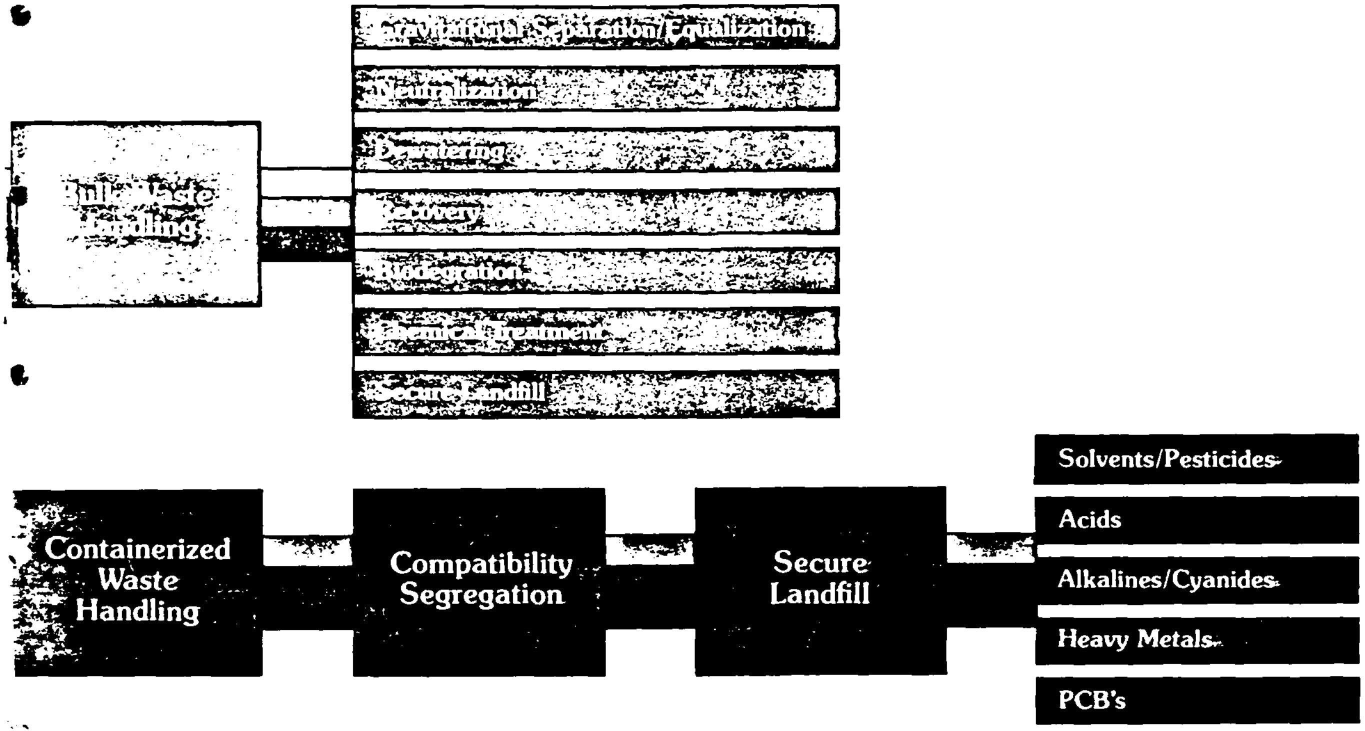
Gravitational separation and clarification basins are designed for liquid waste treatment and ultimate disposal



Containerized wastes are segregated by compatibility group and landfilled in appropriate burial cells

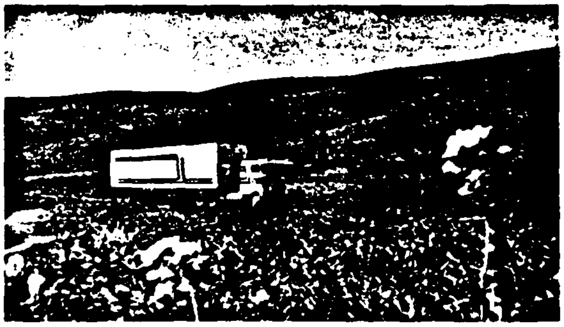
Are any wastes recycled and reused?

Yes. Because of the large amount of oil field waste received, an oil reclamation program has been implemented. In addition, other waste material recovery processes are in review and installation of the required processing facilities is planned in the near future.



Is a transportation service offered?

We operate a transportation program tailored to meet the needs of our customers on a regional basis. We are licensed by the State of California as a hazardous waste hauler and operate in accordance with all Department of Transportation regulations.



One of our well maintained fleet of trucks

Do personnel receive special training?

An intensive formalized instruction program in hazardous waste management is required of all employees to guarantee the safe operation of the facility.

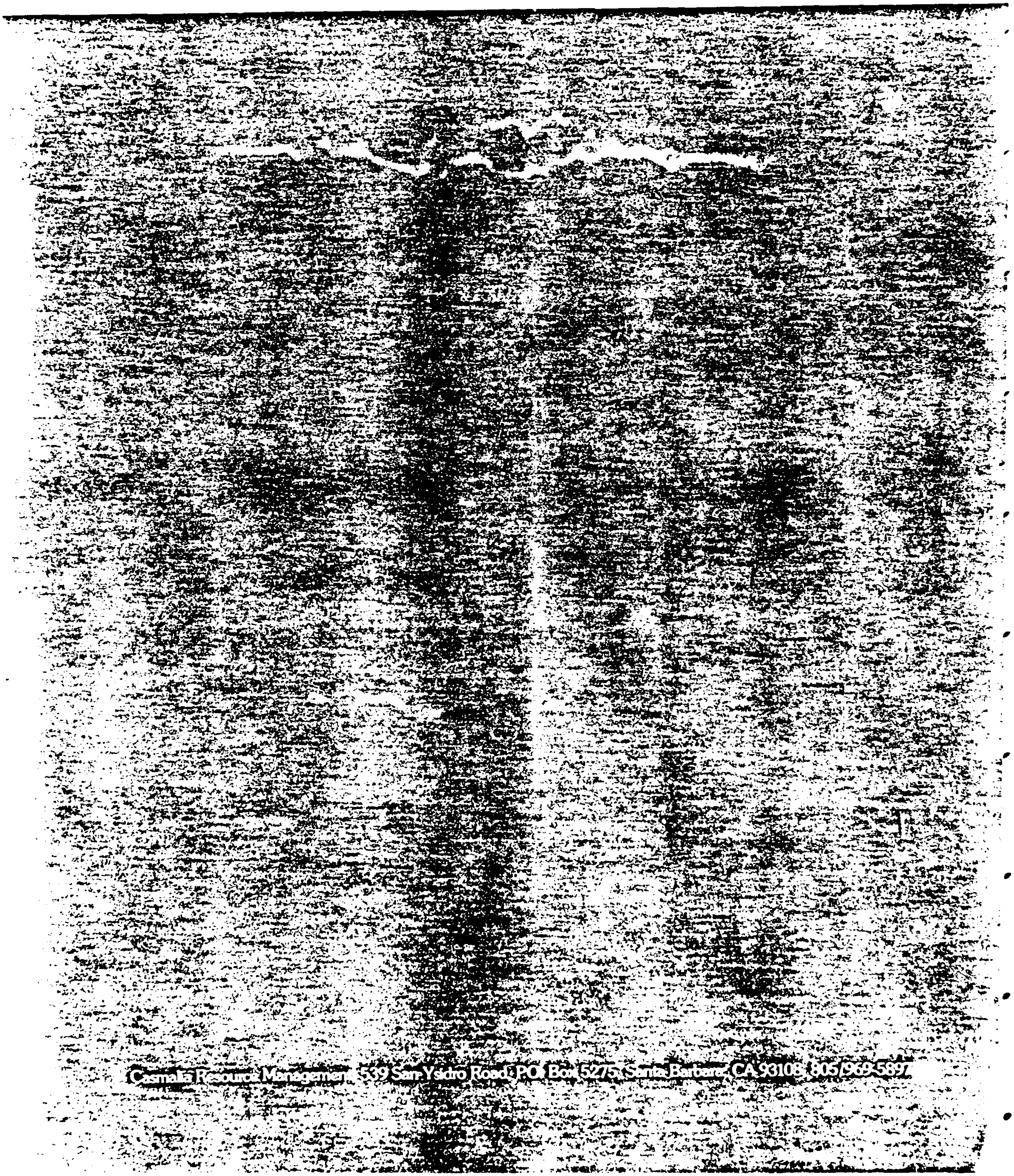
Each employee participates in on-going training programs in hazardous waste management

Composition of wastes is verified by modern analytical equipment in an on-site laboratory.

A complete burial record is kept for each load of waste placed in a landfill area.

What is done to insure environmental and public safety?

Monitoring wells are located throughout the site and the surrounding area. Water sampling is done routinely and analytical studies are performed by an independent testing laboratory. Additionally, numerous local, state and federal agencies monitor the facility on a regular basis.



Casmalia Resource Management 539 San Ysidro Road, P.O. Box 5275, Santa Barbara, CA 93108 805/969-5897

APPENDIX IX

MISCELLANEOUS REFERENCE DOCUMENTS

Southwestern Public Service
Tolk Station, Texas
A111D17197

SILICA REDUCTION BY COLD LIME SOFTENING REVERSE OSMOSIS PRETREATMENT LAB STUDY

Summary

Laboratory tests were conducted on a well water sample from Tolk Station to confirm the reduction of silica from 60 to less than 10 mg/l SiO_2 by cold lime softening as indicated by customer tests. Silt Density Index (SDI) measurements were then made on the cold process effluent, the proposed feed to the Permutit membrane system. Using zeta potential readings, an optimum coagulant dosage was found for reducing the SDI_{15} from 6.5 to 1.4.

Cold lime softening jar tests showed that the silica could be reduced to less than 10 mg/l SiO_2 if sufficient lime was added to obtain a pH of at least 10.5 and a sludge blanket was maintained. However, caution must be exercised not to optimize the silica reduction (5 mg/l SiO_2) by overdosing lime since calcium will be put back into solution, thus nullifying the effect of softening (Table 1, Figures 1, 2, 3).

In order to simulate the in-line coagulation to be used as pretreatment in the Permutit system, the SDI_{15} of the acid stabilized cold lime effluent was reduced from 6.5 to 1.4 by coagulation with Magnifloc 573 followed by filtration through 8.0 µm filter (8.0 µm Millipore filter is used to simulate a sand filter). Zeta potential measurements showed 0.8 mg/l to be the optimum coagulant dosage for Magnifloc 573C. No other coagulants were investigated. Filtering the cold lime effluent without adding a coagulant aid did not substantially alter the sample or the SDI_{15} (Table 3, 4, and 5).

Introduction

The well water was received to determine if the silica could be reduced to less than 10 mg/l SiO_2 by cold lime softening. To determine the optimum conditions for silica removal, jar tests were run and the effluent analyzed for alkalinity, silica, calcium, magnesium, and pH. Parameters investigated included sludge blanket volume, temperature, and lime dosage. An initial 8 volumes of sample were softened in order to generate the sludge blanket for one volume in the final jar test. In both cases an anionic polyelectrolyte of high molecular weight was added as a flocculant. Both unfiltered and samples filtered through 0.1 µm and 8.0 µm Millipore filters were collected on the resulting effluents (with and without sludge blankets).

Zeta potentials were measured on the raw water and the acid stabilized cold lime effluent. The optimum coagulant system required to reduce the zeta potential to near zero was found. The optimum coagulant dosage was added to the sample followed by filtration through an 8.0 µm Millipore filter to simulate sand filtration.

Silt Density Indices for 15 minutes were measured of the raw sample, the cold lime effluent (pH 8.5), 8.0 µm filtrate of the cold lime effluent (pH 8.3), and the coagulated and filtered effluent. The limited sample volume remaining after completing the cold lime softening studies required the use of a smaller filter for SDI determinations. Thus, a 13 mm diameter filter replaced the conventionally used 47 mm filter and the effluent volume collected was reduced proportional to the filter surface area reduction.

Results

- Cold lime softening jar tests

The removal of silica is dependent on several variables including pH, temperature, sludge blanket and magnesium removal. Table 1 summarizes the relationship of these parameters. As can be seen in Figure 1 of pH vs effluent concentration, the silica is reduced almost linearly with pH until pH 10.7 where a minimum is reached (T = 62°F, with sludge blanket). The lowest possible pH should be used since, as seen in Figure 2, an increase in pH after pH 10.4 will add calcium to the solution. Since silica is removed by adsorbing to the $Mg(OH)_2$ precipitate, to effectively reduce the silica from 60 mg/l SiO_2 in the raw water to less than 10 mg/l SiO_2, a larger lime dosage than the stoichiometric dosage for alkalinity removal is required (see analysis of raw water, Table 6). The excess lime dosage removes the magnesium at the expense of adding calcium hydroxide hardness. Figure 3 shows the relationship between magnesium removal and silica removal. This shows that in order to remove 50 mg/l SiO_2 at 62°F, 162 mg/l (as $CaCO_3$) of magnesium must also be removed.

$\times \frac{40}{100} = 65$ mg/l MgO

Table 2 shows the effect of the sludge blanket on silica removal. Samples A and B were run at similar pH with sample B having 100 ml/l (8 vol.:1 vol.) of the precipitate formed in Step 1, and sample A having no sludge blanket. As can be seen from the analysis, the silica was reduced to 6 mg/l SiO_2 in B and 24 mg/l SiO_2 in A. The floc formed in Step A was very small and did not settle completely. The addition of the sludge blanket to Test B created a much larger floc which settled rapidly.

Temperature also affects the efficiency of the silica removal (Table 3). Increasing the temperature from 62 to 69°F increases the silica removal efficiency by 10-16%, depending on the pH.

- Filter vs non-filtered analysis

Measuring the Ca, Mg, and SiO_2 content of the cold lime softened effluent, both unfiltered and filtered through a 0.1 µm Millipore, is a method used to determine the ratio of the dissolved (0.1 µm filtrate) vs the total (non-filtered) constituents. Table 4 showed typical results from filtration of the second step of the jar test. The calcium, magnesium, and silica concentrations remained unchanged by filtration. Since the influent to the Permutit system will be acid stabilized, the jar test effluents were also first pH adjusted to 8.3 with H_2SO_4 followed by filtration and analyses. This analysis shows the cold lime effluent pH adjusted then filtered, to be insignificantly lower in all concentrations than those filtered prior to pH adjustment. As with the pH 10.4 sample, the acid stabilized samples did not show a significant change in analysis for Ca, Mg, or SiO_2 due to filtration of the sample.

- Zeta potentials

Zeta potentials are a measurement of the effective charge on particles. Zeta potential measurements showed the raw water to have a zeta potential of -16 mv while the cold lime effluent was -22 mv. The successive addition of cationic polymer to the cold lime effluent will reduce the zeta potential to zero and eventually reverse it to a positive particle. The optimum coagulant dosage is that necessary to reduce the zeta potential to "0" mv. As seen in Table 5, successive additions of Magnifloc 573C reduces the zeta potential until zero is reached when 0.8 mg/l of the polyelectrolyte is added. This dosage was then added to the sample prior to sand filtration (simulated in this test work by 8.0 µm filtration) and Silt Density Index measurements were made on the filter effluent.

- Silt Density Index (SDI)

The SDI determinations for the raw water and the various lab test effluents are summarized in Table 5. The SDI_{15} for the raw water was 6.4 while the acid stabilized cold lime softened effluent gave an SDI_{15} of 6.5. Filtering the cold lime effluent through an 8.0 µm filter reduces the SDI_{15} to 5.8. The SDI_{15} can be reduced to 1.4 if the effluent is coagulated with 0.8 mg/l of Magnifloc 573 C, then filtered through an 8.0 µm filter.

Caution should be used when interpreting laboratory SDI results. While the laboratory results can be used to indicate trends, the absolute SDI values obtained on a shipped water sample will not necessarily be the same as the SDI values obtained at the source. For this specific application, it is likely that cold lime softening followed by sand filtration will not significantly lower the value of the SDI obtained on the raw water unless a cationic polyelectrolyte is added to the acid stabilized cold lime effluent before it enters the sand filter. Since the laboratory SDI numbers were obtained on a shipped water sample, and a 13 mm filter was used for SDI determinations instead of the standard 47 mm filter, it is likely that the actual field values may differ from laboratory results.

Conclusions and Recommendations

Cold lime softening

- For a 70°F influent, silica can be reduced from 60 mg/l to 10 mg/l SiO_2 if the pH is increased with lime to at least 10.5 and a sludge blanket is maintained.

- Decreasing the temperature of the process from 70°F t 63°F caused a 10% decrease in silica removal.

- Silica removal down to 5 mg/l is possible by overdosing the lime required for alkalinity removal. However, this negates the effect of softening by putting calcium back into solution. ($3.2 \times \frac{40}{100} = 1.28$ MG/L MGO / MG/L SiO_2 REMOVED)

- Approximately 3.2 parts of magnesium removal is required per part of silica removed. Thus, magnesium must be reduced by 162 mg/l as $CaCO_3$ if the silica is to be reduced to less than 10 mg/l.

Coagulation study

- The raw water sample has a zeta potential of -16 mv.

- The cold lime softened effluent has a zeta potential of -22 mv which can be reduced to near zero by the addition of 0.8 mg/l Magnifloc 573C.

- The raw water sample has an SDI_{15} of 6.4.

- The cold lime softened effluent has an SDI_{15} of 6.5.

- The addition of 0.8 mg/l of Magnifloc 573C followed by filtration through an 8.0 µm filter reduces the SDI_{15} to 1.4.

- The above SDI and zeta potential measurements should be used only to determine trends since the measurements were done on a shipped sample.

Nancy J. Lemmo

Nancy J. Lemmo
Technical Service Chemist

TABLE 2. EFFECT OF SLUDGE BLANKET ON SILICA REMOVAL

Test Conditions

A	B
T = 70°F	T = 70°F
Polymer = 1 mg/l Betz 1100	Polymer = 1 mg/l Betz 1100
Lime = 300 mg/l $Ca(OH)_2$	Lime = 250 mg/l $Ca(OH)_2$
Sludge Blanket = 0 ml	Sludge Blanket = 100 ml/liter
pH = 10.5	pH = 10.6

Effluent Analysis

	A	B
Calcium (mg/l as $CaCO_3$)	125	155
Magnesium (mg/l as $CaCO_3$)	128	92.7
HCO_3^- (mg/l as $CaCO_3$)	0	0
$CO_3^=$ (mg/l as $CaCO_3$)	35	23.8
OH^- (mg/l as $CaCO_3$)	4.0	5.4
Alkalinity, Phenolphthalein (mg/l as $CaCO_3$)	21.5	17.6
Alkalinity, total (mg/l as $CaCO_3$)	39.0	29.5
Silica (mg/l as SiO_2)	24	6

Note: Sample A did not settle well even with polymer. Much of the solids remained suspended.

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TABLE 1. SILICA REMOVAL BY COLD LIME SOFTENING

pH	CALCIUM (mg/l as $CaCO_3$)	MgO mg/L	MAGNESIUM (mg/l as $CaCO_3$)	Δ MgO mg/L	ALKALINITY (mg/l as $CaCO_3$)	TEMPERATURE (°F)	SLUDGE VOLUME (ml/l)	SILICA (mg/l as SiO_2)
8.6	165	106	265		156	62	20	59
10.0	123	84	210	22	90	62	20	40
10.2	110	54	136	52	85.3	62	20	32
10.4	128	53	132	53	65	62	20	28
10.4	108		174		45	68	110	18.3
10.5	136	42	105	64	28	70	100	7
10.6	155	37	92.7	69	29.5	70	90	6
10.6	148	41	103	65	39.0	63	90	12
10.7	263	9.6	24	96.4	55	62	100	5.0
10.8	288	5.6	14	100.4	63	62	100	5.6
11.2	355	0	0		153	not measured	100	6.9

Note: These analysis are all of the 0.1μm filtrate

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TABLE 3. EFFECT OF TEMPERATURE ON SiO_2 REMOVAL

pH	Temperature °F	mg/l SiO_2 Influent	mg/l SiO_2 Effluent	% Removed
10.4	62	60	28	53
10.4	68	60	18.3	69
10.6	63	60	12	80
10.6	70	60	6	90

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TABLE 4. EFFECT OF FILTERING A "NON-COAGULATED" SAMPLE

Test Conditions

pH = 10.4

Polymer: 1 mg/l Betz 1100

Sludge Blanket: 65 ml/4 liters

Temperature: 68°F

- Sample Effluent Filtered before Acidification

	FILTER SIZE		
	0.1μm	8.0μm	non-filtered
Calcium (mg/l as $CaCO_3$)	108	108	108
Magnesium (mg/l as $CaCO_3$)	174	174	166
Silica (mg/l as SiO_2)	18	18	19

- Sample Effluent Acidified to pH 8.3 with H_2SO_4 then Filtered

	0.1μm	8.0μm	non-filtered
Calcium (mg/l as $CaCO_3$)	103	99	96
Magnesium (mg/l as $CaCO_3$)	158	164	164
Silica (mg/l as SiO_2)	17	17.5	17

A111D17197

TABLE 5. COAGULATION STUDY

Zeta Potential

Raw Water (Before Softening)	-16 mv
Cold Lime Effluent (Acid Stabilized)	-22 mv
Cold Lime Effluent + 0.2 mg/l Magnifloc 573C	-21 mv
Cold Lime Effluent + 0.4 mg/l Magnifloc 573C	-17 mv
Cold Lime Effluent + 0.6 mg/l Magnifloc 573C	-6 mv
Cold Lime Effluent + 0.8 mg/l Magnifloc 573C	"0" mv

SDI Silt Density Index (SDI)

Sample	SDI_{15}
Raw Water (Before Softening)	6.4
Cold Lime Softened Effluent (Acid Stabilized)	6.5
Cold Lime Softened Effluent (Filtered through an 8μm filter)	5.8
Cold Lime Effluent + 0.8 mg/l Magnifloc 573C then filtered through an 8μm filter	1.4

PERMUTIT®
A ZURN COMPANY

ANALYSIS REPORT

Report Date December 14, 1979
Technical Services No. 9180-260 RT
Job No. A111D17197
Collected 11/79 by
Received 11/8/79 by
Analyzed by
No. of Samples

Sample(s) from SOUTHWESTERN PUBLIC SERVICE CORP.
Address TOLK STATION, TEXAS
Requested by

Remarks

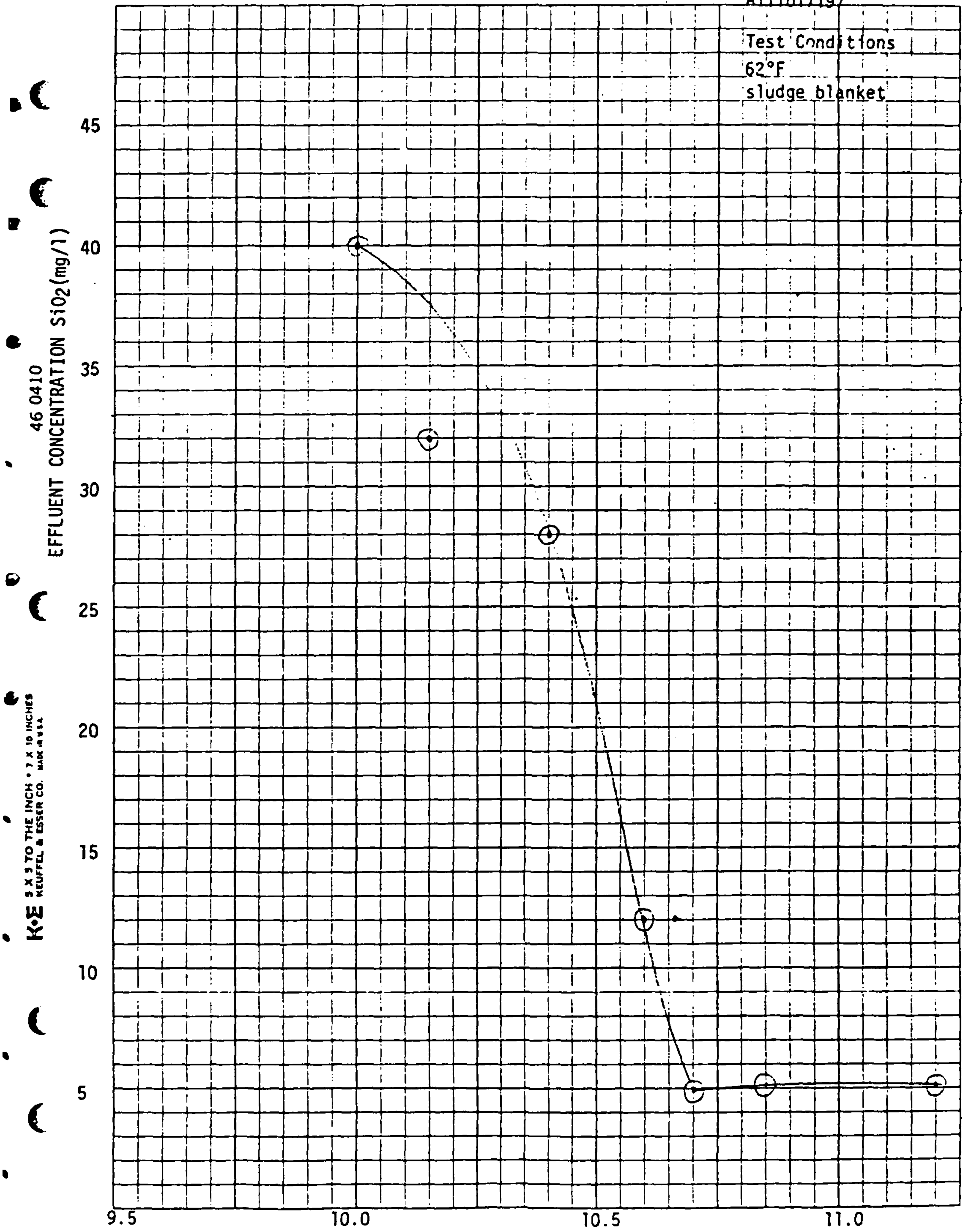
Sample(s) Identification

I. Well Water Received in Drums
Received 11/8/79

Major Cations	Units = mg/1 Expressed as CaCO$_3$	Sample Number					
		I					
Calcium, Ca^{++}		195					
Magnesium, Mg^{++}		247					
Sodium, Na^{+}		229					
Potassium, K^{+}		20					
Acidity (FMA), H^{+}		-					
Σ Major Cations		691					
Major Anions	Units = mg/1 Expressed as CaCO$_3$						
Alkalinity, total		246					
Alk., Phenolphthalein		0					
Chloride, Cl^{-}		141					
Sulfate, SO$_4^{=}$		327					
Nitrate, NO$_3^{-}$		1					
Σ Major Anions		715					
Constituent/Parameter	**Units**						
pH		7.7					
Specific Conductance	µmhos/cm	1190					
Turbidity	NTU	<1					
Color, apparent	color units	<5					
Total Organic Carbon	mg/1 as C	1					
Silica, dissolved	mg/1 as SiO$_2$	60					
Iron	mg/1 as Fe	0.09					
Manganese	mg/1 as Mn	<0.01					
Barium	mg/1 as Ba	0.03					
Strontium	mg/1 as Sr	2.6					
Fluoride	mg/1 as F^{-}	3.7					
Total Dissolved Solids	105°C mg/1	916					

FIGURE 1. pH VS. EFFLUENT CONCENTRATION SiO_2

A111D17197



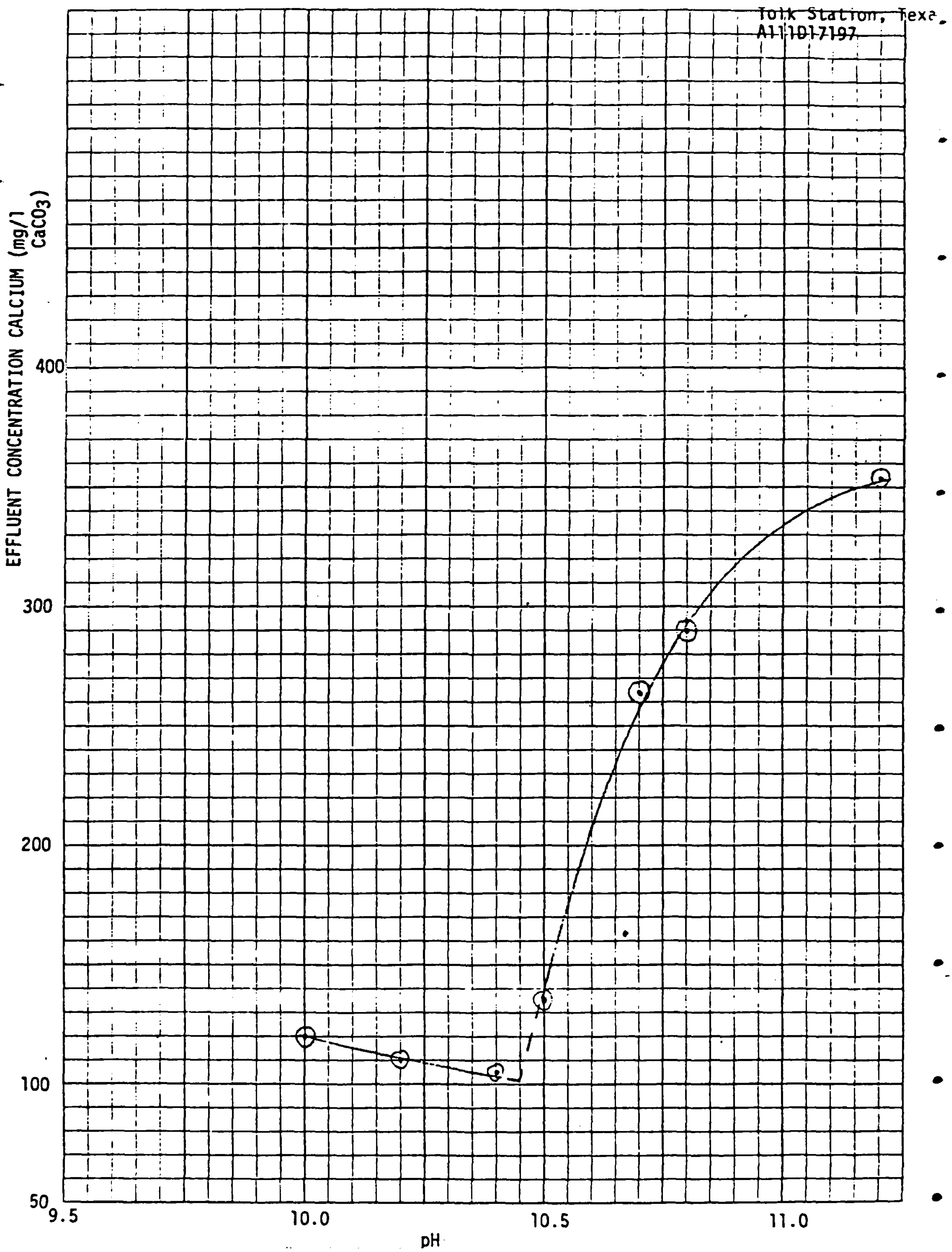
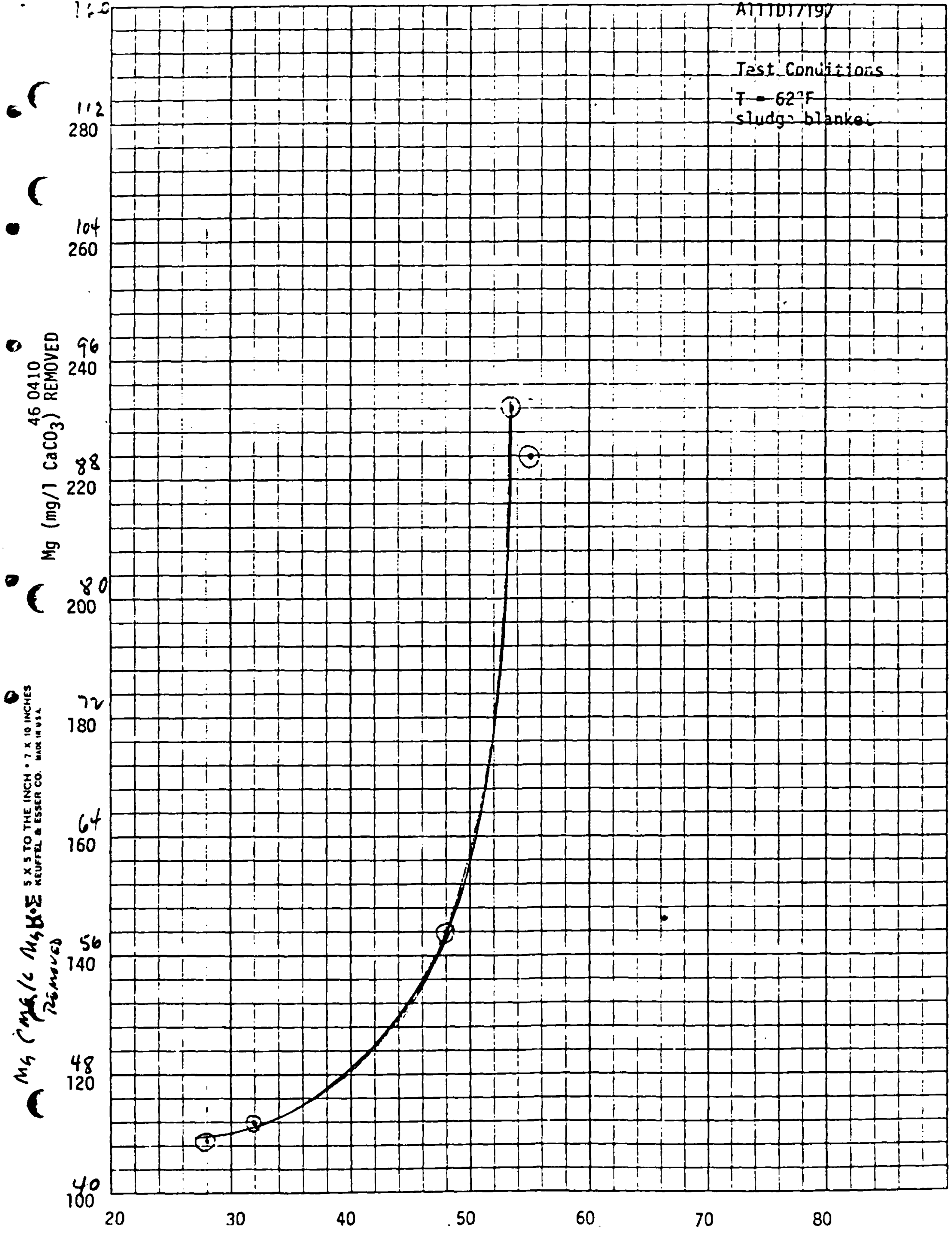

Tolk Station, Texa
A111017197
EFFLUENT CONCENTRATION CALCIUM (mg/l CaCO$_3$)
400
300
200
100
50
9.5
10.0
10.5
11.0
pH

FIGURE 3. MAGNESIUM REMOVAL VS. SILICA REMOVAL



EQUILIBRIUM CONSTANTS

Table 5-5
IONIC PRODUCT CONSTANT OF WATER

This table gives values of pK_w, where K_w is the ionic activity product constant of water, from 0 to 100°C. The values of pK_w from 0 to 60° were given by Harned and Robinson, *Trans. Faraday Soc.*, 36, 973 (1940). Values from 65 to 100° were calculated from Eq. (1-5a) given by Harned and Robinson.

Temp. °C	pK_w	Temp. °C	pK_w	Temp. °C	pK_w	Temp. °C	pK_w
0	14.944	30	13.833	60	13.017	90	12.42
5	14.734	35	13.680	65	12.90	95	12.34
10	14.535	40	13.535	70	12.80	100	12.26
15	14.346	45	13.396	75	12.69		
20	14.167	50	13.262	80	12.60		
25	13.996	55	13.137	85	12.51		

Table 5-6
SOLUBILITY PRODUCTS

The data refer to various temperatures between 18 and 25°C and were primarily compiled from values cited by Bjerrum, Schwarzenbach, and Sillén, *Stability Constants of Metal Complexes*, Part II, Chemical Society, London, 1958.

Substance	pK_{sp}	K_{sp}	Substance	pK_{sp}	K_{sp}
Actinium			$BaCrO_4$	9.93	1.2×10^{-10}
$Ac(OH)_3$	15	1×10^{-15}	$Ba_2[Fe(CN)_6] \cdot 6H_2O$	7.5	3.2×10^{-8}
Aluminum			BaF_2	5.98	1.0×10^{-6}
$AlAsO_4$	15.8	1.6×10^{-16}	$BaSiF_6$	6	1×10^{-6}
cupferrate AlL_3	18.64	$2.3 \times$ [illegible]	$Ba(IO_3)_2 \cdot 2H_2O$	8.82	1.5×10^{-9}
$Al(OH)_3$ amorphous	32.9	$1.3 \times$ [illegible]	$Ba(OH)_2$	2.3	5×10^{-3}
$AlPO_4$	18.24	$6.3 \times$ [illegible]	$Ba(MnO_4)_2$	9.61	2.5×10^{-10}
8-quinolinolate AlL_3	29.00	$1.00 \times$ [illegible]	$BaMoO_4$	7.40	4.0×10^{-8}
Al_2S_3	6.7	$2 \times$ [illegible]	$Ba(NbO_3)_2$	16.50	3.2×10^{-17}
Al_2Se_3	24.4	$4 \times$ [illegible]	$Ba(NO_3)_2$	2.35	4.5×10^{-3}
Americium			[illegible]	[illegible]	1.6×10 [illegible]
$Am(OH)_3$	19.57	[illegible]	[illegible]	7.64	2.3×10^{-8}
$Am(OH)_4$	56	[illegible]	$BaHPO_4$	6.5	3.2×10^{-7}
Ammonium			[illegible]	22.47	3.4×10 [illegible]
$NH_4UO_2AsO_4$	23.77	[illegible]	[illegible]	10.5	3.2×10 [illegible]
Arsenic			[illegible]	[illegible]	[illegible]
$As_2S_3 + 4H_2O \rightleftharpoons$	21.68	[illegible]	8-quinolinolate [illegible]	8.3	5.0×10 [illegible]
$2HAsO_2 + 3H_2S$			[illegible]	[illegible]	[illegible]
Barium			[illegible]	[illegible]	[illegible]
$Ba_3(AsO_4)_2$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
$Ba(BrO_3)_2$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]			[illegible]	[illegible]	[illegible]

Table 5-6 (*Continued*)
SOLUBILITY PRODUCTS

Substance	pK_{sp}	K_{sp}
(OH)$_2$ amorphous	21.8	1.6×10^{-22}
Be(OH)$_2$ + OH$^-$ ⇌ HBeO$_2^-$ + H$_2$O	2.50	3.2×10^{-3}
BeMoO$_4$	1.5	3.2×10^{-2}
Be(NbO$_3$)$_2$	15.92	1.2×10^{-16}
muth		
iAsO$_4$	9.36	4.4×10^{-10}
cupferrate	27.22	6.0×10^{-28}
Bi(OH)$_3$	30.4	4×10^{-31}
BiI$_3$	18.09	8.1×10^{-19}
BiPO$_4$	22.89	1.3×10^{-23}
Bi$_2$S$_3$	97	1×10^{-97}
BiOBr	6.52	3.0×10^{-7}
BiOCl	30.75	1.8×10^{-31}
BiOOH	9.4	4×10^{-10}
BiO(NO$_2$)	6.31	4.9×10^{-7}
BiO(NO$_3$)	2.55	2.82×10^{-3}
BiOSCN	6.80	1.6×10^{-7}
Cadmium		
anthranilate CdL$_2$	8.27	5.4×10^{-9}
Cd$_3$(AsO$_4$)$_2$	32.66	2.2×10^{-33}
[Cd(NH$_3$)$_6$](BF$_4$)$_2$	5.7	2×10^{-6}
benzoate · 2H$_2$O	2.7	2×10^{-3}
Cd(BO$_2$)$_2$	8.64	2.3×10^{-9}
CdCO$_3$	11.28	5.2×10^{-12}
Cd(CN)$_2$	8.0	1.0×10^{-8}
Cd$_2$[Fe(CN)$_6$]	16.49	3.2×10^{-17}
Cd(OH)$_2$ fresh	13.6	2.5×10^{-14}
CdC$_2$O$_4$ · 3H$_2$O	7.04	9.1×10^{-8}
Cd$_3$(PO$_4$)$_2$	32.6	2.5×10^{-33}
quinaldate CdL$_2$	12.3	5.0×10^{-13}
CdS	26.1	8.0×10^{-27}
CdWO$_4$	5.7	2×10^{-6}
Calcium		
Ca$_3$(AsO$_4$)$_2$	18.17	6.8×10^{-19}
acetate · 3H$_2$O	2.4	4×10^{-3}
benzoate · 3H$_2$O	2.4	4×10^{-3}
CaCO$_3$	8.54	2.8×10^{-9}
CaCO$_3$ calcite	8.35	4.5×10^{-9}
CaCO$_3$ aragonite	8.22	6.0×10^{-9}
CaCrO$_4$	3.15	7.1×10^{-4}
CaF$_2$	10.57	2.7×10^{-11}
Ca[SiF$_6$]	3.09	8.1×10^{-4}
Ca(OH)$_2$	5.26	5.5×10^{-6}
Ca(IO$_3$)$_2$ · 6H$_2$O	6.15	7.1×10^{-7}
Ca[Mg(CO$_3$)$_2$] dolomite	11	1×10^{-11}
CaMoO$_4$	7.38	4.2×10^{-8}
Ca(NbO$_3$)$_2$	17.06	8.7×10^{-18}
CaC$_2$O$_4$ · H$_2$O	8.4	4×10^{-9}
CaHPO$_4$	7.0	1×10^{-7}
Ca$_3$(PO$_4$)$_2$	28.70	2.0×10^{-29}
8-quinolinolate CaL$_2$	11.12	7.6×10^{-12}
CaSeO$_4$	3.09	8.1×10^{-4}
CaSeO$_3$	5.53	3.0×10^{-6}
CaSiO$_3$	7.60	2.5×10^{-8}
CaSO$_4$	5.04	9.1×10^{-6}
CaSO$_3$	7.17	6.8×10^{-8}
tartrate dihydrate	6.11	7.7×10^{-7}
CaWO$_4$	8.06	8.7×10^{-9}
Cerium		
CeF$_3$	15.1	8×10^{-16}
Ce(OH)$_3$	19.8	1.6×10^{-20}
Ce(IO$_3$)$_3$	9.50	3.2×10^{-10}
Ce(IO$_3$)$_4$	16.3	5×10^{-17}
CeO$_2$	36.1	8×10^{-37}
Ce$_2$(C$_2$O$_4$)$_3$ · 9H$_2$O	25.5	3.2×10^{-26}
CePO$_4$	23	1×10^{-23}
Ce$_2$(SeO$_3$)$_3$	24.43	3.7×10^{-25}
Ce$_2$S$_3$	10.22	6.0×10^{-11}
(III) tartrate	19.0	1×10^{-19}
Cesium		
CsBrO$_3$	1.7	5×10^{-2}
CsClO$_3$	1.4	4×10^{-2}
Cs$_2$[PtCl$_6$]	7.5	3.2×10^{-8}
Cs$_3$[Co(NO$_2$)$_6$]	15.24	5.7×10^{-16}
Cs[BF$_4$]	4.7	5×10^{-5}
Cs$_2$[PtF$_6$]	5.62	2.4×10^{-6}
Cs$_2$[SiF$_6$]	4.90	1.3×10^{-5}
CsClO$_4$	2.4	4×10^{-3}
CsIO$_4$	2.36	4.3×10^{-3}
CsMnO$_4$	4.08	8.2×10^{-5}
CsReO$_4$	3.40	4.0×10^{-4}
Chromium(II)		
Cr(OH)$_2$	15.7	2×10^{-16}
Chromium(III)		
CrAsO$_4$	20.11	7.7×10^{-21}
CrF$_3$	10.18	6.6×10^{-11}
Cr(NH$_3$)$_6$(BF$_4$)$_3$	4.21	6.2×10^{-5}
Cr(OH)$_3$	30.2	6.3×10^{-31}
Cr(NH$_3$)$_6$(ReO$_4$)$_3$	11.11	7.7×10^{-12}
CrPO$_4$ · 4H$_2$O green	22.62	2.4×10^{-23}
violet	17.00	1.0×10^{-17}
Cobalt		
anthranilate CoL$_2$	9.68	2.1×10^{-10}
Co$_3$(AsO$_4$)$_2$	28.12	7.6×10^{-29}
CoCO$_3$	12.84	1.4×10^{-13}
Co$_2$[Fe(CN)$_6$]	14.74	1.8×10^{-15}
[Co(NH$_3$)$_6$](BF$_4$)$_2$	5.4	4×10^{-6}
Co(OH)$_2$ fresh	14.8	1.6×10^{-15}
Co(OH)$_3$	43.8	1.6×10^{-44}
Co(IO$_3$)$_2$	4.0	1.0×10^{-4}
quinaldate CoL$_2$	10.8	1.6×10^{-11}
Co[Hg(SCN)$_4$]	5.82	1.5×10^{-6}
α-CoS	20.4	4.0×10^{-21}
β-CoS	24.7	2.0×10^{-25}
8-quinolinolate CoL$_2$	24.8	1.6×10^{-25}

Table 5-6 (*Continued*)
SOLUBILITY PRODUCTS

Substance	pK_{sp}	K_{sp}
$CoHPO_4$	6.7	2×10^{-7}
$Co_3(PO_4)_2$	34.7	2×10^{-35}
$CoSeO_3$	6.8	1.6×10^{-7}
Copper(I)		
CuN_3	8.31	4.9×10^{-9}
$Cu[B(C_6H_5)_4]$ tetraphenylborate	8.0	1×10^{-8}
CuBr	8.28	5.3×10^{-9}
CuCl	5.92	1.2×10^{-6}
CuCN	19.49	3.2×10^{-20}
CuI	11.96	1.1×10^{-12}
CuOH	14.0	1×10^{-14}
Cu_2S	47.6	2.5×10^{-48}
CuSCN	14.32	4.8×10^{-15}
Copper(II)		
anthranilate, CuL_2	13.22	6.0×10^{-14}
$Cu_3(AsO_4)_2$	35.12	7.6×10^{-36}
$Cu(N_3)_2$	9.2	6.3×10^{-10}
$CuCO_3$	9.86	1.4×10^{-10}
$CuCrO_4$	5.44	3.6×10^{-6}
$Cu_2[Fe(CN)_6]$	15.89	1.3×10^{-16}
$Cu(IO_3)_2$	7.13	7.4×10^{-8}
$Cu(OH)_2$	19.66	2.2×10^{-20}
CuC_2O_4	7.64	2.3×10^{-8}
$Cu_3(PO_4)_2$	36.9	1.3×10^{-37}
$Cu_2P_2O_7$	15.08	8.3×10^{-16}
quinaldate, CuL_2	16.8	1.6×10^{-17}
8-quinolinolate, CuL_2	29.7	2.0×10^{-30}
CuS	35.2	6.3×10^{-36}
$CuSeO_3$	7.68	2.1×10^{-8}
$CuWO_4$	5	1×10
Dysprosium		
$Dy_2(CrO_4)_3 \cdot 10H_2O$	8	1×10^{-8}
$Dy(OH)_3$	21.85	1.4×10^{-22}
Erbium		
$Er(OH)_3$	23.39	4.1×10^{-24}
Europium		
$Eu(OH)_3$	23.05	8.9×10^{-24}
Gadolinium		
$Gd(HCO_3)_3$	1.7	2×10
$Gd(OH)_3$	22.74	1.8×10^{-23}
Gallium		
$Ga_4[Fe(CN)_6]_3$	33.82	1.5×10^{-34}
$Ga(OH)_3$	35.15	7.0×10^{-36}
8-quinolinolate, GaL_3	32.06	8.7×10^{-33}
Germanium		
GeO_2	57.0	1.0×10^{-57}
Gold(I)		
AuCl	12.7	2.0×10
AuI	22.8	1.6×10
Gold(III)		
$AuCl_3$	24.5	3.2×10
$Au(OH)_3$	45.[illegible]	[illegible]

Substance	pK_{sp}	K_{sp}
AuI_3	46	1×10^{-46}
$Au_2(C_2O_4)_3$	10	1×10^{-10}
Hafnium		
$Hf(OH)_4$	25.4	4.0×10^{-26}
Holmium		
$Ho(OH)_3$	22.3	5.0×10^{-23}
Indium		
$In_4[Fe(CN)_6]_3$	43.72	1.9×10^{-44}
$In(OH)_3$	33.2	6.3×10^{-34}
quinolinolate, InL_3	31.34	4.6×10^{-32}
In_2S_3	73.24	5.7×10^{-74}
$In_2(SeO_3)_3$	32.6	4.0×10^{-33}
Iron(II)		
$FeCO_3$	10.50	3.2×10^{-11}
$Fe(OH)_2$	15.1	8.0×10^{-16}
$FeC_2O_4 \cdot 2H_2O$	6.5	3.2×10^{-7}
FeS	17.2	6.3×10^{-18}
Iron(III)		
$FeAsO_4$	20.24	5.7×10^{-21}
$Fe_4[Fe(CN)_6]_3$	40.52	3.3×10^{-41}
$Fe(OH)_3$	37.4	4×10^{-38}
$FePO_4$	21.89	1.3×10^{-22}
quinaldate, FeL_3	16.9	1.3×10^{-17}
$Fe_2(SeO_3)_3$	30.7	2.0×10^{-31}
Lanthanum		
$La(BrO_3)_3 \cdot 9H_2O$	2.5	3.2×10^{-3}
$La(OH)_3$	18.7	2.0×10^{-19}
$La(IO_3)_3$	11.21	6.1×10^{-12}
$La_2(MoO_4)_3$	20.4	4×10^{-21}
$La_2(C_2O_4)_3 \cdot 9H_2O$	26.60	2.5×10^{-27}
$LaPO_4$	22.43	3.7×10^{-23}
$La_2(SO_4)_3$	4.5	3.2×10^{-5}
La_2S_3	12.70	2.0×10^{-13}
$La_2(WO_4)_3 \cdot 3H_2O$	3.90	1.3×10^{-4}
Lead		
acetate	2.75	1.8×10^{-3}
anthranilate, PbL_2	9.81	1.6×10^{-10}
$Pb_3(AsO_4)_2$	35.39	4.0×10^{-36}
$Pb(N_3)_2$	8.59	2.5×10^{-9}
$Pb(BO_2)_2$	10.78	1.6×10^{-11}
$PbBr_2$	4.41	4.0×10^{-5}
$Pb(BrO_3)_2$	1.70	2.0×10^{-2}
$PbCO_3$	13.13	7.4×10^{-14}
$PbCl_2$	4.79	1.6×10^{-5}
PbClF	8.62	2.4×10^{-9}
$PbCrO_4$	12.55	2.8×10^{-13}
$Pb(ClO_2)_2$	8.4	4×10^{-9}
$Pb_2[Fe(CN)_6]$	14.46	3.5×10^{-15}
PbF_2	7.57	2.7×10^{-8}
PbFI	8.07	8.5×10^{-9}
$Pb(OH)_2$	14.93	1.2×10^{-15}
PbOHBr	14.70	2×10^{-15}
PbOHCl	[illegible]	[illegible]

Table 5-6 (*Continued*)
SOLUBILITY PRODUCTS

Substance	pK_{sp}	K_{sp}
$PbOHNO_3$	3.55	2.8×10^{-4}
PbI_2	8.15	7.1×10^{-9}
$Pb(IO_3)_2$	12.49	3.2×10^{-13}
$PbMoO_4$	13.0	1.0×10^{-13}
$Pb(NbO_3)_2$	16.62	2.4×10^{-17}
PbC_2O_4	9.32	4.8×10^{-10}
$PbHPO_4$	9.90	1.3×10^{-10}
$Pb_3(PO_4)_2$	42.10	8.0×10^{-43}
$PbHPO_3$	6.24	5.8×10^{-7}
quinaldate, PbL_2	10.6	2.5×10^{-11}
$PbSeO_4$	6.84	1.4×10^{-7}
$PbSeO_3$	11.5	3.2×10^{-12}
$PbSO_4$	7.79	1.6×10^{-8}
PbS	27.9	8.0×10^{-28}
$Pb(SCN)_2$	4.70	2.0×10^{-5}
PbS_2O_3	6.40	4.0×10^{-7}
$PbWO_4$	6.35	4.5×10^{-7}
Lead(IV)		
$Pb(OH)_4$	65.5	3.2×10^{-66}
Lithium		
Li_2CO_3	1.60	2.5×10^{-2}
LiF	2.42	3.8×10^{-3}
Li_3PO_4	8.5	3.2×10^{-9}
$LiUO_2AsO_4$	18.82	1.5×10^{-19}
Lutetium		
$Lu(OH)_3$	23.72	1.9×10^{-24}
Magnesium		
$MgNH_4PO_4$	12.6	2.5×10^{-13}
$Mg_3(AsO_4)_2$	19.68	2.1×10^{-20}
$MgCO_3$	7.46	3.5×10^{-8}
$MgCO_3 \cdot 3H_2O$	4.67	2.1×10^{-5}
MgF_2	8.19	6.5×10^{-9}
$Mg(OH)_2$	10.74	1.8×10^{-11}
$Mg(IO_3)_2 \cdot 4H_2O$	2.5	3.2×10^{-3}
$Mg(NbO_3)_2$	16.64	2.3×10^{-17}
$Mg_3(PO_4)_2$	23–27	10^{-23} to 10^{-27}
8-quinolinolate, MgL_2	15.4	4.0×10^{-16}
$MgSeO_3$	4.89	1.3×10^{-5}
$MgSO_4$	2.5	3.2×10[illegible]
Manganese		
anthranilate, MnL_2	6.75	1.8×10[illegible]
$Mn_3(AsO_4)_2$	28.72	1.9×10^{-29}
$MnCO_3$	10.74	1.8×10^{-11}
$Mn_2[Fe(CN)_6]$	12.10	8.0×10^{-13}
$Mn(OH)_2$	12.72	1.9×10^{-13}
$MnC_2O_4 \cdot 2H_2O$	14.96	1.1×10^{-15}
8-quinolinolate, MnL_2	21.7	2.0×10^{-22}
$MgSeO_3$	6.9	1.3×10[illegible]
MnS amorphous	9.6	2.5×10[illegible]
crystalline	12.6	2.5×10[illegible]
Mercury(I)		
$Hg_2(N_3)_2$	9.15	7.1×10[illegible]
Hg_2Br_2	22.24	5.6×10[illegible]
Hg_2CO_3	16.05	8.9×10^{-17}
$Hg_2(CN)_2$	39.3	5×10^{-40}
Hg_2Cl_2	17.88	1.3×10^{-18}
Hg_2CrO_4	8.70	2.0×10^{-9}
$(Hg_2)_3[Fe(CN)_6]_2$	20.07	8.5×10^{-21}
$Hg_2(OH)_2$	23.7	2.0×10^{-24}
$Hg_2(IO_3)_2$	13.71	2.0×10^{-14}
Hg_2I_2	28.35	4.5×10^{-29}
$Hg_2C_2O_4$	12.7	2.0×10^{-13}
Hg_2HPO_4	12.40	4.0×10^{-13}
quinaldate, Hg_2L_2	17.9	1.3×10^{-18}
Hg_2SeO_3	14.2	8.4×10^{-15}
Hg_2SO_4	6.13	7.4×10^{-7}
Hg_2SO_3	27.0	1.0×10^{-27}
Hg_2S	47.0	1.0×10^{-47}
$Hg_2(SCN)_2$	19.7	2.0×10^{-20}
Hg_2WO_4	16.96	1.1×10^{-17}
Mercury(II)		
$Hg(OH)_2$	25.52	3.0×10^{-26}
$Hg(IO_3)_2$	12.5	3.2×10^{-13}
1,10-*phenanthroline*	24.70	2.0×10^{-25}
quinaldate, HgL_2	16.8	1.6×10^{-17}
$HgSeO_3$	13.82	1.5×10^{-14}
HgS *red*	52.4	4×10^{-53}
HgS black	51.8	1.6×10^{-52}
Neodymium		
$Nd(OH)_3$	21.49	3.2×10^{-22}
Neptunium		
$NpO_2(OH)_2$	21.6	2.5×10^{-22}
Nickel		
$[Ni(NH_3)_6][ReO_4]_2$	3.29	5.1×10^{-4}
anthranilate, NiL_2	9.09	8.1×10^{-10}
$Ni_3(AsO_4)_2$	25.51	3.1×10^{-26}
$NiCO_3$	8.18	6.6×10^{-9}
$Ni_2(CN)_4 \rightarrow Ni^{2+} + Ni(CN)_4^{2-}$	8.77	1.7×10^{-9}
$Ni_2[Fe(CN)_6]$	14.89	1.3×10^{-15}
$[Ni(N_2H_4)_3]SO_4$	13.15	7.1×10^{-14}
$Ni(OH)_2$, fresh	14.7	2.0×10^{-15}
$Ni(IO_3)_2$	7.85	1.4×10^{-8}
NiC_2O_4	9.4	4×10^{-10}
$Ni_3(PO_4)_2$	30.3	5×10^{-31}
$Ni_2P_2O_7$	12.77	1.7×10^{-13}
8-quinolinolate, NiL_2	26.1	8×10^{-27}
quinaldate, NiL_2	10.1	8×10^{-11}
$NiSeO_3$	5.0	1.0×10^{-5}
α-NiS	18.5	3.2×10^{-19}
β-NiS	24.0	1.0×10^{-24}
γ-NiS	25.7	2.0×10^{-26}
Palladium		
$Pd(OH)_2$	31.0	[illegible]
$Pd(OH)_4$	[illegible]	6.3×10[illegible]
[illegible]	[illegible]	[illegible]

Table 5-6 (*Continued*)
SOLUBILITY PRODUCTS

Substance	pK_{sp}	K_{sp}	Substance	pK_{sp}	K_{sp}
Platinum			$AgBrO_3$	4.28	5.3×10^{-5}
$PtBr_4$	40.5	3.2×10^{-41}	$AgBr$	12.30	5.0×10^{-13}
$Pt(OH)_2$	35	1×10^{-35}	Ag_2CO_3	11.09	8.1×10^{-12}
Plutonium			$AgClO_2$	3.7	2.0×10^{-4}
PuO_2CO_3	12.77	1.7×10^{-13}	$AgCl$	9.75	1.8×10^{-10}
PuF_3	15.6	2.5×10^{-16}	Ag_2CrO_4	11.95	1.1×10^{-12}
PuF_4	19.2	6.3×10^{-20}	$Ag_3[Co(NO_2)_6]$	20.07	8.5×10^{-21}
$Pu(OH)_3$	19.7	2.0×10^{-20}	cyanamide, Ag_2CN_2	10.14	7.2×10^{-11}
$Pu(OH)_4$	55	1×10^{-55}	$AgOCN$	6.64	2.3×10^{-7}
$PuO_2(OH)$	9.3	5×10^{-10}	$AgCN$	15.92	1.2×10^{-16}
$PuO_2(OH)_2$	24.7	2×10^{-25}	$Ag_2Cr_2O_7$	6.70	2.0×10^{-7}
$Pu(IO_3)_4$	12.3	5×10^{-13}	dicyanimide, $AgN(CN)_2$	8.85	1.4×10^{-9}
$Pu(HPO_4)_2 \cdot xH_2O$	27.7	2×10^{-28}	$Ag_4[Fe(CN)_6]$	40.81	1.6×10^{-41}
Polonium			$AgOH$	7.71	2.0×10^{-8}
PoS	28.26	5.5×10^{-29}	$Ag_2N_2O_2$	18.89	1.3×10^{-19}
Potassium			$AgIO_3$	7.52	3.0×10^{-8}
$K_2[PdCl_6]$	5.22	6.0×10^{-6}	AgI	16.08	8.3×10^{-17}
$K_2[PtCl_6]$	4.96	1.1×10^{-5}	Ag_2MoO_4	11.55	2.8×10^{-12}
$K_2[PtBr_6]$	4.2	6.3×10^{-5}	$AgNO_2$	3.22	6.0×10^{-4}
$K_2[PtF_6]$	4.54	2.9×10^{-5}	$Ag_2C_2O_4$	10.46	3.4×10^{-11}
K_2SiF_6	6.06	8.7×10^{-7}	Ag_3PO_4	15.84	1.4×10^{-16}
K_2ZrF_6	3.3	5×10^{-4}	quinaldate, AgL	17.9	1.3×10^{-18}
KIO_4	3.08	8.3×10^{-4}	$AgReO_4$	4.10	8.0×10^{-5}
$K_2Na[Co(NO_2)_6] \cdot H_2O$	10.66	2.2×10^{-11}	Ag_2SeO_3	15.00	1.0×10^{-15}
$K[B(C_6H_5)_4]$	7.65	2.2×10^{-8}	Ag_2SeO_4	7.25	5.7×10^{-8}
KUO_2AsO_4	22.60	2.5×10^{-23}	$AgSeCN$	15.40	4.0×10^{-16}
$K_4[UO_2(CO_3)_3]$	4.2	6.3×10^{-5}	Ag_2SO_4	4.84	1.4×10^{-5}
Praseodymium			Ag_2SO_3	13.82	1.5×10^{-14}
$Pr(OH)_3$	21.17	6.8×10^{-22}	Ag_2S	49.2	6.3×10^{-50}
Promethium			$AgSCN$	12.00	1.0×10^{-12}
$Pm(OH)_3$	21	1×10^{-21}	$AgVO_3$	6.3	5×10^{-7}
Radium			Ag_2WO_4	11.26	5.5×10^{-12}
$Ra(IO_3)_2$	9.06	8.7×10^{-10}	Sodium		
$RaSO_4$	10.37	4.2×10^{-11}	$Na[Sb(OH)_6]$	7.4	4.0×10^{-8}
Rhodium			Na_3AlF_6	9.39	4.0×10^{-10}
$Rh(OH)_3$	23	1×10^{-23}	$NaK_2[Co(NO_2)_6]$	10.66	2.2×10^{-11}
Rubidium			$Na(NH_4)_2[Co(NO_2)_6]$	11.4	4×10^{-12}
$Rb_3[Co(NO_2)_6]$	14.83	1.5×10^{-15}	$NaUO_2AsO_4$	21.87	1.3×10^{-22}
$Rb_2[PtCl_6]$	7.2	6.3×10^{-8}	Strontium		
$Rb_2[PtF_6]$	6.12	7.7×10^{-7}	$Sr_3(AsO_4)$	18.09	8.1×10^{-19}
$Rb_2[SiF_6]$	6.3	5.0×10^{-7}	$SrCO_3$	9.96	1.1×10^{-10}
$RbClO_4$	2.60	2.5×10^{-3}	$SrCrO_4$	4.65	2.2×10^{-5}
$RbIO_4$	3.26	5.5×10^{-4}	SrF_2	8.61	2.5×10^{-9}
Ruthenium			$Sr(IO_3)_2$	6.48	3.3×10^{-7}
$Ru(OH)_3$	36	1×10^{-36}	$SrMoO_4$	6.7	2×10^{-7}
Samarium			$Sr(NbO_3)_2$	17.38	4.2×10^{-18}
$Sm(OH)_3$	22.08	8.3×10^{-23}	$SrC_2O_4 \cdot H_2O$	6.80	1.6×10^{-7}
Scandium			$Sr_3(PO_4)_2$	27.39	4.0×10^{-28}
ScF_3	17.37	4.2×10^{-18}	8-quinolinolate, SrL_2	9.3	5×10^{-10}
$Sc(OH)_3$	30.1	8.0×10^{-31}	$SrSeO_3$	5.74	1.8×10^{-6}
Silver			$SrSeO_4$	3.09	8.1×10^{-4}
AgN_3	8.54	2.8×10^{-9}	$SrSO_3$	7.4	4×10^{-8}
Ag_3AsO_4	22.0	1.0×10^{-22}	$SrSO_4$	6.49	3.2×10^{-7}

Table 5-6 (*Continued*)
SOLUBILITY PRODUCTS

Substance	pK_{sp}	K_{sp}	Substance	pK_{sp}	K_{sp}
$SrWO_4$	9.77	1.7×10^{-10}	Uranium		
Terbium			UO_2HAsO_4	10.50	3.2×10^{-11}
$Tb(OH)_3$	21.70	2.0×10^{-22}	UO_2CO_3	11.73	1.8×10^{-12}
Tellurium			$(UO_2)_2[Fe(CN)_6]$	13.15	7.1×10^{-14}
$Te(OH)_4$	53.52	3.0×10^{-54}	$UF_4 \cdot 2.5H_2O$	21.24	5.7×10^{-22}
Thallium(I)			$UO_2(OH)_2$	21.95	1.1×10^{-22}
TlN_3	3.66	2.2×10^{-4}	$UO_2(IO_3)_2 \cdot H_2O$	7.5	3.2×10^{-8}
$TlBr$	5.47	3.4×10^{-6}	$UO_2C_2O_4 \cdot 3H_2O$	3.7	2×10^{-4}
$TlBrO_3$	4.07	8.5×10^{-5}	$(UO_2)_3(PO_4)_2$	46.7	2.0×10^{-47}
$Tl_2[PtCl_6]$	11.4	4.0×10^{-12}	UO_2HPO_4	10.67	2.1×10^{-11}
$TlCl$	3.76	1.7×10^{-4}	UO_2SO_3	8.59	2.6×10^{-9}
Tl_2CrO_4	12.00	1.0×10^{-12}	$UO_2(SCN)_2$	3.4	4×10^{-4}
$Tl_4[Fe(CN)_6] \cdot 2H_2O$	9.3	5×10^{-10}	Vanadium		
$TlIO_3$	5.51	3.1×10^{-6}	$VO(OH)_2$	22.13	5.9×10^{-23}
TlI	7.19	6.5×10^{-8}	$(VO)_3PO_4$	24.1	8×10^{-25}
$Tl_2C_2O_4$	3.7	2×10^{-4}	Ytterbium		
Tl_2SeO_3	38.7	2×10^{-39}	$Yt(OH)_3$	23.6	2.5×10^{-24}
Tl_2SeO_4	4.00	1.0×10^{-4}	Yttrium		
Tl_2S	20.3	5.0×10^{-21}	YF_3	12.14	6.6×10^{-13}
$TlSCN$	3.77	1.7×10^{-4}	$Y(OH)_3$	22.1	8.0×10^{-23}
Thallium(III)			$Y_2(C_2O_4)_3$	28.28	5.3×10^{-29}
$Tl(OH)_3$	45.20	6.3×10^{-46}	Zinc		
8-quinolinolate, TlL_3	32.4	4.0×10^{-33}	anthranilate, ZnL_2	9.23	5.9×10^{-10}
Thorium			$Zn_3(AsO_4)_2$	27.89	1.3×10^{-28}
$ThF_4 \cdot 4H_2O + 2H^+ \rightarrow$	7.23	5.9×10^{-8}	$Zn(BO_2)_2 \cdot H_2O$	10.18	6.6×10^{-11}
$ThF_2^{2+} + 2HF + 4H_2O$			$ZnCO_3$	10.84	1.4×10^{-11}
$Th(OH)_4$	44.4	4.0×10^{-45}	$Zn_2[Fe(CN)_6]$	15.39	4.0×10^{-16}
$Th(C_2O_4)_2$	22	1×10^{-22}	$Zn(IO_3)_2$	7.7	2.0×10^{-8}
$Th_3(PO_4)_4$	78.6	2.5×10^{-79}	$Zn(OH)_2$	16.92	1.2×10^{-17}
$Th(HPO_4)_2$	20	1×10^{-20}	ZnC_2O_4	7.56	2.7×10^{-8}
$Th(IO_3)_4$	14.6	2.5×10^{-15}	$Zn_3(PO_4)_2$	32.04	9.0×10^{-33}
Thullium			quinaldate, ZnL_2	13.8	1.6×10^{-14}
$Tm(OH)_3$	23.48	3.3×10^{-24}	8-quinolinolate, ZnL_2	24.3	5.0×10^{-25}
Tin			$ZnSeO_3$	6.59	2.6×10^{-7}
$Sn(OH)_2$	27.85	1.4×10^{-28}	α-ZnS	23.8	1.6×10^{-24}
$Sn(OH)_4$	56	1×10^{-56}	β-ZnS	21.6	2.5×10^{-22}
SnS	25.0	1.0×10^{-25}	$Zn[Hg(SCN)_4]$	6.66	2.2×10^{-7}
Titanium			Zirconium		
$Ti(OH)_3$	40	1×10^{-40}	$ZrO(OH)_2$	48.2	6.3×10^{-49}
$TiO(OH)_2$	29	1×10^{-29}	$Zr_3(PO_4)_4$	132	1×10^{-132}

PROTON-TRANSFER REACTIONS

The pK_a values listed in Tables 5-7 and 5-8 are the negative (decadic) logarithms of the acidic dissociation constant, i.e., $-\log_{10}K_a = pK_a$. For the general proton-transfer reaction

$$HB \rightleftharpoons H^+ + B$$

the acidic dissociation constant is formulated as follows:

Treatment of Heavy Metals in Wastewaters

What wastewater-treatment method is most cost-effective for electroplating and finishing operations? Here are the alternatives.

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The Federal Government has allowed the General Pretreatment Regulations to take effect as of January 31, 1982 (46 *Federal Register* 4518). In addition, regulations for the electroplating industry have been reissued in the January 13, 1982 *Federal Register* with a compliance date of January 28, 1984. These regulations include maximum discharge criteria for heavy metals. These limitations closely parallel the present criteria promulgated for the plating/surface-finishing industry. The heavy-metals limitations can be broken down into two basic classifications — discharges less than 10,000 gallons per day, and those discharges greater than 10,000 gallons per day to Publicly Owned Treatment Works (POTW). There are complicated formulas for removal credits, but most platers will probably opt to comply with one of the two discharge schedules below (Table 1 and Table 2).

This paper will present a discussion of alternative methods used to treat the typical heavy-metal wastewaters most often generated by electro-plating and surface-finishing operations. Before considering any form of wastewater treatment, it is essential that the manufacturer review and reduce his water usage wherever feasible. This can be done with rinse-tank controllers (conductivity), counterflow rinsing, flow restrictors, and foot pedals. Water-usage reductions will permit the manufacturer to reduce the volume of wastewater generated and thus reduce the capital cost of the wastewater-treatment system.

TABLE 1

LIMITATIONS FOR DISCHARGES MORE THAN 10,000 GALLONS PER DAY TO POTW

Pollutant	Maximum Per Day (mg/l)	Maximum for 4 Consecutive Days (mg/l)
Cadmium	1.2	0.7
Chromium[1]	7.0	4.0
Copper	4.5	2.7
Cyanide[2]	1.9	1.0
Gold	1.2	0.7
Lead	0.6	0.4
Nickel	4.1	2.6
Zinc	4.2	2.6
Total Metals[3]	10.5	6.8

After water-saving steps have been taken, flow studies and analyses of the waste streams must be conducted. With this basic information, wastewater treatment equipment can be selected and sized. Batch treatment can be used where flows are small, irregular, or where the strength of the waste may be quite high or extremely variable [1]. A typical batch-treatment system is shown in Figure 1. Batch systems are available in various modes, ranging from completely manual to fully automatic with a programmable controller. With a batch-treatment system, all treatment operations can be performed in one vessel, depending upon the presence of cyanide/chrome-bearing wastes. Continuous systems require the use of separate integral reaction units for each treatment reaction.

Any wastewaters which contain high amounts of oils must first pass through some type of oil-separation equipment. Floating oils can be skimmed mechanically, while emulsified oils can be forced to separate either with chemical aids, a coalescer, or with ultrafiltration. If BOD/COD is present in excess of the discharge criteria, either aeration or carbon adsorption must be used to reduce the BOD/COD to dischargeable levels [2].

ORIGIN OF WASTES

Cyanide-bearing wastes generally originate from cyanide-bearing cleaners, cyanide dips, and plating solutions for the following metals: copper, zinc, cadmium, brass, bronze, silver, and gold. Both concentrated and dilute wastes are possible. Concentrated wastes are the result of discarding spent solutions. Dilute wastewaters are the result of dragout or carry-over from a process solution which is rinsed off the part. The two should be treated together with the concentrated cyanide wastes bled into the dilute stream. Cyanide waste streams should be segregated from other wastes for treatment.

TABLE 2

LIMITATIONS FOR DISCHARGES LESS THAN 10,000 GALLONS PER DAY TO POTW

Pollutant	Maximum per Day (mg/l)	Average of Daily Values For Four Consecutive Monitoring Days Not to Exceed (mg/l)
CN, Amenable	5.0	2.7
Cd	1.2	0.7
Pb	[illegible]	[illegible]

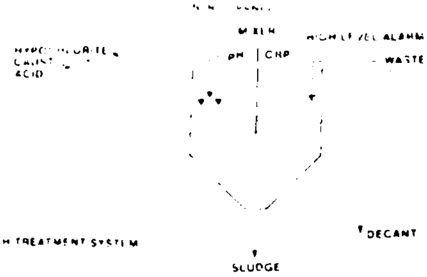


Figure 1. Typical batch-treatment system.

Chromate bearing wastes originate from plating, bright dip, conversion coating, and anodizing. Again, wastes may be dilute or concentrated. Dilute wastes result from drag-out or carry-over from the process solution, which is removed from the work-piece, while concentrated streams result from the periodic dumping of spent baths or solutions. The two streams should be treated together with the concentrated chromate stream being bled into the dilute stream. Chromate streams must be segregated from other wastes for treatment.

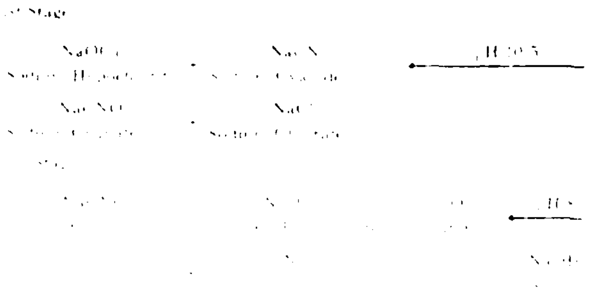
Acid alkali wastes make up the balance of the wastewater stream from most platers finishers. The acids are generated from acid cleaners or pickling solutions, bright dips, acid dips, and their subsequent rinses. Alkalies result from alkaline degreasing and cleaning solutions and their subsequent rinses. The acid alkali wastes, the cyanide-bearing wastes, the chromate-bearing wastes, nickel, copper, and zinc acid plating baths rinses all contain heavy metals.

CONVENTIONAL TREATMENT

The most common method of treatment of cyanide wastes is alkaline chlorination. The chlorine may be added directly as chlorine gas, or in the form of sodium hypochlorite solution. The complete destruction of cyanide, i.e., conversion to carbon dioxide and nitrogen is a two-step oxidation process. The chemical reactions for the process with sodium hypochlorite appear in Figure 2.

When chlorine gas is used, sodium hydroxide must be added in the initial reaction to form sodium hypochlorite. Oxidation of the cyanides then proceeds by the same mechanism. Both stages of the reaction are pH-dependent. With the first stage, the reaction rate decreases as the pH decreases. In the second stage, the reaction rate increases as the pH decreases. It is, however, very important to note that, in the second stage, pH's below 7 must be avoided since at these low pH's cyanate will convert to ammonia.

The use of ozone as an oxidizing agent for cyanides is growing in popularity. The oxidation process occurs at ambient temperatures and can easily be automated. The major disadvantage is that ozone must be generated on-site and is relatively expensive. In addition, oxidation beyond the cyanate level is limited.



1st Stage

$$NaOCl + NaCN \xleftarrow{pH\ 10.5} NaCNO + NaCl$$

[illegible]

Figure 2. Cyanide oxidation.

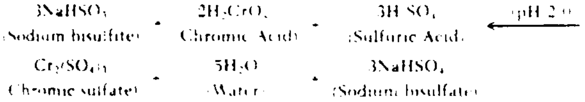
The chromate-bearing wastes must first undergo reduction from the hexavalent state to the trivalent state. This can be accomplished with various reducing agents, the most common being sodium metabisulfite, ferrous sulfate, and sulfur dioxide. The reaction of sodium metabisulfite with chromate is shown in Figure 3.

The oxidation-reduction potential can be used to plot the course of the reduction reaction for chromate and the oxidation reaction for cyanide. Thus, an ORP meter controller is an essential component, along with a pH meter controller to assure proper treatment of cyanide and hexavalent chrome. Once they have been treated they can be combined with the general acid alkali wastes for subsequent pH adjustment and the precipitation of heavy metals.

Single-stage continuous neutralizers are usually suitable for electro-plating wastes, using acids, sodium hydroxide, or lime. If the wastewater is subject to rapid pH variations or flow variations, a two-stage system should be used [1]. The retention time in each vessel is typically ten minutes. The term "neutralizer" is a misnomer today, because of the treatment to a specific pH for optimum heavy-metals removal. Metals precipitate at various levels of pH, depending on various factors such as: the metal itself, the insoluble salt that has been formed (e.g., hydroxide, sulfide, etc.), the presence of complexing agents such as EDTA (ethylene diamene tetraacetic acid), ammonia, acetic acids, etc [3]. Theoretical curves for the precipitation of various metals as hydroxides are shown in Figure 4.

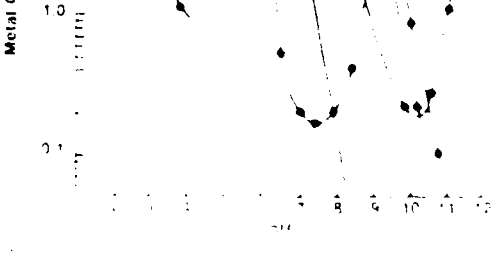
When two or more heavy metals are present in the same waste stream, the optimum pH for precipitation may be different than the optimum pH for one particular ion. In order to determine the optimum treatment process, a bench-scale laboratory testing program should be conducted and should include the use of various chemicals and various pH ranges to determine their effect in producing the best effluent. Various polymers should also be tested for their use in improving the settleability of the metal precipitates. Polymer is typically added immediately after pH adjustment in a flocculation vessel. The flocculated wastewater is then permitted to settle.

Various types of settling vessels are available. They include conventional center feed-peripheral discharge circu-



$$\underset{\text{(Sodium bisulfite)}}{3NaHSO_3} + \underset{\text{(Chromic Acid)}}{2H_2CrO_4} + \underset{\text{(Sulfuric Acid)}}{3H_2SO_4} \xleftarrow{pH\ 2.0} \underset{\text{(Chromic sulfate)}}{Cr_2(SO_4)_3} + \underset{\text{(Water)}}{5H_2O} + \underset{\text{(Sodium bisulfate)}}{3NaHSO_4}$$

Figure 3. Chromate reduction.



[illegible] metals [illegible] hydroxides [illegible] clarifiers and lamella-type clarifier. The slant tube and lamella-type clarifiers offer improved settling while occupying less area than conventional clarifiers. The precipitated sludge from the clarifier is removed at 1-2% solids for further thickening in a sludge thickener and or subsequent dewatering.

The clarifier overflow may contain residual suspended solids requiring removal with a polishing filter. This ensures *maximum removal* of metals. A dual-media gravity filter or pressure filter is the most prevalent choice for filtration. When the filter reaches terminal head loss, it must be backwashed, which takes 15-20 minutes. During this time, it is out of service, with the main sump (feeding the pH-adjustment unit) holding the incoming flow. One alternate to this is to use a duplex filtration system assuring continuous operation. Effluent polishing can also be provided continuously with the DynaSand™ Filter which is a *continuous-backwashing, upflow, deep-bed granular-*media filter. The feed is introduced into the bottom of the unit and flows upward through a series of riser tubes and is then evenly distributed through the distribution hood. The influent flows upward counter to the downward-moving sand bed; the filtered effluent then exists *via* an overflow weir. The sand bed and the accumulated solids are drawn downward into the suction of an airlift pipe at the center of the filter which transfers the slurry upward through the center of the unit. The scouring action frees the solids and they are then separated in the washer/separator which returns the sand to the filter and the solids to the reject stream. This device permits continuous backwashing utilizing 2-3% of the flow. The filtered, treated wastewater is then discharged to the POTW.

After the sludge has been collected from the clarifier, it is pumped to a sludge-thickening device. Usually, a conical-bottom tank is used with decant connections located on the side of the tank. This enables the initial collected sludge to be concentrated from 1-2% solids by weight to a final concentration of 4-8% solids by weight. Thickening improves the performance and efficiency of the final dewatering process and results in substantial volume reductions to reduce both the disposal and handling costs. From the sludge-thickening tank the sludge can be further dewatered with the use of a centrifuge, vacuum filter, or a plate-and-frame filter press.

A vacuum filter can work either continuously or as a batch operation. The common type of vaccum filter is the rotary-drum vacuum filter. This unit has three basic zones of operation: 1) slurry pick-up, 2) cake-drying area, 3) scraper discharge. The system is constructed as a cylinder with various types of filter media. The cylinder is usually submerged about 40% with the speed of rotation set to obtain optimum pick-up, dewatering, and cake removal with the filtrate returned to the main process sump for retreatment. The dewatered cake contains from 20-30% solids [4].

The filter press is one of the most common devices utilized for the dewatering of metal-hydroxide sludges. The system consists of a frame to support the plates. Plates can be either of the gasketed or non-gasketed type. Typically, the press is opened or closed with either a hydraulic system or a hand crank. The hydraulic system reduces the manual cranking labor. Once the press has been closed, the sludge is pumped to the press where it disperses to each chamber simultaneously. Under pressure, the solids deposit uniformly on the surface of the cloth with the initial build-up acting as a filter. In most applications, the cake will build up to completely fill the chambers in about a two-hour period with the [illegible] when the chambers are full. The [illegible] is then [illegible] blown into one of the discharge [illegible] and [illegible]

[illegible] removed from the unit. The press typically produces sludge containing 20-40% solids by weight, while requiring only minimal manual labor.

In applications where the volume of sludge to be dewatered is large, the use of a centrifuge is very economical. The slurry is fed to the center of the unit, where it is accelerated with the rotational speed of the unit and packs on the outside bowl of the unit with the clear liquid collected through a filter screen. The heavier solids are forced towards the sludge discharge where they are typically removed by a screw conveyor. The concentrate is returned to the main process sump for reprocessing. Centrifuges can produce dewatered cakes of 15-25% solids by weight.

Bag filters are also used on occasion to dewater sludge. Some units utilize a series of open filter bags, while others utilize pumps to feed bags in a central housing. The bags can produce cakes ranging from 6-12% solids by weight. Once the sludge has been dewatered, it must be disposed of and this requirement is often the major factor in selecting a more effective dewatering process.

SULFIDE PRECIPITATION

Sulfide precipitation can be more practical than hydroxide precipitation in removing chromium because it directly reduces the hexavalent chrome to its trivalent state, eliminating the need for intermediate pH control. Sulfide precipitation is accomplished with either the soluble-sulfide or insoluble-sulfide process. With the insoluble process, an excess of ferrous sulfide is added, enabling the iron to give up its sulfide and to precipitate any metal with a lower solubility than the ferrous sulfide. With alkaline pH, the iron precipitates in the hydroxide form. In the soluble-sulfide process, a sulfide-ion probe is utilized to measure control the addition of soluble sulfides such as sodium sulfide or sodium hydrosulfide. The soluble-sulfide system typically requires a higher chemical demand and produces a larger volume of sludge than hydroxide precipitation. Sulfide precipitation is relatively insensitive to the presence of most chelating agents and performs well on many complexed heavy metals [2]. But sludge disposal can present a problem with no adequate data available to confirm the existence of sulfide sludges with long-term stability and it therefore may be difficult to obtain regulatory agency approval to dispose of the sludge in some areas [5].

ELECTROCHEMICAL REDUCTION

Chromium reduction is the most common application for electrochemical reduction precipitation. This process utilizes consumable iron electrodes and electricity to generate ferrous ions, which react with the hexavalent chrome to produce trivalent chrome. Because of the introduction of ferrous ions into the waste stream, some additional solids will be generated. Maintenance includes biweekly replacement of electrodes and washing of electrodes (10-15 minutes day). The conventional chemical reduction system has a combined treatment and sludge-disposal cost advantage over the electrochemical method when the influent Cr^{+6} exceeds 5 ppm [2].

INTEGRATED WASTEWATER TREATMENT

The integrated-system approach incorporates the waste-treatment step as part of the actual plating operation. In this type of system, the drag-out on the work-piece is treated in a rinse tank that contains the treatment chemical. For example, immediately following the chromic-acid bath there would be a chromic-acid waste treatment rinse. This rinse would be in a closed loop with a chromic-acid waste treatment reservoir which is continuously dosed with the required make-up sodium bisulfite or other reducing agent. Following the treatment rinse there would be a [illegible] rinse tanks which would discharge [illegible]

[illegible] the trivalent stage. A similar approach is utilized following the cyanide baths.

INSOLUBLE STARCH XANTHATE

Insoluble starch xanthate (ISX) is a recent process developed by the U.S. Department of Agriculture to remove heavy metals from wastewater. ISX is made from commercial crosslinked starch by reacting the starch with sodium hydroxide and sodium disulfide. To give the product additional stability and improve the settling rate, magnesium sulfate is added. ISX acts as an ion-exchange material, exchanging the heavy-metal ions and replacing them with manganese and sodium ions. The process generates a significant amount of sludge, although the sludge does settle rapidly and can be dewatered to 30-90% solids by weight. This sludge is very stable with no leachate problems evident. ISX is very effective in the treatment of complexed copper but can also be used with most heavy metals.

ELECTROLYTIC TECHNIQUES

Electrolytic techniques have recently been utilized to plate out dissolved metals, reduce chromium, and to oxidize cyanide from wastewater. The major operating cost is the electrical current, with no chemical treatment required. The high electrical resistance of dilute solutions has made only more concentrated rinses economically treatable until very recently. Two companies are presently actively marketing electrolytic-treatment systems.

EVAPORATION

The evaporation process has been utilized successfully on virtually all types of plating baths. One of the most important benefits of the evaporative recovery system is that it enables the return of drag-out wastes of higher concentrations than the original bath. In those installations, where the evaporation losses are minimal, and where the drag-in is equal to the drag-out, there is considerable merit in the use of evaporative recovery. There are basically three types of evaporators: vacuum evaporators, thin-film evaporators, and atmospheric evaporators.

Vacuum evaporators utilize reduced pressure to lower the boiling point of the solution, therefore allowing a lower rate of decomposition of cyanide solutions. This also reduces both the carbon-dioxide adsorption and the air entrainment of the solution being boiled.

The thin-film or rising-film evaporators are designed to provide a very fast rate of heat input to a thin film of solution. This minimizes both crystallization and solids precipitation on the heat-exchanger surfaces, resulting in lower maintenance requirements and better efficiency in the heat transfer. The thin-film and rising-film evaporators can be combined with vacuum evaporation to take advantage of the benefits of both processes, inhibiting any thermal degradation of the solution additives and reducing energy consumption.

Atmospheric evaporators are normally operated below the boiling temperatures. The evaporator column is designed similarly to an exhaust scrubber, with a vent fan passing a large volume of air through a packed column where the warm solution is sprayed from the top. The exhaust air is saturated with water. The atmospheric evaporators are very cost effective with chromic acid, when used in conjunction with the scrubbing of the plating tank exhaust.

The savings [illegible] for evaporation [illegible] the concentration [illegible] water being evaporated [illegible] of drag [illegible] acid [illegible]

[illegible]

REVERSE OSMOSIS

The name "reverse osmosis" was originally derived because it is the transport of water in a reverse direction of normal osmosis, where water flows from a less concentrated solution through a semi-permeable membrane to a more concentrated solution. The feed solution flows over the surface of the membrane. The membrane is typically a cellulose acetate film very similar to heavy cellophane. Pressure is utilized to force a percentage of the water in the solution through the membrane while a little of the initial water, enriched in solutes, remains to be transported away. The solution entering the membrane is designated as the feed, while the material forced through the membrane is called the permeate. The enriched solute water is referred to as the concentrate or reject stream.

The major difficulty with reverse osmosis (RO) Systems is the problem of maintaining membrane performance. The pH must be maintained in a pH range of 2.5 to 11 to ensure reasonable membrane life. Good filtration should always be utilized to protect the membrane surface from fouling. Reverse osmosis has great potential for the recovery of raw metal materials in the metal-finishing rinses after plating. At present, systems have been utilized on chrome, nickel, and copper plating-line rinses, producing as the by-product pure water for re-use.

ION EXCHANGE

Ion exchange is a reversible chemical reaction, where an ion from the solution is exchanged for a similarly charged ion attached to a solid particle. Typically, synthetic organic resins are utilized because of their superior capabilities of being manufactured for specific applications. The organic resin is composed of polyelectrolytes with a high molecular weight, which can exchange their mobile ions with those of a similar charge in the surrounding medium. Ion exchange is ideally suited for dilute solutions, with the treated water being of very high purity. Although every known metal has been recovered, separated, and purified by some ion-exchange process in the laboratory, on a commercial scale only a few are treated with ion exchange [9]. Economics plays the major role in determining whether it is feasible to treat with ion exchange.

There are various types of resins, but the two basic classifications are cationic and anionic. The cationic resins have positively charged mobile ions available for exchange, while the anionic have negatively charged mobile ions available for exchange. Both of these groups can be further classified as strong- or weak-base anion exchangers, or strong- or weak-acid cation exchangers, and are so named because of their chemical behavior. Most industrial applications utilize columns with fixed beds of ion-exchange resin. Once the resin has become exhausted, the system must be regenerated. A cationic resin is regenerated with acid, which elutes the collected positively charged ions and replaces them with H^+ ions followed by a slow water rinse to remove any residual acid. An anionic resin is regenerated with caustic which elutes the collected negatively charged ions and replaces them with OH^- ions.

Ion exchange is used in the metals and plating industries to remove trace pollutants from wastewater after a conventional system, or to recover bath solution drag-out from rinse water and to return the purified water for re-use. One example is the use of ion exchange to recover and return chromic acid to the bath. The rinses are first collected in a holding tank where they are pumped at a constant rate through [illegible] and an activated carbon filter. [illegible] cation and [illegible]

[illegible]

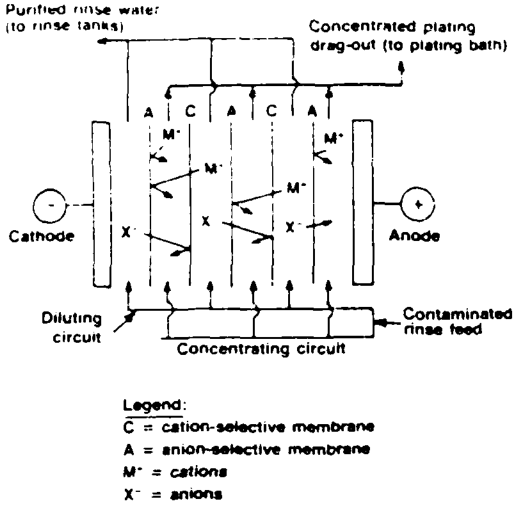


Figure 5. Electrodialysis unit flow schematic.

hausted, it is removed from operation and regenerated with caustic and returned on-line as the second column. The caustic regenerant stream is now sodium chromate and is passed to the second cationic column. The sodium ions are exchanged for hydrogen ions, producing chromic acid and water, and can be returned to the bath. When the cationic columns are exhausted, they must be regenerated with caustic, with the regenerant treated for removal of heavy metals and pH adjustment.

The major disadvantage of the ion-exchange system is the need to be regenerated after exhaustion. This produces a concentrated waste stream which has to either be treated or hauled away for disposal.

ELECTRODIALYSIS

Electrodialysis is used to concentrate or separate ionic species in a water solution. A water solution is passed through alternately placed anionic and cationic permeable membranes with an electric potential applied across the membranes. The electric potential provides the force to enable ion migration. Therefore, there are two hydraulic circuits, one which is ion-depleted while the other is ion-concentrated. The electrical potential across the membrane determines the degree of purification/concentration needed to return the plating chemicals to the bath [2].

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Treatment of Water and Wastewater For Removal of Heavy Metals

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WESTON ENVIRONMENTAL CONSULTANTS-DESIGNERS

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INTRODUCTION

Heavy metal pollution of our waters has received increased attention, because of the toxicity of heavy metals towards individual living organisms and, most importantly, towards human beings. For many years, water treatment plants have been concerned with the levels of Manganese and Iron in water supplies because of the taste and color they impart to the water. More recently, health effects of heavy metals, rather than these aesthetic effects, are becoming a topic of concern. Table 1 summarizes the U.S. Public Health Service Drinking Water Standards for heavy metals. Most of these heavy metals have been found in levels close to or exceeding these standards in distribution systems throughout the country (1).

In 1968, the American Water Works Association adopted water quality goals that in some instances were more stringent than the U.S.P.H.S. Drinking Water Standards. These goals were intended to be more exacting than U.S.P.H.S. Drinking Water Standards with respect to aesthetic qualities. AWWA water quality goals for heavy metals are also summarized in Table 1.

The importance that has been placed on the potential adverse impact of heavy metals on the environment is illustrated by the low permissible ambient concentrations in natural waters and the low effluent standards promulgated by regulatory agencies. Typical ambient and effluent-limiting concentrations are shown in Table 2.

In spite of the critical nature of heavy metals in drinking waters, the removal of heavy metals from drinking water supplies, has in the past, been limited in practice (at least consciously) to removal of iron and manganese for aesthetic reasons. Other heavy-metal removal technology has thus been applied almost exclusively in wastewater treatment. Many industries practice heavy-metal removal as pretreatment prior to discharge to biological treatment systems, to avoid upsets due to the toxicity of heavy metals to bacteria.

In this paper, the primary focus is on review of heavy-metal removal technology, particularly as it applies to removing low concentrations of heavy metals. A number of industries with high concentrations of

Table 1

Water Quality Goals and Drinking Water Standards for Heavy Metals

Heavy Metal	U.S.P.H. Drinking Water Standards (1962)		AWWA Water Quality Goals (1968)
	Mandatory Requirements mg/L	Recommended Requirements mg/L	mg/L
Aluminum (Al)	-	-	0.05
Arsenic (As)	0.05	0.01	-
Barium (Ba)	1.0	-	-
Cadmium (Cd)	0.01	-	-
Chromium (hexavalent)	0.05	-	-
Chromium (Trivalent)	-	-	-
Copper (Cu)	-	1.0	0.2
Iron (Fe)	-	0.3	0.05
Lead (Pb)	0.05	-	-
Manganese (Mn)	-	0.05	0.01
Mercury (Hg)	-	-	-
Nickel (Ni)	-	-	-
Selenium (Se)	0.01	-	-
Silver (Ag)	0.05	-	-
Zinc (Zn)	-	5	1.0

Table 2

Heavy-Metal Water Quality Standards*

Heavy-Metal	Ambient Water Quality Standard mg/l	Effluent Standard mg/l
Aluminum (Al)	--	--
Arsenic (Ar)	1.0	0.25
Barium (Ba)	5.0	2.0
Cadmium (Cd)	0.05	0.15
Chromium (Cr^{+6})	0.05	0.30
Chromium (Cr^{+3})	1.0	1.0
Copper (Cu)	0.02	1.0
Iron (Fe)	1.0	2.0
Lead (Pb)	0.10	0.10
Manganese (Mn)	1.0	1.0
Mercury (Hg)	0.0005	0.0005
Nickel (Ni)	1.0	1.0
Selenium (Se)	1.0	1.0
Silver (Ag)	0.0005	0.10
Zinc (Zn)	1.0	1.0

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*Current Standards of the State of Illinois. Changes recommended by an Effluent Standards Advisory Group include: lower chromium (Cr^{+6}) from 0.30 to 0.10; lower copper (Cu) from 1.0 to 0.50; raise lead (Pb) from 0.10 to 0.20; raise mercury (Hg) from 0.0005 to 0.003; and keep selenium (Se) as an effluent standard rather than an ambient water quality standard.

heavy metals in their wastewaters practice metal recovery; the methods for metal recovery are mentioned, but not emphasized in this paper. The treatment methods covered include:

Precipitation
Ion Exchange
Adsorption
Oxidation/Reduction

Since solids removal is a significant factor in effective heavy-metals removal, settling and filtration are also covered.

PRECIPITATION

Simple precipitation is the oldest and most widely used method for removal of heavy metals. It is also a very effective and well proven method, and one which will probably continue to be the most popular method for removing heavy metals, even to very low concentrations. When designed and operated properly, precipitation methods for removing heavy metals are very effective.

Most metal hydroxides are relatively insoluble in water. Their precipitation is governed by the relative concentrations of the precipitation chemical and of the metal ion in solution, and by the pH. An excess of precipitation chemical beyond the amount needed to meet the stoichiometric relationship is required. This excess can best be determined from practical experience. In most cases, the metal concentration in solution in the effluent is a function of the final chemical equilibrium treatment condition, and is independent of the initial metal concentration. Generally, as the pH increases, the solubility of the metal hydroxide decreases. (This is illustrated in Figure 1.) While heavy-metal precipitation generally depends on this metal hydroxide solubility, other precipitates (e.g., metal oxides and sulfides) are also important in some cases.

Since many of the heavy metals form insoluble hydroxides or oxides at a pH of 11, lime treatment is effective in the precipitation of these metals. To remove the precipitates, lime treatment must be followed by settling, and to achieve low concentrations of heavy metals in the effluent, the settling must often be preceded by coagulation and often followed by filtration. Table 3 summarizes the extent of heavy-metals treatment achievable by lime treatment, as well as other precipitation methods. A review of this Table makes it clear why lime treatment is so important for heavy metals removal. It is a very effective technology.

Many water-treatment plants practice heavy-metal removal incidentally, in the course of lime-soda water-softening. Even without the lime-soda process, water treatment plants practice some degree of heavy-metal removal merely through solids removal (i.e., coagulation, settling and filtration), because many heavy metals are relatively insoluble even at neutral pH's.

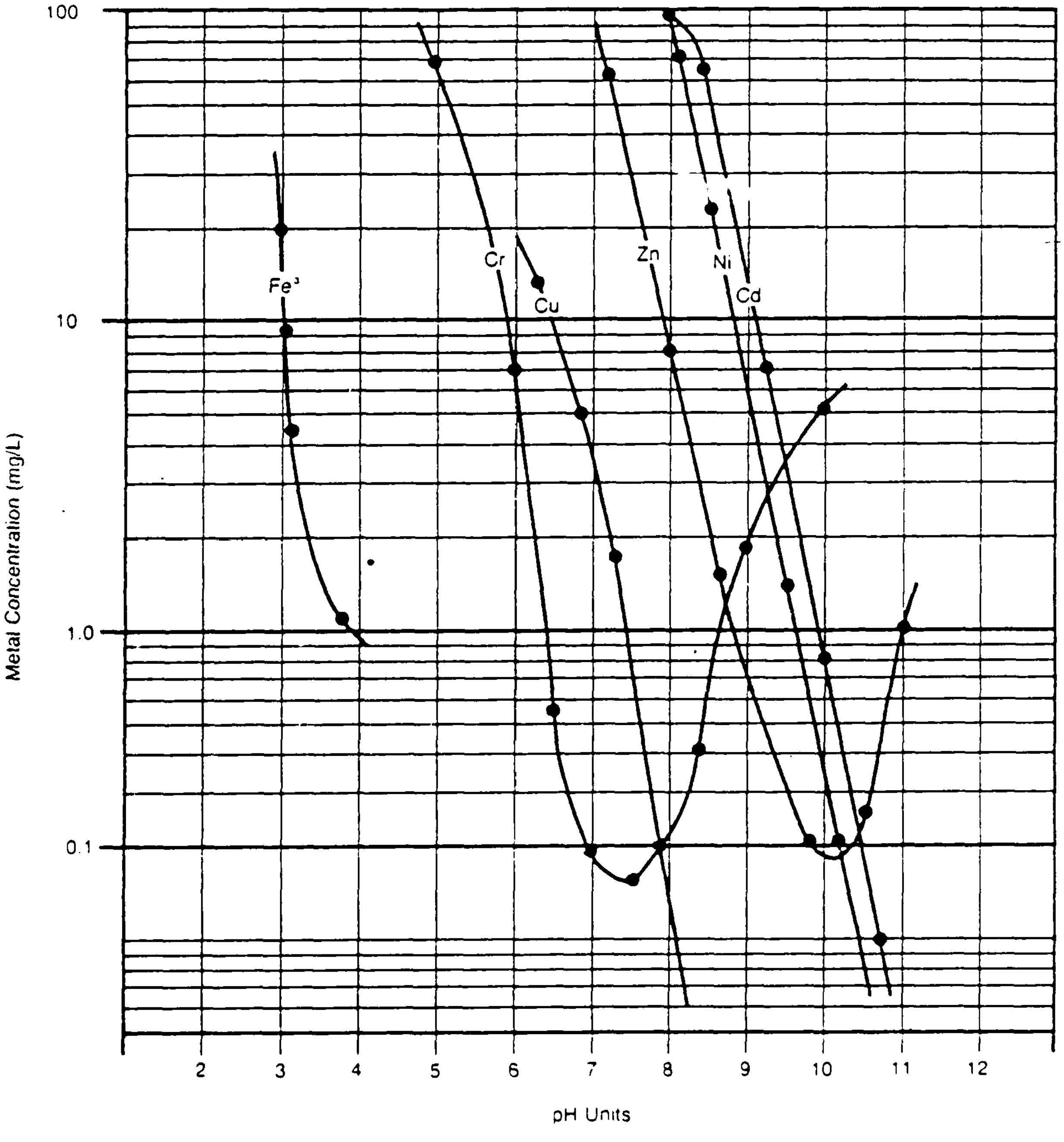

Figure 1   Precipitation as Hydroxide Salts

Table 3

Heavy Metal Removal By Precipitation

Metal	Lime Treatment		Other Precipitation Methods	
	pH	Effluent Concentration mg/L	Concentration mg/L	Description
Arsenic, As	11	0.03	0.05(2)	Sulfide @ pH = 6.7
			0.05(2)	Ferric Chloride Coagulation
Barium, Ba	11.5(2)	0.94(2)	0.03(2)	Ferric Sulfate with Lime @ pH ≈10.
	11.0(1)	1.3(1)	0.27(2)	Ferric Sulfate @ pH = 6
Cadmium, Cd	10(2)	0.1(2)	0.04(2)	$Fe(OH)_2$ & lime @ pH = 10
	11.5(2)	0.014(2)	0.05(2)	$Fe(OH)_2$
Chromium, Cr (hexavalent)		Cannot be precipitated		
Chromium, Cr (trivalent)	9.5(1)	0.4(1)		
	8.5 - 9.5(2)	0.06(2)		
Copper, Cu	9 - 10.3(2)	0.5(2)		
Iron, Fe	10.8(1)	0.1(1)	0.5(2)	Oxidation of Ferrous to Ferric results in precipitation of hydroxide at pH = 7
Lead, Pb	11.5(2)	0.02(2)	0.03	Ferric Sulfate and lime @ pH = 10
			0.03	Ferric Sulfate @ pH = 6.0
Manganese, Mn	10.8(1)	<0.1	0.05	Oxidation of Manganous results in precipitation of hydroxide at pH = 7
Mercury, Hg	Not Applicable		0.1 - 0.3	Sulfide after oxidation to Mercuric Ion
Nickel, Ni	11.5(2)	0.1 - 0.2(2)	0.35(2)	Ferrous Sulfate and lime @ pH = 10
Selenium, Se	Not Applicable		0.5(2) (little supporting data)	Sulfide at pH = 6.5 (little supporting data)
Silver, Ag	11	0.4(2)	1.4(2)	Chloride
			0.1(2)	Lime and Ozone @ pH = 10
			?	Sulfide
Zinc, Zn	?	1.0(2)	very low(2)	Sulfide @ pH = 2
	9.5	0.3(1)		

The effectiveness of heavy-metal precipitation can be greatly reduced by interferences and/or a number of complexing agents. Although various organic materials can form complexes with metals, the most common heavy-metal complexing agent is cyanide, which complexes with many metals thus increasing the overall solubility of the metals. Removal of Cyanide is usually required for effective precipitation of heavy metals. The most common method for such removal is oxidation by chlorination to carbon dioxide and nitrogen.

Precipitation processes are not the complete answer to all heavy-metal removal problems, but are often at least part of the answer. Precipitation is a common process in water-treatment plants, which for years have been involved with unit processes such as lime softening, flocculation, sedimentation, aeration, and filtration. Thus, many water-treatment plants have been achieving some heavy-metals removal, and with some process modification, greater removals may be achieved with existing equipment.

SOLIDS REMOVAL

Effective solids removal is extremely important in heavy-metals removal by precipitation. In removing low concentrations of heavy metals, solids removal, rather than solubility, often becomes the limiting factor. Metal hydroxides, although insoluble, tend to form bulky but light flocculent particles which are often difficult to remove by clarification unless coagulant aids are used.

Filtration following clarification is usually required to achieve very low concentrations of heavy metals. Good examples of the importance of filtration are shown in Table 4, which indicates that filtration makes as much as one order of magnitude difference in the concentration of heavy metal achieved after precipitation and clarification.

Another important role of solids removal is as a pretreatment operation in heavy-metal removal by processes such as ion exchange, reverse osmosis, activated carbon adsorption, and electrodialysis. Accumulation of solids in reverse osmosis and electrodialysis membranes or in ion exchange and carbon media can adversily affect the operation of these processes.

In summary, very good solids removal is invariably required to achieve low heavy-metal concentrations, and filtration is usually required.

ION EXCHANGE

The ion exchange process has been used by many industries for water treatment when extremely high purity of water is required. Ion exchange, however, is capable of removing only ionic species from water; suspended materials (solids) are not removed by ion exchange and are usually detrimental to the process, because they can foul the ion-exchange beds.

Table 4

Attainable Concentration of Various Metals

Metal	Precipitation and Clarification mg/L	With Filtration mg/L	Reference
Lead	0.2	0.019	(2)
	0.25	0.029	(2)
	0.25	0.03	(2)
Chromium (Trivalent)	2.7	0.63	(1)
Copper	0.79	0.32	(1)
Selenium	0.0103	0.00932	(1)
Zinc	0.97	0.23	(1)

Ion exchangers are simply insoluble electrolyte materials which exchange ions with a solution. There are two main classes: cations and anions. A cation exchanger removes only positively-charged ions from solution, while an anion exchanger removes only negatively-charged ions from solution. Ion exchange processes are very effective in removing heavy metals to very low concentrations, but they are relatively non-selective and also remove other ions of like charge. Thus, if the removal of heavy metals in the presence of high concentrations of other dissolved inorganics (e.g., Na^+, Ca^{++}) is desired, ion exchange will not selectively remove the heavy metals, and the resin will be spent rapidly.

Ion exchange resins are usually regenerated, and the spent regenerant is in effect a more concentrated wastewater stream contaminated with the same ions (heavy metals) that were removed from the more-dilute, treated stream. This wastewater must be disposed of, and the disposal often requires treatment for removal of heavy metals. In effect, ion exchange will remove low concentrations of heavy metals very effectively and concentrate them in a stream of less volume, which can be treated by precipitation or other recovery processes. Ion exchange, therefore, is most applicable as a scavenging or polishing treatment unit.

The utilization of ion exchange in water treatment has been mainly in connection with water softening, and a strong acid cation exchanger (sulfonated copolymer resin of styrene and divinylbenzene) is most often used. The ion exchange reactions can be represented as follows:

$$2RSO_3\ Na + Ca^{++}\ (\text{or } Mg^{++}) = (RSO_3)_2\ Ca\ (\text{or } Mg) + 2Na^+$$

A 10 percent (or stronger) solution of NaCl is normally used to regenerate the resin.

Most heavy-metal cations will exchange with the strong acid cation resins used in water softening. As mentioned previously, selectivity for removal of specific ions is not good, but there are conditions where certain ions are more readily exchanged. Concentration and valence are two factors which influence cation exchange. Ions present in high concentrations will exchange more than those in low concentrations. At equal concentration the removal of divalent cations (e.g., Mn^{++}, Cu^{++}, Pb^{++}) will be greater than that of monovalent cations (e.g., Na^+, Li^+, NH_4^+). A consequence of this valency influence is the increase of sodium concentration in the treated water.

ADSORPTION

The use of adsorption for removal of heavy metals has been reported for arsenic, cadmium, chromium, copper, mercury, and nickel. The mechanism for metals removal with adsorptive materials such as activated carbon is not fully understood, but the following can be postulated with reasonable confidence:

1. Heavy metals are known to form soluble complexes with organic compounds. In the presence of such organics, heavy-metals removal may be achieved by complexing followed by adsorption of the organics.

2. Heavy metals can form hydroxide complexes which in effect can act like polymers. It is possible that these hydroxide complexes can form hydrated molecules large enough for adsorption to be effective.

Generally speaking, adsorption processes are not as applicable as precipitation or ion exchange; however, their use should be considered in special applications, particularly those in which precipitation and ion exchange are ineffective.

OXIDATION/REDUCTION

Oxidation/reduction processes play an important role in heavy metals removal, particularly by precipitation. For example, in order to achieve effective precipitation of iron at a near-neutral pH, ferrous iron must be oxidized to ferric, which occurs very readily at neutral pH in the presence of oxygen. Aeration is usually sufficient to accomplish this oxidation.

Manganese is soluble in water in the forms of manganous and permanganate ions. The permanganate ion is a strong oxidant and is reduced under normal circumstances to insoluble manganese dioxide. The manganous ion, however, must be oxidized to the insoluble manganic ion. Unlike iron, the manganous ion is not oxidized readily by means of aeration at neutral pH, and requires either aeration a higher pH ($\approx$10) or chemical treatment. Chemical treatment involves the use of a strong oxidant such as chlorine, ozone, hypochlorate, chlorine dioxide, manganese dioxide, or potassium permanganate.

In order to precipitate mercury as mercuric sulfide, mercurous and organic mercury compounds must be oxidized to mercuric ion. The reduction of mercury ions to free elemental (insoluble) mercury has also been proposed as a method of mercury removal by precipitation.

As indicated in Table 3, trivalent chromium can be precipitated as a hydroxide by means of lime treatment but hexavalent chromium cannot. Reduction of hexavalent chromium from a valence state of plus six to plus three, and subsequent precipitation of the trivalent chromium ion, is the most common method of hexavalent-chromium removal. The most common reduction process is an acid reduction in which the pH is lowered with sulfuric acid to a pH of 3 or below and the hexavalent chromium is converted to trivalent chromium with a chemical reducing agent such as sulfur. Other reducing agents include sodium bisulfite, sodium metabisulfite, sodium hydrosulfite, and ferrous sulfate.

A very common complication to heavy-metal precipitation is the presence of cyanide, a toxic contaminant in its own right, which is often found in wastewater streams with heavy metal contamination. The cyanide forms complexes with heavy metals, thus increasing the solubility of the metals and decreasing the effectiveness of precipitation. Cyanide is an organic structure which can be destroyed by oxidation to carbon dioxide and nitrogen, and the most common oxidant used for its destruction is chlorine. Complete oxidation of cyanide is usually a two-step procedure requiring close control of pH. The first step is oxidation of the cyanide to cyanate at pH 10 or higher. The second step is oxidation of cyanate to CO_2 and nitrogen by addition of excess chlorine at a pH of 8-8.5. Cyanate can also be oxidized to CO_2 and ammonia by acid hydrolysis at pH 2 to 3, usually by the addition of sulfuric acid.

MISCELLANEOUS PROCESSES

A number of other treatment processes are applicable for removal of heavy metals, particularly in specialized applications. Reverse osmosis, electrodialysis, and evaporation processes have been used to achieve concentrations of heavy metals for recovery purposes. Additional treatment is usually required in conjunction with these processes, however, and costs are usually quite high. Other processes that have been considered for removing heavy metals from water include solvent extraction and freezing; generally speaking, these processes warrant consideration only where recovery of a valuable metal is practical.

SLUDGE DISPOSAL

The end result of most heavy-metal removal processes is a sludge; which must ultimately be disposed of. Typically, heavy-metal sludges are landfilled. An important consideration in the disposal of heavy-metal sludges is that many of the solids can go back into solution when the pH decreases. The reversibility of precipitation is such that rainwater, with its relatively low pH, can cause the heavy-metal solids to go back into solution. Treatment of landfill leachates has been proposed, but this merely results in more heavy-metal sludge and thus a cyclic operation.

Landfilling of heavy-metal sludges is indeed a feasible method of disposal, if proper care is taken to segregate it from other sludges and to avoid contact with surface or ground water. Nevertheless, the trend towards more frequent occurrence of leachate problems points to the need and possible future trend towards heavy-metal source control and metal recovery.

INTEGRATED APPROACH (CASE STUDY) (5)

In order to illustrate some of the principles that have been touched on in this paper, a case study of industry discharging metal wastes is presented herein. This case study is based on a Weston industrial client, and was previously presented at AIChE's 82nd National Meeting (1976) (5). Although this particular case study involves the removal of relatively high metal concentrations from water, the principles involved are nevertheless applicable to removal of low concentrations.

The treatment facilities for this industry were designed on the basis of the influent and effluent waste characteristics shown in Table 5, and the effluent quality predicted in Table 5 was based on wastewater treatability studies. A flow diagram of the treatment process involved is shown in Figure 2.

The heart of the process is single-stage lime treatment, a very traditional treatment process. Because of the cyanide and hexavalent chromium present in the wastewaters, the more concentrated streams are isolated and pretreated (through cyanide oxidation and chromium reduction) prior to the lime treatment.

The importance of good solids removal is well reflected in the design of this treatment system, which includes a flocculator-clarifier followed by polishing filters and effluent polishing lagoons. Since a number of heavy metals required precipitation in a single stage, design of the process required knowledge of the effect of pH on solubility. Investigation disclosed that this relationship varied from time to time, and Figure 3 illustrates the typical soluble metal concentration vs. pH data for this wastewater at a given time. The minimum concentration for each metal varies from day to day, depending on many production variables and probably also on the presence of complexing agents. Figure 3 indicates that the optimum pH for Zn removal is between 8 and 9, while for copper it is nearly 11. In order to achieve maximum overall removal of metals, the system was designed to be maintained at a pH of 9-10. Should lower concentrations of metals in the effluent be required, a two- or three-stage precipitation process would be required, because the minimum solubility of each of the metals involved occurs at a different pH.

Table 6 is a summary of the operating records from the plant during the twelve months following start-up. The plant is operated to minimize total metals in the effluent, and an on-site atomic absorption unit provides current operational data needed for pH adjustment and optimal plant control.

The copper problem encountered in this project is of particular interest. Unusually high copper concentrations after lime treatment were often observed, both in the treatibility testing program (see Table 5, which predicts an effluent copper concentration of 2.65 mg/L) and in first two months of operation of the treatment plant (2.33 mg/L in December, 1973

Table 5(5)

Design Influent and Effluent Characteristics

	Influent	Effluent
Total Flow, gpd	274,000	274,000
Cyanide Flow, gpd	12,500	12,500
Chromium Flow, gpd	11,500	11,500
COD, mg/L	300	160 (100)*
Suspended Solids, mg/L	195	10
pH	10.5	8.5
Total Dissolved Solids, mg/L	740	1,025
Copper, mg/L	29	2.65
Zinc, mg/L	5.0	0.50
Cadmium, mg/L	1.8	0.07
Nickel, mg/L	1.5	0.01
Total Chromium, mg/L**	0.16	0.05
Total Heavy Metals, mg/L	37.5	3.28
Cyanide, mg/L	200	0.05

* Permit application stated 100 mg/L average, 150 mg/L maximum (Actual permit did not include any limitations.)

** Based on data from existing plant.

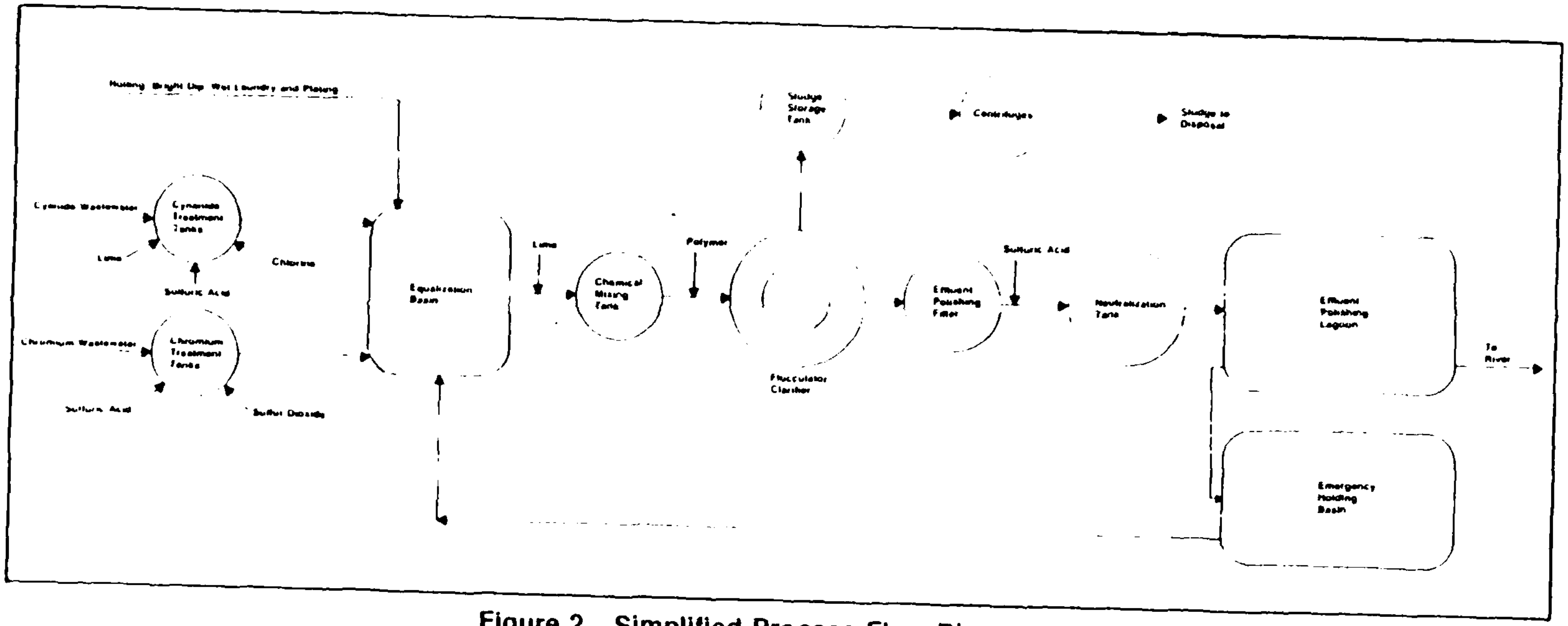

Figure 2 Simplified Process Flow Diagram

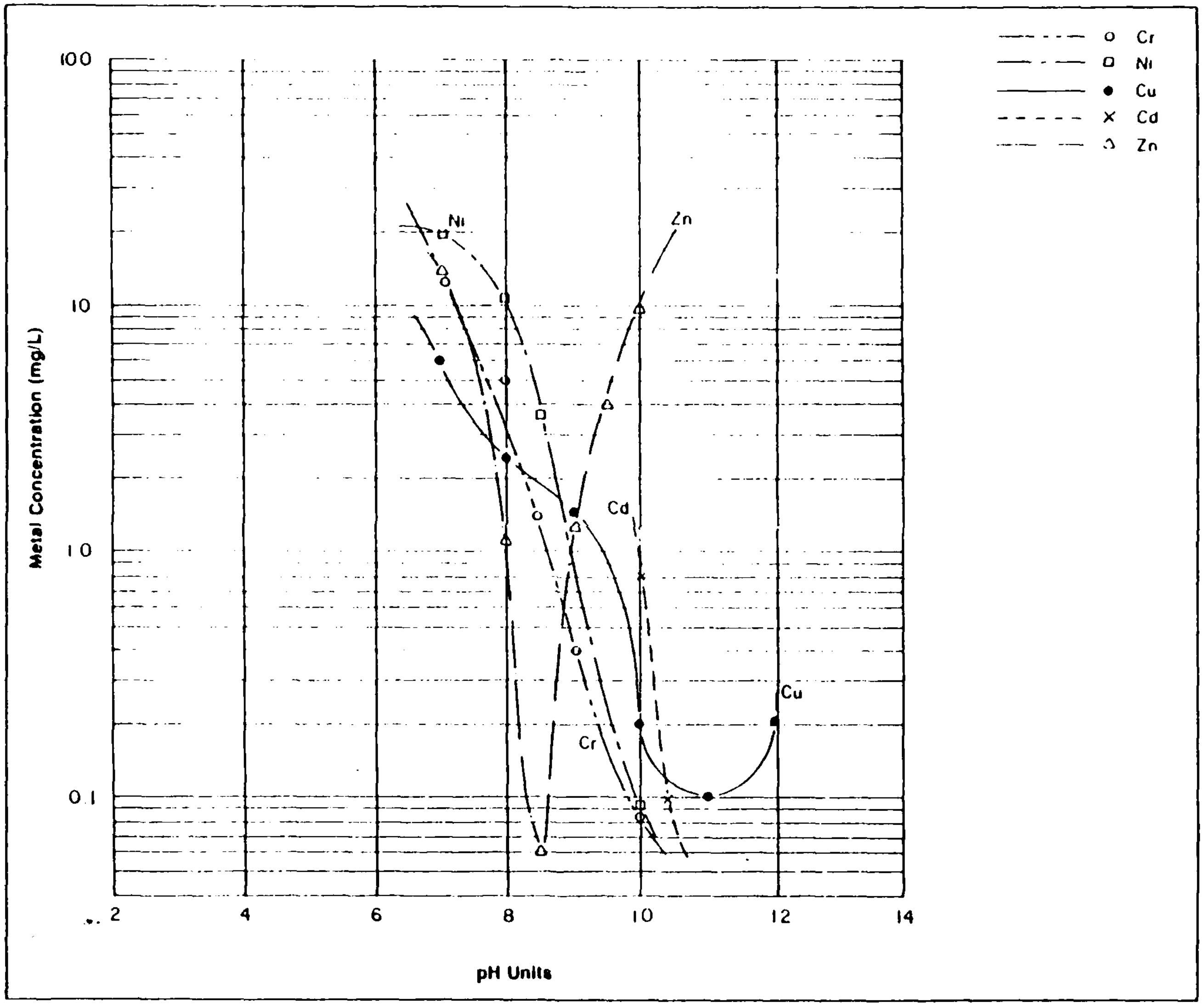

Figure 3 Soluble Metal Concentration vs pH

Table 6 (5)

Average Monthly Effluent Quality

Month	Flow mgd	COD mg/L	S.S. mg/L	Cyanide mg/L	Cadmium mg/L	Total Chromium mg/L	Copper mg/L	Nickel mg/L	Zinc mg/L	Total Metals mg/L	Remarks
Dec. '73	0.235	62	8	0.33	0.05	0.03	2.33	0.44	0.78	3.61	
Jan. '74	0.218	72	5	0.12	0.04	0.03	2.41	0.56	0.42	3.46	
Feb. '74	0.210	66	7	0.04	0.02	0.02	0.69	0.50	0.18	1.40	Isolated stripper problem
Mar. '74	0.271	61	5	0.03	0.01	0.02	0.45	0.22	0.24	0.94	Represents optimum single-stage plant operation
Apr. '74	0.255	62	14	0.03	0.01	0.02	0.46	0.17	0.16	0.80	
May '74	0.219	58	11	0.02	0.01	0.02	0.59	0.17	0.16	0.95	
June '74	0.251	79	24	0.03	0.01	0.02	0.41	0.21	0.01	0.75	
July '74	0.190	81	10	0.02	0.01	0.02	0.39	0.23	0.11	0.76	
Aug. '74	0.253	78	22	0.02	0.01	0.02	0.51	0.26	0.26	1.06	Reduced operating pH
Sept.'74	0.266	71	19	0.04	0.01	0.02	0.59	0.30	0.25	1.17	Conserve chemical cost
Oct. '74	0.283	65	17	0.03	0.01	0.02	0.58	0.45	0.38	1.38	
Nov. '74	0.273	45	2	0.04	0.01	0.02	0.77	0.43	0.44	1.67	

and 2.41 mg/L in January, 1974). Investigation of the problem disclosed that the cause was intermittent discharges of a small quantity of organic material into the process sewer. When this discharge was stopped, the concentration of copper in the effluent decreased substantially (0.39 to 0.77 mg/L, averaging 0.54 mg/L in the next ten months). Apparently, the organic material had been complexing with the copper, thereby increasing its solubility and inhibiting its precipitation.

SUMMARY AND CONCLUSIONS

Heavy-metal removal has historically relied on precipitation and good solids removal by sedimentation and filtration. However, a number of other treatment processes, most notably ion exchange, can also accomplish heavy-metals removal. Other processes, such as adsorption, freezing, reverse osmosis, electrodialysis, evaporation, and solvent extraction have limited practical applicability. Problems associated with the ultimate disposal of heavy-metal wastes indicate a probable future trend toward heavy-metal source control and recovery.

It is important to note that both the precipitation and the ion exchange processes, particularly precipitation, are traditional water-treatment processes. Lime treatment is widely practiced for removal of calcium and magnesium ions in water softening. Ion exchange has also been used for the same purposes; however, because of higher cost, ion exchange normally is used for water softening only in specialized applications where the quality of water must be very high. It is thus likely that many water-treatment plants are already achieving some degree of heavy-metals removal, and that with minor process modifications high degrees of removal could be achieved.

Carbon adsorption may be important where the presence of organic compounds results in metal complexes which interfere with precipitation. Carbon adsorption also is a fairly common water-treatment process.

The use of other heavy-metal removal processes should not be ignored, but their applicability is highly specialized, and their use is justified only after full consideration of the more traditional heavy-metal removal technology.

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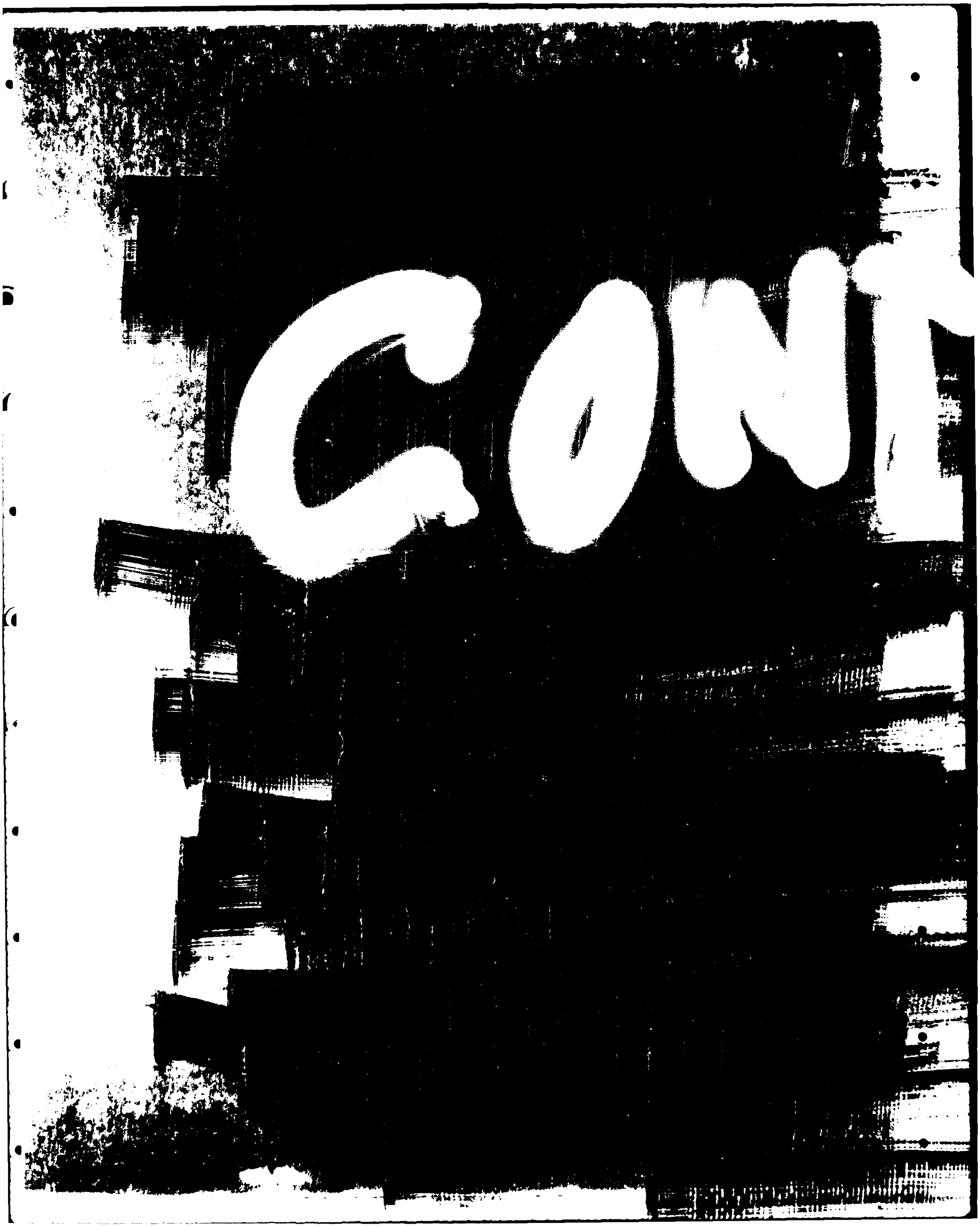
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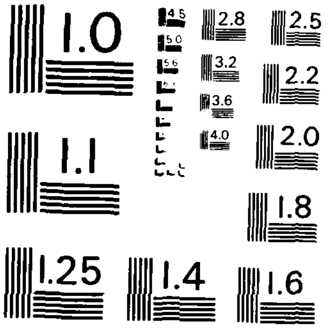

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SUPPLEMENTARY

INFORMATION

Errata

AD-A144 420

The following are blank pages.

Behind Appendix II pages 8, 14, 16, 17, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36 and 38.

DTIC-FDAC
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Errata

AD-B011 949

Page B-10 is not available.

DTIC-FDAC
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AD-B012 924

Page C-2 is blank.

DTIC-FDAC
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Errata

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Errata

AD-B019 151

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DTIC-FDAC
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4. METHOD AND RESULTS.

a. GENERAL.

(1) Modified VSD and MSD LRUs replaced fleet standard MSD and VSD units in the F-111D test aircraft. Mission profiles were selected to evaluate the capability and interoperability of the modified MSD/VSD with the integrated aircraft system.

(2) Fourteen test sorties, ten effective and four noneffective, were flown by the 431 TES expending 105 bombs to evaluate the modified MSD/VSD.

(3) MK 106 and bomb dummy unit (BDU)-33 practice munitions were used for all deliveries. The following weapons deliveries were examined: radar laydown (RLD), RLD beacon (BCN), moving target detection (MTD), low-angle low-drag (LALD), dive, dive toss, low toss (L TOSS), and visual laydown (VLD). These provided data for typical F-111D weapon deliveries and navigation profiles.

(4) Weapon deliveries conformed to procedures and constraints outlined in AFR 50-46, TACM 51-50, TACR 55-111, Naval Air Station Fallon (NASF) Instruction 3710.5L, and appropriate range operation manuals and directives.

b. OBJECTIVE 1. Evaluate the capability of the modified MSD.

(1) Measure of Effectiveness (MOE).

(a) Results of aircrew selected MSD modes/submodes.

(b) Qualitative assessment of displays and mechanization.

(c) Circular error probable (CEP).

(2) Evaluation Criteria. Source: 57 Fighter Weapons Wing (FWW)/DT.

(a) Modified MSD must respond properly 100 percent of the time to all aircrew selected modes, submodes, and functions IAW TO 1F-111D-1-2. Improper responses not attributed to MSD design deficiencies were excluded from consideration.

(b) Test team rating of satisfactory.

(c) Base threshold CEP evaluation criteria were dependent on delivery mode and are listed in Table 1. The base threshold CEP was derived from previous test results or, when there were no previous test results for a delivery mode, 431 TES CEPs demonstrated during training missions. The adjusted threshold was analytically derived by the project operations analyst to give a more meaningful measure for evaluation by relating the "base CEP" to the actual sample size.

Errata

AD-B088 892

Page 220 is not available.

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