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The Effectiveness of Potassium Permanganate in Oxidizing Hydrogen Sulfide and in Aiding Mechanical Dewatering of Pulp and Paper Industry Sludges

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THE EFFECTIVENESS OF POTASSIUM PERMANGANATE IN OXIDIZING HYDROGEN SULFIDE AND IN AIDING MECHANICAL DEWATERING OF PULP AND PAPER INDUSTRY SLUDGES

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TABLE OF CONTENTS

INTRODUCTION

Odorous compounds have long been a significant problem faced by mills treating their own wastewater. This problem can be compounded when mechanical dewatering equipment is used to process primary and secondary sludges.

Plainwell Paper Company, a competitive producer of fine printing and technical specialty papers, is no exception to this rule. Along with the start-up of their new waste water treatment facility, which includes an Arus-Andritz sludge dewatering machine, came an irritating and potetially harmful odor problem. It was determined that the major cause of the odor was hydrogen sulfide.

Plainwell treats their water using primary clarification followed by aerobic digestion and secondary clarification. The combined sludge, largely primary in content, is pumped to a holding tank and subsequently dewatered to about 50% solids.

Changes in the dewatering and handling processes and a change from acid to alkaline papermaking in the mill helped to reduce some of the odor problem. However, the remaining odor neccessitated further action.

After considering pH control, masking, and oxidizing agents, a decision was made to use chlorine dioxide to oxidize the odorous compounds present in the sludge as it entered the dewatering facility. (1)(2)(3) This system is presently quite sucessful at lowering the hydrogen sulfide to a safe and workable level.

Recently, wastewater treatment facilities have reported successful odor elimination and beneficial sludge conditioning using potassium permanganate ($KMnO_4$) as an oxidant. (1)(2)(4)

In this thesis, we will study the odor control and sludge conditioning effects of potassium permanganate on Plainwell Paper Company's combined sludge.

OXIDANT SELECTION

To justify considerations of potassium permanganate for odor control, we took a look at other oxidizing agents that have typically been used in the pulp and paper industry. At this time, Plainwell Paper is using chlorine dioxide for odor control. This is generated using an aqueous solution of sodium chlorite and chlorine gas.[5]

$$NaClO_2 + 1/2Cl_2 \rightarrow ClO_2 + NaCl$$

Chlorine gas and hydrogen peroxide were also considered.

Using the availability of electrons as an indicator of relative oxidizing potential, we looked at the reactions of the oxidants mentioned. Although the reaction rates of the oxidants are not the same, their effect on odorous compounds per available electron should be very similar. The reactions at the pH range of interest (ph 6.5-8) are as listed: (5) (6) (7)

1. $Cl_2 + 2e^- \rightarrow 2Cl^-$

2. $ClO_2 + 1e^- \rightarrow ClO_2^-$

3. $H_2O_2 + 2e^- \rightarrow 2OH^-$

   or $H_2O_2 + 2H_3O^+ + 2e^- \rightarrow 4H_2O$

4. $MnO_4^- + 4H^+ + 3e^- \rightarrow 2H_2O + MnO_2$

Using Cl_2 as a base; H_2O_2, $KMnO_4$ and ClO_2 would cost roughly 1.2, 6.2 and 11.8 times as much respectively for equivalent amounts of available electrons. Generation and handling costs are not included in this estimate.

When contact time is limited, as in the case at Plainwell, reaction rate can be critical. Potassium permanganate reacts almost instantly while hydrogen peroxide can take as long as 15-30 minutes to react. Chlorine gas and chlorine dioxide fall closer to the potassium permanganate for reaction rate.

Potassium permanganate reacts differently depending on the condition of the system. The reactions for alkaline, acidic, and neutral conditions are as follows: (7)

Alkaline

$$8kMnO_4 + 3H_2S \rightarrow 3K_2SO_4 + 2KOH + 2H_2O + 8MnO_2\downarrow$$

Acidic

$$2KMnO_4 + 3H_2S \rightarrow 3S + 2H_2O + 2KOH + 2MnO_2\downarrow$$

Neutral

$$4KMnO_4 + 3H_2S \rightarrow 2K_2SO_4 + 3MnO + MnO_2\downarrow + 3H_2O$$

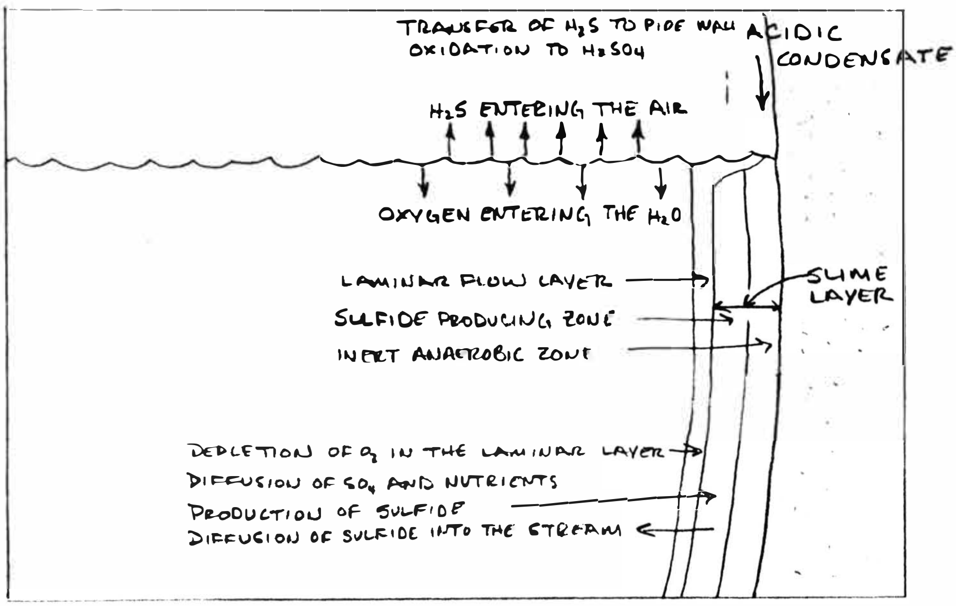
Therefore, alkaline systems would require larger amounts of potassium permanganate than would an acid system to oxidize the same amount of hydrogen sulfide. The typical oxidation for most systems would be the neutral reaction with both elemental sulfur and sulfate being formed.

ODOR CONTROL

Since odor control is our primary concern and hydrogen sulfide our primary contributor, we will discuss this first. Hydrogen sulfide is generated biochemically by sulfate reducing bacteria such as Desulfovibrio desulfuricians. (8)

$$SO_4^{=} + \text{organic matter} \xrightarrow{\text{bacteria}} H_2S + H_2O + CO_2$$

The optimum conditions for this reaction include; a reducing environment (ORP $^-$200 to $^-$300MV), neutral pH (best 7-8), anaerobic conditions and moderate temperatures (86°F). These conditions are readily available in the slime layer that can be found all along the treatment stream. In this layer, oxygen that may be present in the stream is unable to penetrate and a reducing, anaerobic environment is established.



TAKEN FROM 1982 NCASI CENTRAL-LAKE STATES REGIONAL MEETING ADVANCE SUMMARIES OF PRESENTATIONS.

(FIGURE I)

Hydrogen sulfide is an irritating, harmful and dangerous molecule. Levels as low as 0.025 ppm can be detected by the human nose as a "rotten egg" smell. The OSHA limit for eight hours is 20 ppm. (4)(9) It becomes irritating at between 70-150 ppm and fatal at levels over 700 ppm. (Figure I) Detection of the colorless gas by smell is often lost after prolonged exposure. (1) This is especially significant since the safety of personnel could be jeopardized by undetected high hydrogen sulfide levels.

The pH of the system affects the form in which the sulfide is present. At low pH the H_2S form is prominent, while at high pH, the HS^- ion is more prominent. Since HS^- is nonodorous, it is more desirable. (10)(11)

OTHER BENEFITS

Once hydrogen sulfide has formed, sulfuric acid generation is possible. Under the right conditions, bacteria of the genus thiobacillus can use hydrogen sulfide and oxygen to form sulfuric acid.

$$H_2S + 2O_2 \xrightarrow{\text{Bacteria}} H_2SO_4$$

Sulfuric acid is highly corrosive to both metals and concrete.

Consolidated Paper, Inc., feels that the use of potassium permanganate has caused a reduction of sulfides in their press filtrate. They feel that this has reduced the filamentous bacteria in their secondary clarifier. If bulking is a problem, reduced filamentous populations could result in less solids in the effluent. (1)

Potassium Permanganate also oxidized other equally harmful but less predominant odor causing compounds. It is very effective at removing grease and skum from the treatment system. (12)(13)

CONDITIONING EFFECTS

When potassium permanganate oxidizes hydrogen sulfide or other oxidizable compounds, manganese dioxide precipitates out as a solid. (14)

It is thought that manganese dioxide acts similar to iron (III) hydroxide as a sludge conditioner. Manganese dioxide has high surface area and is able to absorb multiple divalent metal cations. The charged molecules may electrostatically attract colloidal particles and act as a flocculating aid. Studies have shown that for certain sludges this conditioning effect can help to reduce polymer consumption for mechanical dewatering. (1)(3)(15)

Some claims have been made that hydrogen peroxide may have a mild sludge conditioning effect. However, there is no documentation available to support this claim.

EXPERIMENTAL DESIGN

The experimentation should give us useful information in two areas:

(1) the effectiveness of potassium permanganate for odor control, and

(2) its ability to aid in mechanical dewatering of sludge.

ODOR

To study potassium permanganate's ability to destroy odor, predominantly hydrogen sulfide, we must devop a hydrogen sulfide generation versus potassium permanganate curve for our particular sludge. We will

be using sludge taken from Plainwell Paper's wastewater treatment facility before any chlorine dioxide or polymer has been added. We will select a sludge that falls very nearly to their average pH value.

A quick preliminary experiment will be run to determine the dosage necessary for complete destruction of hydrogen sulfide. The literature suggests between 90-100 ppm for a predominantly primary sludge. (1)(4)(12)(16)(17) Generally, our sludge solids contain 50% filler (clay, carbonate, TiO_2, etc.) and 50% organic materials. From this experimentation, we can determine the dosage range for complete testing.

We will be using specially equipped reagent bottles for the hydrogen sulfide destruction test procedures. For each test, the bottle will be filled to a specified level with undewatered sludge. The proper amount of potassium permanganate will be added and sufficiently mixed, and a sample of the gas remaining in the air space will be tested using a hydrogen sulfide detection tube and a Dräger Hand Pump. We will be using water to replace the gas taken from the bottle through the detection tube. To insure accurate readings of the hydrogen sulfide, the cap will be designed to allow us to mix the sludge and potassium permanganate, then insert the detection tube without losing any of the gas. (FIGURE II)

A study done by Ken Pisarczyk, of Carcus Chemical Company indicates that mixing time for potassium permanganate has little or no effect on both hydrogen sulfide and conditioning effects. (6) However, for continuity, we will use a thirty second mix time for all experimentation.

CONDITIONING

Studies done by Carus Chemical Company and trials at the Saratoga County Sewer District and Consolidated Paper's wastewater treatment plant have shown that when using potassium permanganate for odor control they have observed significant sludge conditioning effects. (1)(18) This effect appears to be more pronounced for primary sludges. (3)(6)(7)

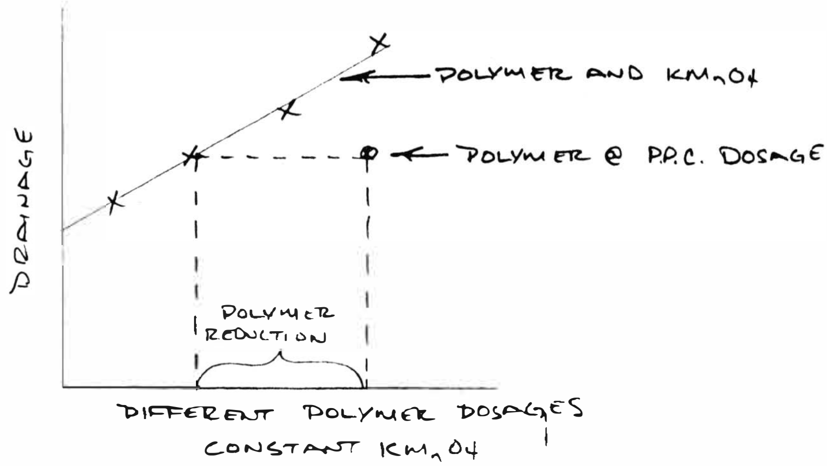
The second part of the experiment will focus on this aspect of potassium permanganate use since sludge conditioning could lead to reductions in polymer consumption while maintaining drainage rates and cake solids.

We will begin by studying the effects of different concentrations of potassium permanganate on sludge dewatering. We will check levels slightly beyond that necessary for odor control as determined by the previous experiment.

To accomplish this, we will place a specified amount of the potassium permanganate oxidized sludge into a device as pictured (Figure III) and measure the volume of filtrate collected in a certain period of time. This time period will be based on the actual operation of the Sludge Dewatering Machine (SDM). It will be related to the time necessary for the belt to travel from the beginning to the end of the gravity zone. Under normal operation, the belt travels about 25-50 feet per minute. Nearly 60% of the water is removed at the gravity zone and the formation of a good floc is most important in this stage. After the wedge zone, the sludge is further dewatered in the "s" section and the roll to roll "press" section (Figure IV).

A second experiment will be run to determine the filtrate volume at Plainwell Paper Company polymer addition rate. Generally, a cationic polyacrylamide is used for conditioning the sludge for dewatering.

Finally, we will determine the filtrate volume for a specified time using differing amounts of polymer and the same potassium permanganate dosage. This can be compared to the filtrate volume for polymer only to determine if there can be a reduction in polymer for the same conditioning.



We will attempt to simulate the "S" and "press" section by running the solids retained from the polymer only and the polymer plus potassium permanganate trials through a press. We plan to use the Noble and Wood sheet press to dewater the sludge mechanically. Each trial will be checked for solids. (Figure VI, VII)

We plan to use Western Michigan's statistics lab as an aid to determining the proper number of trials necessary and to analyze our collected data.

EXPERIMENTATION

SLUDGE CONDITIONS

Presently, Plainwell Paper's sludge is predominently primary in nature. However, in the future we expect a larger portion of the combined sludge to be secondary. For this reason, two samples of sludge were collected and tested. Sludge sample one contained almost 100% primary sludge and sample two contained roughly 80% primary and 20% secondary. Solids, ash and pH data for both samples are listed in figure VIII.

Once collected, the samples were allowed to digest for roughly one week in a covered barrel to allow them to become more septic and increase the H_2S concentration.

HYDROGEN SULFIDE ODOR CONTROL

Literature indicates that paper mill sludges require anywhere from one to two pounds of potassium permanganate per dry ton of sludge. (1)(6) For our testing, we used a one percent solution of potassium permanganate and checked dosages from zero to 40 ppm at five ppm intervals.

We found it necessary to dilute the potassium permanganate in water because in a raw sludge sample the crystals oxidized so fast a manganese dioxide layer formed and prevented complete dissolving. The apporatus shown in figure II was used for all the odor testing. For each run, the appropriate amount of potassium permanganate solution was added to the bottle. Next, 75 ml of sludge was taken directly from the bulk sample and added to the bottle. A four ply layer of saran wrap was placed over the neck of the bottle and the cap was secured. After mixing the bottle by shaking it for 30 seconds, the siphon hose and Drager detection tube were inserted through the two holes at the top of the cap,

and the layer of saran wrap.

Each stroke of the Drager hand pump withdrew 100 cc of the gas above the treated sludge. The vacuum created drew an equal amount of water through the siphon hose to replace the gas.

ODOR CONTROL DATA

The primary sludge required slightly less potassium permanganate to produce hydrogen sulfide levels below the detection level. (Figure IX, X; Table I). The drainage testing will be run using 30 ppm KMnO for sample one and 40 ppm per dry ton for sample two. The cost per dry ton for sample one and two would be $1.08 and $1.27, respectively; at $1:00 per pound.

DRAINAGE TESTING

It is the intent of this part of the experiment to determine if the concentrations of potassium permanganate necessary to control odor offer any conditioning effect on our sludge samples. For this we used the drainage tester shown in figure III. Since this apporatus was designed to simulate the drainage of the gravity zone of the SDM, we tested conditioned sludge to determine the testers capabilities. We found that the tester allowed sufficient accuracy and reproducability for the concentration range of interest. Highly conditioned and lightly conditioned sludge drainages could be determined to within 2.5 ml and 1 ml respectively.

The drainage time of 12 seconds was determined by finding the average time a conditioned sludge sample remains in the gravity drainage zone on Plainwell's SDM.

The polymer only dosage, or Plainwell Paper's dosage, was determined by testing sludge coming directly from the headbox of the SDM. The dose required to obtain simular drainage results was considered appropriate. The dose was 50 pounds of polymer per dry ton of sludge.

The actual drainage testing consisted of an unconditioned sample, a sample with polymer only at Plainwell's dosage and samples with the specified potassium permanganate plus varying doses of polymer. Duplicate or triplicate tests were run for each sample.

For each test, 500 ml of sludge was added to a one liter graduate.

The appropriate polymer dose was added using a syringe.

Finally, the remaining 500 ml was added and the sample thoroughly mixed by inverting the column several times. The sample was then quickly poured into the drainage tester and the volume of filtrate at 12 seconds was measured.

For the samples containing potassium permanganate, a large sample containing the appropriate dosage was mixed and used for an entire set of polymer dosage testing.

The results for both samples one and two, can be seen in figure XI and XII, and tables II and III.

DRAINAGE DATA

The data from sample one indicates that the same drainage could be aquired using 30 ppm $KMnO_4$ and 1000 ppm polymer as would be obtained with 1400 ppm polymer only. This would mean a 400 ppm polymer reduction when potassium permanganate is used.

PRESS TESTING

The press testing was done to determine if potassium permanganate affects the solids of the sludge after mechanical dewatering. A M & K sheet mold press was used to simulate the press section of the SDM. (Figure VI).

All the testing was done using the sample one sludge. Three tests were run:

1. 30 ppm KMnO , 1400 ppm polymer
2. 1400 ppm polymer
3. 30 ppm KMnO , 1000 ppm KMnO

Each test was replicated five times. For each test, the appropriate amount of KMnO was added to 200 ml of sludge. It was mixed thoroughly with a lightening mixer. Next, the polymer was added and also mixed with the lightening mixer. Finally, the sample was poured on a sample SDM wire. The area of wire used was held constant by pouring the sludge within the confines of a mould placed on the wire.

The sample is then run through the press with 50 psi on the nip. The felt sheets were used to pick up the water coming from the sludge.

PRESS DATA

The press data is listed in table IV. The normal curve significance test of statistics (or null hypothesis) was used to determine if there was a "significant" difference between the mean of the sludge solids numbers obtained. Although 30 observations are generally considered a minimum population, adequate results can be obtained using a sample size of five. The confidence interval used for the test was 0.95

with a level of significance of 0.050. The reduced polymer dose had one point, 51.5, omitted from consideration since it fell outside the 90% confidence interval for that test. With this in mind, there is no significant difference in sludge solids after experimental dewatering.

COST CONSIDERATIONS

Potassium permanganate has the potential to reduce costs in two ways, at Plainwell; first, the data suggests that polymer consumption can be reduced, especially for predominently primary sludges. Secondly, Plainwell is presently spending about $1.8 per dry ton for odor control using chlorine dioxide. Potassium permanganate should cost between $1.08 and $1.27 per dry ton. The data is outlined in table V.

CONCLUSION

At a time when many mills are considering using potassium permanganate for odor control, it is very important to know just what can be gained and what may be lost in implementing its use.

The data suggests that potassium permanganate can effectively control odor at a cost that is competative with other oxidants. In addition, polymer rates may be cut back due to the conditioning effect KMnO seems to have on sludge. This is especially true for sludges that are largely primary in nature. There appears to be no loss or gain in sludge solids off the press when $KMnO_4$ is used.

It could be very beneficial for Plainwell Paper Company to run a full scale trial to determine if $KMnO_4$ should replace chlorine dioxide for odor control.

BIBLIOGRAPHY

1. Ficek, Kenneth J., "Potassium Permanganate Controls Sewage Odors" LaSalle, IL.: Carus Chemical Co. (1980)

2. Sheridan, Thomas J., "Potassium Permanganate Odor Control in Maynard." WPCF 17 (July, 1980): #7

3. Rudolph, Donald J., P. E., "Solution to Odor Problem Gives Unexpected Savings" Water/Engineering and Management (November, 1982)

4. Langworthy, Virgil W., "KMnO Gets High Marks in Sludge Dewatering Test" Water/Engineering and Management 128 (Novemeber 1981) 16

5. Gall, R. J., "Chlorine Dioxide An Overview of it's Preparation, Properties and Uses" Niagra Falls, N. Y.: Hooker Chemical and Plastics Corp.

6. Pisarczyk, A.H., "Sludge Odor Control and Improved Dewatering With Potassium Permanganate" LaSalle, IL Carus Chemical Co. (1982)

7. Pisarczyk, A.H., "Odor Control With Potassium Permangantae" LaSalle, IL.: Carus Chemical Co. (1982)

8. Jackson, J.H., "The use of Potassium Permanganate in Waste Water Treatment Plants" Chicago, ILL.: Consolidated Papers, Inc.

9. U. S. Department of Health and Human Services, "NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards" Volume #2

10. Pisarczyk, A.H., "Control of Hydrogen Sulfide in Wastewater" LaSalle, IL.: Carus Chemical Co. (1982)

11. Pisarczyk, A.H., "Interim Report of Potassium Permanganate Sludge Conditioning: LaSalle, IL.: Carus Chemical Co. (1981)

12. Langworthy, Virgil W., "Potassium Permanganate for Grease Removal" Water/Engineering and Management 128 (March 1981):14.

13. Wolfe, Saul and Ingold, Christopher F., "Oxidation of Olefins by Potassium Permanganate" American Chemical Society 103 (February 1981):938-4

14. CARIOX® Usage in Pulp and Paper Mills Brochure, Carus Chemical Company (September 1982).

15. The CARIOX® Method for Water Treatment Brochure, Carus Chemical Company, (1978).

16. Peskator, Howard, "Nothing Fishy About Using Potassium Permanganate" Water and Sewage Works 126 (May 1979):64-7.

17. Swanson, Don, "Plants Control Taste/Odor Problems With $KMnO_4$ Injection" Water and Sewage Works 124(March 1977):72-4.

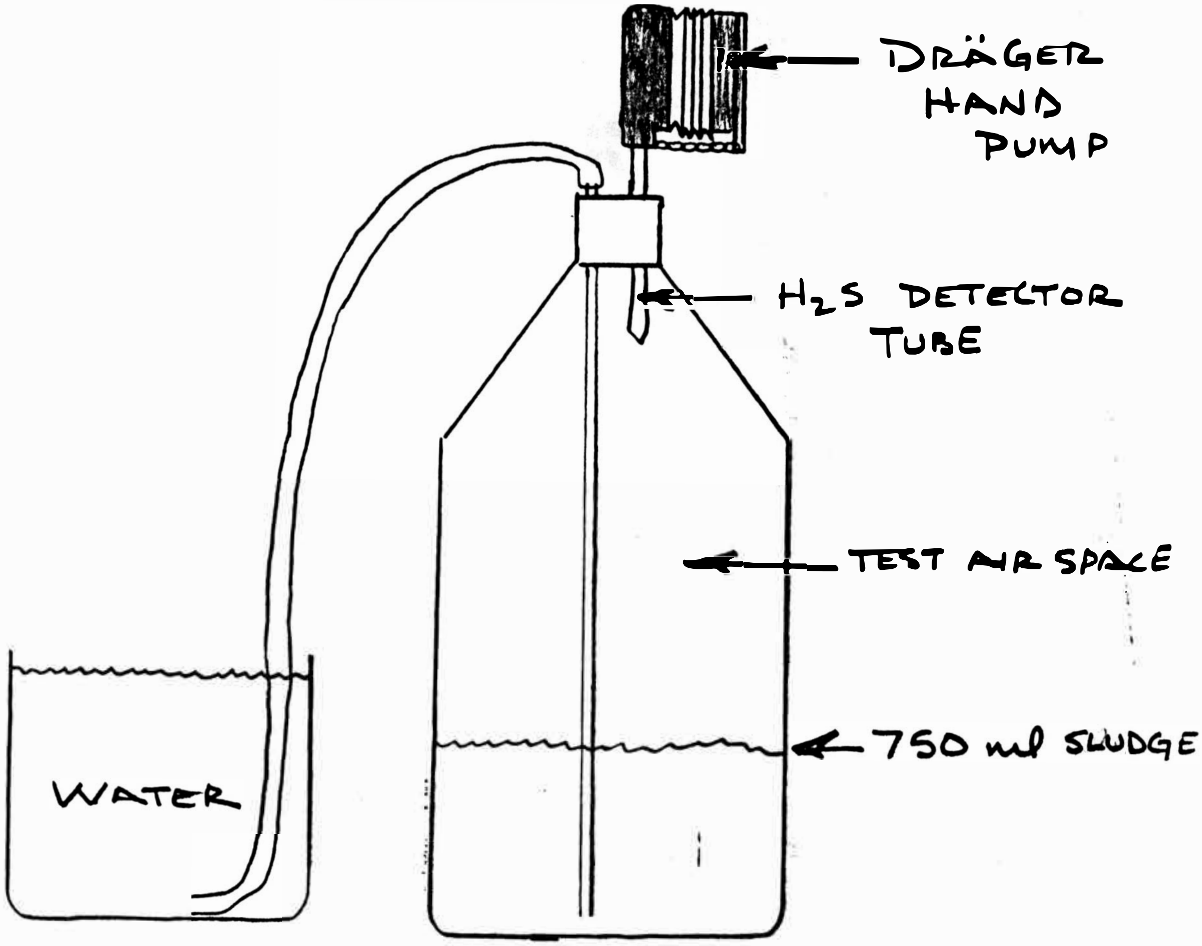
18. CARIOX® For Sludge Odor Control Brochure, Carus Chemical Company.

HYDROGEN SULFIDE

LEVELS(ppm)	
0.025	HUMAN DETECTION
10	TIME WEIGHTED AVERAGE LIMIT
15	SHORT TERM EXPOSURE LIMIT
50	SYMPTOMS OF ILLNESS
200	SEVERE TOXIC EFFECTS
600	LETHAL, 30 MIN EXPOSURE
800	LETHAL, IMMEDIATELY

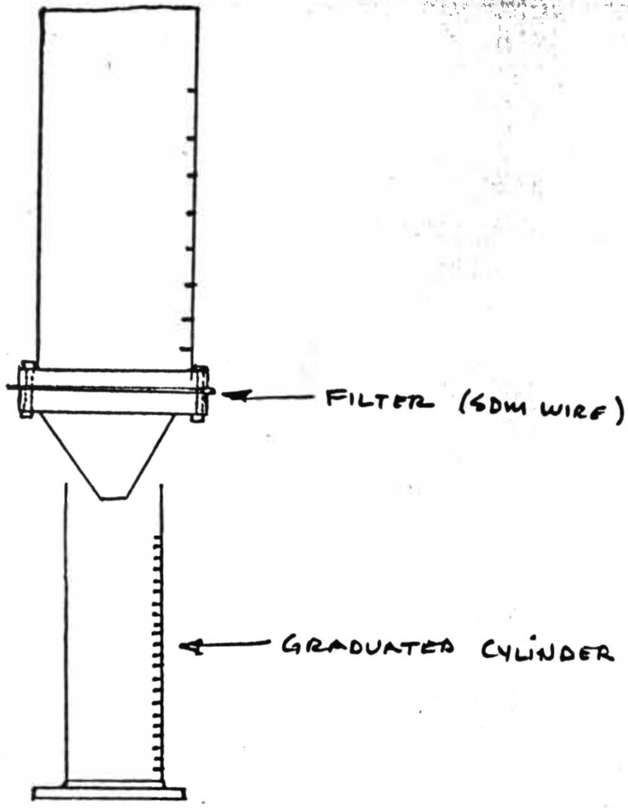
(FIGURE I)

HYDROGEN SULFIDE TESTING APPARATUS

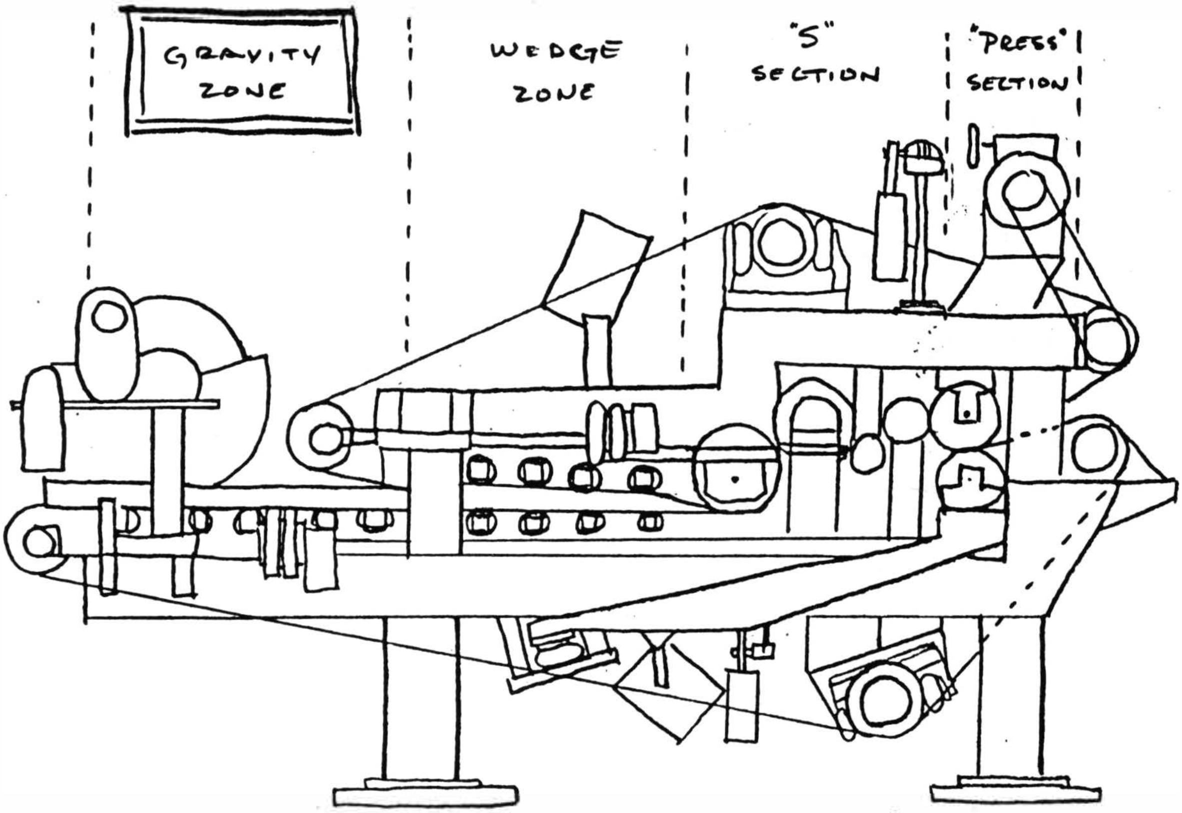


(FIGURE II)

(FIGURE III)



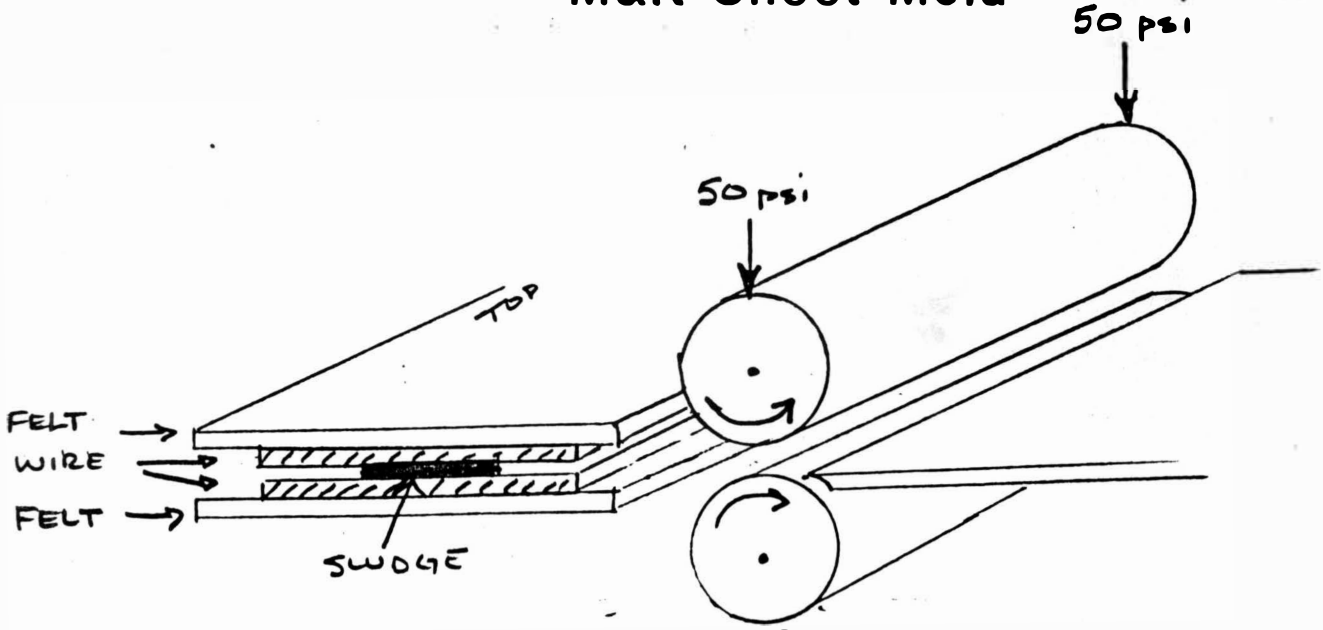
Drainage Tester



Sludge Dewatering Machine

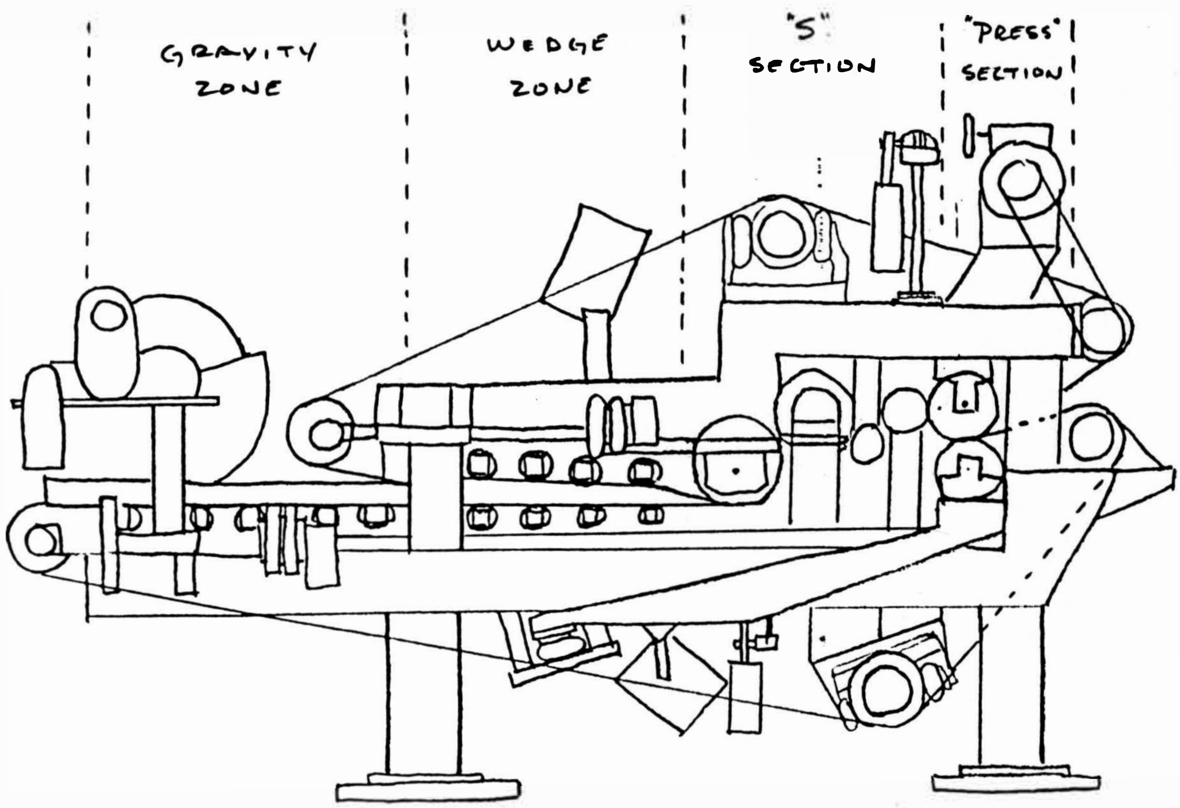
(FIGURE IV)

M&K Sheet Mold



Press Section

(FIGURE VI)



Sludge Dewatering Machine

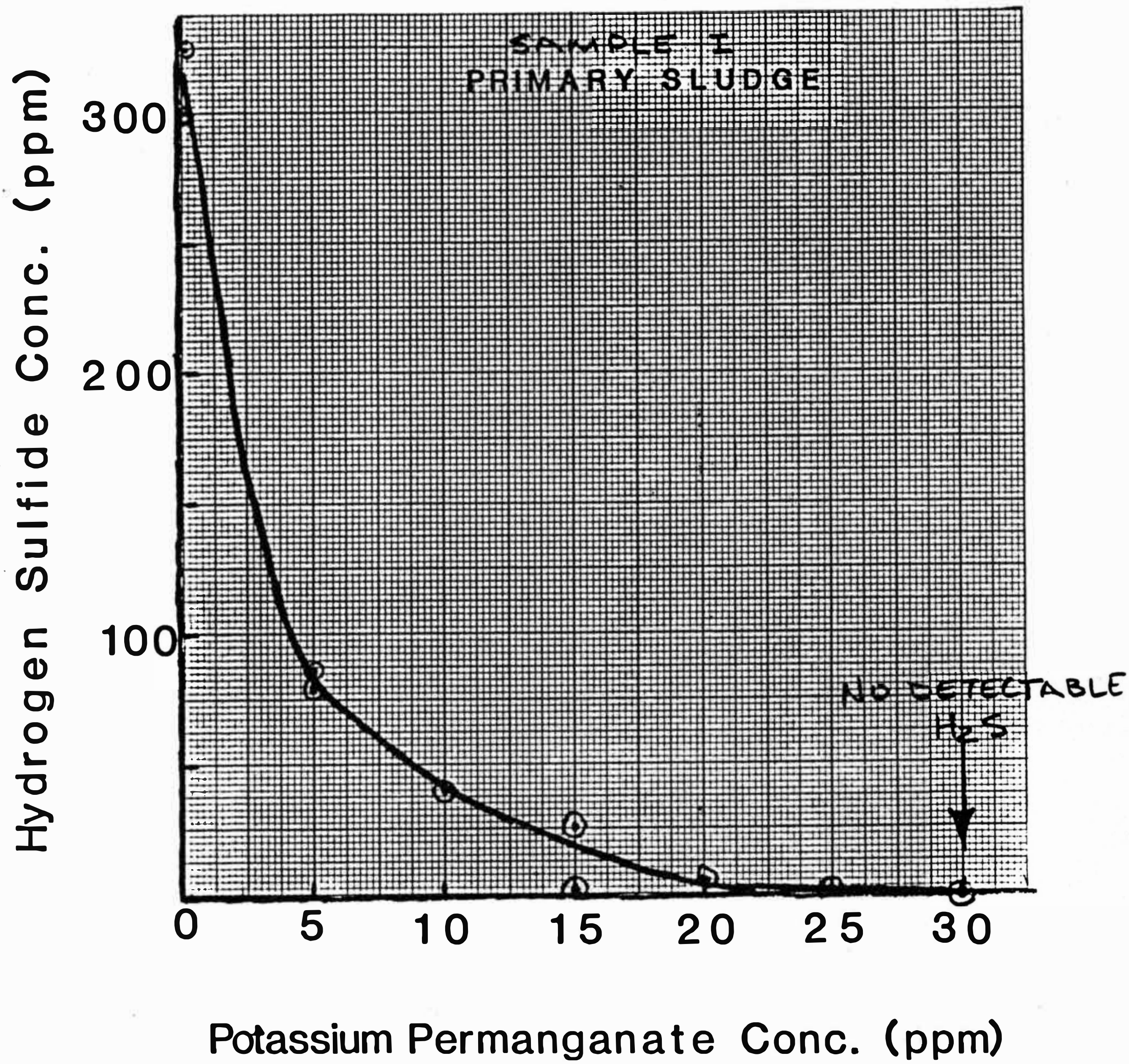
(FIGURE VII)

SLUDGE TESTING CONDITIONS

	Sample 1	Sample 2
COMPOSITION:		
PRIMARY	100 %	80 %
SECONDARY	0 %	20 %
SOLIDS	5.6 %	6.3 %
ASH	47.9 %	47.0 %
pH	7.3	7.1

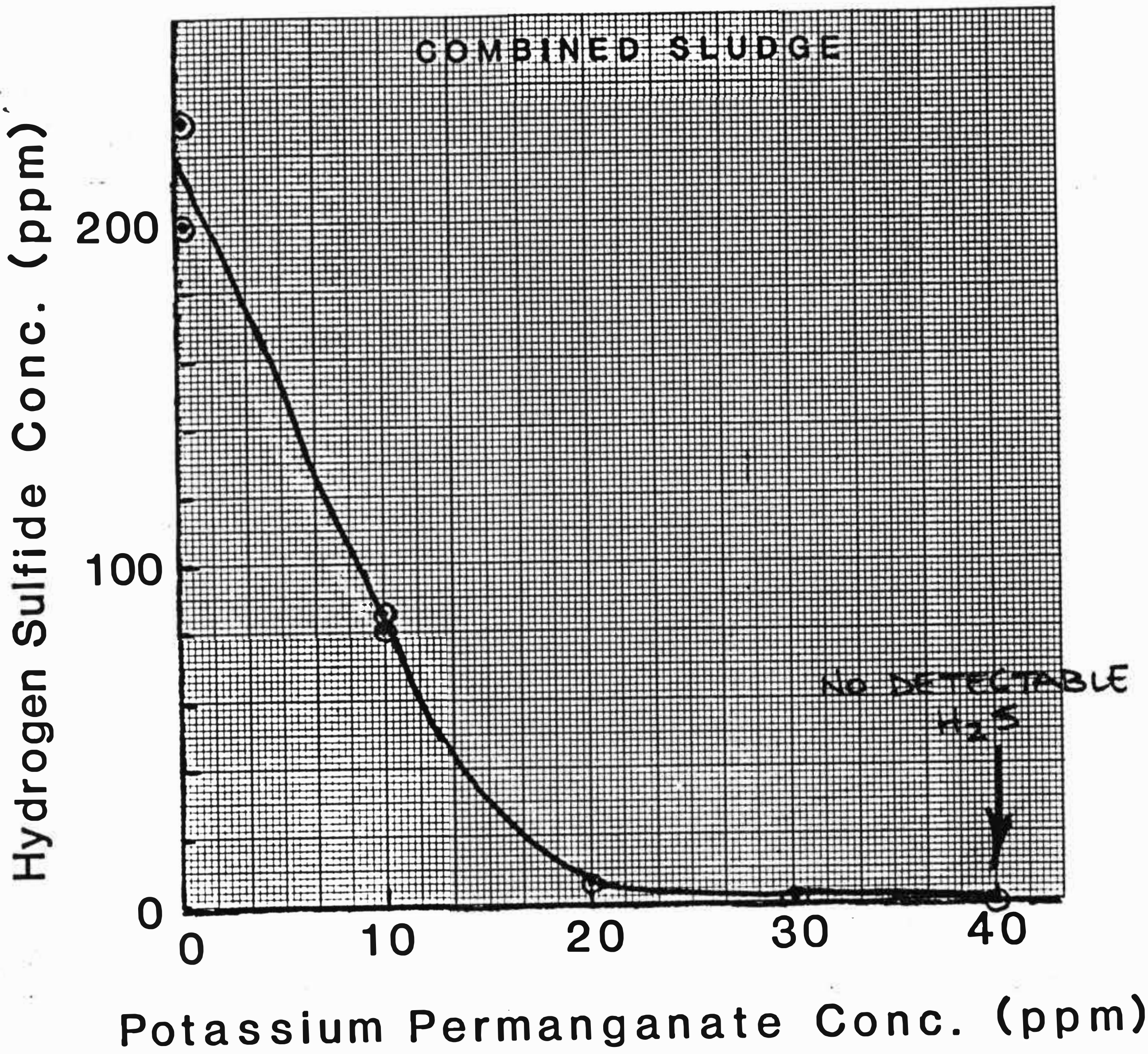
(FIGURE VIII)

HYROGEN SULFIDE
ODOR CONTROL

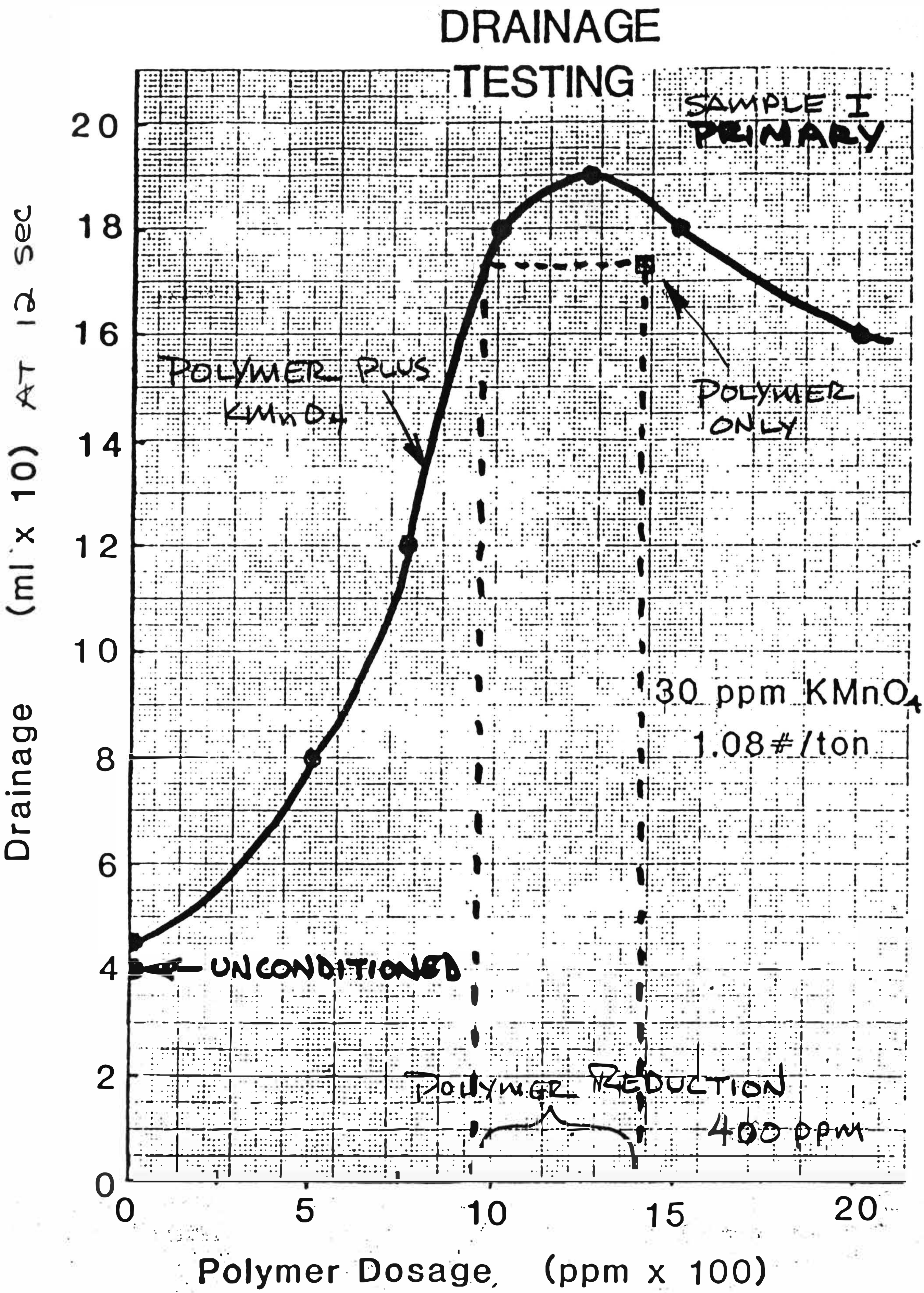


(FIGURE IX)

HYDROGEN SULFIDE
ODOR CONTROL



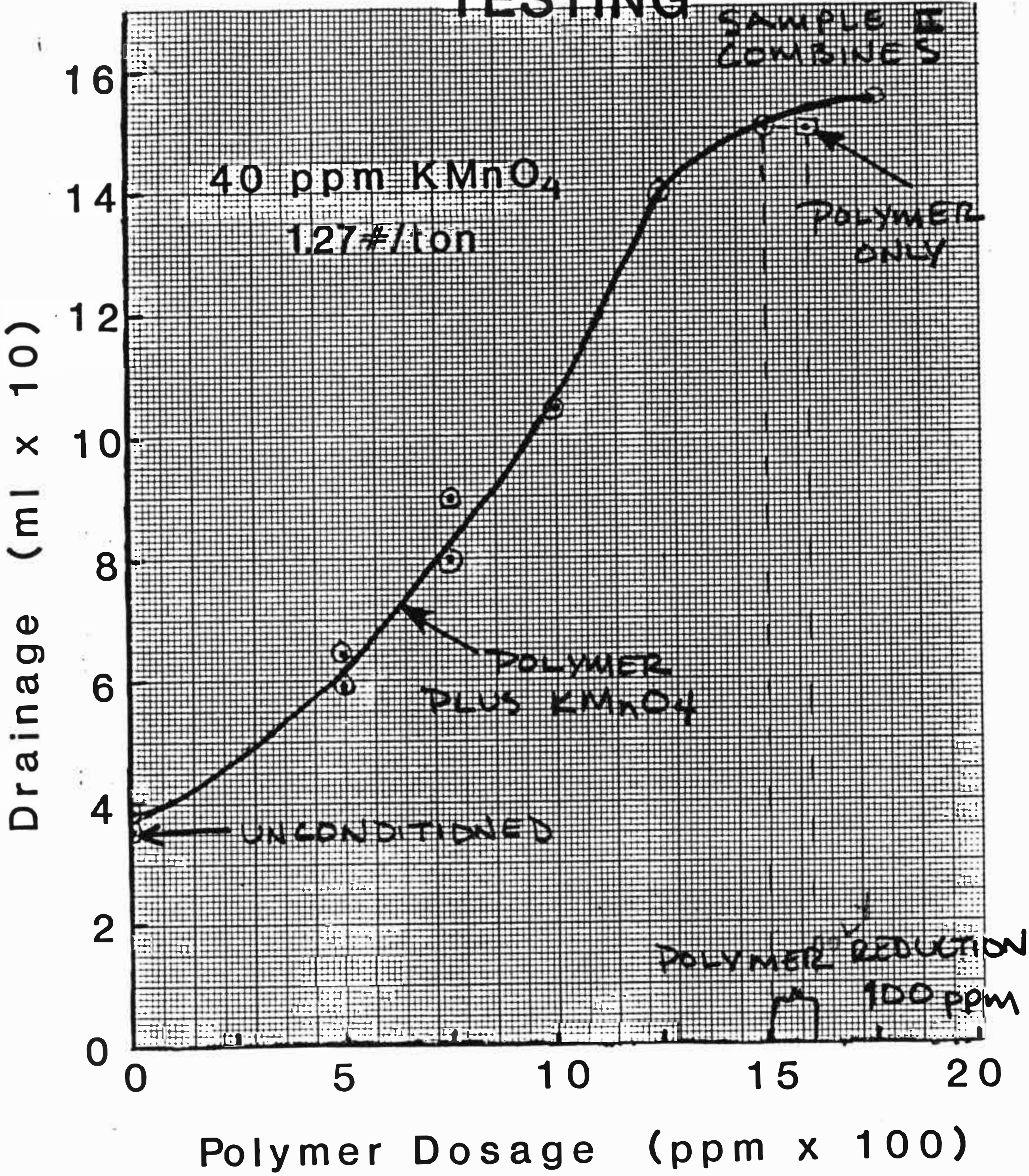
(FIGURE X)



DRAINAGE
TESTING
SAMPLE I
PRIMARY
Drainage (ml x 10) AT 12 sec
20
18
16
14
12
10
8
6
4
2
0
POLYMER PLUS KMnO4
POLYMER ONLY
UNCONDITIONED
30 ppm KMnO4
1.08#/ton
POLYMER REDUCTION
400 ppm
0
5
10
15
20
Polymer Dosage (ppm x 100)

(FIGURE XI)

DRAINAGE TESTING



(FIGURE XII)

ODOR TESTING DATA

SAMPLE ONE

SAMPLE ONE

H_2S CONC. (PPM) #1	H_2S CONC. (PPM) #2	$KMnO_4$ CONC. (PPM)
230	200	INITIAL
85.7	80	10
5.0	5.0	20
2.0	2.0	30
0	0	40

SAMPLE TWO

H_2S CONC. (PPM) #1	H_2S CONC. (PPM) #2	$KMnO_4$ CONC. (PPM)
325	300	INITIAL
85	80	5
40	40	10
2	25	15
4.5	4.5	20
TRACE	TRACE	25
0	0	30

TABLE I

SLUDGE DRAINAGE DATA

SAMPLE ONE

SAMPLE TYPE	VOLUME @ 12 SECONDS (ml) TRIAL 1	TRIAL 2
UNCONDITIONED	40	38
1400 ppm POLYMER	170	180
30 ppm $KMnO_4$	46	44
30 ppm $KMnO_4$ 500 ppm POLYMER	80	80
" " " 750 " "	120	120
" " " 1000 " "	180	180
" " " 1250 " "	190	190
" " " 1500 " "	180	180
" " " 2000 " "	160	160

TABLE II

SLUDGE DRAINAGE DATA

~~SLUDGE~~ SAMPLE TWO

SAMPLE TYPE	VOLUME AT 12 SECONDS (ml) TRIAL 1	TRIAL 2	TRIAL 3
UNCONDITIONED	37	36	35
1600 ppm POLYMER	150	150	
40 ppm KMnO4 500 ppm POLY.	60	60	65
" " " 750 " "	80	80	80
" " 1000 " "	105	105	105
" " " 1250 " "	140	140	140
" " " 1500 " "	150	150	150
" " " 1750 " "	155	155	155

TABLE III

PRESS SECTION
TESTING
DATA

% SOLIDS

30 PPM $KMnO_4$ 1400 PPM POLYMER	1400 PPM POLYMER	30 PPM $KMnO_4$ 1000 PPM POLYMER
55.1	57.1	56.8
56.7	56.7	51.5 OMIT
56.1	57.0	55.0
56.2	56.8	56.0
55.8	57.0	53.3
$\bar{x}$ = 56.0	$\bar{x}$ = 56.9	$\bar{x}$ = 55.3
σ = .589	σ = .16	σ = 1.50

TABLE IV

COST DATA

	PRESENT ClO_2 ODOR CONTROL	WITH $KMnO_4$ ODOR CONTROL
SAMPLE I		
POLYMER	$ 13/TON	$ 9.28 /TON
ODOR	$ 1.8/TON	$ 1.08 / TON
	$ 14.8/TON	$ 10.36 /TON

$ 4.44/TON x 12,600 TONS/YR = $ 55,944 /YR
(SAVINGS)

	ClO_2	$KMnO_4$
SAMPLE II		
POLYMER	$ 13.2 / TON	$ 12.38 / TON
ODOR	$ 1.8 / TON	$ 1.27 / TON
	$ 15 / TON	$ 13.65 / TON

$ 1.35/TON x 12,600 TONS/YR = $ 17,010 /YEAR
(SAVINGS)

TABLE I