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CLASSIFIER BOTTOMS EVALUATION FOR SAFE DETOXIFICATION AND DISPOSAL

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CLASSIFIER BOTTOMS EVALUATION FOR SAFE DETOXIFICATION AND DISPOSAL
LD-2206

INTRODUCTION

The recent accelerating emphasis on protection of the environment has necessitated the need of rapid development in technology to aid in pollution control.

The proper management of hazardous waste is now clearly recognized as one of the major tasks the chemical industry will have to accomplish in the coming decades. As environmental laws and regulation are becoming stricter in the near future, industry's waste disposal options have become increasingly limited and costly.

Recently, the Resource Conservation Recovery Act (RCRA) has helped to promote environmental safeguards, but also has required more costly waste management practices to deal with hazardous waste.

The cost of putting a hazardous waste into a secure landfill in bulk form is about \$0.45/gallon; whereas, in drums, the cost is higher and the practice will soon be ruled out by EPA.

PPG Industries Chemical Division at Lake Charles is paying over \$67,000 annually for the disposal of its Bottoms Plant solids and liquid hazardous waste alone. The future prospect for such disposal is not promising. The ever increasing high cost and possible future restriction on transportation, as well as the limitation of secure landfill facilities are quite unpredictable.

Concerned with all these problems, a need was recognized to have an alternate solution. A project was jointly originated by Process Engineering and the Laboratory to look into such possibilities.

The objective of this project is to present specific information pertinent to the possible in-plant alternate to dispose of such hazardous waste. The laboratory responsibility was considered to provide those design parameters of the unit process which are involved in physical-chemical treatment of the raw waste for detoxification, as well as the analytical data to determine the best suited design criteria in selection of the candidate process. The approach should be environmentally and legally safe, technologically feasible, as well as economically desirable. Also, if possible, this method should be adaptable to our other similar solid waste problems which would be generated by various other operating units.

Classified bottoms sludge contains mostly residue of dopp kettles and those heavies which can neither be incinerated in our existing facilities, nor separated in API Separators. A general characterization and analyses are summarized in Table Nos. I, II and III to show the solid and vaporizable contents and other chemical and physical characteristics.

SL 085454

Table I. General Characteristics of Classifier Bottoms (Untreated)

Physical Characteristics

State	Semi-viscous sludge.
Color	Greenish black with brown specks.
Odor	Pungent and chlorinated organics.
Solids and Vaporizable Contents	8-10% solids and 90-92% vaporizable components.

Chemical Characteristics

BTU/lb (gross)	3376
Residue at 350°C	7.5%
Organic Contents (volatiles)	52% (See Table II)
Inorganic Contents (metals)	6% (See Table III)
pH	Less than one (highly acidic)

Table II. Analysis of Total Organics (weight % volatiles) Present in Classifier Bottoms

Component, wt %	11/21/80	11/24/80	12/02/80	6/16/81	Average
Vinyl Chloride	Trace	-	-	-	
Ethyl Chloride	8.53	0.94	1.01	0.34	2.7
1,1-Dichloroethane	21.21	7.00	5.52	7.99	10.38
cis-1,2-Dichloroethylene	0.13	0.12	0.11	0.16	0.13
Chloroform	0.37	0.22	0.20	1.33	2.12
1,2-Dichloroethane	6.06	6.12	6.50	9.04	6.92
Methylchloroform	0.63	2.96	1.41	0.69	1.42
Carbon Tetrachloride	0.41	0.38	0.35	0.30	0.36
Trichloroethylene	6.43	7.46	7.01	5.61	6.62
1,1,2-Trichloroethane	9.10	2.95	3.54	3.16	4.63
Toluene	0.04	-	-	-	0.04
Perchloroethylene	8.03	8.75	9.53	10.42	8.93
unsym-Tetrachloroethane	4.01	1.26	1.34	1.68	2.06
sym-Tetrachloroethane	3.33	1.09	0.88	3.46	2.19
Pentachloroethane	4.75	1.66	1.80	1.74	2.48
Hexachloroethane	1.64	0.34	0.39	0.79	0.75
Hexachlorobutadiene	0.05	0.69	0.90	1.39	0.75
Total Volatiles Average					52.572

Method of Analysis: Gas Chromatography; methylene chloride extraction.

Table III. Total Inorganic (weight % metals) Present in
Classifier Bottom (Raw Sludge)

<u>Metals</u>	<u>1st Composite</u>		<u>2nd Composite</u>		<u>3rd Composite</u>		<u>Average</u>	
Fe	4.9	%	5.4	%	4.8	%	5.03	%
Cr	< 0.0001	%	0.003	%	0.004	%	0.002	%
Cu	0.02	%	0.023	%	0.033	%	0.025	%
Pb	< 0.0001	%	0.001	%	0.002	%	0.0010	%
Ni	0.01	%	0.005	%	0.015	%	0.01	%
Hg	0.05	ppm	0.3	ppm	0.5	ppm	0.43	ppm
Ca	-		0.117	%	3.20	%	1.10	%
Total							6.17	%

ABSTRACT

Laboratory studies were conducted to develop a means to detoxify bottoms material from the Plant B Classifier. A two step process involving pre-treatment with lime followed by pyrolysis was found to decompose the toxic components of the waste, rendering the resulting solid suitable for landfill. A continuous pilot plant to verify this treatment process is recommended.

EXPERIMENTAL**A. Sampling**

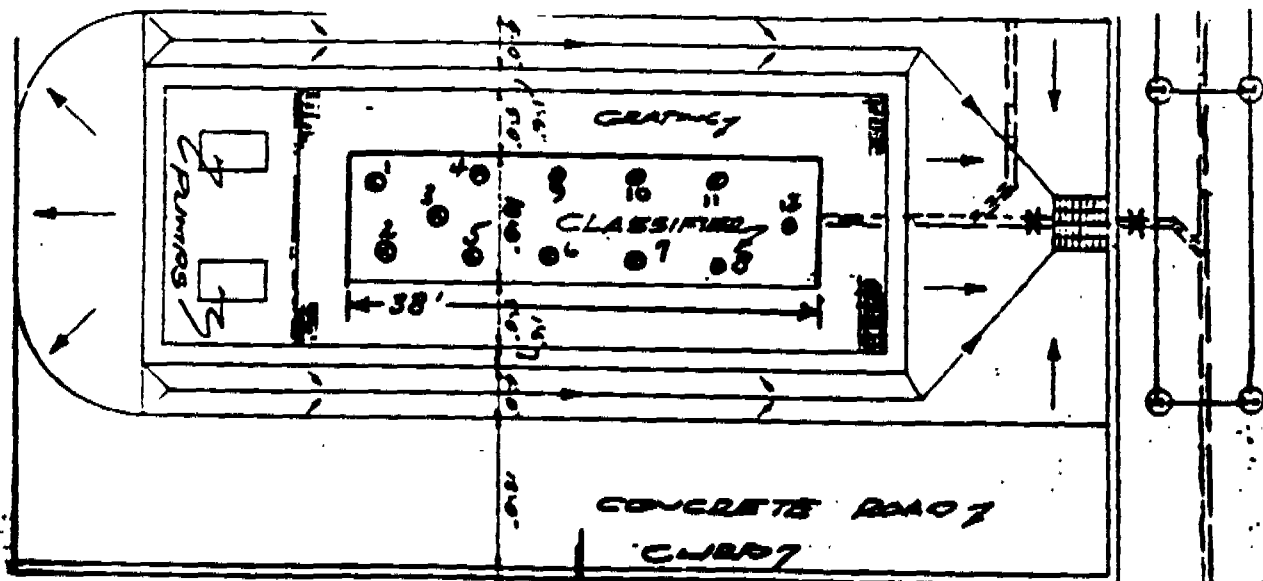
The classified bottoms holding tank is a 38' x 10' x 8' rectangular pond where the tar buggies dump the material from various dopp kettles and vacuum trucks discharge organic waste from other operating units. The solids are separated from organics and water and settle down to the bottom by gravity as well as by the precipitating action of ferric chloride present as the spent catalyst from the dopp kettles.

The sampling scheme (Figure No. 1) was devised to ensure collection of a representative portion of the classified bottoms material. The surface area of the pond was divided into an imaginary grid system and a total of 12 cored samples were taken (using EPA's COLIWASA method) with a 2-1/2" x 5' spun fiberglass pipe operated by two men. The twelve core samples were composited and equal portions were transferred into three one-gallon plastic containers holding about 10 pounds each of sampled material for laboratory experimentation. The sampling was performed in compliance with existing regulations promulgated by the regulatory agencies (EPA 600/2-80-018, January 1980. Samplers and Sampling Procedures for Hazardous Waste Streams, Analytical Operating Procedures Manual, Department of Natural Resources, Office of Environmental Affairs, Hazardous Waste Management Division, Baton Rouge, Louisiana, August 1980).

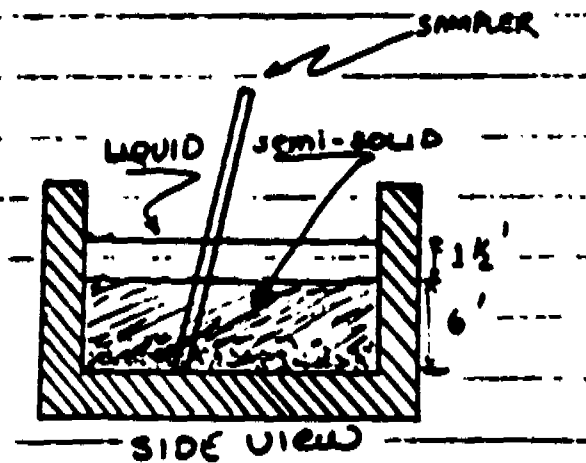
B. Equipment and Apparatus

The initial laboratory pyrolysis experiment was performed in a platinum crucible using an electric heater to study the weight loss relationship to heat and total time period (Table IV). Later, for pilot studies, the apparatus for pyrolyzing the classified bottoms was designed for comparative batch incinerations, ranging from 100-500 grams. The system (Figure No. 2 and Photograph No. 1 of the pilot plant) consisted of a one-liter borosilicate reactor vessel and a trio of Greenberg-Smith 500 mL water scrubbers. An air filter of 0.45 μ m particle retention (Gelman-089-844 8" x 10" size) was installed after these scrubbers to verify that all the particulates of interest were trapped. To collect this sample, Research Appliance Company's particulate Air Sampler (Model GMWL-2000) was used. This air sampling equipment served a dual purpose: first, for collection of the said particulate, and second, as the source of induction air needed for oxidation during the pyrolysis. The entire assembly was a closed system except for an air inlet, provided by a glass tube opening into the reactor vessel. The exhaust was connected to the three water scrubbers followed by the particulate sample equipment. A 750 watt, variable control, electric distillation furnace was used to provide the necessary heat. A digital

Figure 1. Classifier Bottoms Basin and Sampling Scheme



DEVELOP sample location:



Study of Thermal Decomposition and Organics Weight Loss of Classified Bottoms

Small Scale Experimentation)

Weight Lost at 15 Minutes			Weight Lost at 30 Minutes			Weight Lost at 45 Minutes			Weight Lost at One Hour			Weight Lost at One Hour and Fifteen Min.		
Observed Temperature			Observed Temperature			Observed Temperature			Observed Temperature			Observed Temperature		
85-100°C			120-150°C			175-220°C			270°C			310-320°C		
Remaining Weight, g	Weight Lost, g	Weight Lost, %	Remaining Weight, g	Weight Lost, g	Weight Lost, %	Remaining Weight, g	Weight Lost, g	Weight Lost, %	Remaining Weight, g	Weight Lost, g	Weight Lost, %	Remaining Weight, g	Weight Lost, g	Weight Lost, %
9.3	15.7	62.8	3.46	21.54	86.16	2.03	22.97	91.68	1.98	23.02	92.12	1.96	23.04	92.14
7.37	17.65	70.65	2.09	22.91	91.64				1.94	23.06	92.24	1.93	23.07	92.28
9.31	15.92	63.68	4.2	20.03	83.35	2.04	23.19	91.9	1.80	23.43	92.86	1.77	23.46	92.98
8.40	17.13	64.97	2.77	22.66	89.1	1.85	23.58	92.72	1.84	23.59	92.76	1.84	23.59	92.76

Losses in Weight Loss

- A
- 92.54 g
- 0.39

LB-2204/8

SL 085460

- B. pyrometer was used to study the temperature within the reactor, and another pyrometer was attached to the heat source to monitor the heat differentials during the pyrolysis (Figure No. 2).

The entire system was mounted in a hood and all experimentation performed with the hood door closed and hood exhaust on.

C. Procedure

Weighed samples of the material to be pyrolyzed were placed in the reactor vessel along with the thermocouple. Another thermocouple was placed between the heat source and the reactor vessel bottom. The reactor vessel, scrubbing units, and air sampling equipment were connected to each other. The flow of air into the system was adjusted by a bypass valve. The heating of the reactor vessel was controlled manually by monitoring both the sludge and the heat source temperatures. Temperature readings were recorded every two to five minutes depending on the temperature differential.

The three scrubbers were charged with 150 mL water to retain any sublimates and water soluble gases coming out of the reactor. This was followed by the 0.45 μ m filter assembly of the air sampling equipment. This unit retains all the particulates not trapped by the scrubbing units.

DISCUSSION AND RESULTS

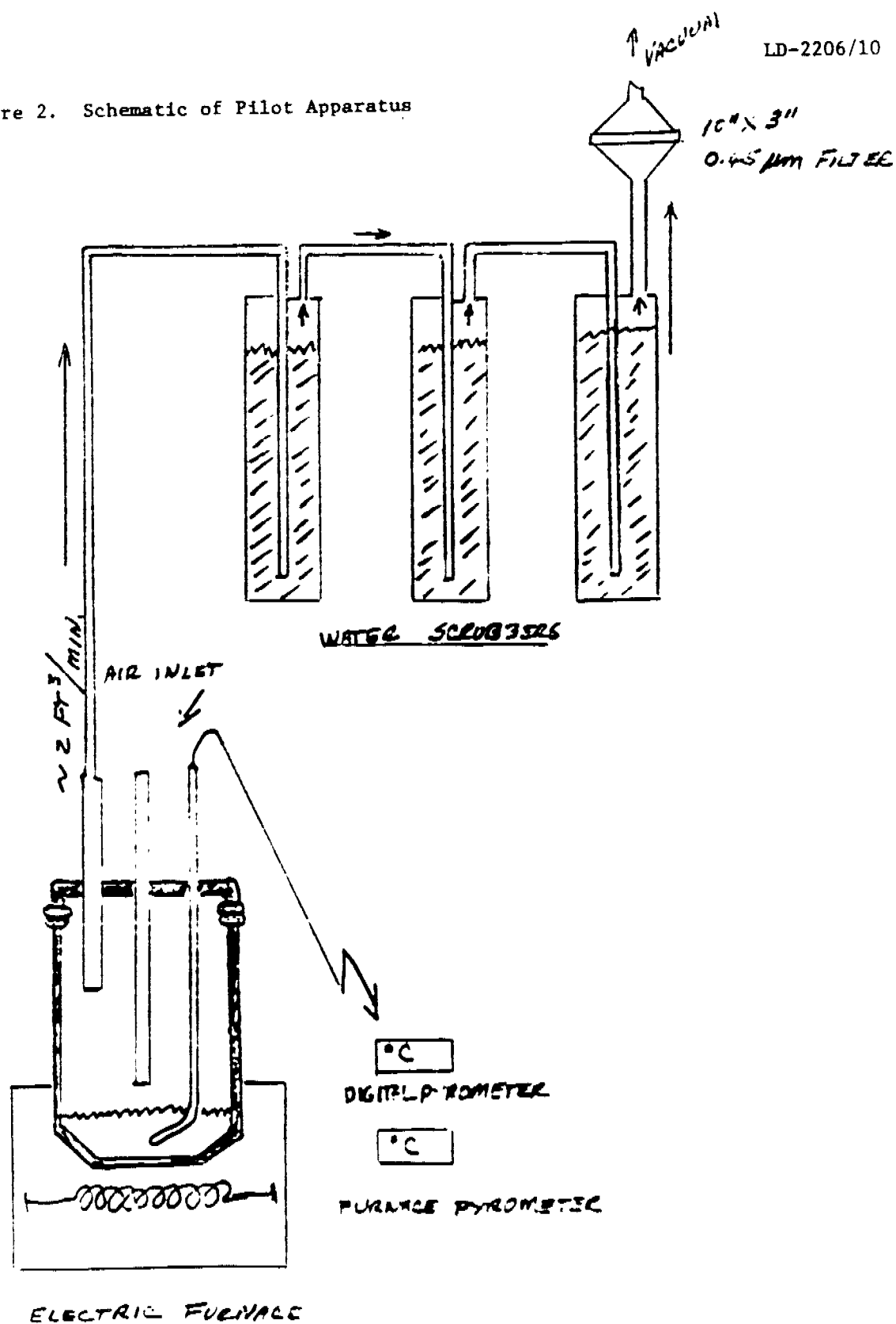
The major constituents of the sludge are: spent ferric chloride catalyst, muriatic acid, sand, chlorinated organics, water, and tar-like heavy sludge.

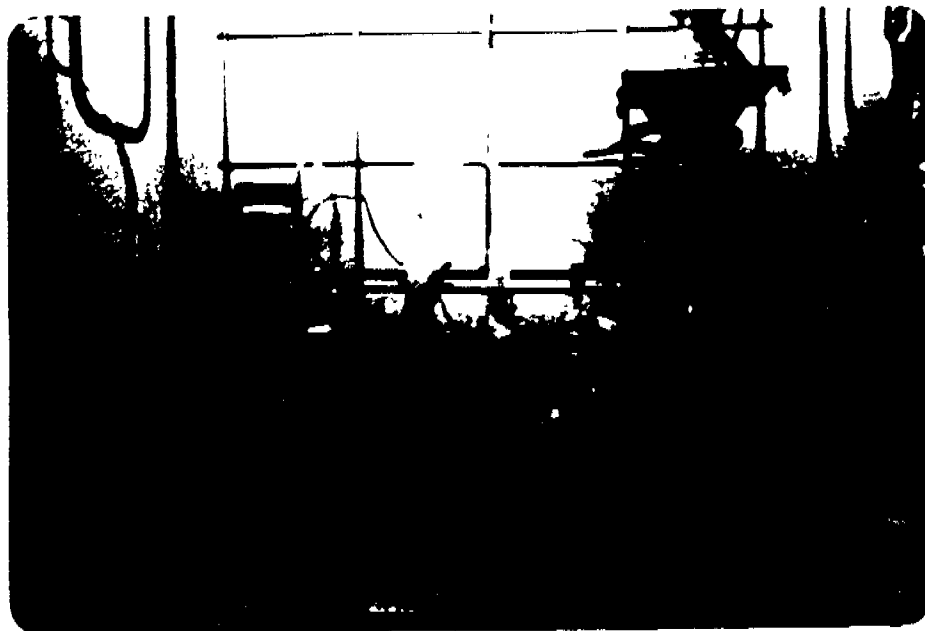
Pyrolysis of these materials offers the opportunity to reduce the volume as well as the toxic components to levels qualifying for disposal at a non-hazardous, sterile landfill.

The results of the preliminary experiments show that the sludge sample contains approximately 92% volatile constituents with 8% solids (Table IV). The spectrographic analysis of the residue indicated that the major constituents were Fe_2O_3 and sand with minor quantities of Hg and Ca (Table V). The vaporizable constituents were largely composed of organics, muriatic acid (HCl), $FeCl_3$, and water.

Although volume reduction of the bulky waste was achieved, as well as detoxification, the resultant particulate emissions, chiefly iron, were highly undesirable (Photograph No. 2). Strict air pollution regulations and highly corrosive gaseous emissions (HCl) prevent such practices. The evolved HCl formed indigenously by hydrolysis of $FeCl_3$, and thermal decomposition of chlorinated organics would have a significant effect on the performance and life of the reactor and its hardware. Therefore, it was necessary to select an agent that would neutralize existing HCl and that formed by the decomposition of chlorinated organics.

Figure 2. Schematic of Pilot Apparatus





SL 085463

Table V. Metal Analysis of Pyrolyzed Sludge
(Untreated Pyrolyzed Residue of Raw Sludge)

<u>Metals</u>	<u>1st Composite</u>	<u>2nd Composite</u>	<u>Average</u>
Fe	35.9 %	39.5 %	37.5 %
Cr	0.24	< 0.0001 (0.18 ppm)	0.120
Cu	0.19	0.15	0.170
Pb	0.004	< 0.0001 (0.04 ppm)	0.002
Ni	0.10	0.04	0.070
Hg	< 0.10 ppm	0.5 ppm	0.30 ppm
Ca	0.24	0.25	<u>0.245</u>
Total			38.11 %



Photomicrograph 2. Pyrolysis of untreated sludge.
(Note the effects of particulates.)



Photomicrograph 3. Pyrolysis of treated sludge.
(All three scrubbers and reactor vessel did not show any particulate deposition.)

Several neutralizing agents were considered including calcium carbonate, calcium oxide (quick lime) and slaked lime. Slaked lime was selected because it is readily available and safe to use. Quick lime releases large quantities of heat upon contacting water which could result in a fire or release of organics in air. Calcium carbonate is not efficient for neutralizing and more expensive.

The typical dose was considered to be 20 g/100 g of waste, but it may range from 18 g-22 g/100 g depending upon the nature of the waste. The 1:5 mix ratio was successfully used for our pilot plant experiments. A pH range of 9.8 to 10.5 was considered a good indication of thorough mixing and complete neutralization of lime and waste. The slight excess alkalinity serves as a reserve for any other HCl produced during the pyrolysis.

The treated waste (20 g/100 g) was heated. At temperatures of 150°-165°C, the charred remains of organics reached the auto ignition point and burned with a slight glow. The pyrolysis was completed without any particulate emissions at 350°C. (Photograph No. 3).

The residues and scrubbing waters were analyzed for organics, inorganics, and leachate testings (Tables VI, VII, and VIII). The filter paper from the air sampling unit was weighed and checked for any retention. Results were negative.

Sabine 'clear well' River Water was used in the scrubbers for one incineration of treated sludge for comparison to the total suspended solids formation when scrubbing with distilled water. Results did not show any difference.

Scrubber efficiency was determined by comparing total suspended solids retained in each scrubbing unit to the total of the three. The scrubber efficiencies were: No. 1 scrubber retained 87.4% of the total particulate, No. 2 scrubber retained 12.5% and No. 3 scrubber collected 0.1%. The scrubber waters were step-filtered through a range of filter pore sizes for size distribution analysis (Table VIII).

CONCLUSION

The results of several tests proved that the lime treatment was quite effective for the neutralization of waste prior to the pyrolysis. It controlled very efficiently the problem of particulate and corrosive gas emissions.

The quantity of final residue resulting from lime treatment was considerably greater but it is offset by the lack of atmospheric emissions and solids loading of the scrubber water by this process.

The observed temperature increase during the mixing of slaked lime with waste was approximately 10°C. The water was not heated to the point of boiling. The waste was not heated to the point of ignition.

The characterization analysis of the residue indicated an EPA "non-hazardous" classification. The EPA toxicity test for heavy metals (Table VII) was negative for toxic metals. Residues were analyzed for high molecular weight organics such as PCB, and results were negative. A detailed analysis and comparative results of treated and untreated pyrolyzed residues are given in Table VIII.

Table VI. Metal Analyses of Treated and Pyrolyzed Bottoms Sludge

<u>Metals</u>	<u>1st Composite</u>		<u>2nd Composite</u>		<u>3rd Composite</u>		<u>Average</u>	
Fe	19.3	X	20.8	X	12.2	X	17.43	X
Cr	0.00005	X	0.009	X	0.018	X	0.009	X
Cu	0.17	X	0.094	X	0.083	X	0.115	X
Pb	0.00005	X	0.004	X	0.004	X	0.0027	X
Ni	0.04	X	0.05	X	0.035	X	0.0416	X
Hg	0.2	ppm	0.1	ppm	0.2	ppm	0.17	ppm
Ca	20.0	X	16.50	X	19.6	X	18.7	X
Total							36.47	X

Table VII. EP Toxicity Analysis for Hazardous and Toxic Metal Evaluation (Residues of Treated and Pyrolyzed Sludge)

<u>Toxic Metals</u>	<u>1st Composite</u>	<u>2nd Composite</u>	<u>3rd Composite</u>	<u>EPA's Limits</u>
Cu	-	0.0 ppm	0.2 ppm	0.733 ppm 5.0 mg/L max.
Ni	-	0.1 ppm	0.3 ppm	0.80 ppm -
Cr	1.0 ppm	0.2 ppm	0.9 ppm	0.70 ppm 5.0 mg/L
Pb	1.0 ppm	0.6 ppm	0.8 ppm	0.80 ppm 5.0 mg/L
Cd	< 0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm 1.0 mg/L
As	< 5.0 ppm	-	-	- 5.0 mg/L
Ba	-	-	-	- 100.0 mg/L
Hg	0.005 ppm	< 0.002 ppm	< 0.002 ppm	< 0.003 ppm 0.2 mg/L

Table VIII. Comparative Study of Chemical and Physical Characteristics of Pyrolyzed, Treated and Untreated Sludge

<u>Characteristics</u>	<u>Sludge Treated (With Lime)</u>	<u>Sludge (Untreated)</u>
State	Small granular, lumpy and and hyroscopic.	Medium to fine grain powder.
Color	Rust brown.	Brownish black.
Odor	None	None
Residue, %	25-35	10-15
Residue pH	10.4	5.8
Volatiles and Sublimates	75-65%	90-85%
Pyrolysis-optimum Temperature	350°C	480°C
T.D.S. (Scrubber Water)	0.0063%	N/A
T.S.S. (Scrubber Water)	10 ppm	500 ppm
Distribution of Particulate		
Size (Scrubber Water)		
30-60 μ m	2	112
10-20 μ m	2	111
- 8 μ m	1	110
5 μ m	3	54
3 μ m	1	50
1.2 μ m	0	36
0.8 μ m	1	2
0.45 μ m	0	25
pH of Scrubber Waters		
Scrubber No. 1	3.7	0.8
Scrubber No. 2	5.0	1.6
Scrubber No. 3	5.2	2.7

RECOMMENDATIONS

There are a few important factors which should be observed for an efficient pyrolysis and detoxification of this waste.

Complete neutralization of waste is necessary, since the majority of pyrolysis problems are caused by HCl. Neutralization is greatly simplified if the lime is added in the form of a thick slurry. This serves two functions: first, water promotes the hydrolysis of FeCl₃, and second, water provides an effective medium for the homogeneous acid neutralization.

The lime mixing ratio (1:5 based on the acidity of sludge) is also an important factor in this process. Exceeding the optimum neutralization level may cause higher pH in the residue. A pH of 12.5 or above classifies any waste as hazardous.

Calcium chloride converts into a porous, hygroscopic, amorphous mass above 200°C. It fuses and begins to decompose at 500°-710° into oxy-chloride, calcium chloride, calcium oxide, and chlorine in the presence of air. Upon rapid cooling, it solidifies into a glass-like crypto-crystalline mass which sticks to the reactor vessel. The safe range was considered to be between 350-400°C to prevent glass formation. Therefore, most experiments were performed up to the range of 350-400°C, although a few of the experiments reached 500°C.

Finally, a larger scale continuous pilot plant is recommended for further analytical testing of emissions to verify the complete detoxification of waste material that was achieved in laboratory scale experiments.

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