

Short Communication

CHEMICAL SUPPRESSION OF AIR POLLUTANTS DURING THE THERMAL DISPOSAL OF HAZARDOUS WASTES

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Introduction

Hazardous waste management has become one of our nation's top priority programs. These wastes are unavoidable by-products of our technology and can pose a serious threat to health and environment if not properly controlled. Major methods under investigation for the disposal of chemical wastes are incineration, physical/chemical treatment, biological methods and land disposal.

None of these methods is ideal, for each has its own environmental implications. Land disposal inclusive of landfill, infiltration/evaporation and encapsulation, if properly performed, is essentially masking our wastes. To say that these procedures safely fix the chemical waste material within our environment is to ignore the long-range impact of leaching, migration and residual toxicity. Biological treatment is the reduction of specific waste material through the use of micro-organisms and enzymes. This approach may require moderate capital investment, but the environmental impact with respect to residual toxicity of the final effluent and sludge, losses to the environment through surface water, volatilization and system upset are not fully characterized. Physical/chemical treatment inclusive of hydrolysis, microwave discharge, carbon adsorption and ozonation, to name a few, lack adequate detailing to define process limitations and their environmental impact [1, 2]. Incineration is the most developed treatment process assuring efficient, 99.9 + %, conversion and effective disposal, by reducing the volume of material to be disposed and the ease of controlling the environmental impact with pollution control equipment. The residual ash may require proper disposal due to toxicity, but in much smaller quantities.

In the thermal oxidation of many waste materials, the problem of air pollutants such as SO₂, HCl, P₂O₅, etc. may require removal prior to the release of the flue gases to the environment. If energy recovery is desired as part of the total system, these acid gases may also have a bearing on the cost effectiveness of that concept due to consideration of corrosion.

Over the past 10 years the concept of the pyrolysis afterburner has been successfully demonstrated and has led to the development of processes and equipment for the thermal disposal of hazardous chemicals, including fluorinated and chlorinated compounds, mustard and nerve agents, styrene tar, rubber waste, API separator bottoms and pharmaceutical sludges [3, 4, 5].

The advantages of pyrolysis over incineration are the flexibility of the process and the potential to minimize the impact of thermal disposal on air quality. Pyrolysis, prior to fume incineration, minimizes the particulate carryout as compared to "conventional" incineration with an afterburner which has more gas flow and resulting product agitation. Pyrolysis implies heating in the absence of air to thermally degrade the material to a volatile gaseous portion and a residual solid comprised of fixed carbon and ash. The flexibility of the process comes about with the availability of a gaseous fuel having many potential heating applications [6].

In the processing of toxic materials such as PCBs, pesticides, herbicides, etc., the effluent gases of any thermal disposal system will require scrubbing. Sulfur, chlorine and phosphorus are some of the typical elements present, either singly or in combination, in these wastes and will volatilize during the thermal process to be carried off into the gas stream. Therefore, because of evolution of these acid gases, a scrubber system will be necessary to remove the pollutants to meet environmental emission standards and special consideration will be required for the materials of construction due to a potential corrosion problem.

Assessing the potential of the pyrolysis—afterburner thermal process, it becomes apparent that control of both temperature and pyrolysis chamber solid and gas chemistry permit the operation to be manipulated. By adding inexpensive reactive compounds to the wastes and allowing them to react with the elements such as sulfur and chlorine, it is possible to form non-vaporizing or very low vaporizing solid compounds of these elements. Binding of these constituents with adequate effectiveness can eliminate or reduce the requirement of the pollution control equipment, and can considerably reduce the corrosion problems in the downstream equipment.

Objective

A program was undertaken by the Midland—Ross Thermal Systems Technical Center, whose objective was to establish the technical feasibility of suppressing the formation of air pollutants during the thermal disposal of hazardous wastes. The purpose was to attempt to convert the undesirable elemental constituents to compounds exerting either no, or very low, vapor pressures during the pyrolysis step. The effectiveness of the additive would then be measured as the percent of feed component remaining in the char.

Laboratory procedure

Test facility

An electrically heated Lindberg oven modified as a muffle furnace was used for the experimental bench scale program. The use of a muffle permitted the pyrolysis process to take place in an inert nitrogen atmosphere. The gas outlet on the muffle furnace was connected to a gas cooler. The cooled effluent gases were passed through water and a caustic scrubbing system to remove the acidic gases before venting. An overall bench scale process schematic is presented in Fig.1.

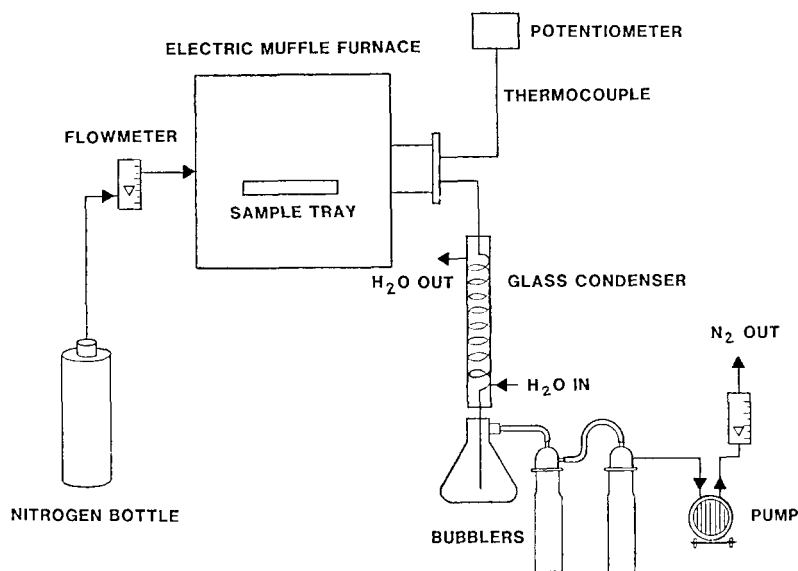


Fig.3. Mole ratio vs. effectiveness.

Test materials

The first bench test series consisted of simulating a chemical waste. The simulated waste was prepared by mixing sand and a pesticide containing sulfur, chlorine and phosphorus to a paste-like consistency. The pesticide used was "Isotox Insect Spray," manufactured by Chevron Chemical Company. The selected additives for this series of tests were technical grade iron oxide (FeO), calcium oxide (CaO) and sodium carbonate (Na₂CO₃). See Table 1, composition of simulated waste.

A second series of bench tests consisted of pyrolyzing an industrial sludge containing both sulfur and chlorine. Samples of this waste, approximately 50% by weight water, were treated with calcium hydroxide (Ca(OH)₂) or sodium hydroxide (NaOH) prior to pyrolysis. See Table 2, composition of industrial sludge.

TABLE 1

Composition of simulated waste

Component	Weight (g)	Concentration (wt %)
Sand	25.0	—
Isotox	20.0	—
Chlorine	0.19	0.42
Sulfur	0.25	0.55
Phosphorus	0.24	0.53

TABLE 2

Composition of industrial sludge feed

Component	Concentration (wt %)
Carbon	17.5
Hydrogen	2.3
Oxygen	17.8
Sulfur	1.5
Chlorine	0.5
Nitrogen	1.1
Ash	19.6
Water	39.7

Test procedure

For the first series of tests, the oven was preheated to the desired temperature. The three additives were tested at 800° F and 1200° F. During each of the six runs, the muffle was loaded with four alloy trays. One run consisted of four trays, the first tray containing weighed quantities of sand and insecticide, the second tray containing a weighed quantity of additive only, and the third and fourth trays containing weighed quantities of sand, insecticide and the additive.

The loaded muffle was closed with a gasketed flange and was purged with nitrogen at a flow rate of 2 to 3 ft³/h. The effluent gases from the muffle were cooled in a glass condenser by circulating water through the jacket. Cooled gases were scrubbed by two bubblers, one containing water and the other caustic solution. Pyrolysis of the simulant waste was carried out for about 1½ hours to assure complete reaction. At the end of the pyrolysis, nitrogen purging was continued during the cooling period. The cooled trays were weighed to measure the weight loss and samples were taken for chemical analysis.

Basically, the same test procedure was used for the second test series, except individual samples of the industrial sludge were pyrolyzed at 1400° F for approximately ½ hour. The time of pyrolysis was governed by the generation of smoke appearing in the furnace purge. The cooled samples were weighed and analyzed.

Discussion of results

Each sample of residue from the simulated waste was analyzed for percent chlorine, sulfur and phosphorus. Additive effectiveness was determined by comparing the residual concentrations with the calculated concentration in the purchased material. The effectiveness of the additives used in the first series of experiments is summarized in Table 3, additive effectiveness — simulated waste bench tests. The results show that of the three additives tested, sodium carbonate was found to be most efficient with suppressant effectiveness of 49.5% for sulfur, 45.9% for chlorine and 27.9% for phosphorus. With respect to temperature effect, sodium carbonate was more effective for phosphorus and chlorine than for sulfur at 1200° F, but greater for sulfur than for chlorine and phosphorus at 800° F.

The results of the industrial sludge bench pyrolysis tests are summarized in Table 4, additive effectiveness — industrial sludge bench tests. All runs during the tests were performed in a flue product atmosphere at 1400° F. The results show sodium hydroxide to be more effective than calcium hydroxide, exhibiting suppressant effectiveness of greater than 90% for sulfur and approximately 80% for chlorine. Both additives exhibited increased effectiveness with increased concentration.

TABLE 3

Additive effectiveness — simulated waste bench tests

Additive	Pyrolysis temperature (° F)	Effectiveness		
		Cl (%)	S (%)	P (%)
Na ₂ CO ₃	800	17.2	49.6	10.0
	1200	45.9	6.4	27.9
CaO	800	18.7	17.6	0.0
	1200	19.3	0.0	15.4
FeO	800	13.5	29.6	1.7
	1200	6.3	12.8	14.6

TABLE 4

Additive effectiveness — industrial sludge bench tests

Additive	Mole ratio	Pyrolysis temperature (° F)	Effectiveness		Weight loss (%)
			Cl (%)	S (%)	
NaOH	1.4	1400	83.1	90.5	75.0
	2.5	1400	79.2	92.1	74.7
Ca(OH) ₂	1.4	1400	77.6	58.6	74.1
	2.1	1400	86.5	80.8	74.8

The successful results of the bench scale program were used to establish the test parameters for a pilot scale demonstration run. Samples of the previously tested industrial sludge were fed to the Technical Center's rotary hearth pyrolyzer-rich fume incinerator system, Fig. 2. The calcium hydroxide concentration in the sludge feed was maintained at 8% by weight establishing a mole ratio of 1.8 : 1 calcium to reactive constituents. Feed, char and stack samples were analyzed for sulfur and chlorine concentrations. During the course of these demonstration runs, the average weight loss for the sludge was 70% to 73%, which compared favorably with the bench tests of 74%. Table 5 summarizes the results obtained for these runs. The effectiveness of calcium hydroxide to suppress the release of sulfur and chlorine was comparable to the results obtained at the bench scale level; that is, approximately 80% for chlorine and 70% for sulfur (refer to Fig. 3).

The results of these tests permit the hypothesis of the synergistic effect of mixed wastes. Proper waste management could permit the mixing of several

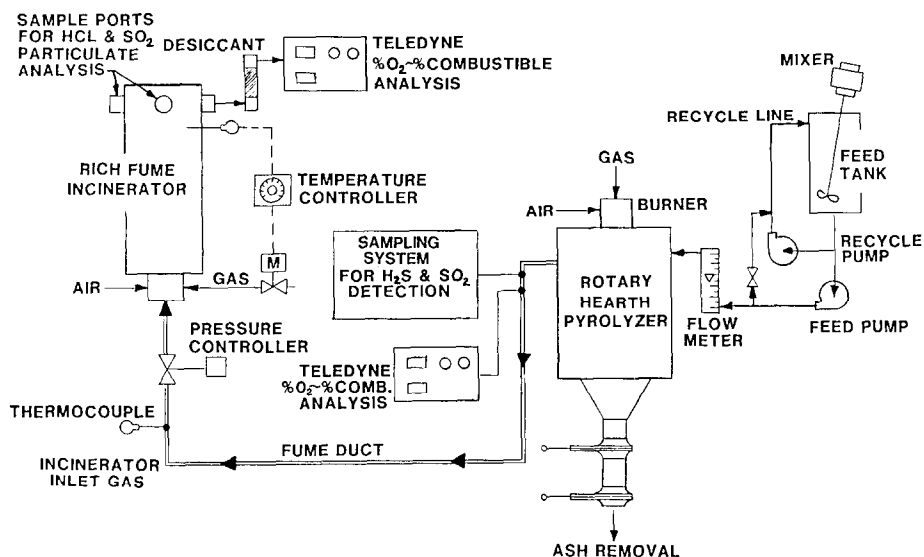


Fig. 2. Schematic of pilot-plant equipment.

TABLE 5

Additive effectiveness — industrial sludge pilot tests

Run no.	Additive	Mole ratio	Pyrolysis temperature (°F)	Effectiveness Cl (%)	Effectiveness S (%)	Weight loss (%)
1	Ca(OH) ₂	1.8	1400	86.4	62.3	73.2
2	Ca(OH) ₂	1.8	1400	81.1	72.6	70.4

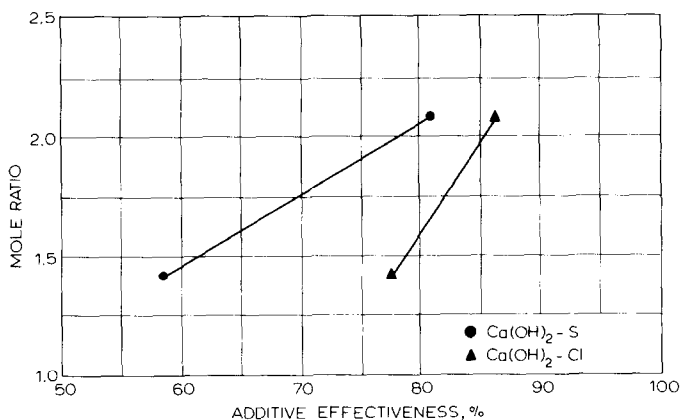


Fig.1. Bench-scale pyrolysis system.

dissimilar waste streams in such a way as to permit two thermally reactive chemical constituents to combine in the pyrolysis step. The binding of these elements with adequate effectiveness to form non-vaporizing or very low vaporizing solid compounds can eliminate the requirement of the control equipment and can considerably reduce the corrosion problems associated with the downstream equipment.

Conclusions

A concept for the chemical suppression of air pollutants has been demonstrated to be technically feasible during the thermal disposal (pyrolysis-afterburner) of hazardous waste. It has been shown that chemical constituents such as chlorine, sulfur and phosphorus can be retained with the ash during the pyrolysis process. The degree of effectiveness varies with type and concentration of additive utilized. Within the parameters of the test program, sodium hydroxide exhibited a greater effectiveness than calcium hydroxide or either of the salts tested. Calcium hydroxide exhibited sufficient reactivity when compared to sodium hydroxide to warrant its use due to its lower cost, availability and ease of disposal.

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