


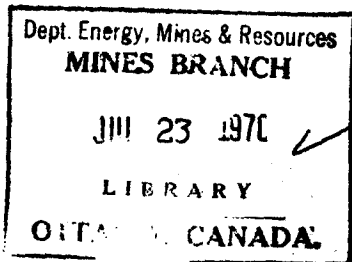
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DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*Mines Branch Program
on Environmental Improvement*

*THE THERMAL DESTRUCTION OF DDT
IN AN OIL CARRIER*



H. WHALEY, G. K. LEE, R. K. JEFFREY AND E. R. MITCHELL

CANADIAN COMBUSTION RESEARCH LABORATORY
FUELS RESEARCH CENTRE

APRIL 1970

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THE THERMAL DESTRUCTION OF DDT
IN AN OIL CARRIER

by

H. Whaley^{*}, G.K. Lee^{*}, R.K. Jeffrey^{**}
and E.R. Mitchell^{***}

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SUMMARY

The report describes combustion tests which established that the safe disposal of DDT in an oil carrier can be achieved by thermal destruction. The tests were conducted in two laboratory pilot-scale installations to determine

- a) the nature of the combustion products produced and the completeness of thermal destruction,
- b) the extent to which any noxious products in the flue gases can be removed by scrubbing and neutralisation procedures, and
- c) the design criteria necessary to construct commercial DDT/oil incinerators.

Complete combustion was readily achieved in both laboratory units, using a "blue-flame" burner with controlled flame recirculation. An important finding was that the chlorine present in the DDT formula was reduced to hydrochloric acid gas which was effectively removed and neutralised by an alkali scrubbing unit.

On the basis of the test data, design criteria were drawn up for commercial DDT/oil incinerators, using combinations of commercially available components.

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Direction des mines

Rapport de recherches R 225

DESTRUCTION THERMIQUE DES MÉLANGES DDT-HUILE

par

H. Whaley*, G.K. Lee*, R.K. Jeffrey** et E.R. Mitchell***

RÉSUMÉ

Le rapport décrit des essais de combustion qui ont montré la possibilité de détruire en toute sécurité les mélanges DDT-huile par incinération. Les essais ont été effectués dans deux appareils pilotes de laboratoire afin de déterminer:

- a) la nature des produits de combustion et le degré de destruction obtenu;
- b) jusqu'à quel point on peut éliminer les produits nocifs dans les gaz de combustion par lavage et neutralisation;
- c) les normes à observer dans la construction d'incinérateurs commerciaux de mélanges DDT-huile.

Dans les deux appareils, on a aisément obtenu une combustion complète à l'aide d'un brûleur à "flamme bleue" avec recirculation sous flamme contrôlée. Il importe de noter que le chlore contenu dans le DDT s'est transformé en acide chlorhydrique gazeux qui a été complètement éliminé et neutralisé par un appareil de lavage alcalin.

Les résultats des essais ont permis d'établir des normes pour la construction d'incinérateurs commerciaux de mélanges DDT-huile, combinant des éléments d'appareils existants.

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INTRODUCTION

On January 1, 1970, the use of the pesticide DDT (p-dichlorodiphenyl trichloroethane) was prohibited in Canada except under control for certain restricted agricultural or extermination purposes. In anticipation of this ban, the Canada Department of Agriculture initiated studies on methods for disposing of present stocks of DDT. One possibility that was considered was incineration or thermal destruction. Because of the overwhelming influence of combustion in such a process, the Department of Agriculture, through Mr. R. Maybury, requested the assistance of the Canadian Combustion Research Laboratory (CCRL) of the Department of Energy, Mines and Resources. The request was accepted and work was undertaken as part of the Mines Branch program on environmental improvement.

The initial feasibility study was based on the thermal decomposition of liquid DDT formulations which may contain up to 30% by weight of DDT in kerosene. Previous small-scale studies* demonstrated that, in an oxidizing atmosphere, DDT decomposes completely at 1000°C, which is well below temperatures found in commercial turbulent diffusion flames.

However, firing DDT through standard industrial burners presents two problems. First, the thermal decomposition of DDT results in certain toxic, residual-chlorine products which must be neutralised before emission to atmosphere. Second, conventional "luminous-flame" burners emit up to 0.25% unburned combustibles, mostly in the form of soot which, having a high adsorptive capacity, provides a means for toxic chlorine products to escape into the environment.

Relatively new fundamental knowledge in the field of combustion offers a solution to the second problem. "Blue-flame" oil burners are now commercially available, which can, through controlled flame recirculation, readily achieve complete, soot-free combustion.

Thus, by employing a "blue-flame" burner, the incineration of DDT appeared feasible, provided a suitable system could be developed to neutralise the toxic products in the flue gas.

* Chemical and Thermal Methods for Disposal of Pesticides. M. V. Kennedy, B. J. Stojanovic, and F. L. Shuman, Jr., *Pesticide Review* (1969) 29, pp. 89-104.

Consequently, CCRL submitted a proposal, on invitation from the Federal Interdepartmental Committee on Pesticides, to demonstrate the feasibility of thermally destroying DDT in kerosene, using a "blue-flame" burner as the primary component of the process. This proposal was accepted by the committee, and CCRL was requested to proceed on a priority basis.

INCINERATOR DEVELOPMENT

Research Model

Incinerator Components

The burner selected for the first incineration experiments was a commercial, air-atomizing, blue-flame burner, modified in the laboratory to give operator control of both combustion air and pressure drop across the flame. It was mounted on a cylindrical, water-cooled flame tunnel, the dimensions of which were selected to meet the requirements of the burner. From the water-cooled chamber, in which 20% of the input combustion heat was removed, the flue gas passed through two water scrubbers in series for removal of hydrochloric acid (HCl) vapour. The primary scrubber used recycled streams of water to cool the walls of the scrubber reservoir in the vicinity of the flame tunnel exit, while fresh make-up water to absorb HCl was supplied through four spray nozzles covering the gas flow path. The flue gas then passed through the secondary scrubber to remove any remaining HCl. Here three spray nozzles, each on the axis of a vertical circular duct, provided a mist of water that passed counter-current to the gas stream into the reservoir below. The final stage of the system was a demister to minimize carry-over of acid droplets in the flue gas. Figure 1 shows where samples were withdrawn for qualitative analysis.

Test Results

The chlorine compounds which might theoretically result from the combustion of the pesticide-oil solution are shown in Table 1. All of these compounds can be relatively dangerous and almost one-half of them are gaseous at room temperature. For this reason, qualitative tests, described in Appendix A, were conducted on samples from both the flue gas and the water-washing streams to determine whether any of the chlorinated compounds listed in Table 1 were formed in the combustion process. From thermochemical considerations, the first two, HCl and $\text{HCl} \cdot x\text{H}_2\text{O}$, should be the most dominant species present; the remaining compounds are shown

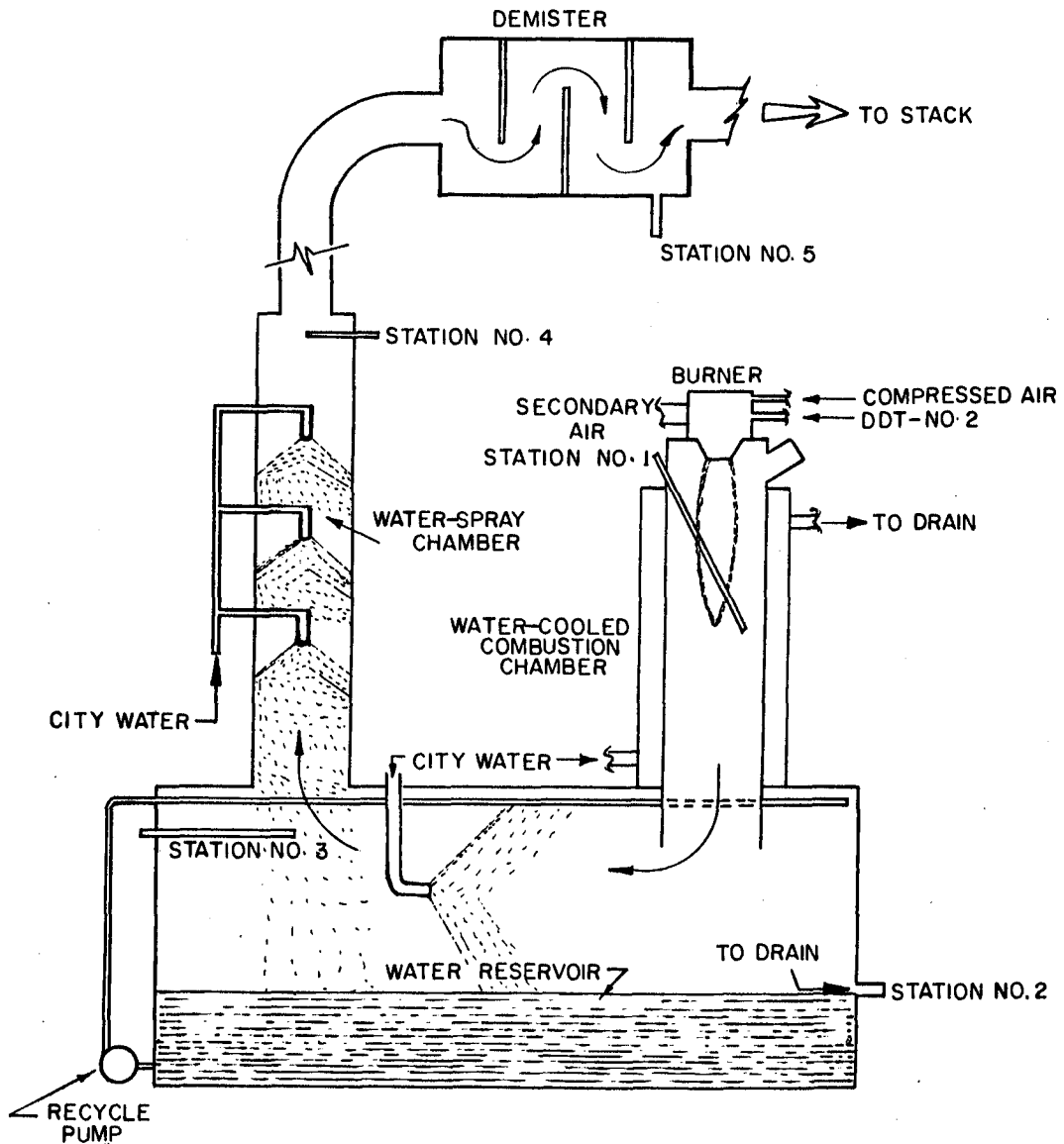


Figure 1. Illustration of research model DDT incinerator.

TABLE 1

Possible Chlorinated Compounds from the Thermal Decomposition of DDT*

Name	Formula	Form at Room Temp.	Boiling Point, °C	Solubility in Cold Water
Hydrogen Chloride	HCl	Gas	-85	82.3 cc in 100 g (0°C)
Hydrochloric Acid	HCl.xH ₂ O	Liquid	Decomposes	
Chlorine	Cl ₂	Gas	-34.06	1.46 cc in 100 g (0°C)
Chlorinated Water	Cl ₂ +H ₂ O	Liquid	Decomposes	-
Hypochlorous Acid	HClO	Liquid	-	Soluble
Chlorous Acid	HClO ₂	Liquid	-	Soluble
Chloric Acid	HClO ₃	Liquid	40, decomposes	Very soluble
Perchloric Acid	HClO ₄	Solid	16 at 18 mm pressure	Soluble
Chlorine Monoxide	Cl ₂ O	Gas	3.8	2 x 10 ⁴ cc in 100 g (0°C)
Chlorine Dioxide	ClO ₂	Gas	9.9	2 x 10 ³ cc in 100 g (4°C)
Chlorine Hexoxide	ClO ₆	Liquid	Decomposes	Soluble
Chlorine Heptoxide	Cl ₂ O ₇	Liquid	82, explosive	Soluble but decomposes
Chlorine Hydrate	Cl ₂ .8H ₂ O	Solid	10, decomposes	Soluble
Chlorates	ClO ₃ ⁻	Solid	-	Soluble

*Compiled from Chemical Engineers' Handbook, Editor J. H. Perry, 4th Edition, McGraw-Hill, 1963, and Handbook of Chemistry, Editor N. A. Lange, 10th Edition, McGraw-Hill, 1961.

in order of their possible existence in the combustion gases. The safe incineration of DDT depended largely on which of these compounds were present in the combustion products, since many would be extremely difficult to remove. Some of the compounds are either extremely toxic or malodorous in trace quantities, and if released untreated would result in a local air pollution problem.

Operating data for the research incinerator are given in Table 2, and a list of the qualitative analyses conducted on both gaseous and aqueous incinerator effluents is given in Table 3. Chlorides (Cl^-) were positively identified in all samples, indicating the presence of HCl, whereas no residual chlorine was detected in any sample after reduction, indicating the absence of chlorine gas (Cl_2), hypochlorites (ClO^-), chlorates (ClO_3^-), perchlorates (ClO_4^-) and oxy-chlorine compounds (see Table 1). The research incinerator established conclusively, and somewhat unexpectedly, that no Cl_2 was present outside of the flame envelope. After consultation with other experts, it was concluded that this is due to the presence, in the reaction zone, of chlorine (Cl^-) ions and hydrogen (H^+) ions which react preferentially to form HCl at the fringes of the flame. The combination of two chlorine ions to form chlorine gas is unlikely to occur, because the energy required for union is greater than that required for the formation of HCl.

Development Model

Incinerator Components and Test Procedure

The research incinerator described above showed that the complete destruction of DDT presented no problems. However, severe overheating of the water in the reservoir proved to be a major difficulty. This was due largely to the high proportion of recycled water required for scrubbing purposes and the low over-all water throughput necessary for accurate effluent analysis. Therefore, a second incinerator, known as a development model, was constructed using a waste-heat boiler. In this system, the same blue-flame burner, water-cooled combustion chamber, vertical scrubber, and demister were used without change from the research apparatus but the primary scrubber assembly was replaced by a 40-hp, locomotive-type boiler. A schematic illustration of the development model incinerator is shown in Figure 2, along with locations of the sampling stations. Photographs of the incinerator are shown in Figure 3.

The development model incinerator also included provisions for chemically neutralising the hydrochloric acid in the combustion gas. Altogether, three alternatives were tried: (a) removal of HCl by water scrubbing and neutralisation of the resulting dilute acid in a limestone-bed reactor; (b) direct neutralisation by using sodium hydroxide solution in combination with water in the scrubber, and (c) chemical neutralisation in

TABLE 2

Typical Operating Data for the Research Model Incinerator

Fuel		Combustion Air		Flame		Stack	
Type	Input (lgph)	Primary (psig)	Secondary (in. W.G.)	Type	Temp., °F (°C)	Pressure (in. W.G.)	Temp., °F (°C)
No. 2 oil	3.5	50	3.25	Blue	2700 (1660)	0.8	180 (82)
30% DDT in oil	3.25	65	4.4	Green	2300 (1340)	0.8	200 (93)

Heat absorbed by water-cooled combustion chamber, using both No.2 oil and 30% DDT in oil, was about 21.5% of the heat input.

TABLE 3

Qualitative Analyses of Effluents from Research Model Incinerator

Sampling Station	Type of Sample	Sampling Method	Absorbent	Ions in Sample	
				Test*	Present
1	Gas	Vacuum Flask	-	Cl ⁻	Yes
	Gas	"	AgNO ₃	Cl ⁻	Yes
	Gas	"	NaOH	Residual Cl	No
2	Liquid	Aliquot		Cl ⁻	Yes
				Residual Cl	No
3	Gas	Absorption	10°C H ₂ O	Cl ⁻	Yes
	"	"	20°C H ₂ O	Cl ⁻	Yes
	"	"	NaOH	Residual Cl	No
4	Gas	Absorption	10°C H ₂ O	Cl ⁻	Yes
	"	"	20°C H ₂ O	Cl ⁻	Yes
	"	"	NaOH	Residual Cl	No
5	Liquid	Aliquot		Cl ⁻	Yes
				Residual Cl	No

* Residual Cl is defined by ASTM as (Cl₂ + ClO⁻ + ClO₃⁻ + ClO₄⁻).

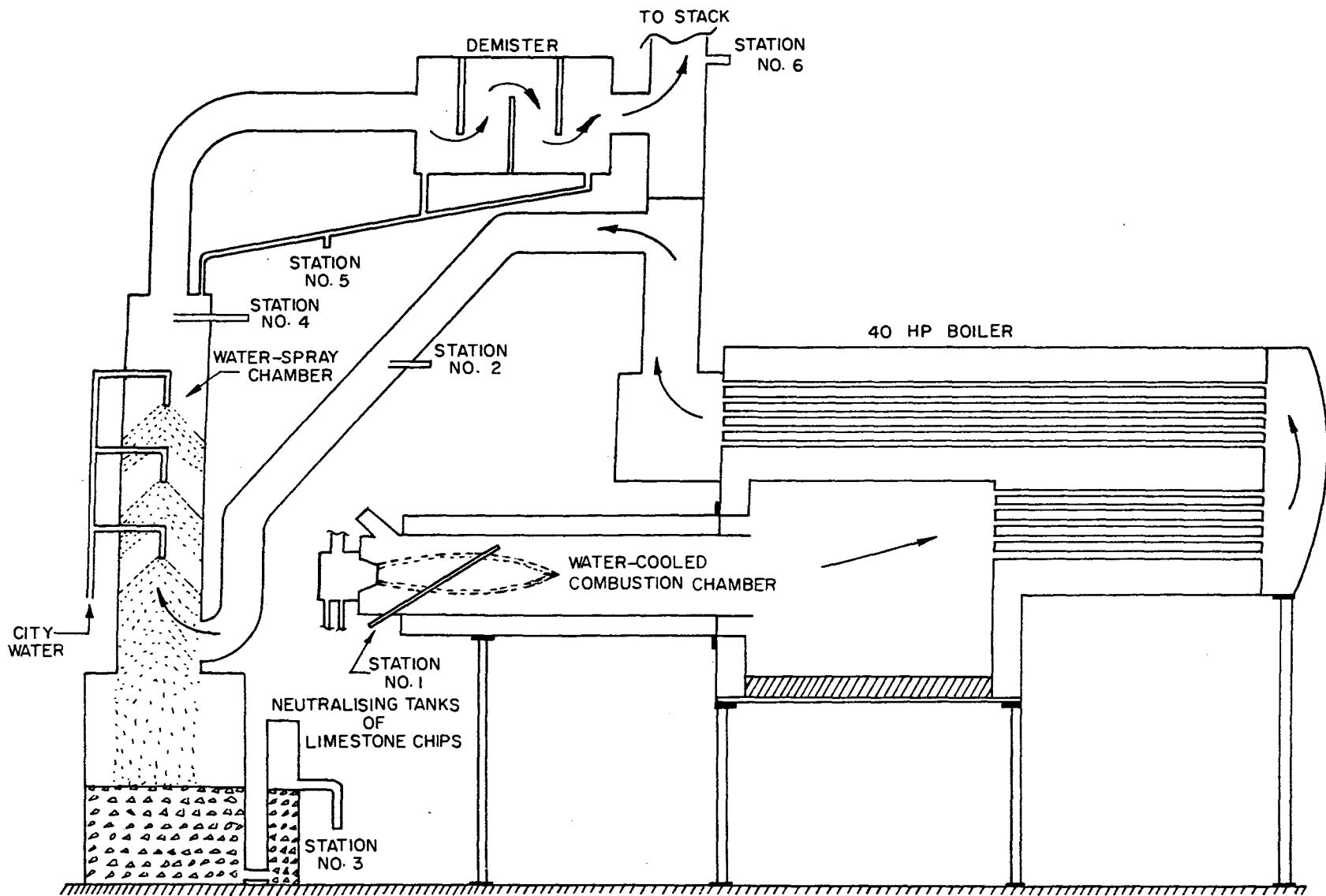
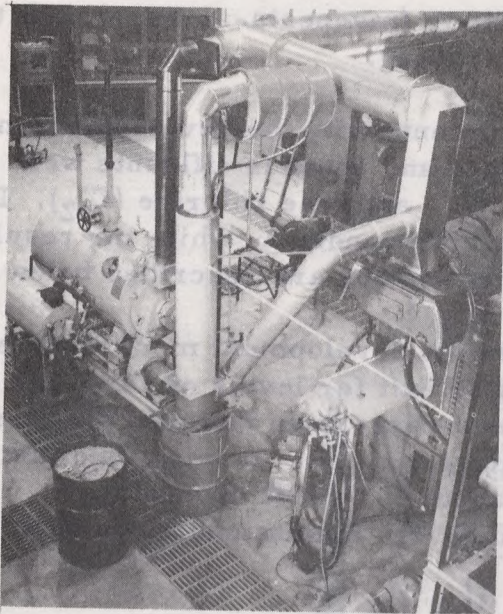
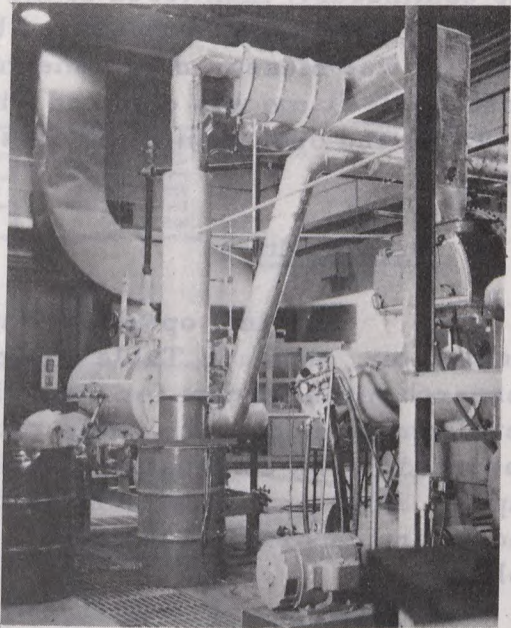


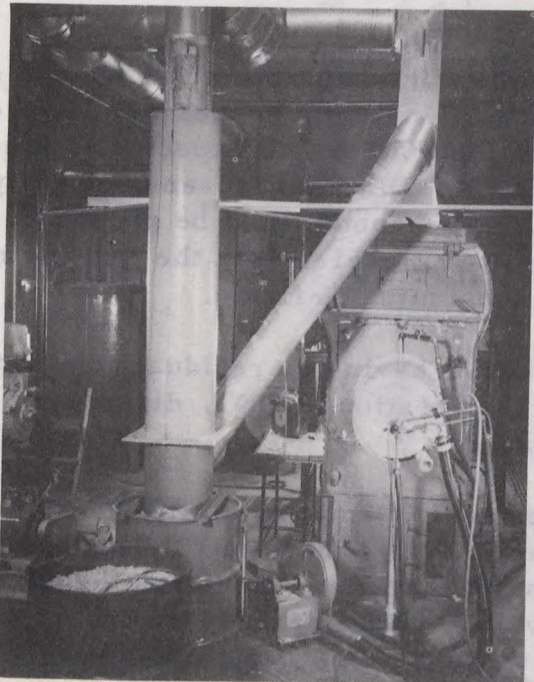
Figure 2. Illustration of development model DDT incinerator.



(a) Top view.



(b) Side view.



(c) Front view.

Figure 3. Views of the development model DDT incinerator showing the burner, combustion chamber, spray system, demister, and neutralising beds of limestone chips.

the flame by injection of a fuel oil additive (magnesia-alumina) with the DDT, thus eliminating the need for water scrubbing.

During combustion experiments with the development model incinerator, samples of both the gaseous and aqueous effluents were quantitatively analyzed for both chlorides (Cl^-) and free chlorine (Cl_2). Details of the analytical procedures are given in Appendix A, while the results from each of the three methods of acid neutralisation are described below.

The flue gas generated in the development model incinerator was continuously monitored at the boiler exit for levels of CO_2 , CO and O_2 ; CO_2 and CO were measured by non-dispersive infrared analyzers, while O_2 was measured by a thermomagnetic cell. It was found that the most stable flame was obtained with about 20 to 40% excess air (3.6 to 6.1% O_2), and operation within this range was maintained throughout the tests.

Test Results

Typical operating data obtained from the development model incinerator, shown in Table 4, were similar to those obtained from the research model except for the firing rate and heat absorption. With the development model, the firing rate was increased to 4.9 Igph and the heat absorbed by the combustion chamber and boiler amounted to 78% of heat input. Additional details of the thermal efficiency of the development model are reported on the ASME short forms, Tables 4 A and 4 B, that follow.

For one series of combustion tests, the water-cooled combustion chamber was removed and the blue-flame burner was fired directly into the oversized firebox of the boiler. As expected, a blue flame was obtained with No. 2 oil, but with 30% DDT in kerosene, only a yellow flame containing soot and gaseous hydrocarbons could be produced. Clearly, the shape and large size of the furnace interfered with the gas-recirculation pattern necessary for producing a non-luminous flame.

Since non-luminous flames having no residual combustible matter are essential for complete incineration of DDT, direct firing into the locomotive boiler was discontinued.

During these tests, periodic flame-instability created some difficulty. The cause of this was eventually traced to DDT which had re-crystallized in the carrier. The solid particles tended to clog the burner nozzle and cause the flame to blow off. This difficulty was eliminated satisfactorily by passing the DDT through a coil heated by hot boiler water, and in this way the crystalline DDT was redissolved.

TABLE 4

Typical Operating Data for the Development Model Incinerator

Fuel		Combustion Air		Flame		Stack	
Type	Input (lgh)	Primary (psig)	Secondary (in.W.G.)	Type	Temp., °F (°C)	Pressure (in. W.G.)	Temp., °F (°C)
No.2 oil	4.5	55	3.5	Blue	2750 (1550)	-0.02	160 (71)
30% DDT in oil	4.9	65	4.5	Green	2350 (1310)	+0.01	200 (93)

TABLE 4A

DDT DEVELOPMENT MODEL INCINERATOR FEBRUARY 10TH, 1970

SUMMARY SHEET ASME TEST FORM FOR ABBREVIATED EFFICIENCY TEST PTC 4.1-a(1964)

Typical Thermal Efficiency of DDT Incinerator (48% of rated capacity of boiler)			
OWNER OF PLANT Can. Comb. Research Lab. (CCRL)		LOCATION Fuels Research Centre	
TEST CONDUCTED BY H. Whaley	OBJECTIVE OF TEST Research	DURATION 6 hr	
BOILER, MAKE & TYPE Locomotive, Hot Water	RATE CAPACITY 40 hp		
STOKER, TYPE & SIZE -	(1.34 x 10 ⁶ Btu/hr)		
PULVERIZER, TYPE & SIZE -	BURNER, TYPE & SIZE Blue Flame		
FUEL USED 30% DDT in Oil	MINE -	COUNTY -	STATE - SIZE AS FIRED -

PRESSURES & TEMPERATURES				FUEL DATA					
1	STEAM PRESSURE IN BOILER DRUM	psia	15	COAL AS FIRED PROX. ANALYSIS		% wt		OIL	
2	STEAM PRESSURE AT S. H. OUTLET	psia		37	MOISTURE		51	FLASH POINT F(PM)	205
3	STEAM PRESSURE AT R. H. INLET	psia		38	VOL MATTER		52	Sp. Gravity (70F)	1.091
4	STEAM PRESSURE AT R. H. OUTLET	psia		39	FIXED CARBON		53	VISCOSITY AT BURNER (70F)	3.7 cs
5	STEAM TEMPERATURE AT XXX boiler OUTLET	F	168	40	ASH		44	TOTAL HYDROGEN % wt	10.08
6	STEAM TEMPERATURE AT R. H. INLET	F		TOTAL			41	Btu per lb	15,543
7	STEAM TEMPERATURE AT R. H. OUTLET	F		41	Btu per lb AS FIRED				
8	WATER TEMP. ENTERING (6600) (BOILER)	F	45	42	ASH SOFT TEMP.* ASTM METHOD		GAS % VOL		
9	STEAM QUALITY % MOISTURE OR P. P. M.			AS FIRED DDT ULTIMATE ANALYSIS			54	CO	
10	AIR TEMP. AROUND BOILER (AMBIENT)	F	70	43	CARBON	74.48	55	CH ₄ METHANE	
11	TEMP. AIR FOR COMBUSTION (This is Reference Temperature) †	F	70	44	HYDROGEN	10.08	56	C ₂ H ₂ ACETYLENE	
12	TEMPERATURE OF FUEL	F	70	45	Chlorine	15.00	57	C ₂ H ₄ ETHYLENE	
13	GAS TEMP. LEAVING (Boiler)	F	200	46	NITROGEN	-	58	C ₂ H ₆ ETHANE	
14	GAS TEMP. ENTERING AH (If conditions to be corrected to guarantee)	F		47	SULPHUR	0.49	59	H ₂ S	
UNIT QUANTITIES				40	ASH		60	CO ₂	
15	ENTHALPY OF SAT. LIQUID (TOTAL HEAT)	Btu/lb		37	MOISTURE		61	H ₂ HYDROGEN	
16	ENTHALPY OF (EXHAUSTED) (EXHAUSTED) water leaving boiler	Btu/lb	135.9	TOTAL		100.00	TOTAL		
17	ENTHALPY OF SAT. FEED TO (BOILER)	Btu/lb	13.06	COAL PULVERIZATION			TOTAL HYDROGEN % wt		
18	ENTHALPY OF REHEATED STEAM R. H. INLET	Btu/lb		48	GRINDABILITY INOEX*		62	DENSITY 68 F ATM. PRESS.	
19	ENTHALPY OF REHEATED STEAM R. H. OUTLET	Btu/lb		49	FINENESS % THRU 50 M*		63	Btu PER CU FT	
20	HEAT ABS/LB OF STEAM (ITEM 16 - ITEM 17)	Btu/lb		50	FINENESS % THRU 200 M*		41	Btu PER LB	
21	HEAT ABS/LB R. H. STEAM (ITEM 19 - ITEM 18)	Btu/lb	122.84	50			ITEM 31 x 100 = 77.59 ITEM 29		
22	DRY REFUSE (ASH PIT + FLY ASH) PER LB AS FIRED FUEL	lb/lb		64	INPUT-OUTPUT EFFICIENCY OF UNIT %				
23	Btu PER LB IN REFUSE (WEIGHTED AVERAGE)	Btu/lb		HEAT LOSS EFFICIENCY			Btu/lb A. F. FUEL	% of A. F. FUEL	
24	CARBON BURNEO PER LB AS FIRED FUEL	lb/lb	0.7448	65	HEAT LOSS DUE TO DRY GAS			2.97	
25	DRY GAS PER LB AS FIRED FUEL BURNED	lb/lb	14.81	66	HEAT LOSS DUE TO MOISTURE IN FUEL			-	
HOURLY QUANTITIES				67	HEAT LOSS DUE TO H ₂ O FROM COMB. OF H ₂			6.19	
26	ACTUAL WATER EXPOSED heated	lb/hr	5234	68	HEAT LOSS DUE TO COMBUST. IN REFUSE			-	
27	REHEAT STEAM FLOW	lb/hr		69	HEAT LOSS DUE TO RADIATION			15.00	
28	RATE OF FUEL FIRING (AS FIRED wt)	lb/hr	53.31	70	UNMEASURED LOSSES (assumed)			0.5	
29	TOTAL HEAT INPUT (Item 28 x Item 41) / 1000	kB/hr	828.60	71	TOTAL			24.66	
30	HEAT OUTPUT IN BLOW-DOWN WATER	kB/hr		72	EFFICIENCY = (100 - Item 71) %			75.34	
31	TOTAL HEAT OUTPUT (Item 26 x Item 20) + (Item 27 x Item 21) + Item 30 / 1000	kB/hr	642.94						
Dry, Acid-free Flue Gas Anal. (boiler) outlet									
32	CO ₂	% VOL	12.7						
33	O ₂	% VOL	5.0						
34	CO	% VOL	-						
35	N ₂ (BY DIFFERENCE)	% VOL	82.3						
36	EXCESS AIR	%	29.29						

* Not Required for Efficiency Testing

† For Point of Measurement See Par. 7.2.8.1-PTC 4.1-1964

TABLE 4B

DDT DEVELOPMENT MODEL INCINERATOR FEBRUARY 10TH 1970

PTC 4.1-b (1964)

ASME TEST FORM

CALCULATION SHEET

FOR ABBREVIATED EFFICIENCY TEST

Revised September, 1965

OWNER OF PLANT	TEST NO.	BOILER NO.	DATE
30	HEAT OUTPUT IN BOILER BLOW-DOWN WATER = LB OF WATER BLOW-DOWN PER HR x $\frac{\text{ITEM 15} - \text{ITEM 17}}{1000}$ = kB/hr		
24	<p>If impractical to weigh refuse, this item can be estimated as follows</p> <p>DRY REFUSE PER LB OF AS FIRED FUEL = $\frac{\% \text{ ASH IN AS FIRED COAL}}{100 - \% \text{ COMB. IN REFUSE SAMPLE}}$</p> <p>CARBON BURNED PER LB AS FIRED FUEL = $\frac{\text{ITEM 43}}{100} - \left[\frac{\text{ITEM 22}}{14,500} \times \frac{\text{ITEM 23}}{\dots} \right] = 0.7448$</p>	<p>NOTE: IF FLUE DUST & ASH PIT REFUSE DIFFER MATERIALLY IN COMBUSTIBLE CONTENT, THEY SHOULD BE ESTIMATED SEPARATELY. SEE SECTION 7, COMPUTATIONS.</p>	
25	<p>DRY GAS PER LB AS FIRED FUEL BURNED = $\frac{11\text{CO}_2 + 8\text{O}_2 + 7(\text{N}_2 + \text{CO})}{3(\text{CO}_2 + \text{CO})} \times (\text{LB CARBON BURNED PER LB AS FIRED FUEL} + \frac{3}{8} \text{S})$</p> <p>= $11 \times \frac{\text{ITEM 32}}{12.7} + 8 \times \frac{\text{ITEM 33}}{5.0} + 7 \left(\frac{\text{ITEM 35}}{82.3} + \frac{\text{ITEM 34}}{\dots} \right) \times \left[\frac{\text{ITEM 24}}{0.7448} + \frac{\text{ITEM 47}}{267} \right] = 14.81$</p>		
36	<p>EXCESS AIR † = $100 \times \frac{\text{O}_2 - \frac{\text{CO}}{2}}{.2682\text{N}_2 - (\text{O}_2 - \frac{\text{CO}}{2})} = 100 \times \frac{\text{ITEM 33} - \frac{\text{ITEM 34}}{2}}{.2682(\text{ITEM 35}) - (\text{ITEM 33} - \frac{\text{ITEM 34}}{2})} = 29.29$</p>		
HEAT LOSS EFFICIENCY			
65	<p>HEAT LOSS DUE TO DRY GAS = $\frac{\text{LB DRY GAS PER LB AS FIRED FUEL}}{\text{Unit}} \times C_p \times (t_{\text{vg}} - t_{\text{air}}) = \frac{\text{ITEM 25}}{14.81} \times 0.24 \times \frac{(\text{ITEM 13}) - (\text{ITEM 11})}{200 - 70} = \dots$</p>	Btu/lb AS FIRED FUEL	LOSS %
66	<p>HEAT LOSS DUE TO MOISTURE IN FUEL = $\frac{\text{LB H}_2\text{O PER LB AS FIRED FUEL}}{100} \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T GAS LVG}) - (\text{ENTHALPY OF LIQUID AT T AIR})] = \frac{\text{ITEM 37}}{100} \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T ITEM 13}) - (\text{ENTHALPY OF LIQUID AT T ITEM 11})] = \dots$</p>		
67	<p>HEAT LOSS DUE TO H₂O FROM COMB. OF H₂ = $9\text{H}_2 \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T GAS LVG}) - (\text{ENTHALPY OF LIQUID AT T AIR})]$</p> <p>(i.e. after formation of HCl) = $9 \times \frac{\text{ITEM 44}}{100} \times [(\text{ENTHALPY OF VAPOR AT 1 PSIA \& T ITEM 13}) - (\text{ENTHALPY OF LIQUID AT T ITEM 11})] = 9 \times 0.0965 (1145.9 - 38.04) = \dots$</p>		
68	<p>HEAT LOSS DUE TO COMBUSTIBLE IN REFUSE = $\text{ITEM 22} \times \text{ITEM 23} = \dots$</p>		
69	<p>HEAT LOSS DUE TO RADIATION* = $\frac{\text{TOTAL BTU RADIATION LOSS PER HR}}{\text{LB AS FIRED FUEL}} = \frac{\text{ITEM 28}}{\dots} \text{ (ABMA Chart)}$</p>		
70	<p>UNMEASURED LOSSES ** (Assumed)</p>		
71	TOTAL		
72	EFFICIENCY = (100 - ITEM 71)		

† For rigorous determination of excess air see Appendix 9.2 - PTC 4.1-1964

* If losses are not measured, use ABMA Standard Radiation Loss Chart, Fig. 8, PTC 4.1-1964

** Unmeasured losses listed in PTC 4.1 but not tabulated above may be provided for by assigning a mutually agreed upon value for Item 70.

Neutralisation of Inorganic Chlorine Effluents

In tests where the combustion gas was scrubbed by water sprays, a limestone-bed reactor was used to neutralise the wash water. As is shown in Table 5, the limestone-bed reactor, which had a residence time of 65 minutes, neutralised only about 20% of the HCl in the wash water.

A scrubbing system using sodium hydroxide (NaOH) sprays in combination with a water spray proved to be a more effective means of neutralisation of the HCl gas than the limestone-bed reactor. This system, using 1.8 N NaOH at 8 Igph, and an additional water-flow rate of 4 Igph, instantaneously removed and neutralised all of the HCl vapour entering the scrubber, and the liquid to drain contained no free acid. Although the scrubbing efficiency was the same as with the aqueous sprays (~95%), HCl neutralisation with the NaOH spray reduced corrosion in the scrubbing and flue systems, thereby increasing operating efficiencies and life of the apparatus. As an example, during the tests with the water-spray system, the HCl removal efficiency was observed to drop to about 78% due to deterioration of the water-spray pattern caused by excessive corrosion of the leading spray nozzle. From Table 5 it is evident that about one-third of the HCl generated in the flame was condensed in the boiler; therefore, the normality of the NaOH solution can be adjusted for stoichiometric removal of the remaining HCl.

The fuel-oil additive tests, which were of a short-term nature, utilized a magnesia-alumina formulation developed by the CCRL for the prevention of corrosion in boilers. It was envisaged that the additive would neutralise the HCl vapour within the combustion zone, thus eliminating the necessity for the ancillary spraying equipment. Due to limitations of the additive metering pump, the rate of additive injection into the burner was only about 70% of the theoretical requirement and all of the injected additive reacted with HCl. As is shown in Table 5, about 30% of the HCl generated was exhausted to the stack and all the fireside deposit in the boiler contained some free acid. There is little doubt that with the correct additive injection rate all of the HCl can be neutralised. However, even with 70% of the correct additive injection rate, severe fouling of the burner quarl and electrodes occurred, as shown in Figure 4. In addition, heavy deposits of magnesium chloride encrusted the fireside surfaces of the boiler. For these reasons the additive neutralisation tests were discontinued.

As can be seen from Table 5, tests on the liquid effluents from the neutralising systems, and on the Mg/Al boiler deposits, showed no excessive levels of unburnt pesticide during normal operating conditions. However, during periods of flame instability, caused by operating changes or other factors such as recrystallized DDT in the fuel, DDT levels in the effluents were observed to increase temporarily by up to one order of magnitude.

TABLE 5

Quantitative Data on Chlorinated Effluents from the Development Model Incinerator

Neutralization Test	Sample		Ion present, ppm			Cl ⁻ as acid	Cl ⁻ Removal %		Remarks
	Station	Type	Cl ⁻	Residual Cl	Cation	ppm	Boiler	Scrubber	
(a) Limestone Reactor and Water Spray System	1	Gas	8260*	0	-	8260*	35.3	94.5	(i) Boiler Cl ⁻ removal efficiency based on theoretical Cl ⁻ generated in the flame. (ii) Scrubber removal efficiency based on actual Cl ⁻ entering scrubber. (iii) CaCl ₂ solution having a pH < 7 is mildly corrosive. (iv) DDT in CaCl ₂ solution < 0.1 ppm under normal operating conditions.
	2	Gas ^{1/}	5345**	0		5345**			
	6	Gas ^{2/}	294**	0					
	3	Liquid ^{1/}		0					
(b) Sodium Hydroxide Spray System (1.8 N NaOH solution)	1	Gas	8260*			8260*	33.7	96.5	(i) Boiler Cl ⁻ removal efficiency based on theoretical Cl ⁻ generated in the flame. (ii) Scrubber removal efficiency based on actual Cl ⁻ entering scrubber. (iii) No acid in NaCl effluent from scrubber. (iv) NaCl solution having a pH of 7 is chemically neutral and weakly corrosive. (v) DDT in NaCl solution < 0.1 ppm under normal operating conditions.
	2	Gas ^{3/}	5474**			5474**			
	6	Gas ^{4/}	190**						
	3	Liquid ^{5/}	Excess OH radicals present, indicating no free acid						
(c) Mg/Al fuel-oil additive injection with the fuel.	1	Gas	8260*			8260*	68.7	-	(i) Additive Cl ⁻ removal efficiency based on theoretical HCl in flue gases. No scrubber. (ii) All of the additive injected was effective in neutralizing HCl. (iii) DDT in MgCl ₂ deposits < 20 ppm under normal operating conditions.
	6	Gas ^{4/}	2583**			2583**			

* Theoretical level at 5% O₂ from Appendix 2.

** Corrected for deviations in flue gas O₂ level and DDT content.

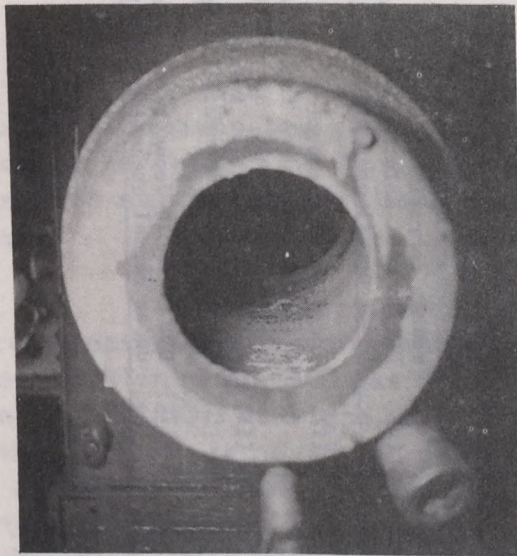
^{1/} Average of 6 samples.

^{2/} Average of 3 samples.

^{3/} Average of 4 samples.

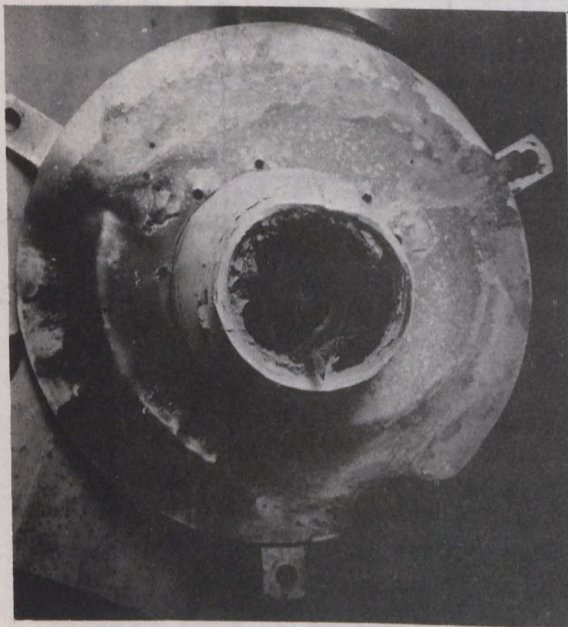
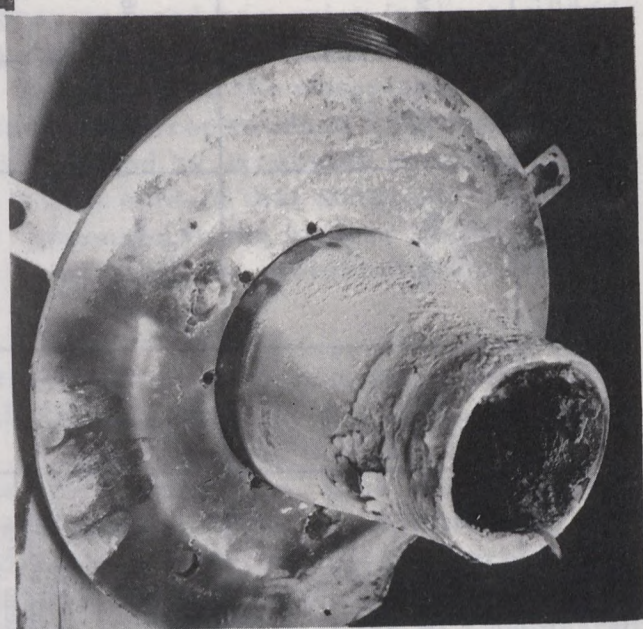
^{4/} Average of 2 samples.

^{5/} Average of 7 samples.



(a) Water-cooled combustion chamber.

(b) Burner mouth and exterior surface of quarl.



(c) Front view of burner, showing build-up around ignition electrodes.

Figure 4. Fouling of the burner and combustion chamber which restricts the use of a fuel-oil additive to neutralise hydrogen chloride from the thermal destruction of DDT.

To summarize, intimate scrubbing of the flue gas with NaOH sprays in combination with a water wash provided instantaneous neutralisation of virtually all the HCl present. Removal of HCl from the flue gas by water washing, followed by neutralisation of the wash water in a limestone-bed reactor, was only partially effective because of low reactivity between the wash water and the limestone chips.

The fuel-oil additive can neutralise 100% of the HCl in the flue gas but severe fouling of burner components and boiler fireside surfaces by the additive reaction product overrides any benefits.

DESIGN CRITERIA FOR A PROTOTYPE INCINERATOR

General design specifications for a prototype incinerator to burn DDT in an oil carrier, together with the ancillary spraying and demisting systems, are detailed below. If such a system is built it seems important that CCRL personnel supervise its initial operation and determine the removal efficiencies of heat and acid.

Burner Unit

The main consideration in the thermal destruction of DDT is that the combustion process emit negligible amounts of unburnt hydrocarbon and soot. It has been established that complete thermal destruction of DDT can be achieved using a blue-flame combustion system which converts all of the organo-chlorine in DDT to HCl. A suitable unit for this purpose is the compressed-air-atomizing "Selectos" blue-flame burner, Type 60, Model IBF, modified with a special manifold for control of pressurized combustion air. The specifications of the burner are as follows:

Fuel capacity (M5 nozzle)	0.8 to 8 Igph No. 2 oil 0.8 to 5 Igph 30% DDT in oil
Atomizing air pressure	25-75 psig
Atomizing air volume	20 cfm at maximum pressure
Combustion air pressure	7 in. W.G.
Combustion air volume	400 cfm at 30°F
Flame temperature	1660°C No. 2 oil
(measured with a suction pyrometer)	1340°C 30% DDT in oil

The combustion-air fan should be equipped with an inlet damper to permit control of secondary air.

DDT Supply to Burner

To ensure an adequate supply of DDT/oil to the burner, it is necessary to have at least a ten-foot head for gravity feed. An alternative is a low-pressure oil pump having a supply pressure of about 5 psi and a capacity of at least 8 Igph.

Winter storage outdoors or in unheated premises may result in the precipitation of DDT crystals from solutions of DDT in oil. These crystals do not readily redissolve at room temperature, and can cause considerable operating difficulty, as described on page 10. It is strongly recommended that any solution of DDT in oil which may have been subjected to sub-zero ($^{\circ}\text{F}$) temperatures be reheated to at least 150°F before use. This may be easily achieved by use of a suitable heat exchanger between the storage tank and the burner, capable of utilizing the hot water from the boiler to raise up to 8 Igph of DDT/oil to the specified temperature.

Heat Exchanger

A standard, package fire-tube boiler can be used to remove most of the heat liberated during the combustion of the DDT/oil. Since the maximum firing rate of DDT recommended represents a heat input of about one million Btu/hr, a Scotch marine dry-back package boiler having a full-load rating of at least 30 boiler hp is suggested. Since the degree of flame recirculation is critical in stabilizing the non-luminous DDT/oil flame, and since recirculation is affected by furnace geometry, the flame tunnel should be 14 in. to 16 in. ID and at least 8 ft long. The flue-gas temperature at the boiler exit should be 250°F or above, to avoid excessive acid condensation in the boiler. Boilers suitable for this service appear to be the 40-hp two-pass Napanee (Series 500), the 30-hp four-pass Cleaver-Brooks (Model CB), or their equivalents.

If there is no convenient way of utilizing the steam generated in the boiler, or if it is advantageous to eliminate need for the ancillaries required for steam generation, the boiler may be used as a heat exchanger by flooding with water which is discharged to drain. At 1,000,000 Btu/hr heat input and 80% boiler efficiency, assuming a 100°F temperature rise in the water, this represents a water requirement of 800 Igph. If there is an economic advantage in using an existing fire-box boiler, then a water-cooled combustion chamber could be incorporated as illustrated in Figure 2.

Flue-gas Scrubbing and HCl Neutralisation Systems

The combustion system just described will produce about 8,000 ppm of HCl from 1.5 million cu ft/hr of flue gas at 250°F . Since up to one-third of this acid may be condensed in the boiler, the gas-scrubbing system must be capable of removing the remainder. This can be accomplished by scrubbing with 12 Igph of 1 N NaOH, followed by a water wash of 5 Igph.

To summarize, intimate scrubbing of the flue gas with NaOH sprays in combination with a water wash provided instantaneous neutralisation of virtually all the HCl present. Removal of HCl from the flue gas by water washing, followed by neutralisation of the wash water in a limestone-bed reactor, was only partially effective because of low reactivity between the wash water and the limestone chips.

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A vertical spray arrangement similar to the one in the development model may be used (Figure 2). The flow rate and normality of the NaOH scrubbing solution can be adjusted to ensure that the liquid discharged to drain has a pH between 6 and 7. However, a total spray rate of at least 15 Igph is advisable to ensure adequate washing of the flue gas. Suitable spray nozzles for the scrubber are the fogging, wide-spray whirljet type, supplied by Spraying Systems Company. It is suggested that the nozzles be fabricated from P. V. C. because of the relatively short operating life of stainless steel nozzles in the corrosive flue-gas stream. However, if P. V. C. nozzles are used care must be taken to ensure that the flue-gas temperature does not exceed 300°F at the scrubber inlet. These are available at flow rates from 2.5 Igph upward, at a pressure of 10 psi.

Alternatively, the combustion gas may be scrubbed with water sprays and the acidic wash water may be neutralised in a bed of limestone chips. However, as explained earlier, neutralisation rates in the limestone reactor are low, hence this system may be impractical.

Alternative Heat Extraction and Scrubbing Unit

The package boiler and scrubber specified in the preceding sections are similar in principle to the development model incinerator (Figure 2). However, earlier experience with the research model incinerator (Figure 1) does not eliminate a combined heat extraction and scrubbing unit from consideration as an alternative system. Such a unit is the Buffalo Forge hydraulic cooling tower which is commercially available for fume removal in certain chemical process and furnace operations. The unit employs tangentially-injected water sprays for fume and soluble-gas removal as well as for cooling purposes. Provision can be made for recycling part of the scrubbing water, provided the cooling requirements are met by the net water throughput. At least 800 Igph of water are required for removal of the input heat of about one million Btu/hr (8 Igph 30% DDT/oil); therefore this would be the minimum net water throughput specified for the system. Since the water throughput, rather than physical size, is of major significance in design considerations, any of the three Buffalo Forge scrubbing towers in the range 3 to 4 ft diameter can be recommended.

Neutralisation of the HCl with NaOH solution can be achieved in various spray combinations in this system, e. g. by simply using a more concentrated solution in the flushing waters at the base of the scrubbing tower. Whatever spray combination is used for neutralisation purposes, care must be taken that sufficient NaOH is injected into the system for complete neutralisation of the HCl in the combustion gases as previously outlined. Limestone-bed neutralisation is not considered as an ancillary to this unit, due to the throughput requirement of at least 800 Igph of water for cooling purposes, necessitating an excessively large bed before sufficient liquid residence time would be obtained for adequate dilute-phase acid neutralisation.

Flue-gas Demister

Entrained aerosols can be removed from the flue gas at the scrubber exit by a highly-efficient, acid-resistant demister having polypropylene screens. These units are commercially available with a guaranteed removal efficiency of 99.5%. However, to prevent damage to the plastic screens, the firing rate must be controlled to prevent flue-gas temperatures in excess of 300°F at the demister inlet.

Flue-gas System and Stack

For best results the acid-free flue gas should be exhausted into the breeching or stack of an operating heating plant in such a way that the incinerator will operate under a slightly negative pressure. This is desirable for two reasons: a negative pressure will eliminate leakage of toxic gas from the combustion system into the boiler room, and, by mixing the flue gas from the DDT incinerator with the flue gas from a heating plant, the high humidity in the scrubbed gas will be reduced and the plume will be given sufficient buoyancy for good dispersion.

Safety Controls

In addition to the normal controls required for operation of the burner and the boiler, the DDT incineration system should be equipped with the following protective devices:-

- (a) A conventional flame safeguard to shut off the fuel supply in case of flame failure for any reason.
- (b) Pressure switches to shut off the fuel supply in case of failure of either the atomizing air or the combustion air.
- (c) A protectorelay at the inlet to the demister, preferably arranged to energize an alarm at 275°F, and to shut off the fuel supply at 300°F. This will protect the demister from overfiring, or loss of the scrubbing liquid supply.
- (d) A pH monitor on the wash-water drain, to energize an alarm in case of unacceptable deviations from the desired pH level.

Operation of Prototype Incinerators

Start-up and shut-down operation with No. 2 oil is advisable, due to the difficulties of flame stabilization when firing DDT/oil into a cold system. It is also desirable to burn No. 2 oil for a few hours after washing

boiler fireside surfaces as described below. Regular boiler plant staff can be trained to operate the prototype incinerators and ancillary equipment if these are equipped with automatic controls and the safety devices described above.

Maintenance Provisions

It is essential that critical components of the DDT incinerator, such as the burner nozzle, the alkali and water-spray nozzles and the demister, be accessible for inspection, removal and, if necessary, replacement. All mild-steel surfaces, including the flue-gas duct and boiler tubes, are subject to acid corrosion and must have access doors for copious water-washing procedures. It is also recommended that complete water-washing of the system be conducted weekly, and certainly at the beginning of any lengthy shut-down period.

Capital Equipment Cost

It is estimated that both of the prototype incinerators described above would, at the present time, cost approximately \$8,000. This price includes the burner, safety devices, atomizing air compressor, combustion air fan, a chemical feed pump, a pH monitor, the package boiler, and the flue-gas scrubbing and demisting systems or the alternative hydraulic scrubbing system.

CONCLUSIONS

DDT in an oil carrier can be completely destroyed in an incinerator utilizing a commercially available blue-flame burner. It has been shown that the organo-chlorine in the DDT/oil mixture breaks down into chlorine ions in the flame and is entirely converted to HCl at the flame fringes; no residual chlorinated hydrocarbons or Cl₂ is produced. The formation of HCl is desirable since the acid vapour is easily removed from the flue gas by conventional scrubbing procedures. It is, however, important to have an effective scrubbing and demisting system, since emissions of HCl vapour to the atmosphere can be both toxic and corrosive. The most effective means of removing HCl vapour from the flue gas has proved to be a combined sodium hydroxide and water-spray system.

Effective removal of HCl from flue gas was obtained by water scrubbing only, but neutralisation of the acidic wash water by a limestone bed reactor was only partially effective.

A magnesia-alumina additive developed for the control of low-temperature corrosion in boilers proved 100% effective in chemically combining with HCl, but because of excessive burner and boiler fouling it was not regarded as a feasible neutralisation method.

On the basis of experiments first conducted in a research model, and subsequently in a development model incinerator, the operating and design criteria given above for a prototype incinerator are considered to be realistic for the safe destruction of DDT in an oil carrier.

ACKNOWLEDGEMENTS

Thanks are due to R. Maybury and D. L. Campbell of the Analytical Services Section of the Department of Agriculture for the analyses of effluent samples and boiler deposits for unburnt DDT content. The technical assistance of F. D. Friedrich of the C. C. R. L. staff, and of the Solid Fuels and Gas Analysis sections of the Fuels Research Centre, Mines Branch, is gratefully acknowledged. The combustion-rig tests were carried out under the supervision of D. G. Savignac of the C. C. R. L. staff.

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APPENDIX A

SAMPLING AND ANALYSIS OF COMBUSTION PRODUCTS

Gas-sampling Probes

Two types of probes were used to sample the gas stream from the DDT incinerator. In zones where temperatures were below 480°C, a 3/8-in.-O. D. by 12-in.-long stainless steel tube was used. In the combustion chamber, where flame temperatures exceeded 1250°C, a 3/8-in.-O. D. by 24-in.-long, inert silica-glass tube was used to prevent any reaction between the probe material and chlorinated residues in the flue gas.

Gas-sampling Methods

Two sampling methods, the vacuum flask and the gas-absorption train, were used for qualitative and quantitative measurements of the combustion products.

In general, the following requirements were met for both sampling methods:-

- (i) The samples were representative of the conditions existing at the point of extraction.
- (ii) The samples were of sufficient volume and were taken frequently enough that accuracy of analysis was limited only by the analytical methods employed.
- (iii) The time interval between sample collection and analysis was kept to a minimum, and all samples were protected from light and heat.

Vacuum-flask Method

Essentially two vacuum-flask sampling methods were used. In the first an evacuated flask, shown in Figure 5, was used to sample flue gas for determination of relatively stable components such as CO₂, O₂, CH₄, CO, H₂, and N₂. This method is not suitable for sampling reactive gases such as hydrogen sulphide, hydrogen chloride, oxides of nitrogen, or sulphur dioxide, because such gases are known to react with dust particles, moisture, and to some extent, even with the glass flask. To overcome the possibility of interactions, a second method was employed, in which the evacuated flasks were charged with a chemical absorbent to selectively remove specific gases. Determination was then carried out by analyzing the absorbent: e. g., a flask

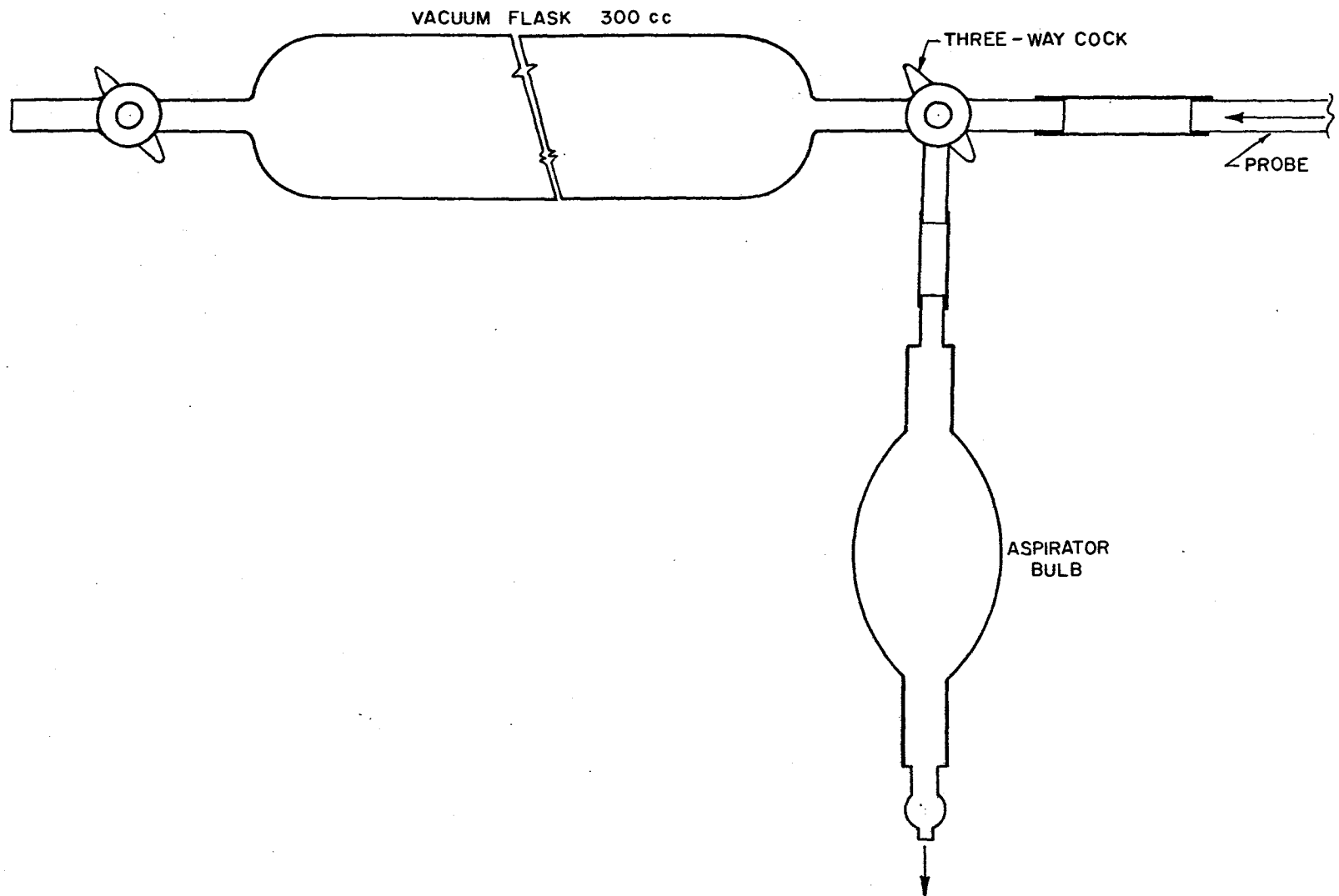


Figure 5. Vacuum flask and aspirator bulb for gas sampling.

charged with 0.025 N AgNO₃ would give a positive indication of the presence of Cl⁻ and/or OCl⁻ in gases or liquids.

The vacuum flasks were prepared in an uncontaminated atmosphere and evacuated to 1 mm Hg or less. The volume of sample at barometric pressure was calculated as follows:-

$$V_s = V_f \times \frac{P_1 - P_2}{P_1}$$

where V_s = volume of gas sample at barometric pressure,

V_f = volume of flask,

P_1 = barometric pressure, and

P_2 = pressure in evacuated flask.

In collecting a sample of gas by the vacuum-flask method, the sample probe was first purged with the sample gas by means of a bulb aspirator connected to one port of a 3-way cock as shown in Figure 5. The sample gas was then drawn into the flask by turning the 3-way cock to connect the probe and the flask. The stopcock was closed when the pressure in the flask and that in the sample probe were equal.

Absorption Method

1) Absorbers

The gas-absorption train consisted of two U-shaped absorbers each having a fritted-disc bubbler. The two absorbers, equipped with spray traps, were connected in series by means of standard taper joints and tygon tubing as shown in Figure 6. All taper joints were lubricated with silicone grease.

Any combination of two or more absorbers could be used to collect specific gases by use of the appropriate absorbents and glassware. A typical flow system for the selective absorption of hydrogen chloride gas and residual chlorine gas is shown schematically in Figure 7. The first bubbler, which contained 100 ml of distilled de-ionized H₂O at 20°C, absorbed Cl⁻ radicals, and the second, which contained 100 ml of 0.2 N NaOH, absorbed residual Cl (Cl₂, ClO⁻, ClO₃⁻ and ClO₄⁻).

2) Metering and Pumping System

The pumping system was composed of a pump and a vacuum manifold equipped with a by-pass valve to control the rate of gas flow. The pump provided a steady flow of 2 cfh of gas through the absorption train while maintaining a constant manifold vacuum of about 3 in. Hg. The sample gas volume was measured with an integrating wet-test meter.

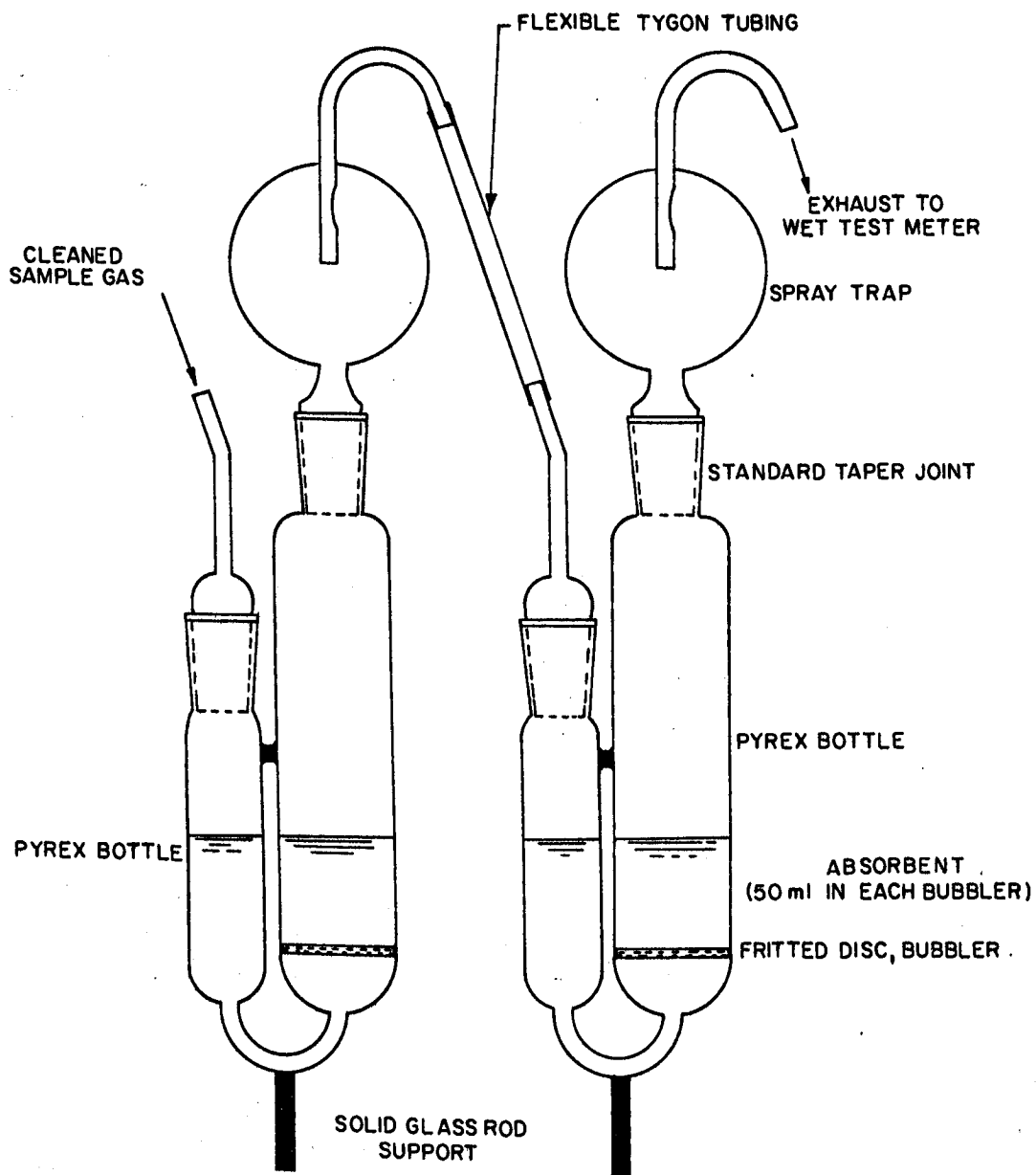


Figure 6. Details of gas absorption bubblers.

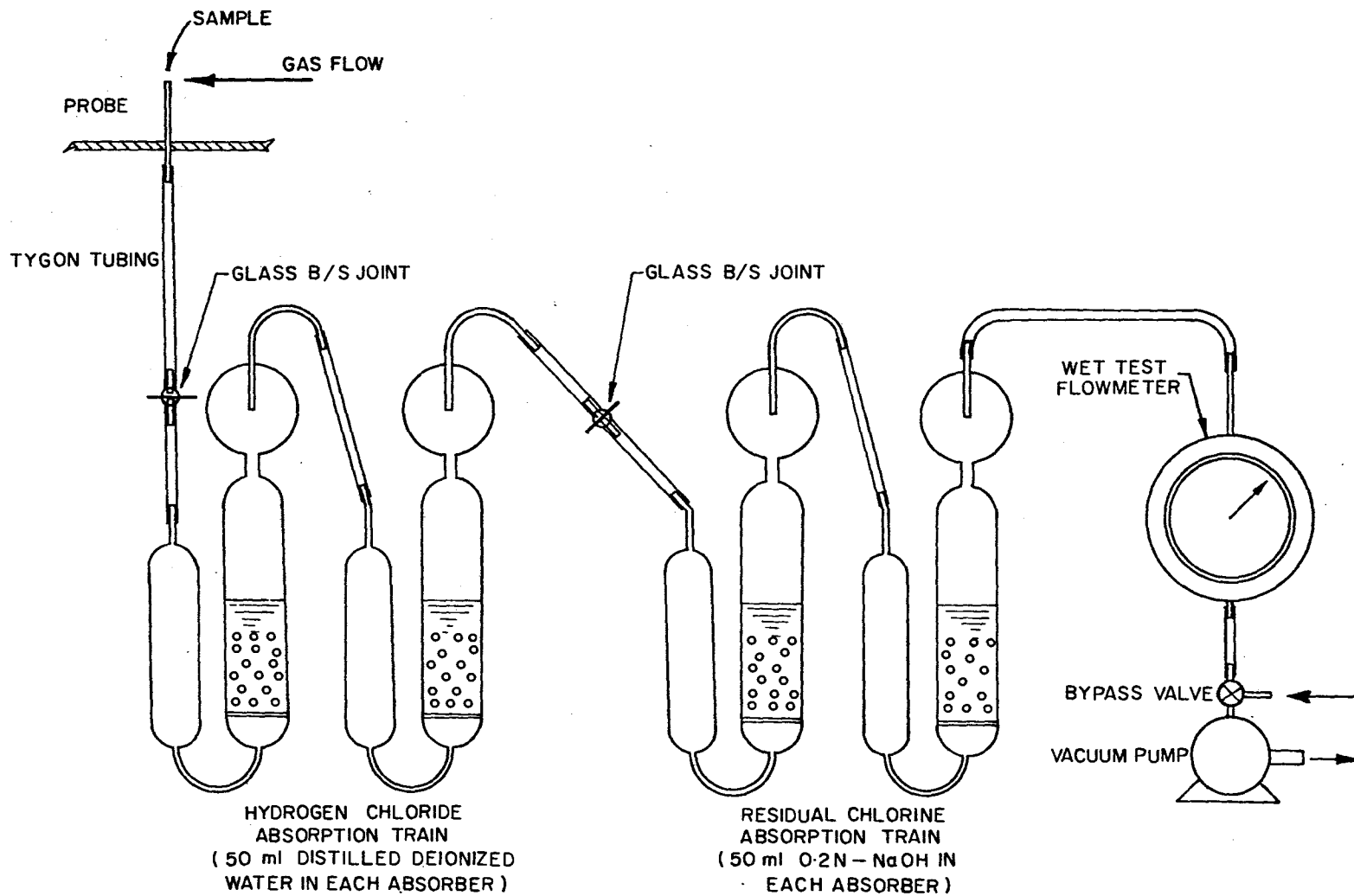


Figure 7. HCl and Cl₂ absorption system.

3) Additional Equipment:

Stop watch, recording tables;
Two wash bottles;
Clips for ball and socket joints;
Rubber and tygon tubing;
Silicone grease.

4) Operation of Absorption Apparatus

After the sampling train had been assembled as illustrated in Figure 7, the by-pass valve was fully opened, the vacuum pump was turned ON, and the by-pass valve was then adjusted to give a flow rate of 2 cfh. The following data were recorded:

V_i = initial meter volume (cu ft);
 T_m = temperature of meter;
 P_b = barometric pressure;
 D_p = pressure drop across flowmeter.

It was found that a sample of 1 cu ft taken over a 30-min sampling period was sufficient to ensure a pollutant concentration consistent with the detection range of the analytical procedure.

After the desired volume of gas had passed through the system, the vacuum pump was turned OFF and the sampling train was disconnected from the probe. The final volume of the meter (V_f) was then recorded, the probe was removed from the sampling station, and the vacuum pump was turned ON for 1 minute to purge the gas from the sampling lines.

Correction of gas volume to 20°C:

$$V_{20} = (V_f - V_i) \left(\frac{293}{273} \right) \left(\frac{P_b - D_p}{P_b} \right) \text{ cu ft.}$$

Qualitative Analyses for Chlorinated Compounds

This section outlines the procedures used for sampling and qualitative analysis of the flue-gas samples from the research model DDT incinerator.

Sampling Methods

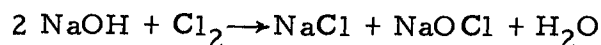
Gas samples were taken by the following four methods:-

- A. Absorption system for HCl and residual Cl,
- B. Evacuated vacuum flask for analyses of CO₂, CO, O₂, CH₂, N₂ and H₂,
- C. Evacuated vacuum flask charged with 50 ml of 0.025 N AgNO₃ for detection of chlorides,
- D. Evacuated vacuum flask charged with 50 ml of ice-cold, distilled, de-ionized H₂O for detection of residual Cl.

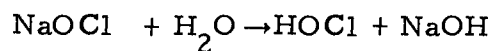
Chlorine Gas (Cl₂)

1) Test 1

The presence of chlorine gas (Cl₂) leads to the following reaction in the residual chlorine gas bubbler used in sampling method A:



The resulting solution tends to bleach a filter paper previously soaked in the organic dye azobenzene and dried. Boiling the solution causes the reaction



and the presence of OCl⁻ can be determined by the procedure described in Test 2.

2) Test 2

Hot turpentine (C₁₀H₁₆) on a filter paper burns in chlorine gas (collected by sampling method B), yielding black carbon fumes plus HCl.

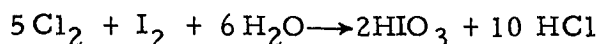
3) Test 3

The cold chlorine-in-water sample (sample method D), when added dropwise to a solution of 0.1 N iodide, liberates the iodine to yield a brown-coloured solution according to the reaction:



If the brown solution is shaken with 2 ml of CCl₄, the colour of the solution changes to violet and settles out below the aqueous layer.

If an excess of chlorine-in-water is added to the iodide solution, the liberated iodine will be oxidized to yield a colourless iodic acid solution according to the equation:



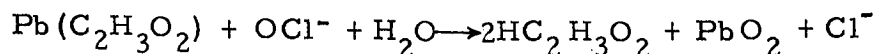
Hypochlorites (OCl^-)

1) Test 1

In the presence of OCl^- (and Cl^-), 0.025 N silver nitrate (sampling method C) will yield a white turbid solution when shaken.

2) Test 2

Add 10 drops of 0.5 N lead acetate to a 10-ml aliquot of the ice-cold water sample (sampling method D). Stir the mixture and bring to a slow boil in a hot-water bath. If OCl^- is present in the mixture, a brown lead-oxide precipitate will result through the reaction:



If OCl^- is not found in the cold-water sample, all of the I_2 released in the potassium iodide test for chlorine gas (see page 29) is then assumed to be Cl_2 . However, if OCl^- is present, a correction must be made in the Cl_2 determination because I_2 is also released by OCl^- .

Chloride (Cl^-)

Pipette a 10-ml aliquot of aqueous sample from the HCl gas bubbler (sampling method A) into a test tube. Acidify with 3 M HNO_3 . Add 5 drops of 2 M H_2SO_4 and bring the contents of the test tube to a boil in a hot bath. Continue boiling and test the escaping fumes for H_2S which interferes with the Cl^- test. If H_2S is present, a filter paper moistened with lead acetate solution will turn black. If no H_2S is present, cool the solution and add 1 drop of 0.2 M AgNO_3 . A white, curdy precipitate (AgCl) proves the presence of chlorides.

Chlorate (ClO_3^-)

Filter the precipitate produced in the above test for chloride. Introduce to the filtrate a little chloride-free sodium nitrate to reduce the chlorate, if present, to chloride. Add 1 drop of 0.2 M HNO_3 to the solution. A white, curdy precipitate (AgCl) indicates the presence of chlorates.

Perchlorate (ClO_4^-)

Filter the precipitate produced on the above test for chlorate. Remove any excess of silver in the filtrate with a solution of sodium carbonate. Evaporate the resulting solution to dryness, and heat to dull red to convert any perchlorate to chloride. Extract the residue with H_2O , and test for chloride with dilute HNO_3 and 0.2 M AgNO_3 .

Quantitative Analyses for Chlorinated Compounds

This section describes the procedures used for quantitative analyses of the flue-gas samples from the development model DDT incinerator.

Residual Chlorine (Cl_2)

1) Method

The method is an iodometric titration for total chlorine, without regard to type, utilizing phenylarseneoxide as the titrating agent. When a filtered, iron-free aliquot taken from the residual chlorine bubbler is treated with iodide, the iodine liberated at the proper pH is stoichiometrically proportional to the residual chlorine present. The iodine so liberated is titrated with standard phenylarseneoxide solution in the presence of starch until the iodine is completely reduced. The end point of the titration occurs when the next addition of phenylarseneoxide solution causes the blue colour to disappear in the sample.

2) Reagents

(a) Buffer Solution

Dissolve 243 g of sodium acetate trihydrate and 480 g of glacial acetic acid in water and dilute to 1000 ml.

(b) 0.00564 N Phenylarseneoxide Solution

Dissolve 0.8 g of phenylarseneoxide in 150 ml of NaOH (12 g per litre). To 110 ml of this solution add 800 ml of water, and bring to a pH of 9.0 by slowly adding 1.1 HCl. Continue to acidify with HCl until a pH of between 6 and 7 is reached; then dilute to 1000 ml and add 1 ml of chloroform for preservation. Standardize to 0.00564 N against 0.0282 N iodine solution.

(c) Potassium Iodide Solution

Dissolve 50 g of KI in water and dilute to 1 litre.

(d) Starch Indicator

Make a paste of 1 g of arrowroot starch or soluble iodometric starch with water. Pour the paste into 100 ml of boiling water and boil for several minutes. Store in a glass-stoppered bottle in a refrigerator. Starch solution, prepared in this manner, will remain chemically stable for three days.

3) Procedure

To a 50-ml filtered sample in a 500-ml Erlenmeyer flask, add 1 ml of KI solution, while stirring. Immediately following, add buffer solution in sufficient quantity to ensure a pH of 4.0. While stirring, add 0.00564 N phenylarseneoxide solution dropwise from a 50-ml burette until the colour is reduced to a pale yet discernible yellow. Add 1 ml of starch solution, which will turn the sample blue. Continue the dropwise addition of the phenylarseneoxide solution, while stirring, until the next addition eradicates the blue colour. Record the total volume of the phenylarseneoxide solution added.

4) Calculation

$$\text{Residual chlorine, ppm (v/v)} = \frac{(V_T)(12.64)}{(V_a)(V_{20})}$$

where

V_T = millilitres of 0.00564 N phenylarseneoxide solution required for the titration,

V_a = millilitres of sample used in titration, and

V_{20} = volume of gas sample in cubic feet, corrected to 20°C and 760 mm Hg.

Chloride Ion (Cl⁻)

1) Method

A liquid aliquot from the hydrogen chloride bubbler (sampling method A) is adjusted to a pH of 8.3 and then titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the brick-red silver chromate colour.

2) Interferences

Bromide, iodide and sulphide are titrated along with the chloride. Sulphite and objectionable colour or turbidity must be eliminated. Compounds which precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

3) Reagents

(a) Potassium Chromate Indicator

Dissolve 50 g of potassium chromate (K_2CrO_4) in 100 ml of water, and add silver nitrate ($AgNO_3$) until a slight red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 hr. Filter the solution to remove the precipitate and dilute to 1000 ml with water.

(b) Silver Nitrate Standard Solution (0.025 N)

Crush approximately 5 g of $AgNO_3$ crystals and dry to constant weight at $40^\circ C$. Dissolve 4.2473 ± 0.0002 g of the crushed, dried crystals in water and dilute to 1000 ml. Standardize against 0.025 N NaCl.

(c) Others

- 30% hydrogen peroxide solution
- 0.2 N NaOH solution
- 1:19 H_2SO_4 solution (1 volume of conc. H_2SO_4 to 19 volumes of water)

4) Procedure

Step 1. Pipette 10 ml of the sample into a 150-ml beaker and dilute to about 50 ml with water. Adjust the apparent pH to 8.3, using H_2SO_4 (1:19) or 0.2 N NaOH.

Step 2. Add about 1 ml of K_2CrO_4 indicator, and mix. Add standard $AgNO_3$ solution dropwise from a 50-ml burette until the brick-red (or pink) colour persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles.

Step 3. Repeat the procedure as described above, using exactly one-half as much original sample, diluted to 50 ml with halide-free water.

Note: If sulphite ion is present in the two samples, first add 0.5 ml of H_2O_2 to each and mix for one minute. Adjust the pH, and proceed with titration.

5) Calculation

The chloride ion concentration in the original sample can be calculated as follows:-

$$\text{Total chloride, ppm v/v} = \frac{(V_1 - V_2)(N)(448.02)}{(V_a)(V_{20})}$$

where V_1 = ml of standard $AgNO_3$ solution added in titrating the sample as prepared in Procedure Step 1,

V_2 = ml of standard $AgNO_3$ solution added in titrating the sample as prepared in Procedure Step 3,

N = normality of standard $AgNO_3$ solution,

V_a = aliquot volume (ml) of original sample in the 50-ml test sample prepared in Procedure Step 1, and

V_{20} = volume of gas sample in cubic feet, corrected to 20°C and 760 mm Hg.

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APPENDIX B

THEORETICAL COMBUSTION REQUIREMENTS FOR A
30% DDT IN OIL MIXTURE

Properties of Fuel

Typical No. 2 oil analysis	C	0.8600
	H	0.1330
	S	0.0070
DDT (C ₁₄ H ₉ Cl ₅)	C	0.4744
molecular weight 354.46	H	0.0256
	Cl	0.5000

Calculated composition of a 30% by weight mixture of DDT:

C = 0.7 x 0.8600 + 0.3 x 0.4774	=	0.7443
H = 0.7 x 0.1330 + 0.3 x 0.0256	=	0.1008
S = 0.7 x 0.0070	=	0.0049
Cl = 0.3 x 0.5000	=	<u>0.1500</u>
		1.0000

Combustion Calculations for 30% DDT/Oil

(a) Stoichiometric Flue Gas Formation

C, lb mol/lb fuel	=	0.7443/12.01	=	0.06197
∴ CO ₂ formation	=	0.06197 lb mol/lb fuel		
S, lb mol/lb fuel	=	0.0049/32.06	=	0.00015
∴ SO ₂ formation	=	0.00015 lb mol/lb fuel		
Cl ₂ , lb mol/lb fuel	=	0.1500/35.45 x 2	=	0.00212
∴ HCl formation	=	2 x 0.00212	=	0.00423 lb mol/lb fuel
Total H ₂ lb mol/lb fuel	=	0.1008/2 x 1.008	=	0.05000
H ₂ required to form HCl, lb mol/lb fuel	=	<u>0.00212</u>		
H ₂ remaining to form H ₂ O, lb mol/lb fuel	=	0.04788		

(b) Stoichiometric Combustion Air Requirement

$$\begin{aligned} \text{Stoichiometric O}_2, \text{ lb mol/lb fuel} &= 0.06197 + 0.00016 + 0.03495 \\ &= 0.08607 \\ \text{Stoichiometric N}_2, \text{ lb mol/lb fuel} &= \frac{79}{21} \times 0.08607 = 0.32378 \\ \text{Stoichiometric air, lb mol/lb fuel} &= 0.08607 + 0.03238 = 0.40986 \end{aligned}$$

(c) Dry Stoichiometric HCl ppm v/v in Flue Gas

Dry flue gas	CO ₂	0.06197
lb mol/lb fuel	SO ₂	0.00015
	HCl	0.00423
	N ₂	<u>0.32378</u>
Total		0.39013

∴ Stoichiometric HCl concentration = 10,845 ppm v/v

(d) HCl ppm for 5% O₂ in Flue Gas

$$\begin{aligned} \text{Additional oxygen,} &= \frac{0.21 \times 0.05 \times 0.39013}{(0.21 - 0.05)} \\ &= 0.025603 \\ \text{Additional dilution air} &= 0.02560/0.21 \\ \text{lb mol/lb fuel} &= 0.12192 \\ \text{Total dry flue gas} &= 0.39013 + 0.12192 \\ \text{lb mol/lb fuel} &= 0.51205 \end{aligned}$$

∴ HCl concentration at 5% O₂ = 8,263 ppm v/v
