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EXPERIMENTAL INVESTIGATION OF CFBC TECHNOLOGY FOR THE DECONTAMINATIO[N] OF HIGHLY CHLORINATED PCB WASTES

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JANUARY 1994

THIS WORK WAS SUPPORTED IN PART BY CINTEC ENVIRONMENT INC. AND THE FEDERAL PROGRAM ON ENERGY RESEARCH AND DEVELOPMENT (PERD)

DIVISION REPORT ERL 94-01 (TR)

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SYNOPSIS

CINTEC ENVIRONMENT INC. was contracted by the Province of Quebec to treat PCB-contaminated wastes in its transportable circulating fluidized bed combustor (CFBC) - the Quebec project. Tests were conducted in a pilot-scale research facility at CANMET's Energy Research Laboratories in Ottawa (Natural Resources Canada). The test program was designed to confirm stable steady-state operation under the Quebec project conditions expected during commercial operation and to measure the stack emissions of significant pollutants.

The results confirm that the commercial unit will exhibit stable and reliable operation under the operating conditions of the Quebec project and that it will comply with all applicable regulatory and project specific requirements.

BACKGROUND

Polychlorinated Biphenyls (PCBs)

PCBs are organic compounds in which two or more chlorine atoms are substituted for hydrogen atoms on a biphenyl molecule. These chemicals were first manufactured at the end of the 19th century, when their remarkable properties were discovered: high stability, high heat capacity, low flammability and low electrical conductivity. PCBs became widely used in electrical equipment, such as transformers and capacitors, as well as heat transfer fluids and in other various specific applications[1,2].

It was not until the 1960s that their potential threat to human health was first reported. Although their toxicity is still a matter of controversy, it is now well documented that the biodegradability of PCBs with four or more chlorine atoms is extremely slow. They accumulate in the food chain, where they end up in the fatty tissues of fish. Such accumulation has been detected in the fish stocks in the Great Lakes. Furthermore, it was found that poor combustion of PCBs such as in electrical fires (300-500°C) leads to the formation of dioxin.

No commercial PCBs were manufactured in Canada since they were all imported from the U.S. In 1977, the U.S. EPA, via the Toxic Substance Control Act (TSCA), generally prohibited the manufacture, processing, sale and use of PCBs in the U.S. At the same time, the Canadian government prohibited importation and regulated utilization of these compounds.

PCBs are no longer produced, but major amounts are stored worldwide as askarels (pure PCBs diluted with trichlorobenzenes), blends with mineral oil, contaminated pieces of electrical equipment, and soils and debris. These wastes must be treated and disposed of.

PCB Events in Quebec

In August 1988, a fire erupted in a privately owned PCB storage facility located in St-Basile-le-Grand, a small community near Montreal, Quebec. As a precautionary measure, government authorities evacuated the 3500 local residents. The Quebec government then took over the storage facility in St-Basile, cleaned it up, repacked the PCBs, confined the contaminated soils/debris, and finally secured the site. Although no effects on the health of the population were reported, these events received intensive media coverage. Subsequently, the Province of Quebec implemented a strategy for the destruction of PCBs under its custody (this represents less than 10% of all PCBs stored in the Province of Quebec).

In 1989, Quebec set up a commission to investigate the toxic waste issue. Its final report[3] clearly indicated that any recommended elimination process for PCBs, in order to get public acceptance, must be transportable and implemented on a regional basis.

In 1991, the Quebec Ministry of the Environment and Wildlife (MEW) created a task force (PCB-Quebec) with the mandate of implementing a phased program for the complete elimination of PCBs held by the Quebec government. The program phases are:

1. Definition of standards and criteria
2. Identification of proven technologies
3. Identification of the most suitable treatment sites
4. Preparation of a request for proposal (RFP) document
5. Preparation of impact studies
6. Public hearings
7. Destruction of PCBs.

The RFP document defined the types and quantities of PCB-contaminated waste to be treated and identified the sites where the wastes were to be treated. The RFP document was issued

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for public tender in September 1992. In January 1993, CINTEC ENVIRONMENT INC., owner of the OGDEN 36-in. circulating fluidized bed combustor (CFBC) was awarded the contract. For the Quebec project, CINTEC is associated with SNC•LAVALIN Inc., Canada's largest engineering firm that provides project management services, internal quality control and laboratory analyses.

Types of PCB Waste

Three types of PCB contaminated materials are to be treated:

- liquids, including essentially pure askarels and contaminated oils;
- solids, mainly soils and some debris, generally lightly contaminated;
- electrical equipment, consisting of transformers and capacitors.

The liquids and solids are to be incinerated with minimal pretreatment, while the decontamination of electrical equipment is a two-step process:

1. PCB extraction is achieved in an autoclave using a solvent (perchloroethylene or PCE) as the carrier;

2. PCBs and the solvent are then separated by distillation. The PCE is recycled to the extraction process, and the PCBs are combined with other PCB contaminated liquids for direct injection into the combustion chamber.

The types and quantities of contaminated waste at each site are given in Table 1.

CFBC TECHNOLOGY

Circulating fluidized bed combustion (CFBC) is an advanced generation of incineration technology that uses high-velocity air to entrain circulating solids in a highly turbulent combustion loop. The technology was initially developed in Germany and Finland during the 1960s for catalytic processes and efficient production of energy from biomass and low-rank coals. Since then, the technology has been successfully adapted for the incineration of a variety of organic wastes and residues[4-7].

The principal advantage of CFBC is that combustion takes place uniformly under very high turbulence. This turbulence ensures excellent mixing and gas-solid contact, thus resulting in efficient oxidation of organic wastes at temperatures lower than those of other incineration processes and no high temperature post-combustion like that in conventional processes. Other significant advantages include: improved heat and mass transfer, more complete chemical reactions, reduced NO_x emissions (due to the lower operating temperatures), and the possibility of injecting limestone (mostly $CaCO_3$) for the *in-situ* capture of sulphur and/or chlorine[5]. In addition, the simplicity of its design allows for precise process control and also for reliable long-term operation.

CFBC Incineration of PCBs

In the 1980s, General Atomic Technologies (GAT) of San Diego, California, constructed a 16-in. CFBC pilot plant to adapt the technology to the destruction of toxic organic wastes. GAT used this pilot plant to demonstrate the incineration of a wide variety of contaminated liquids, solids and sludge[8]. In 1985, GAT conducted a series of U.S. EPA-supervised tests on PCB-contaminated soils[9]. The program consisted of a triplicate test burn using soil spiked at 10,000 ppm PCBs with askarel. The test results are summarized in Table 2.

In 1986, OGDEN Environmental Services (OES) purchased the CFBC incineration technology and pilot plant equipment from GAT. Using the pilot plant test experience, OES then designed and constructed four 36-in. transportable units. These units were intended to be used for the on-site treatment of contaminated soils and halogenated liquids and sludge. They were successfully operated in Stockton (California)

Table 1: Total Quantities (Metric Tonnes) of Contaminated Wastes - Quebec Project

Site	Type of Waste				Total PCBs
	Electrical Equipment	Liquids	Solids[a]	Total	
Baie-Comeau	622	230	1652	2504	185
St-Basile-le-Grand	575	174	13,985	14,734	198
Shawinigan-South	77	35	9	121	31
Total	1274	439	15,646	17,359	414

[a] Principally soils contaminated with low levels of PCBs.

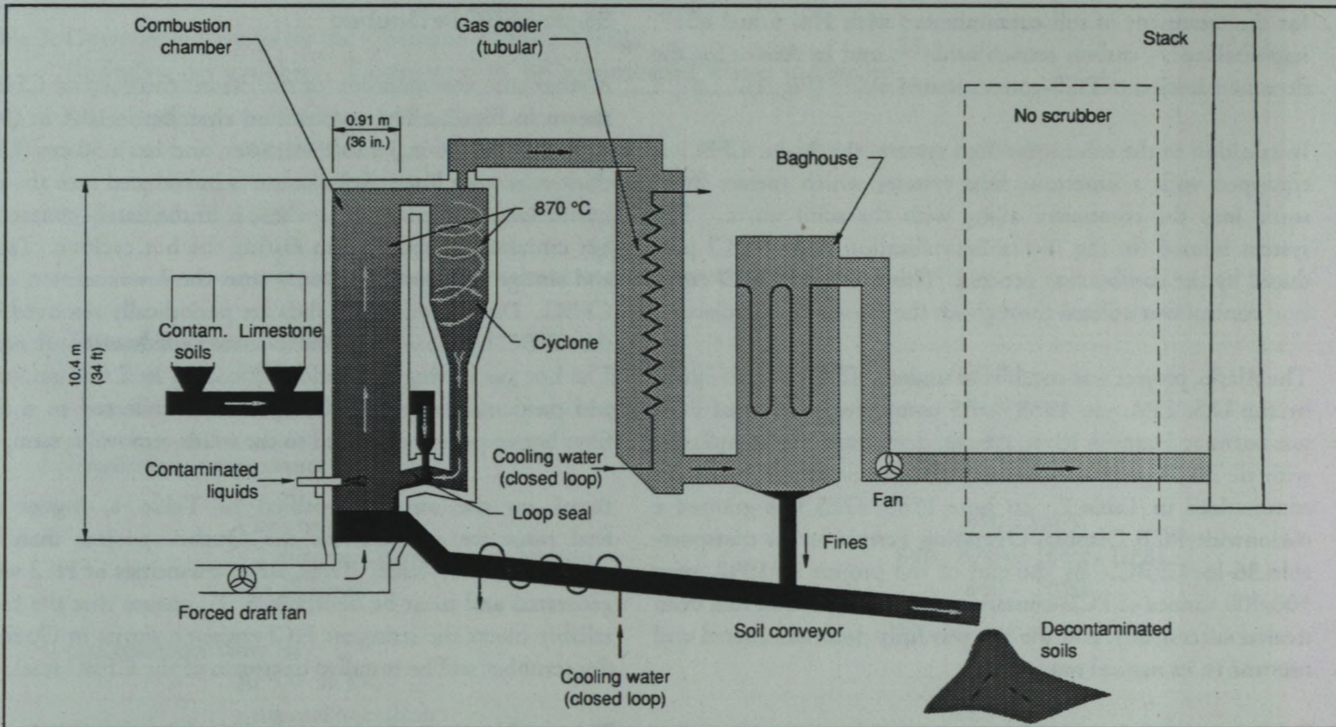

Fig. 1: Schematic Flow Diagram of OGDEN's 36-in. CFBC for the Swanson River Remediation Project (Alaska)

TABLE 2: PCB-Contaminated Soil Test Burn Results from 16-in. Pilot Plant and 36-in. Commercial Plant, Both Owned and Operated by OGDEN Environmental Services

		16-in. Pilot Plant(San Diego)	36-in. Commercial Unit (Swanson River, Alaska)	
Test Parameter		Tests 1, 2, 3, 4	Tests 1, 2, 3	Tests 4, 5, 6
Combustion temp	(°C)	985	880	923
Gas residence time	(s)	1.21	1.68	1.51
Soil throughput	(kg/h)	169	3850	4127
Soil PCB	(ppm)	11,000	683	507
PCB throughput	(kg/h)	1.86	2.63	2.09
Limestone throughput	(kg/h)	18.2	68.2	68.0
$Ca:Cl_2$	(mole ratio)	10:1	42:1	52:1
Flue gas oxygen, dry	(%)	6.9	7.1	6.8
CO	(ppm)	48	14	11
NO_x	(ppm)	37	88	89
Combustion efficiency	(%)	99.92	99.98	99.99
DRE	(%)	> 99.9999	> 99.99993[a]	> 99.99993[a]
Stack dioxin/furan	(ng/Nm^3)	< 20[a]	< 1[a]	< 1[a]
Treated soil PCB content	(ppm)	0.06	< 0.009[a]	< 0.012[a]
Treated soil dioxin/furan	(ppb)	< 0.8[a]	< 0.1[a]	< 0.1[a]

[a] No detectable amount in the sample collected. The values reported are the detection levels of the analytical system.

for the treatment of soil contaminated with No. 6 fuel oil[10], naphthalene[11], carbon tetrachloride[12], and in Alaska for the decontamination of PCB-contaminated soil[13] (Fig. 1).

In addition to the solid waste feed system, the 36-in. CFBC is equipped with a limestone feed system, which meters limestone into the combustor along with the solid waste. The system is used for the *in-situ* neutralization of any HCl produced by the combustion process. This method of HCl emission control was utilized throughout the Alaska PCB project.

The Alaska project was conducted under a TSCA permit issued by the U.S. EPA. In 1988, OES completed a series of PCB test burns at Swanson River, Alaska, demonstrating compliance with all TSCA performance criteria[13]. Relevant test results are summarized in Table 2. In June 1989, OES was granted a nationwide PCB Disposal Operating Permit for its transportable 36-in. CFBC. By the end of the project in 1992, over 100,000 tonnes of PCB-contaminated gravel/silt soil had been treated successfully, and the site was fully decontaminated and restored to its natural state.

Table 2 suggests that the 36-in. commercial unit may be somewhat more efficient than the 16-in. pilot plant unit. With comparable flue gas oxygen levels, the CO levels in the larger unit are one-third those of the smaller one. These lower CO levels were also recorded during the commissioning test conducted prior to the test burns[14]. The higher NO_x levels in Alaska were probably due to organic nitrogen present in the contaminated soil.

36-in. CFBC in Quebec

A schematic configuration of the 36-in. commercial CFBC is shown in Fig. 2. The combustion chamber is 10.4 m (34 ft) high, 0.91 m (36 in.) inside diameter, and has a 30 cm (12 in.) thick refractory liner. Solid waste is introduced into the combustor loop at the loop seal where it immediately contacts the hot circulating solids stream exiting the hot cyclone. Liquids and sludge are injected directly into the lower section of the CFBC. Decontaminated solids are periodically removed from the CFBC by means of a water-cooled solids removal system. The hot gas leaving the cyclone is cooled in a flue gas cooler, and particulate escaping the cyclone is collected in a fabric filter baghouse and conveyed to the solids removal system.

Based on the wastes identified in Table 1, higher PCB feed rates are expected for the Quebec project than were encountered in Alaska. Thus, larger quantities of HCl will be generated and must be neutralized. To ensure that the facility reliably meets the stringent HCl emission limits in Quebec, a dry scrubber will be installed upstream of the CFBC stack.

This scrubber system consists of a Venturi-type vertical reactor with hydrated lime ($Ca(OH)_2$) injection at the bottom. The gas is then filtered into a baghouse while the excess lime is recirculated. The solid residue produced is a mixture of inert $CaCl_2$ and unreacted $Ca(OH)_2$. This type of scrubber has been in operation for several years in Europe on chlorinated solvent incinerators and has an excellent record in terms of reliability and performance[15]. The dry scrubber has the ad-

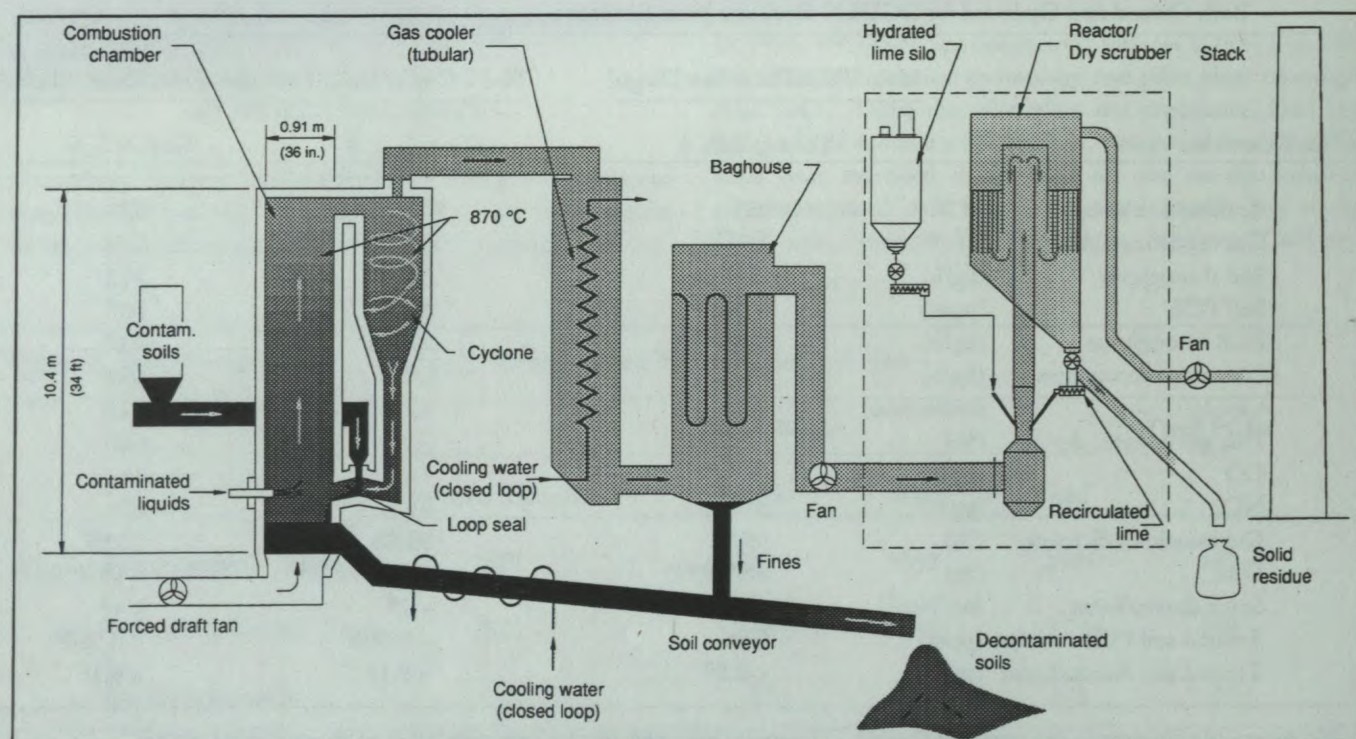

Fig. 2: Schematic Flow Diagram of 36-in. CFBC System for the Decontamination of PCB Contaminated Wastes in Quebec

Table 3: Operational Criteria for the Operation of 36-in. CFBC (including dry scrubber) - Treatment of PCB-Contaminated Wastes in Quebec

Stack emissions (at 7% O_2, dry basis):			
	DRE[a,b]	(%)	>99.9999
	Particulate matter[b]	(mg/Nm^3)	<50
	HCl[b]	(ppmv)	<50
	SO_2[b]	(ppmv	<76
	2,3,7,8-TCDD equiv.[c]	(ng/Nm^3)	<5
Treated soils and solid residues:			
	PCBs[c]	(µg/g)	<0.5
	2,3,7,8-TCDD equiv.[c]	(ng/g)	<1.0
Combustor temperature (°C)			
	- normal operation		870 - 1065
	- 2 minutes allowed for correction		840 - 870 or 1065 - 1090
	- at all times		840 - 1090
Gas residence time (s)			
	At T < 925°C		
	- normal operation		1.7
	- 2 minutes allowed for correction		1.5 - 1.7
	- at all times		>1.5
	At T > 925°C		
	- normal operation		1.5
	- 2 minutes allowed for correction		1.35 - 1.5
	- at all times		>1.35
O_2 (% - wet)			
	- normal operation		4.6
	- 2 minutes allowed for correction		3.0 - 4.6
	- at all times[c]		>3.0
CO[c] (ppmv at 7% O_2)			
	- normal operation[c]		<70
	- 2 minutes allowed for correction[c]		70 - 140
	- at all times[c]		<140
Combustion efficiency (%)			
	- at all times[b]		>99.9

a Destruction and removal efficiency
b Regulatory requirements (MEW)
c Project specific criteria (MEW)

vantage of capturing not only any HCl exiting the CFBC but also any traces of dioxin and furan present in the flue gas[16].

Regulatory Considerations in Quebec

The regulatory and performance criteria for the Quebec project are presented in Table 3. These performance criteria are based on existing provincial regulations and policies from MEW for the operation of new hazardous waste incinerators. They closely follow comparable regulations issued by the U.S. EPA.

Expected Operating Conditions

The operating parameters of the 36-in. CFBC in Quebec will be similar to those demonstrated in the Alaska project. Based on these process conditions, the expected waste feed rates for the Baie-Comeau and St-Basile-le-Grand and Shawinigan-South sites are shown in Table 4.

Total Chlorine Throughput

The only significant difference between the Quebec project's expected feed rates and prior OGDEN's experience is the amount of chlorine being fed to the system. Table 5 compares values for chlorine throughput in past test burns and projects with projected chlorine throughput for the Quebec project.

The first remediation site for the Quebec project will be Baie-Comeau. The equipment will be transported to the site, installed, and tested. Trial test burns will be done with the aim of establishing reliable and steady state conditions.

Since CANMET's Energy Research Laboratories has an identical technology configuration (the CANMET CFBC design was based on the San Diego pilot plant), it was decided to replicate the expected process conditions of the Baie-Comeau demonstration test. This will allow cost and time savings when the commercial 36-in. unit is commissioned in Baie-Comeau in 1994.

CANMET PILOT PLANT TESTS

Test Objectives

The pilot plant test program was designed to meet the following objectives:

1. Confirm the stable and reliable operation of the CFBC at the process conditions expected for the Quebec project

2. Determine the flue gas emissions of CO, CO_2, NO_x, SO_2 and N_2O. Measure the stack emissions of chlorobenzenes and dioxin and furan, and the dioxin, furan and chlorobenzene content in the treated solids. Calculate combustion efficiencies and DREs
3. Examine the effects of limestone addition on process performance

4. Evaluate the performance of various components such as pumps and feeders.

The 36-in. CFBC will be thoroughly tested at Baie-Comeau, although the CANMET test objectives are shown to be met.

Test Facility

CANMET is the science and technology arm of National Resources Canada. CANMET is one of Canada's foremost technology development organizations in mineral and energy research.

CANMET has its own research group in fluidized bed technology. Several bench and pilot-scale reactors have been designed and installed, including a 16-in. CFBC based on

Table 4 Expected Feed Rates to 36-in. CFBC

Type of Feed	Baie-Comeau (kg/h)	St-Basile-le Grand (kg/h)	Shawinigan-South (kg/h)
Total solids (dry basis)	884	2244	55
Contaminated mineral oil	120	25	120
Water[a]	165	382	10
Auxiliary fuel	0	76	0
PCBs and chlorobenzenes (CBs)	140	65	140
Solvent (PCE)[b]	13	4	12
	1322	2796	337

[a] As moisture in the solid waste stream
[b] Perchloroethylene (C_2Cl_4)

Table 5: Comparative Chlorine Throughput in Past Test Burns and Projects using CFBC Technology

	Alaska Swanson River	San Diego Pilot Plant[a]	Quebec St-Basile-le-Grand	Quebec Shawinigan -South	Quebec Baie-Comeau	CANMET Pilot Plant
Chlorine (kg/h)						
- from PCBs	2.4	8.3	26.6	44.1	44.1	0
- from CBs	0	1.3	0	12.6	12.6	77.1[b]
- from PCE	0	0	3.4	10.3	11.1	0
Total chlorine (kg/h)	2.4	9.6	30.0	67.0	67.8	77.1

[a] Test successfully achieved under U.S. EPA surveillance[9] on a 16-in. CFBC. The values have been scaled up by a factor of 7.7 (ratio 36-in. to 16-in. reactor volumes) for comparison.
[b] Average value, with surrogate (Dichlorobenzene (DCB)), scaled up by a factor of 7.8

OGDEN's 16-in. San Diego pilot plant. The unit is 0.405 m (16-in.) in diameter and 6.60 m (22 ft) high with a maximum rating of about 0.8 MW-th and is shown in Fig. 3. The main components of the incinerator are combustor, cyclone, loop seal, flue gas cooler, baghouse, solids and liquids handling and feed systems, and air supply system. It is equipped with comprehensive instrumentation, control and data acquisition systems. The facility is extensively described in a separate report[17].

The test unit, having been designed by GAT for CANMET, is identical to the one built and operated by GAT in San Diego, California. As such, it is a small version of the 36-in. CFBC to be used for the Quebec remediation projects.

For these tests, solids (sand and limestone) were fed to the incinerator through two independently-controlled feed systems. Each feed system consisted of (1) a storage bin, (2) a weigh feeder, (3) an airlock valve, and (4) a common screw conveyor. The weigh feeders meter and maintain constant solids feed rates. The two systems discharge their output to a common solids feed chute which enters the combustor 480 mm above the base of the combustor.

Two separate feed systems for the liquids have been used for these tests. Each liquid feed system consists of a storage drum or tank, variable speed pump, and associated piping. The liquids are fed through a common injection nozzle located 0.6 m above the base of the combustor. The liquid storage drums are placed on weigh scales, and the feed rates are measured by recording drum weight changes over time.

A variety of liquid pumps were employed for feeding the liquid waste. In test 1, it was difficult to provide a uniform and easily controlled feed rate. Subsequent tests were conducted using either a Moyno pump or a gear pump. Both were properly sized. The commercial CFBC is expected to use a gear pump therefore this type of pump was included in the test program.

The combustor temperature was controlled by using up to four water-cooled bayonet tubes. Each tube could be inserted or retracted through the top of the combustor using a motorized winch system.

The hot flue gas exiting the combustion loop is cooled by the flue gas cooler to about 190°C and then conveyed to a fabric filter baghouse. Fine particulate collected in the baghouse is transferred to a storage barrel via an airlock valve. The flue gas is then conveyed via an induced-draft fan to the stack where it is sampled and discharged to the atmosphere.

Hot bed material was drained continuously from the return leg of the combustion loop at a rate sufficient to maintain the solids inventory in the combustion loop at constant value. This material was collected in a storage drum placed on an electronic weigh scale.

Continuous on-line monitoring of flue gas concentrations of CO, CO_2, O_2, SO_2 and NO_x is accomplished using a gas sample conditioning train and a bank of gas analyzers. The flue gas sample is taken from the system at the outlet of the cyclone. The SO_2, CO and CO_2 analyzers operate on the non-dispersive infrared (NDIR) principle, the O_2 analyzer is

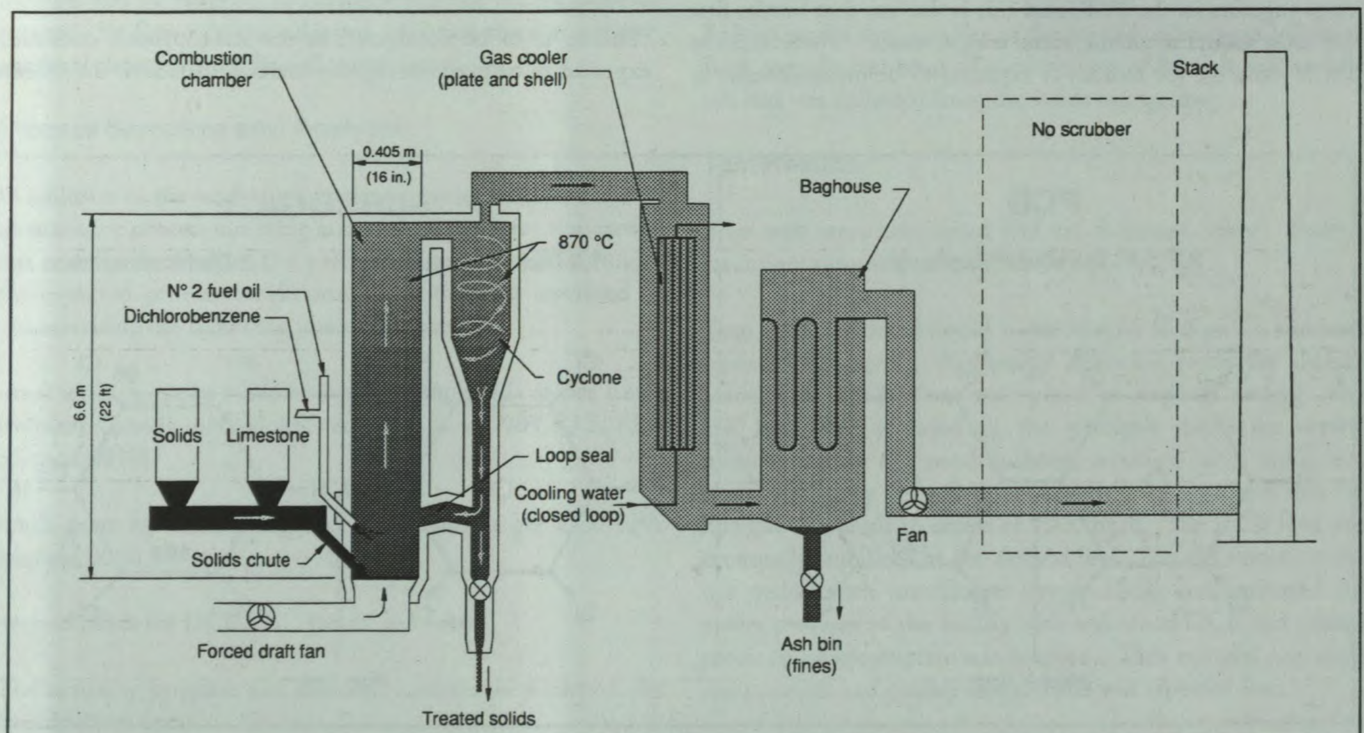

Fig. 3: Schematic Flow Diagram of CANMET's 16-in. CFBC Test Facility

paramagnetic and the NO_x analyzer operates on the chemiluminescence principle. N_2O concentrations were determined by collecting samples of flue gas and analyzing them by gas chromatography.

Process parameters such as loop temperatures and pressures, air flow rates, waste feed rates and flue gas composition were shown on a video display terminal in the control room as part of a schematic diagram of the pilot facility. The same process data were recorded on a data logger and on a dedicated data acquisition system.

Approach

Selection of Waste Surrogates

Because the CANMET facility is not permitted to incinerate PCB-containing materials, a chemical surrogate was used to simulate the PCBs. The surrogate was required to: (1) be an identical aromatic compound in terms of ring structure and chlorine content, (2) be commercially available, (3) be essentially non-toxic. We selected meta(1,3)-Dichlorobenzene (DCB) for the PCB surrogate because it met all the above requirements. DCB was fed to the CFBC at a rate that provided somewhat higher chlorine and aromatic ring feed rates than expected during commercial operation.

The chemical structure of the DCB is compared to that of a typical PCB in Fig. 4. On the basis of thermodynamics, it is expected that the DCB will be even more difficult to destroy than PCBs. As shown in Fig. 4, the weakest chemical bond of either molecule is the one binding the two benzene rings together in the PCB, and this is the one that breaks first (or most easily) at incineration temperatures. Therefore, the DCB molecule (or radical) is expected to be more difficult to destroy. Once that bond is broken, the PCB molecule becomes, in effect, two DCB molecules (or radicals).

In terms of reaction kinetics, radical processes dominate the chemical reactions[18]. There is very little difference between chlorine-substituted benzene products such as DCB and PCB in the oxidizing environment of the CFBC. Attack is expected to commence on the bond joining the two benzene rings, followed by attack on the atoms attached to the aromatic rings and finally ring breakage. This mechanism is substantiated by literature on the decomposition of benzene and aromatic-substituted products[18,19].

Furthermore, DCB may represent a more severe test of the efficiency of the CFBC as a PCB incinerator for dioxin and furan formation. There is some evidence to suggest that this formation may be correlated to the presence of chlorinated substituted benzene compounds[20]. Thus, one might expect a compound like DCB to exhibit higher dioxin and furan production than PCB.

To simulate the solid waste expected at Baie-Comeau, 32 mesh silica sand was used, and for the non-PCB liquid fraction, No. 2 fuel oil was used.

The compositions of the various process feeds are summarized in Table 6.

Feed Rate "Scale-down"

The appropriate surrogate waste feed rates were calculated as follows:

·Testing is to be conducted at the same process conditions expected to be used during commercial operation. In order to

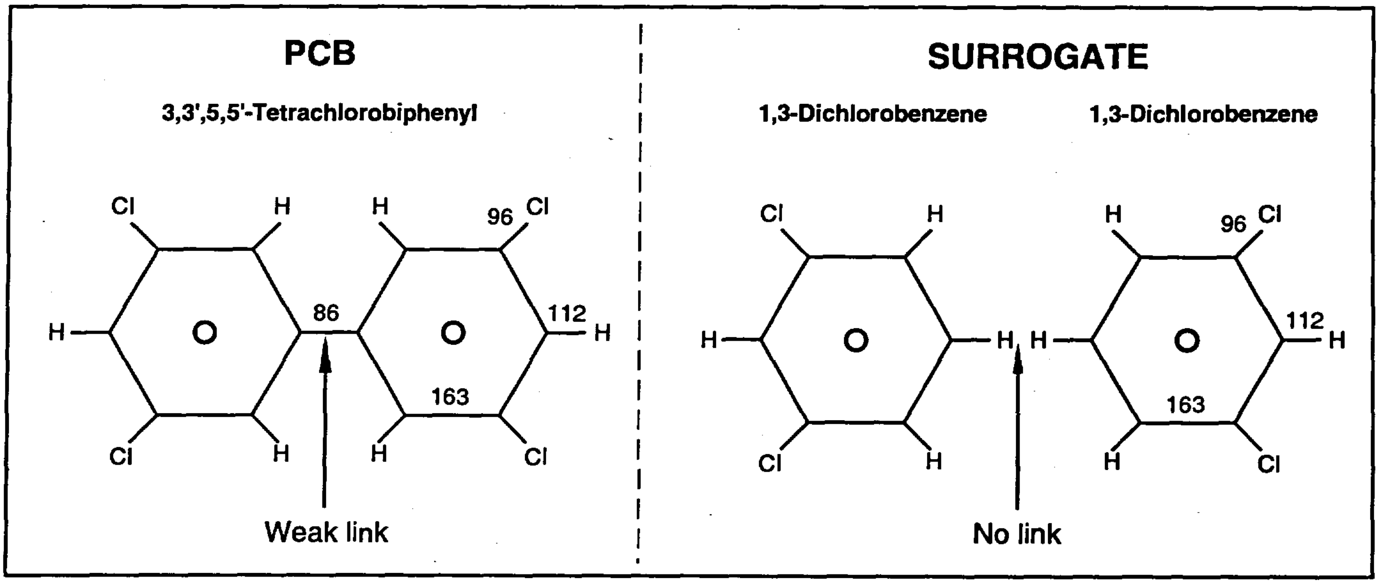

Fig. 4: Comparison of the Molecular Structures of PCB and DCB.
The strengths of the chemical bonds (in kcal/mole) are indicated.

provide a measure of conservatism, the gas residence time for the tests is somewhat less than that expected for commercial operation.

·To maintain the same combustion chemistries, all mass flows into the CFBC (waste, air, and auxiliary fuel) must be reduced by the ratio of the combustion chamber volumes:

$$\frac{36\text{-in. combustor volume}}{16\text{-in. combustor volume}} = \frac{\pi x(36")^2 x 4 x 34'}{\pi x(16")^2 x 4 x 22'} = 7.8$$

·At Baie-Comeau (see Table 5), we expect to feed 67.8 kg/h of chlorine, which is the highest chlorine feed rate expected during commercial operation. At CANMET, this corresponds to 8.72 kg/h of chlorine or 18.1 kg/h of DCB. Somewhat higher DCB feed rates (19-22 kg/h) have been employed to provide an additional measure of conservatism, resulting in scaled up chlorine feed rates in excess of 70 kg/h. Therefore, the PCB concentration in the liquid feed rate at Baie-Comeau (420,000 ppm, or 42%) is simulated at CANMET with a mixture of DCB and No. 2 fuel oil containing 420,000 ppm (or 42%) of DCB.

·At St-Basile-le-Grand (see Table 4), we expect to feed an average of 2244 kg/h of dry solids. This is the highest solids feed rate expected during commercial operation. In these tests, this corresponds to 289 kg/h of dry silica sand. As a conservative measure, we fed an average of 300 kg/h of sand during these tests.

No. 2 fuel oil was used to simulate the non-PCB liquid fraction and to function as auxiliary fuel for the incineration process. Its flow rate was adjusted to obtain the flue gas oxygen level chosen for the Baie-Comeau tests.

Process Sampling and Analysis

In addition to the on-line process monitoring described above, an extensive process sampling and analysis program was carried out to fully characterize the performance of the CFBC under the expected process conditions. This program consisted of characterizing the following process streams:

·stack gases for semi-volatile organic compounds as per Environment Canada method EPS 1/RM/2, June 1989 (U.S. EPA Method 0010).

·stack gases for volatile organic compounds as per U.S. EPA Method 0030.

·treated solids for DCB, CB, dioxin and furan.

The sampling program and chemical analyses were carried out by accredited firms.

In parallel, extensive quality control was implemented by SNC•LAVALIN, which included general testing and sampling surveillance, detailed calculations and verification of all data and reports.

Test Procedure

At the start of each test run, the combustor and return leg were charged with No. 32 sand. The combustion loop was heated using an 1800 MJ/h natural gas-fired burner. When the combustion loop reached about 600°C, No. 2 fuel oil was introduced at a low rate. The combustion air and oil flows were then gradually increased to the desired values and the burner was shut off. The facility was then maintained at the desired operating temperature for several hours, allowing the system to attain thermal equilibrium. When all conditions were stable, the desired sand feed rate was established and the fuel oil flow rate adjusted to maintain proper operating conditions. The DCB was then introduced at a low rate (6-8 kg/h). Over an interval of about 45 min., the DCB flow rate was increased to its target value and the fuel oil flow rate was reduced to maintain the desired flue gas oxygen value. The bayonet tubes were adjusted as necessary to maintain the desired operating temperature. Once all test conditions were achieved, the facility was operated for at least 1 h prior to stack sampling.

The duration of each test was determined by the time required to complete the stack sampling, a period of several hours. Process conditions were maintained at constant values throughout the sampling period. Following sampling, the DCB feed was terminated and system operation returned to fuel oil for at least 30 minutes. The facility was then shut down.

Following the test, samples of the treated solids were collected. Each sample consisted of a composite of bottom ash and fly ash and was collected from the solids storage drums.

Test Results

Four tests were conducted and are discussed below. Process results are summarized in Table 7.

<u>Test 1</u>: An oversized liquid waste Moyno feed pump was used initially. However, this pump delivered twice the desired amount of DCB than anticipated at a given setting. The test unit was operated in the pyrolysis mode for several minutes before the condition was rectified. This mode was characterized by (1) a flue gas oxygen level near zero and (2) flue gas CO levels in excess of 1000 ppm. The DCB feed was eventually stabilized at the desired level, but the operation for the period with insufficient oxygen likely contaminated the cooler portions of the facility with unburned DCB and related products of incomplete combustion. This run did not meet test protocol and quality control, and was repeated later.

Test 1 was repeated with a variable-speed piston pump of appropriate capacity. Although the pump delivered the DCB

Table 6: Feed Compositions[a]

DICHLOROBENZENE[b]

Constituent	Concentration
Benzene	<0,5 %
Chlorobenzene	<0.5 %
1,2-Dichlorobenzene	<0.5 %
1,3-Dichlorobenzene	100%
1,4-Dichlorobenzene	<0.5 %
Dioxin/furan	0.022 ng/g

No. 2 FUEL OIL

Constituent	Concentration
Carbon	86.8 (w/w) %
Hydrogen	13.0 (w/w) %
Sulphur	0.3 (w/w) %
Nitrogen	0.011 (w/w) %
Benzene	<20 µg/L
Chlorobenzenes	<20 µg/L
Dioxin/furan	0.0012 ng/g
Calorific value	45.0 MJ/kg

No. 32 SAND[c]

Constituent	Concentration	Size Distribution	
		U.S. mesh	Mean % Retained
SiO_2	99.6 (w/w) %	20 (850 µm)	0.1
Fe_2O_3	0.03	30 (600 µm)	9.0
Al_2O_3	0.01	40 (425 µm)	50.5
CaO	0.03	50 (300 µm)	34.7
K_2O	0.10	70 (212 µm)	4.9
TiO_2	0.10	100 (150 µm)	0.8
L.O.I.	0.12	140 (106 µm)	Trace
Dioxin/furan	0.000017 ng/g		
			100 %

LIMESTONE[d]

Constituent	Concentration	Size Distribution	
		U.S. mesh	Mean % Retained
$CaCO_3$	94.0 (w/w) %	16 (1,180 µm)	37.3
SiO_2	4.50	20 (850 µm)	5.7
SO_3	0.79	40 (425 µm)	12.1
MgO	0.43	100 (150 µm)	15.6
Na_2O	0.33	200 (75 µm)	9.5
K_2O	0.32	400 (38 µm)	5.7
Al_2O_3	0.28	-400	14.9
			100 %

[a] Dioxin/furan data are reported as 2, 3, 7, 8 - TCDD equiv.
[b] From HOECHST Canada Inc.
[c] BARCO 32 sand, from Barmin Inc., Watertown, Ontario, Canada.
[d] CALPO limestone, from Nova Scotia, Canada.

at the required rate, it did not do so uniformly. At the desired DCB feed rate, it operated at about 2 cycles per second and, being a single-stroke pump, probably delivered alternate rich and lean pockets of DCB into the combustor.

Test 2: A properly sized Moyno pump was used and the DCB feed was both easily controlled and uniform.

Test 3: Test 3 was conducted immediately following test 2. Test 3 differed from test 2 by the addition of a limestone feed. Limestone was fed at a rate such that the amount of $CaCO_3$ fed was three times the amount required for the complete neutralization (as $CaCl_2$) of all HCl produced. This gives a mole ratio of $Ca:Cl_2$ = 3.0. The sand feed rate was reduced somewhat to maintain a constant solids feed rate. The observed reduction in the measured flue gas CO level is discussed below.

Test 4: A gear pump similar to that planned for the 36-in. CFBC was used. Test 4 was conducted using a lower limestone feed rate (Ca: Cl_2 mole ratio of 1.0) than that used in test 3.

DISCUSSION OF TEST RESULTS

DCB DRE

The DCB DRE (Destruction and Removal Efficiency) was calculated from the test data as follows:

$$DRE\ (\%) = [\frac{M_{in} - M_{out}}{M_{in}}]\ x\ 100$$

where M_{in} = DCB feed rate to the CFBC (g/s), and M_{out} = rate of release of all chlorobenzenes to the stack (g/s) and is usually expressed as a percentage. The sum of all the detected chlorobenzenes is used to determine the DCB DRE. This convention follows that used for reporting PCB test results, wherein all of the PCB congeners are used to calculate the PCB DRE. This approach is significantly more conservative than that using only the measured release of the m(1,3)-Dichlorobenzene, which was used as the PCB surrogate.

The CANMET CFBC demonstrated a DCB DRE in excess of 99.9999% (six nines), which is the Quebec regulatory standard, in all tests performed. In addition, the DREs were obtained without the beneficial use of a scrubber.

If the CANMET CFBC had been equipped with instrumentation and waste interlocks similar to those of the CINTEC CFBC, the problems encountered at the beginning of test 1 would not have occurred. In the CINTEC CFBC, the control system would have automatically terminated waste feeding as soon as the measured flue gas oxygen dropped below 3%. This

Table 7: CANMET Dichlorobenzene Test Results[a]

		Test 1 07-29-93	Test 2 08-18-93	Test 3 08-18-93	Test 4 10-14-93
PROCESS CONDITIONS					
Type of DCB pump		Piston	Moyno	Moyno	Gear
Sand feed rate	(kg/h)	300	300	255	284
DCB feed rate	(kg/h)	21.6	20.7	18.8	21.1
Chlorine feed rate	(kg/h)	10.4	10.0	9.1	10.2
Fuel oil feed rate	(kg/h)	30.0	29.0	32.0	NA[b]
Limestone feed rate	(kg/h)	0	0	45	16
$Ca:Cl_2$	(mole ratio)	–	–	3.0	1.0
Combustor temperature	(°C)	875	877	885	880
Gas residence time	(s)	1.50	1.50	1.50	1.46
O_2	(%)	6.7	6.7	6.9	6.6
MEASURED RESULTS[c]					
CO	(ppmv)	84	97	21	36
CO_2	(%)	10.9	10.8	12.2	11.3
NO_x	(ppmv)	30	30	38	29
N_2O	(ppmv)	0.53	NA	0.27	0.48
SO_2	(ppmv)	150	154	43	86
Combustion efficiency (CE)	(%)	99.92	99.91	99.98	99.97
DRE	(%)	99.99995	99.99994	99.99997	99.99999
Stack TCDD[d]	(ng/Nm^3)	42.0	7.5	3.3	8.0
Total CBs in treated solids	(μg/g)	<0.04	<0.003	0.002	<0.002
TCDD in treated solids[d]	(ng/g)	0.37	0.024	0.035	<0.01

[a] The reported data consist of time-averaged measurements with the averaging time coinciding with the period of stack sampling.
[b] Due to an instrumentation problem, the data were not recorded.
[c] All flue gas concentrations are reported on a dry basis and normalized to 7% O_2 (except O_2)."< " indicates that no detectable quantities were found. The reported values are the detection limits.
[d] Data for dioxin and furan are reported as 2, 3, 7, 8-TCDD equiv. (corrected at 7% O_2 for gas emissions)

action would have occurred only a few seconds after the liquid pump had been started.

Dioxin/Furan

Dioxin and furan concentrations in the stack gas appear to be somewhat sensitive to the selection of the waste liquid feed pump:

·in tests 2, 3 and 4, where appropriate pumps were used, dioxin/furan emissions were low, averaging about 6 ng/Nm^3 (2,3,7,8-TCDD equiv. at 7% O_2) and were not sensitive to the limestone feed rate;
·in tests 1, due to the type of pump utilized, dioxin/furan emissions were higher at 42 ng/Nm^3 (2,3,7,8-TCDD equiv. at 7% O_2).

The data for tests 2, 3 and 4 (average of 6 ng/Nm^3 TCDD equiv.) agree with those obtained from industrial chlorinated waste incinerators. Indeed, dioxin content after gas cooling, for a feed containing 15% chlorine, typically ranges from 1 to 4 ng/Nm^3 TCDD equiv. Use of a dry scrubber with hydrated lime leads to a 90% dioxin removal efficiency, or 0.1 to 0.4 ng/Nm^3 TCDD equiv. at the stack, which is well below the Quebec regulatory limit of less than 5 ng/Nm^3 [ref 13].

Dioxin and furan levels in the treated solids in all cases were well below the Quebec regulatory limit of 1.0 ng/g.

CO Levels and Combustion Efficiency

Combustion efficiency (CE) is defined as:

$$CE\ (\%) = [\frac{(CO_2)}{(CO_2)+(CO)}] \times 100$$

where $[CO_2]$ and [CO] are the measured volumetric stack gas concentrations of carbon dioxide and carbon monoxide, respectively. The quantity is normally expressed as a percentage.

In all four tests, the resulting CE was above the Quebec regulatory limit of 99.9%.

On the other hand, the average CO concentrations are quite sensitive to limestone feeding. This is summarized below:

Test	$Ca:Cl_2$ (mole ratio)	Average CO (ppm at 7% O_2)
1, 2	0.0	91
3	3.0	21
4	1.0	36

In tests 1 and 2, the measured stack CO exceeded the Quebec project regulatory standard of 70 ppm even though acceptable DREs and combustion efficiencies were demonstrated. Tests 3 and 4 clearly met the regulatory standard of less than 70 ppmv.

The regulatory limits on CE and CO levels, unlike those for DRE and dioxin/furan, are not imposed for direct environmental concerns. Rather, high combustion efficiency, low CO levels and low CO transients are indicators of efficient combustion. However, in presence of high concentrations of halogens (such as chlorine), the CO level is somewhat less indicative, given that chlorine inhibits the rapid oxidation of CO to CO_2, but does not decrease the DRE. As demonstrated in tests 1 and 2, CO levels exceed the regulatory standard of 70 ppm, while DREs are well above the required 6 nines.

This phenomenon (high CO levels in the absence of limestone and low levels in its presence) is probably due to the HCl liberated during the incineration process. At the combustion temperatures used in this test series, direct oxidation of CO to CO_2 does not occur very rapidly, and CO is oxidized principally via a OH radical[21-24]. High levels of HCl within the combustion process interfere with the flame radical chemistry which generates the OH radical and therefore inhibit the oxidation of CO. This interference has been noted before[22-27].

The influence of limestone addition in this situation is then understandable, if difficult to quantify. In the CFBC, limestone($CaCO_3$) calcines to CaO + CO_2, with the CO_2 being released to the stack. In Table 7, the effects of this limestone calcination on the measured CO_2 levels are evident. The calcined limestone then reacts with HCl in the combustion gases. At CFBC operating temperatures, this reaction is highly reversible, and significant HCl capture does not occur[25,26]. Clearly, however, this reaction (or the catalytic effect of limestone) is sufficient to reduce chlorine inhibition of the CO oxidation reaction.

The OGDEN PCB tests (see Table 2) were carried out with the addition of limestone giving Ca: Cl_2 mole ratios in excess of 10:1 that are much higher than the ratios tested in the CANMET program. Based on the above test data, there was sufficient limestone in the OGDEN tests to eliminate any possibility of chlorine inhibition of the CO oxidation reaction. Therefore, the earlier observations on process scale-up are probably correct: the larger commercial CFBC should, under comparable process conditions, exhibit lower CO levels than the CANMET CFBC.

The absence of limestone in the waste feed is a result of selecting silica sand as a solid waste surrogate. The sand was intended to simulate the PCB-contamination soils that are expected during commercial operation. Unlike most native soils in Quebec, this sand contains negligible amounts of limestone (see Table 6). Had typical Quebec soil been used for the solid waste surrogate, it is likely that no additional limestone would have been required.

Indeed, the St-Basile contaminated soil has a natural limestone content of 7% (w/w). Use of this soil at CANMET would have resulted in 21 kg/h of $CaCO_3$, which is slightly above the 16 kg/h fed in test 4.

The combined effect of the presence of natural limestone in the soil and the decrease in CO with a 36-in. plant leads us to conclude that CO levels during the Quebec project will be maintained within regulatory limits without external limestone addition.

CONCLUSIONS

The test program has successfully met all of its objectives:

1. Reproducibility and stable operation of the CFBC were demonstrated under commercial CFBC operating conditions.

2. Flue gas sampling showed that emissions of pollutants were very low and well under regulatory limits. Waste DREs in excess of 99.9999% and contaminate-free solid byproducts were proven in replicate testing. Stack dioxin and furan levels were slightly above regulatory limits in the absence of a scrubbing system. Tests were done under more conservative conditions than those expected for commercial operation: lower gas residence time, higher chlorine and solid feed rates.

3. The presence of limestone within the bed leads to a reaction with the HCl produced or to a catalytic reaction and is sufficient to reduce chlorine inhibition of the CO oxidation reaction.

4. The performance of various components was evaluated and led to the following observations:

   -The test program demonstrated that the CANMET CFBC, when properly operated, can easily and efficiently incinerate the PCB surrogate. It was demonstrated that proper operation includes (1) the use of appropriate liquid waste feed pumps and (2) use of an automatic interlock system to prevent waste incineration under non-typical process conditions. Due to the absence of a scrubbing system in the CANMET plant, the only regulatory requirement not fully satisfied is the limit on stack emissions of dioxin and furan. Even here, operation within 20% of the regulatory limit was demonstrated. CINTEC's planned addition of a dry scrubber to treat stack gases guarantees that this stack limit will be satisfied[16].

   -The test program showed the need to co-feed some limestone with the solid waste surrogate in order to meet the regulatory CO standards. It is likely that the larger commercial CFBC will not require supplemental limestone for two reasons: (1) much of the PCB-contaminated waste to be treated already contains native limestone, and (2) lower CO emissions are expected in the commercial CINTEC CFBC than in the smaller CANMET pilot plant CFBC[14].

ACKNOWLEDGMENTS

This experimental program was a collaborative effort among several groups. The authors gratefully acknowledge the contributions of the engineering and technical staffs from CANMET, SNC•LAVALIN, CINTEC, and a number of other parties that contributed to the success of this experimental investigation.

List of Acronyms:

CANMET	:	Canada Centre for Mineral and Energy Technology
CB	:	Chlorobenzene
CE	:	Combustion Efficiency
CFBC	:	Circulating Fluidized Bed Combustor
DCB	:	Meta (1,3)-Dichlorobenzene
DRE	:	Destruction and Removal Efficiency
GAT	:	General Atomic Technologies Inc.
MEW	:	Ministry of the Environment and Wildlife
NA	:	Not Available
OES	:	OGDEN Environmental Services
PCB	:	Polychlorinated Biphenyl
PCE	:	Perchloroethylene
RFP	:	Request For Proposal
TCDD	:	Tetra-Chloro-Dibenzo-Dioxin
TSCA	:	Toxic Substance Control Act
U.S. EPA	:	United States Environmental Protection Agency

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