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Experimental Burning of Waste Oil as a Fuel in Cement Manufacture

S P E C I M E N

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EXPERIMENTAL BURNING OF WASTE OIL

AS A FUEL IN CEMENT MANUFACTURE

by

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ABSTRACT

An experimental program was carried out at the St. Lawrence
Cement Company Limited, Mississauga, Ontario, in which 330,000 gallons
of used lubricating oil were burned as a portion of the total fuel
requirement for a dry-process cement kiln. The system tested uses a
dual four-stage preheater with a by-pass. The oil was primarily composed
of automotive crankcase drainings and contained approximately 0.6 percent
lead, 0.15 percent bromine, 0.1 percent zinc and 0.1 percent phosphorus.

Lead, zinc and phosphorus emissions in the kiln exhaust
gases were not found to be increased during waste oil burning. A
small reduction in particulate emissions was found during waste oil
burning. A small increase in bromide emissions was also found to occur.

A material balance was carried out for Pb, Br, Zn and P
to confirm the emission data. It indicated that these elements were
retained in the process solids. Lead, zinc, phosphorus and some of
the bromine was retained in the collected dust from the precipitator
on the by-pass system.

RESUME

Un programme expérimental de combustion de 330,000 gallons
d'huile de graissage usée a été réalisé à la St. Lawrence Cement Company
Limited de Mississauga, Ontario. Cette quantité n'était qu'une fraction
de tout le combustible nécessaire à la marche d'un four à ciment fabriqué
par voie sèche. Le procédé étudié comportait l'utilisation d'un pré-
chauffeur double à quatre étages pourvu d'un dispositif de dérivation.
L'huile provenait surtout de carters de moteurs et avait une teneur
approximative de 0.6% en plomb, 0.15% en brome, 0.1% en zinc et 0.1% en
phosphore.

En cours k'expérience on n'a pas observé d'augmentation des
émissions de plomb, de zinc et de phosphore dans les gaz du four. On
a cependant observé une modeste réduction des émissions de particules
et une augmentation mineure de celles du brome (bromures).

On a établi le bilan matière du Pb, Br, Zn et P pour confirmer
les données sur les émissions. On a pu montrer que ces éléments demeu-
raient dans les solides produits, les trois derniers et un peu du premier
demeurant aussi dans le clinkerer; la plus grande partie du brome se retrou-
vait dans la poussière recueillie dans le précipitateur couplé au dispositif
de dérivation.

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EXECUTIVE OUTLINE

Safe disposal of used lubricating oil to meet environmental and health criteria presents a serious problem. Some 188 million gallons of lubricating oils were sold in Canada during 1972, and, as sales have increased since then, the problem is one of mounting concern.

Traditionally, primitive disposal methods, such as road oiling, have been used with little regard for environmental effects. When used lubricating oil is employed as a dust palliative as little as one percent remains on the road; the remainder, with its toxic content is released into the environment.

In June, 1974 Environment Canada issued a report (1) on the nature and magnitude of the used lubricating oil problem in Canada. Its findings revealed that most current disposal practices are both wasteful of a non-renewable resource and pose significant pollution hazards.

Although recycling may at first appear to be the prefered solution, economic and other factors restrict it to a small proportion of used lubricating oil generated each year. Some railway companies have diesel lubricating oil custom re-refined for them.

Among the more promising means of disposal cited in the report was that of used lubricating oil as part of the fuel requirement in the manufacture of cement. Preliminary studies suggested that toxic substances could be trapped in the clinker, permitting used lubricating oil to be a fuel source in an environmentally acceptable method of disposal.

Between March 23, 1974, and May 30, 1974, an extensive experiment was performed utilizing used lubricating oil as a partial fuel in a dry process rotary kiln with a four-stage suspension preheater and electrostatic precipitator. The experiment was monitored by Environment Canada, the Ministry of the Environment of Ontario and the Ontario Research Foundation. Results indicated that emissions of toxic substances into the atmosphere were negligible. In fact, the total particulate emission was slightly reduced when using a mix of used lubrication oil and No. 6 fuel oil as compared with normal operations.

As there were no significant deleterious effects on the quality of cement produced under experimental conditions, burning used lubricating oil, for this purpose, appears to be a highly satisfactory disposal method. An additional benefit lies in the fact that in Canada cement kilns are usually located close to urban areas which generate the largest proportion of used lubricating oil. This minimizes transportation and collection costs. The results show that the burning of waste oil in a cement kiln presents an acceptable solution to this difficult waste disposal problem.

SUMMARY

During 1974, 330,000 gallons of used lubricating oil were burned in a carefully controlled experimental trial as a partial fuel in the St. Lawrence Cement Co. dry-process cement kiln at Mississauga, Ontario. The experiment was conducted to determine whether the gas-scrubbing action of the kiln (already known to be effective in removing sulphur from kiln exhaust gases) would permit waste oil to be burned without an adverse effect on air pollution.

The oil came from automotive crankcase drainings and was found to contain an average 0.6 percent lead, 0.15 percent bromine, 0.1 percent zinc and 0.1 percent phosphorus.

It is known that waste automotive oils when burned in conventional oil-fired boilers or furnaces cause about 50 percent of the lead to be emitted to the atmosphere during normal periods of burning and the remainder to be emitted during soot-blowing. No data on the emission of the other pollutants are available but it is presumed that these too will be entirely emitted from conventional combustion equipment. Similarly, use of these oils for dust control on roads requires the direct application of the polluting elements to the environment.

Atmospheric emission measurements were made before, during and after a test period of waste oil burning in the cement kiln. Data from these tests showed that burning waste oil in a suspension preheater kiln did not contribute to emissions of lead, zinc and phosphorus to the atmosphere. A small emission of bromine (presumably as bromide) was attributed to waste oil burning.

In contrast to reported findings with oil-fired boilers the results of this program showed that, on the average, emissions from the cement kiln were restricted to approximately 0.03 percent of the lead and 0.7 percent of the bromine put in with the waste oil.

In addition to the emission measurements a mass balance was carried out on lead, bromine, zinc and phosphorus. This showed that the lead, bromine, zinc and phosphorus were retained in the process solids. Lead, zinc and phosphorus were largely retained in the cement

clinker along with some of the bromine. Most of the bromine was retained as bromide in a pelletized dust, collected from the electrostatic precipitator on the by-pass system.

Both the mass balance and air emissions data from this experiment have illustrated the effectiveness of the gas-scrubbing action of the cement kiln.

Burning waste oil caused no detrimental effects on the hydraulic properties of the cement produced.

Used lubricating oils are largely available at any location in proportion to population. Similarly, the manufacture of Portland cement is carried out in plants located close to most of the major population centres in Canada. This proximity of the used oil supply and the cement plants offers advantages in terms of transportation costs.

It is recommended that used lubricating oils may be employed as fuels in cement kilns, where particulate emissions are reasonably under control, without adverse effects on air pollution. Burning used oils in cement kilns is considered a valuable means of destroying this form of pollutant while recovering useful heat values and hence conserving a non-renewable natural resource.

RECOMMENDATIONS

Burning used lubricating oil as a partial fuel in a dry process rotary cement kiln, with a dual four-stage preheater and electrostatic precipitators, has been shown not to cause an adverse effect on air pollution. This is in contrast to published findings on air pollution caused by burning used oils in conventional oil-fired boilers and furnaces. Under these circumstances it has been reported that about 50 percent of the lead in the used oil will be emitted to the atmosphere during normal burning periods and the balance during soot-blowing (1).

The following recommendations are the outcome of the present report:

1. Used lubricating oils may be employed as fuels in cement kilns, where particulate emissions are reasonably under control, without adverse effects on air pollution. Burning used oils in cement kilns is considered a valuable means of destroying this form of pollutant while recovering useful heat values and hence conserving a non-replaceable natural resource.

2. Burning used lubricating oil in cement kilns offers a significant environmental improvement over burning in conventional oil-fired boiler systems or used as road-oil without pretreatment.

As this experiment was done on a suspension preheater dry process kiln, a comparable experiment using a long-straight kiln (dry process or wet process type) would confirm the extrapolation of these findings to other types of kiln. In any future studies, it is considered sufficient to monitor lead and bromine in the cement production process.

1.   INTRODUCTION

Sales of lubricating oils in Canada reported for 1972 totaled approximately 188 MM gallons (1). Each year, up to 80 MM gallons end up as "waste-oil" requiring disposal or destruction. The disposal of these used oils, in particular automobile crankcase oils which are contaminated with lead, zinc, phosphorus and other chemical elements, is a national problem of considerable magnitude. The concept of using contaminated oils as fuels in a manner which does not present a pollution hazard is a very attractive alternative to disposal. The manufacture of Portland cement demands a high consumption of hydrocarbon fuel and is carried out in plants generally located close to most of the major population centres in Canada. The availability of used oil at any location is proportional to population. Its use as a cement kiln fuel could provide a practical means of local disposal, since collection and transportation cost can be prohibitive beyond a 150 mile radius of the disposal site.

This research program has been carried out to determine whether waste oils can be used in a suspension preheater cement kiln without causing adverse air pollution. The approach taken was to monitor atmospheric emission of selected elements present as contaminants in used oils. A material balance on these elements was made to confirm the emission findings.

2. CEMENT MANUFACTURING

2.1 General Principles

Portland cement is produced by igniting (burning) an accurately proportioned mixture (raw feed) of finely ground limestone, silica, alumina, and iron oxide. The kiln discharge (clinker) is a chemically complex mixture of calcium silicates, aluminates and ferrites which when ground and blended with from 2 to 5 percent of calcium sulphate is sold as Portland cement. A more detailed description is given in Appendix F. Typical raw materials and the necessary elements that they provide are given in Table 1.

The principal process methods used in cement manufacture are given in Table 2 together with their approximate heat requirements. The 80 MM gallons of used lubricating oils could amount to about 15% of fuel needs of the Canadian cement industry based on a total annual cement production of 15×10^6 tons. The lowest heat requirement is in a dry kiln with a suspension preheater. This more efficient utilization of fuel is attained by the heat recovery in the preheater, with the raw material being fed into and counter current to the hot gases exiting from the rotary kiln, (see Section 2.2.1 (b)).

In addition to the cement oxides (CaO, SiO_2, Al_2O_3 and Fe_2O_3), the raw materials (raw feed or raw mix) frequently contain a percentage of other elements in minor proportions. Magnesia (MgO) is found in varying degrees (see Table 1) and acts as a flux which renders burning slightly easier, although an excess of MgO in finished cement is undesirable since it causes deleterious expansion in concrete products. It is therefore limited by such material specifications as CSA A-5 and ASTM C-150. Alkalies (K_2O and Na_2O) frequently are found in raw materials. In excess they are deleterious in the kiln and in the finished cement. MgO, K_2O and Na_2O may be controlled by choice of raw materials while process controls may be used to reduce alkalies. Sulphur as sulphate is present in all Portland cements. It is usually derived by absorption of sulphur oxides from fuel and raw materials into the clinker, additional sulphate is added as gypsum when clinker is ground to form Portland cement. The ability of cement processes to absorb

TABLE 1. TYPICAL RAW MATERIALS USED IN CEMENT MANUFACTURE AND THEIR COMPOSITIONS

	wt %				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Limestone	5.7	0.8	0.3	52.0	0.4
High silica limestone	36.8	1.8	0.6	33.6	0.5
Cement stone	18.0	5.0	1.5	40.0	2.0
Shale	53.8	18.9	7.7	3.2	2.2
Sand	70.0	15.0	5.0	0.8	0.2
Clay	61.0	16.9	12.4	0.5	0.4

TABLE 2. HEAT CONSUMPTION (APPROX.) OF THE VARIOUS CEMENT PROCESSES

Wet	Kcal/Kg	Btu/lb
Long kiln	1650	2900
Calcinator and short kiln	1300	2300
Semi-Wet		
Preheater and short kiln	1000	1800
Dry		
Long Kiln	1300	2300
Suspension preheater and short kiln	875	1500

PRECIPITATOR

KILN EXH. FAN

DUST RETURN

STAGE I

RAW MEAL FEED

STAGE II

STAGE III

STAGE IV

TO BY-PASS

MATERIAL FLOW

GAS FLOW

KILN

Figure 1   Principle of Fuller-Humboldt
Suspension Preheater

This procedure, being swept up with hot gases into one stage and then being dropped into the stream entering the next lowest stage, is repeated in stages 3 and 4 before the partially calcined feed enters the kiln.

The average retention time of the system is less than one minute.

A detailed description of the operation of the Humboldt preheater has been given by G. A. Schroth (7) from which article these notes have been abstracted.

The raw material enters Stage 1 and is preheated to approximately $600^{\circ}F$ while the gas temperature drops from 990 to $650^{\circ}F$. Corresponding heat exchanges occur in stages 2, 3 and 4 such that the material enters the rotary kiln at approximately $1475^{\circ}F$ having been decarbonated to a degree up to 50 percent. The gas temperature at the point of exit from the kiln into the preheater is 1900 to $2000^{\circ}F$.

The St. Lawrence Cement Co. preheater is a dual Fuller-Humboldt unit with the normal four stages in each.

(c) The alkali by-pass system is an important unit in relation to this study. In common with other plants using suspension preheater systems, special measures have to be taken to reduce the build-up of chlorides and alkalies (as sodium and potassium sulphates and chlorides principally) in the system. At the St. Lawrence plant, a system is in use where a fraction of the kiln exhaust gases is by-passed through a conditioning tower. In the conditioning tower, water is sprayed into the gas stream to lower the temperature and condition the gases for precipitation. Concurrently, the gas velocity is reduced since the cross section of the tower is greater than that of the by-pass duct. The net effect of cooling and velocity reduction is to divide the particulate matter carried in the gas stream into two fractions.

A high alkali fraction (termed by-pass dust) becomes concentrated in a material stream which is ultimately collected in an electrostatic precipitator, pelletized and discarded. A fraction of lower alkali content (termed conditioning tower solids) is returned to the raw feed silos and ultimately recycled into the raw feed stream.

3.   WASTE OIL CONTAMINANTS AND THE SELECTION OF ELEMENTS FOR STUDY

A summary of the generally reported contaminants of used lubri-
cating oils is given in Table 3 (1), together with their expected ranges
of concentration. Those elements reported in waste oils with minimum
contamination concentrations greater than 100 ppm were initially selected
from this list. After rejecting those elements already present in
large quantities in cement manufacture (i.e. Ca, Si, Al, Fe and S), Pb,
Zn and P were selected for study.

Prior work at ORF and at St. Lawrence Cement Co. had shown
that bromine is frequently a significant contaminant in waste oils,
particularly automobile crankcase drainings. Analytical work associated
with combustion tests at Gulf Research and Development Co. in 1969, (8)
also showed bromine as a significant constituent of boiler deposits
after waste oils had been used as fuels. Surprisingly, other reports
of waste oil analyses have not included bromine or have reported very
low concentrations. The presence of bromine is to be expected from
the composition of the organo-lead anti-knock additives used in auto-
motive gasolines, which contain ethylene dichloride and ethylene
dibromide, (9). All of these elements have been identified by a number
of workers as present in automotive exhaust emissions (10, 11) and
some transfer of such compounds as lead chlorobromide to the crankcase
is to be expected in most auto engines.

For these reasons bromine was included in the mass balance
study. No attempt was made to obtain a balance on chlorine due to
the relatively large concentrations of this element in normal cement
process materials (about 0.04% in the raw meal, 0.015% in the clinker,
and 4.5% in the by-pass dust).

TABLE **3.** RANGE OF PROPERTIES OF USED LUBRICATING OILS

Property		Min.	Max.
Gravity, API at 60°F		20.7	27.9
Specific Gravity		0.887	0.934
Density	lb/US gal	7.40	7.78
	lb/Can gal	8.90	9.35
Viscosity, SUS at 100°F		87	837
	centistokes	17.3	180.6
Pour Point	°F	< -40	-30
Flash Point	°F	75	415
Heating Value	BTU/lb	13,571	19,300
	BTU/US gal	105,555	143,360
	BTU/Imp gal	126,560	171,890
Neutralization Number	mg KOH/g	4.0	14.3
B S & W	%v/v	0.1	22.0
Sulphur	%w/w	0.21	0.65
Ash	%w/w	0.03	3.78
Silicon	ppm	10	875
Calcium	ppm	700	3,000
Sodium	ppm	16	300
Iron	ppm	50	2,000
Magnesium	ppm	10	1,108
Lead	ppm	800	21,700
Vanadium	ppm	3	39
Copper	ppm	5	348
Barium	ppm	10	2,000
Zinc	ppm	300	3,000
Phosphorus	ppm	500	2,000
Tin	ppm	5	112
Chromium	ppm	8	50
Beryllium	ppm	6	
Manganese	ppm	5	10
Nickel	ppm	3	30

TABLE 3. (CONT'D)

Property		Value Min.	Max.
Cadmium	ppm	4	
Silver	ppm	1	
Strontium	ppm	10	30
Aluminum	ppm	10	800
Boron	ppm	3	20
Molybdenum	ppm	2	3
Titanium	ppm	5	30

NOTE: ppm - parts per million by weight.

Typical results, over a 4 year period, found at the St. Lawrence cement company were:

Lead	0.42
Zinc	0.05
Bromine	0.08
Water	19% w/w (MAX.)
Viscosity	1219 centistokes at $10^{\circ}F$
	220 centistokes at $60^{\circ}F$
Specific gravity*	0.9 at $60^{\circ}F$
Heat value	130-160 x 10^3 BTU/Imp. gal

* As a guide, if specific gravity exceeds 0.96, there is too much water for fuel use.

4.   DISCUSSION

The experimental work of this study has been designed to
examine the interaction between major waste oil contaminants and the
total production system. The work was carried out to test the hypothesis
that waste oil could be burned in the cement kiln without the adverse air
pollution concomitant with burning it in conventional boilers or
incinerators which do not have extensive abatement facilities to cope
with both normal and soot-blowing emissions.

The approach taken was to monitor normal plant kiln emissions
before, during and after a period of waste oil burning to determine
experimentally the effect of waste oil burning on air quality. In
addition a mass balance on the elements lead, bromine, zinc and phosphorus
was carried out to determine where each element was collected in the
process materials and the approximate extent of the retention.

The experimental program comprised three stages. The first
period was from March 9, 1974 to March 20, 1974 when the kiln was running
steadily with normal No. 6 fuel oil as the only fuel. From March 21
to March 30, 1974 attempts were made to start up waste oil feeding.
This was unsuccessful due to pump and meter failures (see Appendix D).
A kiln breakdown followed due to refractory failure. This resulted
in no production until April 13, 1974. This failure was not attributed
to the use of waste oil. From April 17 to May 7, 1974 waste oil was
fed as a partial substitute fuel at the daily rates indicated in Table
B.10. The study then continued to May 30, 1974 during which time the
kiln returned to normal running on No. 6 fuel oil with one short kiln
shutdown on May 15 and May 16, 1974. A total of 330,000 gal of waste
oil was burned.

4.1   Emissions

Generally, examination of stack emissions in the cement indus-
try has been limited to reporting particulate concentrations. Recently,
a survey was made of emissions from Canadian cement plants (12). The
data below are taken from this report to demonstrate the relative
particulate emissions measured during this experiment in comparison

with figures from the survey. From these data it may be concluded that the kiln emissions from this plant are low by current Canadian rates.

TABLE 4. KILN EMISSION FACTORS FOR CANADIAN CEMENT PLANTS, 1970 (12)

Region	Kiln Emissions (lb/ton clinker)
Ontario (average of 7 plants)	19.83
Quebec (average of 5 plants)	43.29
Balance of Canada (average of 12 plants)	17.12
Lowest	0.27
Highest	180.08
Average from present work	0.956

Three sets of data are available from the present test program. The first prior to burning waste oil, under normal plant operating conditions. The second was taken at intervals throughout the waste oil burning period. The third was taken some time after waste oil burning had ceased. From the data collected, this third period seems to have been a time of some routine minor disturbances in the process, since marked differences between the emissions from the two preheater stacks were found and a generally higher particulate emission was noted than during the first test series.

Table 5 summarizes the mean loadings (mg/m^3) and the mean emission rates (lb/hr) for each set of tests, reported individually for particulates, lead, zinc, bromine and phosphorus. Detailed results for each of the 36 tests are given in Table 6.

A review of the sampling data showed that in 11 of the 36 tests sampling was super-isokinetic but to a degree not over 110%. This means that emission rates may be lower than those reported in some cases.

Comparison of average particulate loading data shows that between the first series of tests and the tests carried out during used oil burning there was a reduction in total particulate emissions. Part of this improvement may have been due to the additional water introduced

TABLE 5. SUMMARY OF EMISSIONS

Stack	Test Period	Fuel	Mean Flow (DSCFM)	Mean Loading (mg/m^3)					Mean Emission Rate (lb/hr)				
				Particulate	Pb	Zn	Br	P	Particulate	Pb	Zn	Br	P
NW	11/3/74		61000	320.4	.0456	.0279	.0784	.1169	73.5	.0104	.0062	.0180	.0278
NE	to	No. 6	63000	162.0	.0145	.0175	.0374	.0519	38.7	.0034	.0042	.0090	.0125
SE	15/3/74		9500	89.0	.0305	0	.5458	-----	3.42	.0011	0	.0210	-----
Total									115.6	.0149	.0104	.0480	.0393
NW	22/4/74	No. 6	60000	251.8	.0297	.0267	.2496	.0792	56.6	.0067	.0060	.0561	.0178
NE	to	+	61300	103.0	.0140	.0116	.0866	.0307	25.0	.0032	.0027	.0199	.0071
SE	2/5/74	W.O.	10500	86.6	.0901	.0166	.6017	-----	1.72	.0032	.0007	.0243	-----
Total									83.3	.0131	.0094	.1003	.0249
NW	28/5/74		57200	87.9	.0221	.0100	.0411	.0223	18.8	.0048	.0021	.0087	.0048
NE	to	No. 6	62500	547.6	.0399	.0580	.1669	.1678	128.3	.0118	.0134	.0391	.0392
SE	30/5/74		15200	264.3	.1230	.0019	1.1732	----	14.4	.0068	.0001	.0639	-----
Total									* 161.5	.0234	.0156	.1117	.0440

* - Note precipitator difficulties on third test period.

TABLE 6.   EMISSION RATES

Test Date	Stack	Stack Gas Conditions				Emission Rates (lb/hr)					% Isokinetic
		Flow (dscfm)	Velocity (ft/sec)	Temperature (°F)	Moisture (%)	Particulate	Pb	Br	Zn	P	
11/3	NW	60700	56.09	580	8.5	65.61	.0087	.0161	.0055	.0224	97.63
12/3	NW	61800	57.67	589	8.5	75.38	.0067	.0226	.0074	.0304	98.69
12/3	NW	61100	57.10	591	8.4	79.46	.0158	.0153	.0057	.0276	99.44
22/4	NW	60900	58.75	588	10.3	71.14	.0089	.0581	.0091	.0216	104.09
23/4	NW	59900	58.09	588	9.3	59.59	.0056	.0348	.0049	.0181	98.41
30/4	NW	59600	56.79	601	8.4	70.89	.0049	.0644	.0089	.0248	102.97
30/4	NW	60100	60.00	599	11.2	54.94	.0080	.0548	.0048	.0190	105.76
1/5	NW	60100	58.94	600	11.0	58.12	.0046	.0708	.0055	.0162	103.53
2/5	NW	59400	56.09	594	8.9	24.99	.0080	.0538	.0029	.0071	103.68
29/5	NW	56300	54.34	604	8.5	18.77	.0007	.0163	.0016	.0045	107.94
29/5	NW	57500	55.43	600	8.7	16.05	.0007	.0049	.0024	.0038	108.71
30/5	NW	57700	55.84	611	8.5	21.68	.0129	.0050	.0024	.0060	108.84
11/3	NE	62600	58.82	598	8.3	33.37	.0031	.0077	.0033	.0108	98.16
12/3	NE	63800	59.43	600	7.5	33.09	.0062	.0078	.0047	.0101	99.25
12/3	NE	64700	60.16	599	7.3	49.73	.0010	.0114	.0045	.0163	100.00
22/4	NE	62100	59.93	607	8.7	21.28	.0045	.0135	.0035	.0071	103.38
23/4	NE	62900	60.30	593	8.9	21.30	.0044	.0146	.0028	.0082	97.51
30/4	NE	62200	59.75	613	8.0	18.93	.0017	.0190	.0020	.0068	102.03
30/4	NE	58200	56.79	609	9.9	18.09	.0019	.0136	.0018	.0061	104.40
1/5	NE	61400	59.32	606	9.1	21.85	.0036	.0188	.0033	.0071	103.18
2/5	NE	61100	58.33	606	9.0	40.42	***	.0398	***	***	102.28
29/5	NE	61100	60.48	619	9.5	120.77	.0113	.0395	.0112	.0423	109.39
29/5	NE	62200	61.38	620	9.0	114.14	.0117	.0311	.0138	.0342	108.70
30/5	NE	64000	61.63	600	9.0	149.95	.0124	.0467	.0152	.0412	108.89

TABLE 6.   (CONT'D)

| Test Date | Stack | Stack Gas Conditions | | | | Emission Rates (lb/hr) | | | | | % Isokinetic |
		Flow (dscfm)	Velocity (ft/sec)	Temperature (°F)	Moisture (%)	Particulate	Pb	Br	Zn	P	
14/3	SE	12100	32.15	272	22.5	3.71	.0002	.0153	0	*** ----	102.05
14/3	Se	10400	27.13	274	22.1	3.08	.0010	.0321	0	----	103.98
15/3	Se	8800	22.45	269	19.7	3.49	.0020	.0157	0	----	89.86
22/4	SE	11400	30.63	278	21.5	0.66	.0006	.0042	.0011	----	93.56
23/4	SE	12000	33.69	291	23.5	4.92	.0030	.0839	.0019	----	95.69
30/4	SE	10300	28.45	305	21.6	0.76	.0025	.0094	0	----	96.57
30/4	SE	9830	27.25	310	21.3	1.96	.0019	.0259	.0007	----	101.59
1/5	SE	8780	24.01	300	21.1	1.58	.0084	.0178	.0004	----	95.15
2/5	SE	8220	21.23	293	18.0	0.42	.0027	.0048	0	----	105.53
29/5	SE	14500	36.93	261	18.9	12.95	.0075	.0687	0	----	97.16
29/5	SE	14400	37.01	265	19.0	27.61	.0118	.1130	.0003	----	97.46
30/5	SE	16700	42.64	255	20.1	2.67	.0010	.0100	0	----	97.07

***   No Data Available

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with used oil. That water can improve precipitator efficiency even at
600° F has been discussed by White (13) with particular reference to cement
manufacturing processes.

No significant changes were noted in the measured average loadings
or emission rates of Pb, Zn or P. A small increase in average emissions
for Br did occur during used oil burning. Lead and bromine were found
in increased concentrations in the particulate materials collected during
used oil burning. This effect is not reflected in the average loading
recorded for these elements due to the reduction in total particulate
emissions discussed above.

Concentrations of zinc and phosphorus in filter particulates
were not found to be related in any way to used oil burning. This is not
surprising since these elements are largely present in the system as
a result of solid raw material composition, rather than being supplied
by the fuel.

Considering the kiln system, it is to be expected that the pre-
heater emissions will consist largely of partly-calcined raw-meal, conta-
minated with components generated during burning, for example alkali
halides and sulphates. The extent to which the particulate materials
are contaminated is illustrated by the comparison of the particulate
analyses for lead, bromine, zinc and phosphorus with typical raw-meal
analyses given in Table 7.

TABLE 7.   COMPARISON OF RAW-MEAL AND PREHEATER PARTICULATE ANALYSES
            FOR Pb, Br, Zn and P

	Average Raw-Meal Analysis (%)	Average Particulate Analysis (%)	
		Baseline	Test Period
Pb	0.0006	0.0031	0.0088
Br	0.0008	0.035	0.104
Zn	0.0049	0.0089	0.0094
P	0.038	0.035	0.036

Using the emission rates found by this study, three cases
were examined by Dr. F. Frantisak of Ontario Ministry of the Environment,
Air Resources Branch to compute ground level concentrations (GLC).
The Air Resources Branch multi-stack, point of impingement program
was used and the following results were obtained for particulate maximum
GLC. (see Appendix G for explanation of dispersion.)

TABLE 8. PARTICULATE MAXIMUM GROUND LEVEL CONCENTRATIONS (GLC)

Case	Maximum Particulate GLC ($\mu g/m^3$)	
	C Stability	D Stability
1. Initial base tests, 12/3/74.	24.4 at 1900 m	15.5 at 6100 m
2. Waste Oil Burn Tests, 23/4/74	16.1 at 1900 m	10.2 at 5900 m
3. Final base tests, 29/5/74	33.9 at 1700 m	22.6 at 5100 m

These point of impingement levels (calculated ground level
point or point of impingement level concentrations) are well within
the Ontario regulation of 100 $\mu g/m^3$. Considering that the lead
composition of the particulate emissions are < 0.01%, similarly computed
lead impingement values would be less than 0.01 $\mu g/m^3$ which is substan-
tially below the Ontario regulation maximum permitted value of 5
$\mu g/m^3$.

A detailed comparison of the data from these emission tests
with data from reported waste oil burns in the conventional equipment
is given in Section 4.6 of this report. On the average, emissions from
the kiln were restricted to approximately 0.03 percent of the lead and
0.7 percent of the bromine introduced with the waste oil.

4.2   The Mass Balance

Four solid materials, raw-meal, clinker, by-pass dust and
conditioning tower solids together with No. 6 fuel oil and waste oil
were monitored for the elements Pb, Zn, Br and P. To determine a
mass balance, raw-meal feed and fuel are the only input streams.

Clinker (the product) and by-pass dust (a pelletized waste product) form the output streams. Conditioning tower solids are returned by a long-term cycle (of unknown duration) to the raw-meal storage silos. In order to avoid accumulative accounting of the elements carried in this stream, the conditioning tower solids were accounted as an output stream in the daily mass balance calculations. To calculate the mass balance, each stream was sampled and quantified using a period of 24 hours as the unit base for calculation. Tables 9 and 10 summarize the mass balance findings. Separate balances were calculated, one for the whole test period using data from St. Lawrence Cement Co.; the other for the period April 27 to May 10 using data from Ontario Research Foundation. Methods of sampling and quantifying material streams are detailed in Appendix A. Details of analytical results, comparisons of analytical agreement, calculations and tables of daily mass balances are given in Appendix B.

4.2.1 Significance of Mass Balance

In common with other material balance experiments on large scale production systems, the material accounting in this experiment shows apparent losses and gains when the data are expressed in percent input or retention. These should not be regarded as real system losses or gains. Rather they reflect the aggregate effects of random or minor systematic errors in weighing and quantifying very large quantities of materials and in analysing samples at concentrations as low as 1×10^{-4} percent. Some measure of the limitations imposed by these practical conditions may be obtained by considering the following illustration:

Material Stream	Quantity (tons/day)	lb/24 hr Equivalent to 0.0001%
Raw meal feed	5,000	10
Clinker	3,000	6

Thus, an analytical error of $\pm$ 0.0001% imposes a quantitation uncertainty of approximately $\pm$ 10 lb/24 hr on the material account for the analysed element.

TABLE 9. ACCUMULATED MASS BALANCES *

ACCUMULATION PERIOD	FUEL **	ELEMENT	ACCUMULATED INPUT (LB) (T_I)	% OF T_I DERIVED FROM WASTE OIL	ACCUMULATED RETENTION (LB) (T_R)	% OF T_I RETAINED IN: CLINKER	BP DUST	TOTAL
9/3 to 20/3	#6	Pb	502	0	627	117.1	7.8	124.9
		Br	590	0	564	55.4	40.2	95.6
		Zn	5,125	0	5,909	114.9	0.3	115.2
		P	40,260	0	39,500	98.0	0.1	98.1
17/4 to 7/5	#6 + WO	Pb	13,731	96.6	12,246	85.0	4.2	89.2
+		Br	6,187	52.3	4,466	35.3	36.9	72.2
8/5 to 30/5	#6	Zn	22,168	10.6	24,526	110.6	0.2	110.8
		P	150,135	1.7	147,833	98.2	0.1	98.3

*   Calculated from SLC data

** #6 Indicates Bunker "C" fuel oil as the only fuel.

#6 and WO indicates Bunker "C" fuel oil and waste oil as fuels.

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TABLE 10. COMPARISON OF ACCUMALATED MASS BALANCES
(for period 27/4/74 to 10/5/74)

ELEMENT	LABORATORY	ACCUMULATED INPUT (lb) (T_R)	ACCUMULATED RETENTION (lb) (T_R)	%OF T_I RETAINED IN:		
				CLINKER	BP DUST	TOTAL
Pb	ORF	7,447	6,766	86.5	4.4	90.9
	SLC	7,432	6,239	79.7	4.2	83.9
Br	ORF	2,429	1,827	17.0	58.3	75.3
	SLC	2,655	1,981	31.0	43.6	74.6
Zn	ORF	6,479	5,729	88.0	0.2	88.2
	SLC	8,069	8,876	109.8	0.2	110.0
P	ORF	50,831	53,441	105.0	0.1	105.1
	SLC	52,469	53,305	101.6	0.04	101.6

Consider the following example of typical lead balance accounting from analytical data:

Material Stream	Quantity	Analytical Limit of Detection	Approximate Variability Range
	(lb/day)	% w/w	(lb/day)
Raw Meal Feed	10×10^6	$\pm$ .0003	$\pm$ 30
Clinker	6×10^6	$\pm$ .0004	$\pm$ 24
Waste Oil	180×10^3	$\pm$ .002	$\pm$ 4
Total Variability Range			$\pm$ 58

Approximate Average Lead Input: 800 lb/day

Clearly no attempt should be made to equate material balance losses with true losses from the process. Losses due to emissions were accounted by the separate emissions testing in this program. The material balance serves to show the overall order of retention, the material stream in which the elements studied are found, and confirms the emission data.

4.2.2   Lead retention

The results of the mass balance show that 89 percent of the total lead in the system, most of which originates from waste oil, is retained in the process solids; from 75 to 85 percent in the clinker and 9 percent in the conditioning tower solids.

The by-pass dust, the only material discarded (in pelletized form), was found to retain about 4% of the total lead.

No literature data have been found to explain the behaviour of lead in cement burning although Blaine et al (3) have found up to 0.05% Pb in some production cements. At first sight, considering the removal of alkali metals from clinker with halides it might be expected that lead halide volatization should occur.

Consider the vapour pressure data shown in Table 11. Clearly lead halides boil well below maximum kiln temperatures. The finding that lead is largely concentrated into the clinker would suggest that lead injected with fuel must be either oxidized or taken into solid solution in the clinker in the body of the kiln.

TABLE 11. VAPOUR PRESSURES OF SELECTED COMPOUNDS (14)

Compound or Element	Temperature (^{o}C) of indicated vapour pressure
	1 mm	10 mm	40 mm	100 mm	400 mm	760 mm
KBr	795	940	1050	1137	1297	1383
KCl	821	968	1078	1164	1322	1407
NaBr	806	952	1063	1148	1304	1392
NaCl	865	1017	1131	1220	1379	1465
$PbBr_2$	513	610	686	745	856	914
$PbCl_2$	547	648	725	784	893	954
Pb (metal)	973	1162	1309	1421	1630	1744
PbO	943	1085	1189	1265	1402	1472

4.2.3 Phosphorus and zinc retention

Both phosphorus and zinc were found to be completely contained by the system. The containment was almost entirely within the clinker with only very minor percentages reported in the conditioning tower solids and by-pass dusts. Both elements were predominantly supplied by raw meal rather than through introduction from waste oil.

The behaviour of phosphorus in cement burning has been examined by a number of workers who have shown it to be combined as ortho-phosphate in the silicate phases (15). Steinour (16) studied production cements with up to 0.37% P_2O_5, while Blaine et al found commercial cements to contain up to 0.57% P. Sichov (17) indicated that the permitted phosphorus in clinker is 0.1 to 0.2%, calculated as P_2O_5, this restriction being for the quality of the clinker rather than a limitation on how much P_2O_5 clinker will absorb. It is known that P_2O_5 will be retained in clinker to much higher concentrations. For example, in Uganda, clinker with 2% P_2O_5 is commercially produced (15).

Zinc has been shown to replace calcium in the tricalcium silicate lattice (18, 19). The study by Blaine et al reported up to 0.2% Zn in production cements. The findings of this work are therefore consistent with previous research reports.

4.2.4   Bromine retention

It is general knowledge that chlorine in various forms has been used extensively for many years as an additive to reduce alkalies in the clinker (20, 21, 22). Alkali chlorides are readily formed in the burning zone and are volatilized in the kiln. Ultimately they are collected in the precipitator system. Although data is lacking on bromine, it was expected, due to the great similarity between bromine and chlorine, that the same association with alkali would occur. Evidence to this effect can be seen by the low concentration of bromine in the clinker and the higher concentration in the by-pass dust. Despite levels so low as to make analyses extremely difficult, a fairly good balance was obtained; greater than 70 percent of the total bromide was found in the process solids. As would be expected the majority of the bromide was reported in the collected by-pass precipitator dust. This indicates that the bromine leaves the kiln in a form which is readily collected in the by-pass precipitator. It can be assumed that the bulk of the bromine is collected as potassium bromide, since the potassium halides are more easily volatilized than sodium halides.

4.2.5   Minor contaminants of waste oil

As stated previously, the average analyses of waste oils indicate trace quantities of other elements at concentrations too low for the balance measurements. Assuming complete absorption of each of the trace elements reported from waste oils into clinker produced under conditions similar to the present program, it is possible to calculate the percent absolute increase of these elements in the clinker. The results of such calculations are given in Table 12 and demonstrate the impracticality of attempting a material balance.

The results obtained for lead, phosphorus, bromine and zinc allow some predictions to be made in the following manner. Calcium, silicon, magnesium, iron and aluminum are all major cement components. Their inclusion in the system is therefore expected to be normal for these elements as components of all the relevant process solids. Their emission will be restricted to the low levels of particulate emission normal to production. Barium has been shown to substitute in the

TABLE 12. CALCULATED INCREASE IN CLINKER OF ELEMENTAL OXIDES FROM WASTE OIL

Element	Pounds of Combustion Product per 10,000 U.S. Gallons*	% Absolute Increase of Oxide in Clinker
lead	720	0.0315
phosphorus	264	0.0114
calcium	220	0.0095
silicon	64	0.0028
magnesium	61	0.0026
zinc	58	0.0025
barium	57	0.0025
iron	42	0.0018
aluminum	6.3	0.00027
boron	5.9	0.00025
chromium	4.8	0.00021
nickel	2.4	0.00010
copper	1.6	0.000069
tin	1.3	0.000056

* Data from W.C. McCrone provided by Environment Canada.

Assumptions: Oil Sp. Gr. = 0.9
Waste Oil Feed = 15 Can. gpm.
Clinker Production = 3000 TPD

dicalcium silicate lattice (23) with up to 0.2% BaO being reported in production cements (24). Manganese has been found in slag cements at up to 1% (24), and in regular Portland cements at up to 0.2% (3) as Mn, Mn^{2+} being capable of substituting for Ca^{2+} in dicalcium silicate in clinker (18, 25). Greater than 0.2% SrO is normal in cement clinkers. (24). These elements then may be expected to behave similarly to zinc and be contained in the clinker when present in waste oil.

With some of the remaining elements of used oil, the possibility exists that some volatile compounds could be formed. This is not likely however and in the case of most elements the reactions in the cement kiln are known. Even if some or any of these elements should form a volatile compound, it is likely, as in the case of lead, to be trapped.

Guinier and Regourd (18) indicated that a solid solution can form with 2% B_2O_3 in dicalcium silicate. The solubility even at $1430^{o}C$ is 0.01% B_2O_3 in dicalcium silicate (26).

Chromium in cement clinker has been extensively studied. Sichov (17) as well as Boikova (27) state that the maximum solubility of Cr_2O_3 in tricalcium silicate is 2%, while Guinier and Regourd (18) indicate that Cr^{3+} can substitute for Ca^{2+} in the dicalcium silicate lattice. Sakurai et al (28) indicate that the tetracalcium aluminoferrite phase in clinker can also absorb Cr_2O_3. Values of 0.01 to 0.02% Cr_2O_3 are normal in Portland cement. (3, 24).

4.3   Cement Quality

Midgley (29) has reported that small additions of lead cause very serious strength reduction and retardation of setting in Portland cement. Lea (24) indicates that these effects are obtained when as little as 0.001 percent soluble lead is added. While also observing set retardation, Lieber (30) obtained an improved compressive strength at late stages of hydration with the addition of lead compounds. In each of these studies soluble lead compounds were introduced to the hydrating cement/ water system. Conversely, Blaine et al (31) in studying trace elements present in cement in the form of clinker components did not find cor-

relation between lead content and compressive strength in samples hydrated normally for up to 28 days. These workers examined samples containing from 0 to 0.05 percent lead.

Zinc has also been found to be a set retarder (24, 30) and several patents exist for zinc compounds to be employed for this purpose (32). Blaine et al (31) considered zinc containment and found that compressive strengths may be higher after five years in cements with higher zinc content. The zinc content ranged up to 0.2 percent in the Blaine study.

Steinour has shown (16) that while soluble phosphate compounds added to cement act as retarders, little retardation is found due to phosphate in clinkers.

The reported effects made it necessary to examine the hydraulic properties of the cements produced from clinkers manufactured during waste oil burning. The details of the experimental work carried out to this purpose are given in Appendix C. Of the three elements lead, zinc and phosphorus, only lead was increased significantly in concentration in the clinkers as a result of burning waste oil. Cements containing lead over the range of concentrations produced during the burn were examined and no conclusive correlation between lead content and cement quality was found. The lead introduced from the waste oil did not appear to have any detrimental effect on the quality of the finished Portland cement (see Appendix C).

4.4 Trace Elements in Hydrated Portland Cement

The hydraulic properties of cement depend upon the formation of insoluble hydrates. These hydrates are complex solid solutions and contain many elements in variable relative proportions. For example, Al^{3+}, Fe^{3+}, and SO_4^{2-} can all enter the structure of the calcium silicate hydrate gel (24, 33). There is also evidence that hydrated magnesium silicates analogous to naturally occurring minerals such as serpentine can form in the hydration of cement (24). Cements can be produced by replacing calcium with strontium (24) or barium (24, 34) or by replacing silicon with germanium (24), the hydration products being analogous to those found in normal cements (24).

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Quaternary hydrates can be formed with calcium aluminate hydrates. Included among species which can enter this structure are Ga_2O_3, $CrO_4^{\cdot}$, SeO_4, Cl, Br, I, MnO_4, ClO_3, IO_3, BrO_3 and SiO_3 (20, 24, 35). The sulphate in cement adds a complication but substitution into the calcium aluminate sulphate hydrates by for example Cr_2O_3 (24) and Cl (24) has been reported. Complexes with Cl (20, 24, 35) and Br (36) (entering the calcium aluminate hydrate structure) have been extensively reported and the reactions are similar.

The retarding action of lead, copper and zinc salts discussed in section 4.3 has been attributed to the formation of insoluble hydrate salts of these elements on the surface of clinker particles (37). Lieber (30) in his study suggests that zinc and lead enter the structure of the insoluble calcium silicate hydrates. As indicated by Steinour, the phosphate in the clinker is insoluble in water. Thus for a substantial number of the contaminants in used lubrication oils, enough is known to state that most or all will remain within the insoluble structure of the hydrated compounds in concrete.

4.5   Extrapolation of Observations to Other Kiln Types

Because of the considerable variability of process types in the cement manufacturing industry, direct extrapolation of the observations of this research to other types of kilns is difficult. However, some broad generalizations may be made by considering the ways in which some elements are trapped in the kiln system. Three mechanisms operate in combination to build up an overall equilibrium concentration of these elements:

(i)   Gas scrubbing by process materials;

(ii)   the development of internal cycles;

(iii) electrostatic precipitator action.

The gas stream, flowing in opposition to the process materials in the cement kiln, contains dust, alkalies (Na_2O and K_2O), sulphur, and halides. These are produced by vaporization and dissociation of process solids and fuel components. Those elements, introduced with the waste oil, which are volatile at kiln and flame temperature will be expected also to travel with the gas stream. The raw mix in cement

processing has been shown to provide an excellent scrubbing action for sulphur compounds (2). In addition, the dry-process kiln with a preheater system is well known to have a scrubbing action in the case of alkali chlorides.

The concepts of kiln gas reaction chemistry are summarized by Locher, Sprung and Opitz (38). To illustrate the general principles, consider a kiln-preheater combination operating at normal clinkering temperature using a raw mix containing alkali metals and chlorides. Alkali halides have sufficiently high vapour pressures that they are volatilized in or before the burning zone of the kiln (material temperature in the burning zone is approximately $2650^{o}F$). The volatilized alkali chlorides are carried in the gas stream to the preheater where there is extensive mixing of gases with the cooler kiln feed in the cyclones. The alkali chlorides condense upon these particles and return to the kiln to again be volatilized, thereby setting up an internal cycle (39). The development of a cycle is characterized by a gradual build-up of the concentration of alkali chlorides to a steady (equilibrium) state in the clinker and dust components. This characteristic is a useful indication of the relative volatility of elemental components. The effect is illustrated by the behaviour of lead and bromine in the present study. An examination of the data in Tables B.15 and B.16 (Appendix B) shows how these two elements gradually increased in the clinker, bypass-dust and conditioning tower solids after waste oil was introduced and gradually declined after waste oil feeding was discontinued. Phosphorus exhibited no cycle whatsoever which would preclude formation of volatile compounds. A slight cycle may have been present in the case of zinc.

In trying to predict the possible effects of waste oils used in kilns, some consideration should be given to the influence of dust collection facilities on volatile component emissions. Norbom (40) has discussed these points at some length and some of the following items are condensed from his article.

When dust is removed from a gas stream using an electrostatic precipitator, the coarse dust will precipitate close to the collector inlet and the fine dust will precipitate close to the outlet. At low

precipitator efficiencies the smallest particles are the most likely ones to be emitted to the atmosphere. This would not present a serious potential problem except that there is a concentrating effect operating which causes volatile components to collect in the finest particulate matter in some process types.

Volatile components may enter the precipitator system in one of two ways:

(i)   They may crystallize into individual minute particles;

(ii) they may condense on particles of dust or feed materials.

Dust from a four-stage preheater kiln contains alkalis predominantly condensed onto solid particles of dust. In long open kilns (particularly long dry-process kilns) a large proportion of individually crystallized particles of small size are formed which collect preferentially in the outlet end of the precipitator.

Particulate matter from the fuel can reach the precipitator in two ways:

(i)   When injected with the fuel, the particle size is very small and these are liable to be carried directly to the precipitator in the gas stream;

(ii) Some fuel contaminants can react with material in the cement kiln to form volatile compounds which, in turn, are carried to the precipitator.

Without a by-pass, the four-stage suspension preheater is extremely efficient in scrubbing action since all the gas after passing through the straight kiln section is subjected to extensive mixing in four cyclones. Each subsequent mix occurs with material of lower temperature. Virtually no alkali chloride escapes to the precipitator, and this material is then trapped betwen the burning zone and the preheater (with the exception of traces retained in the clinker). The amount of alkali chlorides cycling in the kiln can become high enough that their condensation can cause severe plugging in the lowest stage of the preheater. Presently, it is claimed that a four-stage suspension

preheater cannot be operated without a by-pass if the chloride concentration in the raw meal exceeds 0.015%. The exit gas temperature of the four-stage suspension preheater kiln is approximately $615^{\circ}F$ to $660^{\circ}F$.

The addition of a by-pass to the four-stage preheater kiln adds a complication to a discussion of relative efficiencies of different kiln systems as scrubbers. Approximately 95% of the gas from the kiln is subjected to mixing with raw meal through the four cyclones. The remaining 5% is removed from the kiln with the volatile components still in the gaseous state or in the form of finely divided particulate matter. This portion of the gas is conditioned and cooled by a water spray to the optimum temperature for precipitator efficiency. The four-stage suspension preheater with a by-pass is still an excellent gas scrubber although the effectiveness of the scrubbing action will be reduced as compared to a four-stage preheater without by-pass. The scrubbing action of a four-stage preheater with by-pass is probably at least as good as a two-stage preheater kiln.

The two-stage suspension preheater kiln has two cyclones in which mixing raw meal with the gas stream occurs. The exit gas temperature is about $750^{\circ}F$ to $840^{\circ}F$. Therefore, this kiln is less efficient than the four-stage preheater kiln in its scrubbing action and for this reason has been recommended for use at chloride levels slightly higher than allowed in the four-stage preheater kiln.

The one-stage preheater has an exit gas temperature of about $840^{\circ}F$ to $930^{\circ}F$. There is only one cycle of mixing of gas and raw meal. This type of kiln is less efficient as a scrubber than either the two or four-stage preheater kiln and does not trap alkali chlorides to the same extent as either.

Long straight kilns with chain system heat exchangers are less efficient as gas scrubbers than are preheater kilns since the mixing of gas stream and materials is less efficient. Additionally, these kilns are the ones which are most susceptible to volatile component segregation in the electrostatic precipitator. As water in the slurry helps to absorb materials from the gas stream and wet materials adhere better to kiln walls and chains, the long straight wet process kiln will

presumably be a more efficient scrubber than a long straight dry process kiln.

In summary, it may be presumed from the studies carried out during this program that lead and bromine, once in the dust control system, will behave similarly to alkalis and chlorine. Three factors should then be considered in predicting the possible effects of waste oils in kilns of other types:

(i) Long open kilns will be more subject to concentration of volatile components in the dust fraction of finest particle size and hence more subject to adverse emissions if total dust control is not efficient.

(ii) In any system, good precipitator performance would be important for successful emission control when burning used oils.

(iii) It can be expected that virtually all of the bromine will be found in the kiln precipitator, presumably as alkali halide, in any kiln system except the four-stage preheater without by-pass. In all systems, the main portion of lead is expected to be in the clinker. The portion of lead collected at the precipitator can be expected to follow an inverse order of efficiencies of the kiln as a scrubber. No emission problem is to be expected in any system for zinc and phosphorus, although slight increase in levels at the precipitator of straight kilns will occur.

Since the present study shows that the zinc and phosphorus are retained almost completely in the clinker, it should not be necessary to monitor these elements if an experimental study of used lubricating oils is carried out on another cement kiln system. Lead is the contaminant of highest concentration in used lubricating oil and can form volatile compounds. The study of lead balances should indicate whether any detrimental effect on air quality would occur by burning used lubricating oil in other cement kilns. Bromine should also be monitored since

this element forms such volatile compounds, although it is expected that mainly alkali bromides will be formed.

It should be pointed out that the scrubbing action of the cement kiln only applies when there is adequate feed material being supplied. Under conditions of kiln start-up and shut-down, waste oil should not be fed as a fuel since at these times the kiln and preheater are empty of raw meal or clinker.

In summary the findings of this study should be applicable to kilns which have:

      (i)   good scrubbing of the combustion gases with the solids in the kiln.

     (ii)   electrostatic precipitators or other suitable means of recovering the finest particle matter.

As the precipitator efficiency decreases, this decrease would be greatest for the finest particulate matter, with which the contaminants of waste oil will be concentrated in open kilns. Thus, it would imply that as particulate emission increases, the emission of contaminants from the waste oil would increase at an even greater rate.

The present authors believe that future experiments, if carried out, will demonstrate that used lubricating oils can be burned in most types of cement kilns where current particulate emissions are reasonably under control. It should also be pointed out that in all such studies, due to build up of volatile compounds by internal cycles, stack sampling to determine emission of contaminants from waste oil should not be conducted until the oil has been burned for sufficient time to allow the system to reach steady state.

4.6   Comparison of Cement-Kiln Burning With Other Uses and Disposal Methods for Waste Oils

Of the estimated 80 million gallons of waste oil generated in Canada each year only 5-6 million gallons is being re-refined and put back into service as lubricating oil (1). The remainder is used on roads as dust suppressant, blended with fuels so that it can be burnt, or released into sewers. The findings of the present work should be considered in the perspective of these unsatisfactory and hazardous alternative methods of disposal.

Road oiling is the end use of most of the used oil picked up by waste oil collectors. To date this appears to have been economically attractive. However, a study by the EPA (41) on one particular road found that:

(a) 70-75% leaves the road by dust movement and runoff;

(b) 25-30% is lost by volatilization, adhesion to vehicles and biodegradation;

(c) as little as 1% remains on the road.

This study also showed that the vegetation in adjacent fields was high in metallic compounds that came from the road oil.

Used lubricating oils contain both portions of original additives and impurities acquired during service, and at the time of collection. The oils are generally undesirable for road surfacing because of the content of water oil emulsifiers included in their original formulation and because of the pollutants inherent in their chemical composition. To remove possibly dangerous contaminants and to improve their properties as dust suppressants, road oils would have to be treated before application. Treatment would consist of thermal dehydration, stripping to remove low flash point materials followed by sulphuric acid contacting. These or other alternative processes would add substantially to the costs of road oiling while doing nothing to reduce the loss of a non-renewable natural resource. In these respects the use of waste oil as a dust palliative must be regarded as an unsatisfactory disposal method.

Another use of waste oil is in the form of fuel. However, when employed indiscriminately the emission of non-combustible components in the oil make fuel use a method subject to considerable pollution hazards.

An extensive review of experimental burning of waste oil in conventional oil-fired boilers and furnaces is provided by Skinner (1). In this review, an EPA summary of ten burning trials is quoted with the conclusion that on average, about 50% of the lead present in waste oil fed to a burner is emitted during normal burning periods, the balance is emitted during soot blowing. The quantitative studies that have been reported have been confined to determining lead emissions in conventional combustion procedures.

A comparison of the present data with three published reports is given in Table 13 for lead emissions. The very substantial differences in the ratio Pb Out/Pb In (%) between the conventional burner tests and the cement plant experiment shows the potential overall improvement in terms of environmental impact to be gained by burning in the cement kiln rather than burning in conventional oil fired furnaces. There is also an advantage inherent in cement kiln burning that is not immediately apparent from much of the literature data. In the results shown in Table 13 only on one test are the effects of soot-blowing indicated. Test #10 reported for the Shell Oil experiment showed over 100% of the lead to be emitted during soot-blowing.

Soot-blowing is a pollution hazard of considerable importance when burning waste oils that may be illustrated by considering the following reported incidences.

The "Shell Oil Company Wood River Refinery Waste Oil Burning Test" (8) concluded:

"Even though stack samples do not account for loss of more than 50% of the lead during normal operations, it must be concluded that much larger amounts leave during soot-blowing operations. This is also confirmed by the absence of deposits in the boiler except in equilibrium amounts on the tubes."

The "Humble Oil and Refinery Company Waste Oil Burning Test" (1) at Sewell's Point Terminal showed ground level concentrations of less than 0.05 $\mu g/m^3$ during normal operation, rising to 0.67 $\mu g/m^3$ while soot-blowing. The soot from tubes contained 43% lead.

Data from the API waste oil burning test performed at Hawaiian Electric Co. Plant in January 1974, showed soot-blowing produced flakes up to 3-5 inches in size. In the earlier waste oil burning tests at this installation, large amounts of stack deposits were flaked off and sporadically discharged from the stacks, even at full load conditions (56 mw). The analysis of these flakes showed the major components to be iron (36.5% w/w), lead (4.3% w/w), calcium (1.7% w/w), zinc 0.4% w/w) and magnesium 0.3% w/w).

During these discharges, the lead emitted from the stack exceeded the lead in fuel fed to the boilers. This indicated emission

TABLE 13. COMPARISON OF LEAD EMISSIONS DURING WASTE OIL BURNING
AT ST. LAWRENCE CEMENT WITH OTHER TYPES OF COMBUSTION

Test Location	Sample Identification	Pb (lb/hr)		$\frac{Out}{In}$ (%)
		Total In	Total Out	
St. Lawrence Cement	22/4	45	0.014	.031
	23/4	42	0.013	.031
	30/4(1)	32	0.009	.029
	30/4(2)	32	0.012	.037
	1/5	32	0.017	.052
Humble, Baltimore Terminal (1)	15/8/72(1)	0.235	.104	44.8
	15/8/72(2)	0.235	.156	66.4
	18/9/72	0.227	.160	70.5
	22/9/72	1.17	.504	45.1
	23/9/72	1.17	.389	33.2
	6/9/72	1.14	.400	35.1
	8/9/72	0.914	.424	46.4
	11/9/72	0.933	.480	51.4
	13/9/72	1.05	.496	47.2
	11/10/72	3.77	.806	21.4
	17/10/72	3.11	.746	24.0
	18/10/72	3.57	.849	23.8
Shell Oil (8)	1	22.6	7.75	34
	2	22.6	7.50	33
	3	22.6	6.26	28
	4	17.0	4.35	26
	5	17.0	3.40	20
	6	17.0	4.02	24
	7	17.0	3.67	22
	8	9.2	4.50	49
	9	9.2	3.83	42
	10	9.2	9.73	102*
Northern States Power Company (coal-fired)	12/6/73	4.19	<.007	0.167

* Included 3 min. soot blower operation

of the accumulated ash and other material deposits.

The manufacturing of cements in a rotary kiln never involves any operation comparable to soot-blowing and hence is not subject to the hazardous emissions concomitant with this procedure.

The use of waste oil as an additional fuel in coal-fired boilers has been less fully studied than in oil-fired systems. An experimental burn was carried out a Northern States Power Company in which some 29,000 gallons of used oil was burned. Oil was fed at 155 gal/hr and was computed to introduce lead at 4.036 lb/hr with 0.159 lb/hr from coal to give a total of 4.19 lb/hr. Lead emissions were monitored by isokinetic stack sampling and found to be less than 6.99×10^{-3} lb/hr. This gives an average of 0.167% of the lead input emitted during burning. The retention in this system was through lead containment in the fly-ash which was captured in the electrostatic precipitator system.

It is to be expected that Br, Zn, P and other elements will all be substantially emitted when waste oil is burned in a conventional oil-burning system. No information is available to allow assessment of the behaviour of these other elements when using waste oils in a coal-fired unit.

5.   CONCLUSIONS

The concept of using waste oil as a fuel in cement processing derives from the already well known action of cement kilns as "dry-lime scrubbers" in relation to sulphur and halogens in the kiln gases. It was believed that this scrubbing action would be effective as a means of removing other chemical elements.

In this program lead, zinc and phosphorus emissions in the kiln exhaust gases were not increased as a result of waste oil burning. A small increase in bromide emissions and a small decrease in total particulate emissions were observed.

Combustion in conventional oil-burning boilers is considered to result in practically all of the lead and unknown but probably high proportion of the bromine, zinc and phosphorus being emitted to the atmosphere. Road oiling using waste oil requires the direct application of the pollutant elements to the environment and has been reported to cause considerable water pollution. In contrast, the results of this program showed that on average emissions from the cement kiln were restriceted to approximately 0.03 percent of the lead and 0.7 percent of the bromine put in with the waste oil.

A mass balance was carried out on trace quantities of these elements in the cement kiln. The results of the study showed that 89 percent of the lead, 72 percent of the bromine and 100 percent of both zinc and phosphorus were retained in the process solids. Lead, zinc and phosphorus were largely retained in the cement clinker along with some of the bromine. Most of the bromine was retained as bromide in a pelletized dust, collected from the electrostatic precipitator on the by-pass system.

Both the mass balance and air emissions data from this experiment have illustrated the effectiveness of the gas-scrubbing action of the cement kiln.

Consideration of the data from this study and examination of the general literature on cement manufacturing has led the authors to conclude that used lubricating oils may be employed as fuels in cement kilns, where particulate emissions are reasonably under control, without adverse effects on air pollution.

REFERENCES

(1)   Skinner, D.J., "Preliminary Review of Used Lubricating Oils in
        Canada". Environment Canada, Economic and Technical Review,
        Report EPS 3-WP-74-4. Ottawa, 1974.

(2)   "Analysis of Retention and Emission of Fuel Sulphur in the
        Manufacture of Portland Cement", Table 12, ref. (12).

(3)   Blaine, R.L., Bean, L. and Hubbard, E.K., "Occurrence of
        Minor and Trace Elements in Portland Cement; Interrelations
        Between Cement and Concrete Properties", Part 1, Section 3,
        Building Science Series 2, NBS. Aug. 1965. p. 33.

(4)   Lea, F.M., "The Chemistry of Cement and Concrete", 3rd Edn.,
        Edward Arnold (Publishers) Ltd. (1970).

(5)   Herod, B.C., "St. Lawrence Cement Expands Clarkson Operation";
        Pit and Quarry, July, 1968.

(6)   Coles, C.W. and Dainton, D.G., "St. Lawrence Cement Co.,
        Clarkson Plant", Cement Technology, 1 (2), 43, (1970)

(7)   Schroth, G.A., "Suspension Preheater System Consumes Less Fuel"
        Rock Products 75 (5), 70, (1972).

(8)   "Final Report of the Task Force on Used Oil Disposal", API Publ.
        No. 4036.

(9)   Gruse, W.A. and Stevens, D.R., "Chemical Technology of
        Petroleum", 3rd Edn., McGraw-Hill (1960) p. 440

(10)   Hirschler, D.A., Gilbert, L.F., Lamb, F.W. and Niebylski, L.M.,
        "Particulate Lead Compounds in Automobile Exhaust Gas", Ind.
        Eng. Chem. 49 (7), 1131, (1957).

(11)   Ter Haar, G.L. and Bayard, M.A., "Composition of Airborne Lead
        Particles", Nature 232, 553, (1971).

(12)   Gagan, E.W., "Air Pollution Emission and Control Technology-
        Cement Industry", Environment Canada, Economic and Technical
        Review, Report EPS 3-AP-74-3.

(13)   White, H.J., "Industrial Electrostatic Precipitation", Addison-
        Wesley Pub. Co. Inc. 1963 p. 326.

(14)   Perry, J.H., Chilton, C.H. and Kirkpatrick, S.D., "Chemical
        Engineers Handbook", 4th Edn. McGraw Hill, p. 3-45.

(15)   Gutt, W., "Manufacture of Portland Cement from Phosphatic Raw
        Materials", Proceedings of the 5th Internationl Symposium on
        the Chemistry of Cements, Tokyo, 1968, Published 1969.

REFERENCES (CONT'D)

(16)   Steinour, H.H., "The Effect of Phosphate in Portland Cement
        Clinker", PCA. Res. and Dev. Bull No. 85.

(17)   Sichov, M.M., "Problem of Admixtures" ref; (15), Vol I, p. 157

(18)   Guinier, A., and Regourd, M., "Structure of Portland Cement
        Minerals" ref. (15), Vol. 1, p.1.

(19)   Hahn, T., Eysel, W., and Woermann, E., "Crystal Chemistry
        of Tricalcium Silicate Solid-Solutions", ref (15), Vol I.
        p. 37.

(20)   Bogue, R.H., "The Chemistry of Portland Cement", Reinholt
        Publishing Co., 2nd Edn., 1955.

(21)   Gilliand, J.L., "Removal of Alkalies by Use of Hydrochloric
        Acid", Symposium on Alkali Removal and Problems, PCA: M-15B

(22)   Woods, H., "Reduction of Alkalis in Cement Manufacture" PCA;
        M-14G.

(23)   Suzuki, K., and Yamaguchi, G., "A Structural Study of $\alpha^1\text{-Ca}_2$
        SiO_4", ref (15) Vol. I, p. 67.

(24)   Rengade, E., Revue Mater. Constr. Trav. Publ. 239, 290,
        (1929)

(25)   Midgley, H.G., "The Minor Elements in Alite and Belite" ref
        (15) Vol. I, p. 226.

(26)   Regourd, M., Bigare, M., Forest, J., and Guinier, A., "Synthesis
        and Crystallographic Investigation of Some Belites", ref (15),
        Vol. I, p. 44.

(27)   Boikova, A.I. "The Effect of Chromium Oxide on the Structural
        Transformations in Tricalcium Silicate", ref. (15), Vol. I
        p. 234.

(28)   Sakurai, T., Sato, T., and Yoshinaga, A., "The Effect of Minor
        Components on the Early Hydraulic Activity of the Major Phases
        of Portland Cement Clinker", ref. (15), Vol. I, p. 300.

(29)   Midgley, H.G., "The Effect of Lead Compounds in Aggregate upon
        the Setting of Portland Cement". Mag. Concr. Res. 22, (20),
        42, (1970).

(30)   Lieber, W. "The Influence of Lead and Zinc Compounds on the
        Hydration of Portland Cement". ref. (15). Vol. II, p. 444

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APPENDIX A

APPENDIX A

QUANTIFYING, SAMPLING AND ANALYSIS OF PROCESS MATERIALS

A schematic illustration of material flow through the production system is shown in Figure A.1. To obtain the material balance, seven materials were quantified, sampled and analyzed. Table A.1 lists the materials examined with approximate relative quantities under normal production conditions.

Normal plant installations and procedures were available for sampling all of these materials except by-pass precipitator dust, for which a sampling port was installed for this program.

A.1.   Weighing and Sampling Raw-Feed and Clinker

Raw-feed is supplied preblended from the silo storage system to the kiln by a parallel feed of two screw conveyors. The two conveyors discharge onto Gilmore belt weigh-scales from which material (about 110 ton/hr from each) flows into the duct between the first and second preheater stages. For normal production control, the weight of material is continously monitored and 24-hour composite samples are collected from the free-falling feed stream. These composite samples were blended and riffled into two sub-samples for analysis.

The clinker leaves the cooler by conveyor (about 125 ton/hr). For normal production control, samples are taken from the conveyor at intervals of 2 hours to form a routine 24-hour composite. The clinker composite sample is mixed, reduced by 'cone and quartering' and a portion ground. Each day, about 2 lb of the ground sample was collected blended and riffled into two equal sub-samples for analysis.

In common with general practice in the industry, there is no provision in the plant for continous weighing of clinker. Further, the weigh-belt scales are installed largely to aid kiln control; they are not considered reliable enough for accurate continuous weighing of raw meal. It is frequent in cement plants to calculate the clinker production from fuel consumption using long-term inventory figures to establish a relationship.

Figure A.1 Schematic of the Material Flow

2×60,000 dscfm

N.W. AND N.E. PRECIPITATORS

RAW MEAL FEED 5,010 t.p.d. *

WEIGH BELT

9,500 dscfm

B.P. PRECIPITATOR

SUSPENSION PREHEATER

SILO

C.T.

RAW MEAL SILO

46

* BUNKER 'C'

KILN

RAW MEAL

* C.T. SOLIDS 20 t.p.d.

PELLETIZER

* WASTE OIL 11.7 g.p.m.

CLINKER * 3,000 t.p.d.

DISCARD B.P. DUST 6 t.p.d.

* INDICATES SAMPLING AND METERING POINTS FOR TEST BURN.

.
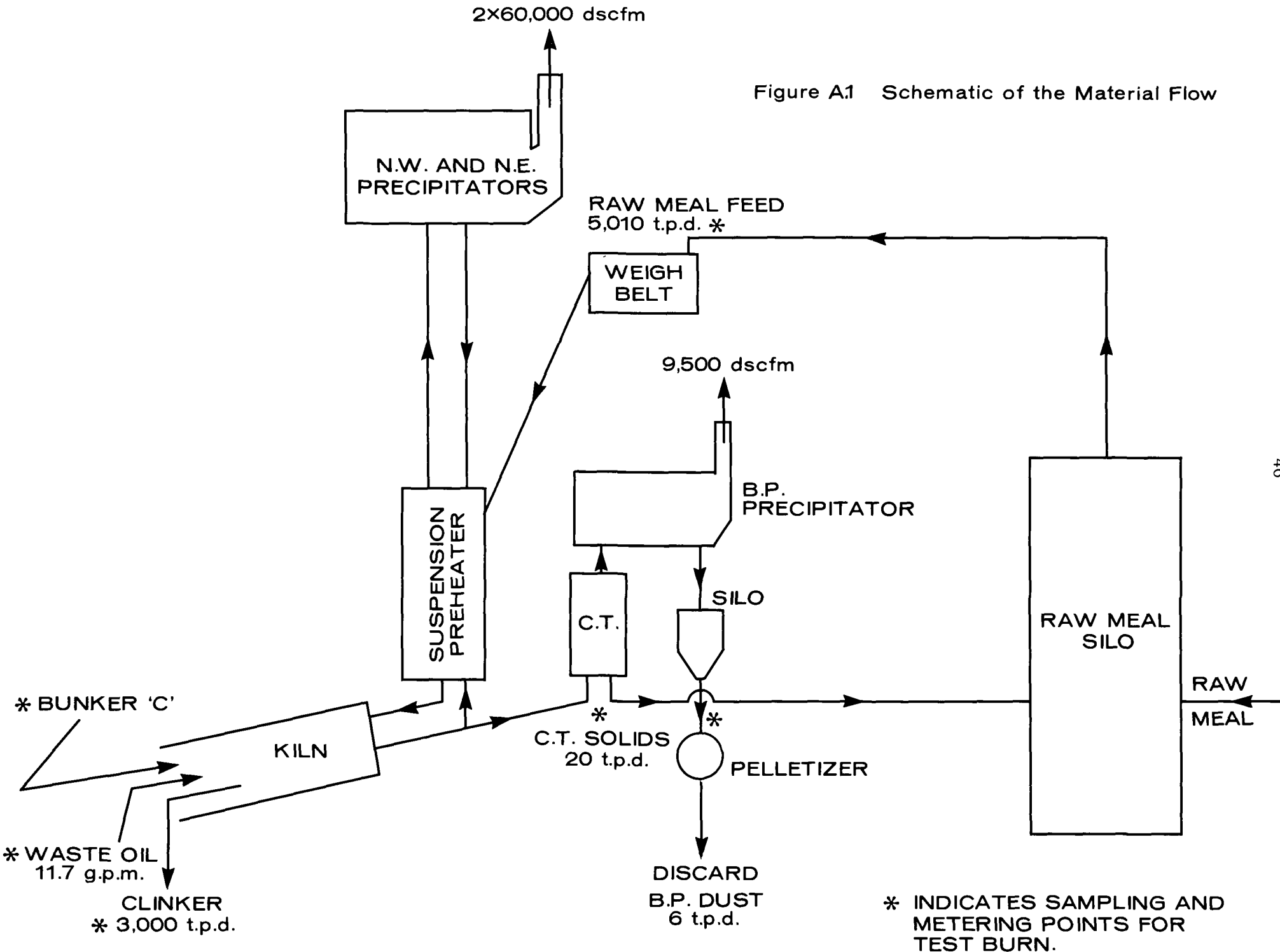
TABLE A.1. PROCESS MATERIALS STUDIED AND APPROXIMATE NORMAL PRODUCTION QUANTITIES

Material	Approximate Quantity
Raw feed	210 tons/hr
Clinker	125 tons/hr
By-pass precipitator dust	5-10 tons/day
Conditioning tower solids	18-25 tons/day
Bunker 'C' fuel oil	-
Waste-oil	10-15 gal/min
Kiln exhaust gases (3 stacks)	Total: 130,000 dscfm

This relationship is treated as proprietary information by most companies and is not recorded in this report. In order to obtain a true value for raw meal consumed, a calculation is usually made over a period of steady plant conditions, of the relationship between raw meal and clinker quantities to effectively calibrate the weigh scales. This approach was taken in the present program. A period at the start of the program from the 10th March to 20th March was chosen. During this time, the daily clinker production figures were calculated using accurately known fuel consumption data and the plant calculation factor determined from annual inventory. A total material balance may then be written as follows:

$$RM = \frac{100}{(100 - LOI_{RM})} \left[C + BPD \left(\frac{100 - LOI_{BPD}}{100} \right) + CT \left(\frac{100 - LOI_{CT}}{100} \right) \right] \quad (1)$$

where RM = quantity of raw meal

C = quantity of clinker

BPD = quantity of by-pass dust

CT = quantity of conditioning tower solids

LOI_{BPD} = loss on ignition of by-pass dust = 14%

LOI_{RM} = loss on ignition of raw meal = 34.66%

LOI_{CT} = loss on ignition of conditioning tower solids = 22%

C is calculated from oil consumption as noted above; BPD and CT were determined as described later in this report from experimental weighings combined with the plant data recording the hours per day when the by-pass was operating.

This allows a weigh-belt calibration to be made such that

$$RM = A \times RM_W$$

where RM_W = weight record from weigh-belt

A = calibration factor

When waste oil was being burned, the clinker production weight could not be reliably calculated from oil consumption. Equation (1)

was then used in the form:

$$A \times RM_W = \frac{100}{65.34} \left[C + BPD \times \frac{86}{100} + CT \times \frac{78}{100} \right]$$

to determine C, the clinker produced. To check the accuracy of the whole calculation, a weighing of clinker during production was carried out on May 1.

The clinker conveyor discharges into an area inside and near the west wall of the storage hall. To weigh the clinker, a period of twelve hours was selected through which the discharged material was moved by overhead crane to an area accessible from outside the building. Front-end loaders then put the clinker into trucks which were weighed on the plant truck-scale. The data obtained over this 12-hour calibration period are given in Table A.2. The total daily production measured at this time was 2932 tons to be compared with a calculated value of 3106 tons, this is an error of 5.6% and is acceptable.

Potential sources of error in the weighing procedure are: (a) the area where the clinker enters the hall must be completely empty at exactly the times the test begins and ends, (b) some loss may occur during handling of clinker, and (c) each of the trucks used was tared only once during the day. The errors are not expected to be significant as clinker handling and timing were well supervised and clinker flows freely from trucks.

A.2   Weighing and Sampling By-Pass Dust

Although the by-pass system operates continuously during normal running of the kiln, the quantity of material is relatively small. To obtain efficient operation of the pelletizing process, a holding silo is used. The silo fills continously and is emptied by screw conveyor to the pelletizer for three, 75 minute periods. During these times, samples were taken at 15-minute intervals to form a 24-hour composite from a sample port directly below the silo. Each sample was passed through a 60 mesh screen, mixed on a twin-shell blender and riffled down to provide two, 1-lb samples for analysis.

Prior to disposal, the by-pass dust is normally pelletized. This is accomplished by dropping the dust into a rotating drum and spray-

TABLE A.2. CLINKER WEIGHTS, MAY 1, 1974

TIME	GROSS WEIGHT	TARE	NET WEIGHT	TIME	GROSS WEIGHT	TARE	NET WEIGHT
8:22 am	83560	34420	49140	3:49 pm	91700	34420	57280
8:30 am	75750	37030	38720	4:05 pm	77490	37030	40460
8:42 am	76180	34420	41760	4:25 pm	87580	34420	53160
8:48 am	76370	37030	39340	4:29 pm	77120	37030	40090
9:02 am	85310	34420	50890	4:50 pm	90660	34420	56240
9:10 am	77290	37030	40260	4:54 pm	87550	37030	50520
9:22 am	75490	34420	41070	5:08 pm	94560	34420	60140
9:30 am	75030	37030	38000	5:11 pm	77730	37030	40700
9:46 am	80880	37030	43850	5:21 pm	74090	34420	39670
10:22 am	75060	37030	38030	5:24 pm	75170	37030	38140
10:39 am	76350	37030	39320	5:35 pm	75710	34420	41290
10:54 am	79080	37030	42050	5:38 pm	78170	37030	41140
11:15 am	75780	37030	38750	5:49 pm	76100	37030	39070
11:39 am	75640	37030	38610	5:57 pm	78910	34420	44490
12:27 pm	72380	34420	37960	6:07 pm	82040	37030	45010
12:41 pm	86060	34420	51640	6:11 pm	91620	34420	57200
1:38 pm	97640	30940	66700	6:25 pm	85150	34420	50730
1:42 pm	75960	37030	38930	6:38 pm	76190	34420	41770
1:41 pm	84640	34420	50220	6:53 pm	78500	34420	44080
1:54 pm	90240	30940	59300	6:57 pm	83400	37030	46370
1:58 pm	76750	37030	39720	7:06 pm	78920	34420	44500
1:59 pm	85200	34420	50780	7:11 pm	82300	37030	45270
2:27 pm	82850	30940	51910	7:19 pm	91070	34420	56650
2:45 pm	81780	34420	47360	7:23 pm	79360	37030	42330
2:46 pm	74040	37030	37010	7:33 pm	88050	34420	53630
2:57 pm	86910	34420	52490	7:37 pm	75930	37030	38900
3:02 pm	73950	37030	36920	7:46 pm	78890	34420	44470
3:18 pm	92510	34420	58090	7:51 pm	78210	37030	41180
3:32 pm	91910	34420	57490	8:01 pm	90320	34420	55900
3:20 pm	78830	37030	41800	8:07 pm	84540	37030	47510
3:31 pm	76280	37030	39250	8:16 pm	91460	34420	57040
3:42 pm	71920	37030	34890	8:27 pm	81200	37030	44170
				TOTAL			2,931,350

2,931,350 pounds = 1466 tons/12 hrs = 2932 tpd.

ing with water. From the drum, the pellets fall into a concrete bin
from which a front-end loader can load them into trucks. Usually,
the pellets are removed only every third day as the daily accumulation
is small. For this study, the pelletized dust was weighed daily during
a two-week period and on two further days which coincided with weighing
of conditioning tower solids. The results were corrected for the water
added during pelletizing.

The greatest source of error in a single day's weight could be
through having the storage silo at different levels when the pellets
were removed from the bin. As this would appear to be the case from
the fluctuations found in the data collected, the average weight per
day (6.02 tons) has been used for the mass balance.

To calculate the daily quantities, the number of hours on each
day during the program that the by-pass was running (obtained from plant
records) was used such that:

$$BPD = \frac{H}{24} \times 6.02$$

where BPD = daily quantity of by-pass dust

H = hours of by-pass running

A.3   Weighing and Sampling Conditioning Tower Solids

Solids leave the base of the conditioning tower by a screw
conveyor system and returned to the raw-feed storage silos. A sampling
point is available in the conveyor system and samples were taken at
intervals of 2 hours to obtain a 24-hour composite. This was sieved
to pass 60 mesh (coarse materials were crushed to pass 60 mesh) blended
in a twin shell blender and riffled down to two convenient samples for
analysis.

To weigh this material, use was made of the emergency system
whereby a screw conveyor at the bottom of the tower can be reversed
causing the dust to drop to the concrete floor. From there, it was loaded
onto trucks and weighed.

It was planned to have weighings of this dust at different
times in the program. However, through operational difficulties, only two

weighings (on consecutive days) were accomplished from six attempts. This necessitated the use of the average (20 tons) of the two weighings throughout the report. To calculate the daily accumulation, a similar procedure was used to that given above for by-pass dust.

As the by-pass was operated at very nearly the same percentage throughout the program, the amount generated was not likely to alter significantly day by day.

A.4   Measurement and Sampling Bunker 'C' Oil

While it was considered unlikely that the bunker 'C' fuel used in the plant would contribute measurable quantities of the elements of concern to this study, in case some traces of Pb, Zn, Br or P were found, it was necessary to retain samples throughout the burn. This was accomplished by retaining a portion of the normal daily composite collected for plant control purposes. The composite was collected over a 24-hour period at intervals of two hours. Fuel quantities are continuously monitored and recorded in the production data but are not given in this report.

A.5   Measurement and Sampling Waste Oil

Sampling waste oil was carried out by withdrawing material from the feed system at two-hour intervals to form daily composite samples. These were collected and shaken vigorously (a 'Red-Devil' paint mixer was found very convenient for this purpose) and divided into two equal volumes for analysis. It should be noted that the waste oils examined in this study separated fairly rapidly to give a sediment. In this work, great care was taken when removing samples for analysis, or when removing samples to send to other laboratories for analysis, that the material was well mixed by vigorous shaking prior to subdivision into aliquots.

Initially, it was intended to meter oil volume flow continously. For this purpose, a target meter was installed in the line to monitor oil quantities. Shortly after starting to burn the oil, the meter became extremely erratic. Apparently, the clearances inside a target meter are so critical that build-up of particulate material from the oil caused greater opening of the meter than the rate of oil warranted. After

cleaning and repairing the meter twice, only to have the problem re-occur several hours after start-up, it was decided that the meter could be used only to indicate complete failure of the system. As a result, oil quantities were measured by taking dip stick readings of the waste oil tanks every three hours. Trucks delivering reclaimed oil were weighed in and out of the plant, the time of weighings being automatically recorded on the weigh scale ticket. By combining dip stick volumes with deliveries made, the amount of reclaim oil burned each day could be calculated.

It should be pointed out that not all reclaimed oil affects the target meter in this manner. St. Lawrence Cement Co. had successfully used this meter for this purpose previously, but some oils or sources of supply can generate this problem.

A.6   Sampling Kiln Gas Emissions

A.6.1   Program Requirements

The kiln and dual preheater installation is exhausted by a pair of 150,000 cfm Joy fans. Gases pass through the parallel electro-static precipitator units to two stacks located at N.W. and N.E. corners of the preheater building, each of which were found to carry gases at a volume flow of 60-65,000 dscfm. A fan located on the outlet side of the by-pass precipitator exhausts the by-pass system to a stack located at the S.E. corner of the preheater building. This was found to carry gases at a volume flow of 9-10,000 dscfm during this study.

The experimental program required that emission tests were performed on each stack according to Environmental Protection Service (A 1) and Ontario Ministry of the Environment (A 2) source testing codes. It was required to provide for three tests on each stack during a period prior to burning waste oil, six tests on each stack during the experimental burning period, and a further three tests on each stack during a period after the experimental burn. The testing schedule is given in Table A.3, with a record of the fuel conditions for each test. The testing was required to be consistent with determination of emissions of particulate matter, and the elements Pb, Zn, P, and Br. None of these elements was expected to be emitted in elemental form, rather as complex silicates or as oxides, alkali halides or sulphates.

TABLE A.3.   SCHEDULE OF EMISSIONS TESTING

Test #	Test Date	Stacks Tested	Fuel Conditions
1	March 11	NW, NE*	
1(a)	March 14	SE	
2	March 12	NW, NE*	
2(a)	March 14	SE	Bunker 'C' only
3	March 12	NW, NE*	
3(a)	March 15	SE	
4	April 22	NW, NE, SE*	
5	April 23	NW, NE, SE*	
6	April 30	NW, NE, SE*	
7	April 30	NW, NE, SE*	Bunker 'C' + Waste-(
8	May 1	NW, NE, SE*	
9	May 2	NW, NE, SE*	
10	May 29	NW, NE, SE*	
11	May 29	NW, NE, SE*	Bunker 'C' only
12	May 30	NW, NE, SE*	

*Simultaneous tests.

A.6.2   Stack Sampling Locations

From each of the three stacks, samples were taken by traversing
the stack diameters from two sampling ports located in the same plane
at right angles to each other. The stacks are located on a flat-roof
at 267'9" above grade. Details of the port positions in each stack
with respect to flow disturbances are given below.

Stack	Designation	Port Positions Relative to Nearest Flow Disturbance (Stack Diameters) Upstream	Downstream	Stack Diameter (ft)
Preheater	NW	1.4D	2.6D	7.0
Preheater	NE	1.4D	2.6D	7.0
By-pass	SE	2.5D	3.3D	3.75

Code procedures require that for 'ideal' sampling the sampling
site on a stack or duct should be at least eight stack diameters downstream
and two diameters upstream of any flow disturbance. In this respect
the available sampling locations were 'non-ideal'. After examination of
stack gas velocity profiles, it was agreed with Environment Canada and
the Ontario Ministry of the Environment that sampling should be carried
out isokinetically at 24 points on each traverse of the two preheater
stacks (NW and NE), and at 16 points on each traverse of the by-pass
stack. During tests #4 through #12, all three stacks were sampled simul-
taneously.

A.6.3   Equipment and Methodology

Joy Emission Parameter Analyzers (EPA, Model CU-2) were used
for sampling. A schematic of the Joy EPA sampling train is shown as
Figure A.2. The cyclone collector was not used for these tests as the
dust loadings in the effluent after pollution control devices were not
considered to be heavy. 10' and 5' stainless steel probes were used
for preheater and by-pass stacks respectively, with nozzle size 1/4"
I.D. Preliminary measurements were made at each stack prior to each test to
determine average stack gas velocity, gas temperature, moisture content
and gas composition, as specified in the Codes. Isokinetic sampling
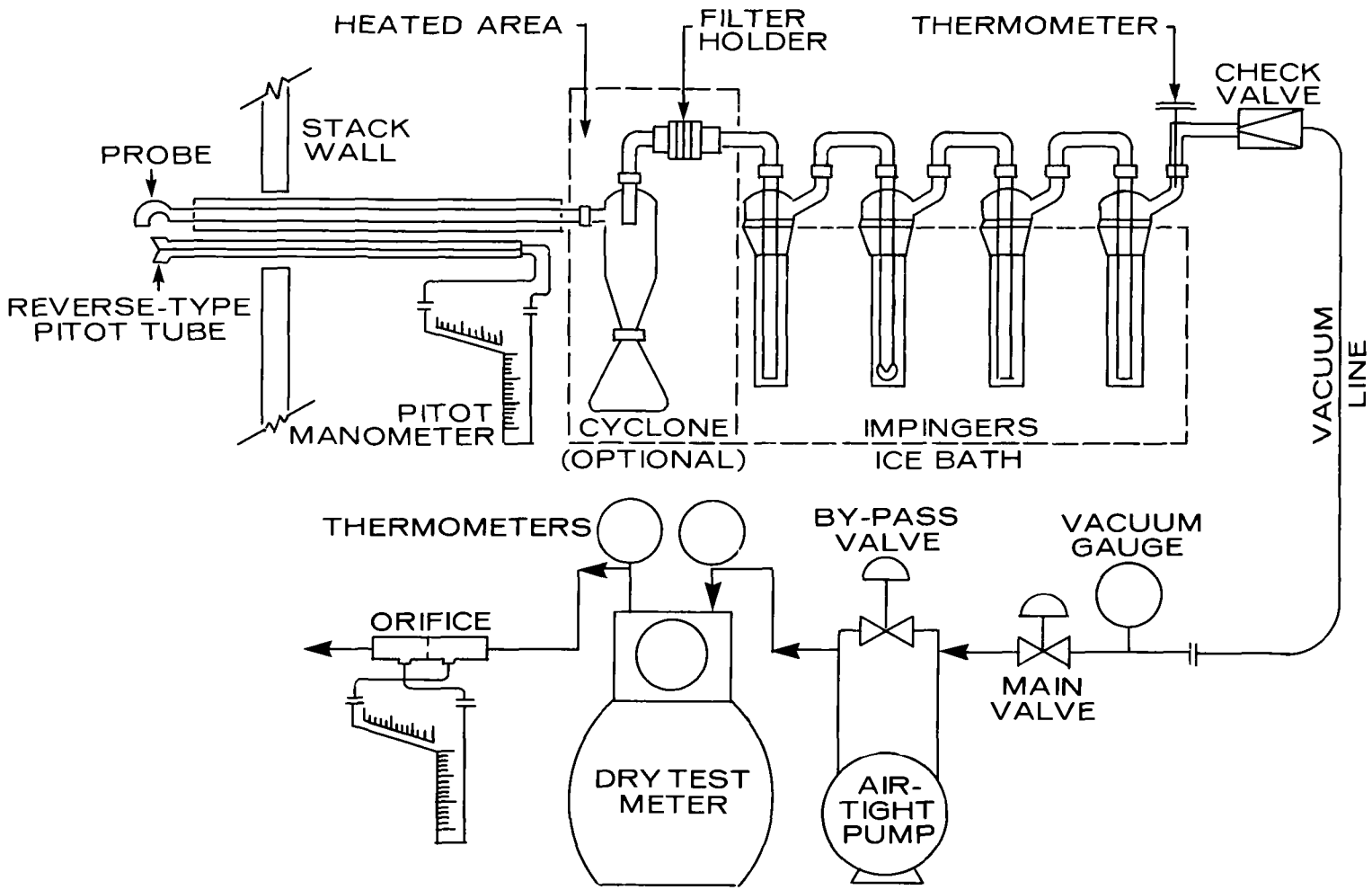
Figure A2   Sampling Train

conditions were established for each test, sampling for five minutes at
each sampling point and recording data at 2.5 minute intervals.

The gas temperature was measured at each traverse point with
a thermocouple and monitored on the Joy EPA console. An S-type pitot
tube, which is part of the sampling probe assembly, measured the dynamic
pressure. The pitot coefficient of each probe used was 0.85. At the
North-West and North-East stacks, stainless steel lined sampling probes
#5 and # 6 respectively were used. Sampling probes #3 and #4 were used
on the South-East (by-pass) stack. Test sampling was started at the
wall opposite to the port. Sampling points along each traverse were
determined using the calculations given in the Ontario Ministry of
the Environment Source Testing Code (A 2). These points are chosen
to be at the centre of equal areas.

The volume flow rate is calculated by multiplying the average
of the gas velocities measured at each point by the stack cross sectional
area at the sampling location. The calculation methods for stack gas
flow rate, moisture content, particulate loading and emission rate are
presented in the Source Testing Code (A 2).

A 0.205 inch I.D. sampling probe tip was used on each probe to
give an isokinetic sampling rate of approximately 0.4 cfm. Probe and
filter holder compartments were maintained between 250 and 300°F.
Reeve Angel, grade 900AF, 12.5 cm glass fiber filters were used to collect
the particulate matter. All parts in the sampling train from the filter
end of the sampling probe to the fourth impinger are made of glass.

The first two impingers of the sampling train were filled with
250 ml of distilled water; the third impinger was empty and the fourth
contained silica gel for the removal of moisture in the gas being metered.

Three Orsat analyses were made on each stack during each sam-
pling day.

At the end of each test, the filter was carefully removed and
placed in a holder for transportation to the laboratory. The inside
of probes were brushed through and rinsed with either acetone or distilled
water. During the first base line tests, from March 11 to March 15,
acetone was used to rinse deposits from the inside of the sampling probe
and top half of the filter holder. The remainder of the glassware was

rinsed with distilled water. It was found that the acetone probe rinse
was contributing to the total amount of particulate collected in the
sampling probe due to formation of a resinous deposit on evaporation
of the acetone. In the remaining tests, distilled water was employed
as a probe rinsing agent. Rinsings of the filter holder assembly,
after filter removal, were added to the probe rinsings. Rinsings
were stored in polyethylene bottles.

The total volume of water in the impingers was measured and then
transferred to polyethylene bottles. Silica gel in the fourth impinger
was removed and stored in another container. In the laboratory, filters
were reconditioned and reweighed. Probe rinsings were filtered through
nucleapore filters to give soluble and insoluble fractions. The mositure
removed from the sampled gas was determined by the sum of gain in
weight of the silica gel and increase in volume of impinger solutions.

The particulate concentration in the gas stream was determined
from the sum of the increase in weight of the particulate collection
filters and the total amount of materials found in the probe rinse,
divided by the volume of gas sampled (corrected to standard conditions).
The impinger catch is not considered as particulate material by the Air
Resources Branch and is reported separately. Particulate concentrations
and emission rates for each test were computed by the methods given in
the Source Testing Code (A 2).

A.7   Analysis of Process Solids

For the purposes of obtaining a mass balance during this
experimental used-oil burn, it was required to carry out chemical analyses
of clinker, raw feed, conditioning tower solids and by-pass precipitator
dust for the elements lead, bromine, zinc and phosphorus. While analyses
for the major component elements of cement process materials are widely
and routinely carried out, the quantitative analysis of trace elements
is not well documented in the literature. Blain, Bean and Hubbard (A 3)
analyzed 186 Portland cements for trace elements using an emission
spectrographic technique to give semi-quantitative data for elements at
concentrations down to 0.001 weight percent.

Atomic absorption AA methods have been considered for the analysis of major components in cement process materials. However, some raw mixes and process dusts are not completely soluble in acidic media. In particular, the possibility of $PbSO_4$ precipitation was of concern in this study. The Portland Cement Association have used fusion with lithium metaborate to form samples that can be dissolved in acid for AA examination. As is shown below, this method is not applicable to Pb or Zn determinations due to volatilization of these elements during fusion. Further, AA offers no means to analyze for bromine and phosphorus.

An alternative method, applicable to all of the elements is X-ray fluorescence (XRF) analysis.

In recent years, the technique has been widely used for trace analysis of silicate minerals containing multiple elements at very low levels of concentration (see for example, Cowgill (A 4)). To determine the suitability of the method, it was necessary to determine whether there are any systematic errors specific to the materials under investigation. A series of preliminary experiments was carried out to assess the method for the purposes of this experimental material balance.

It was first required to examine the process solids to determine which elements were present and what matrix effects were likely to apply limitations to the procedure. Three types of experiments were carried out: (i) examination of fusion techniques as a means to reduce (or standardize) matrix effects; (ii) semi-quantitative analysis of process solids; (iii) preparation of concentration versus intensity curves for required elements by the method of additions.

A.7.1   Preliminary Experiments

One of the most common sources of matrix errors in XRF analysis results from gross particle size differences between samples. A common method of overcoming this difficulty is to homogenize the specimens by fusion with glass forming materials such as lithium tetraborate. In the case of the analyses of the materials in this study, it was considered likely that Pb, Zn and Br would be lost from samples under fusion conditions. A series of test fusions were made under a range

of typical time and temperature conditions using a sample of conditioning tower solids. The results are given in Table A.4 (as changes in count-ratio) and show clearly that fusion would not be suitable for these samples.

The method of internal standardization known as "spiking" was considered a more acceptable approach for these samples. The method is well established as a trace analysis procedure but depends for its accuracy on control of matrix errors.

A.7.2   Analytical Procedures

Analytical methods were developed largely independently at the two laboratories (ORF and SLC). This approach was taken so that if any systematic errors in method or technique were introduced into the program, these would become apparent as systematic discrepencies between the two sets of results. In this section of the report, the detailed methods employed by the two laboratories are given.

Pelletized discs were used at both laboratories. At ORF, pellets were prepared by adding 2 grams of sample to 0.5 grams of Methocel binder. The mix was milled for 10 minutes in a SPEX 8000 Mixer Mill using a tungsten carbide vial. The whole mix was then pelletized at 25 tons pressure into a 1.25 inch diameter pellet. At St. Lawrence Cement, 10 gram samples were ground without binder for 1 minute in a SPEX Shatterbox with tungsten carbide containers and pucks. From this material, 1.25 inch diameter pellets were pressed at 8 tons pressure.

For the X-ray fluorescence method to be applied, it is necessary that there is a linear relationship between elemental concentration (over the full range of concentration required) and the measured fluorescence intensity. The slope of the line representing this relationship then can be used directly as a calibration constant usually in the form of the ratio, counts per second/percent element. When a calibration line is generated by known additions of the test element to a material being analyzed ("spiking"), the line intercept gives the percent of the element present in the original sample prior to any additions.

In addition to linearity, reproducibility of the calibration constant is a prerequisite if it is to be applied across a range of materials having some degree of matrix variability.

TABLE A.4. X.R.F. INTENSITY LOSSES ON FUSION OF C.T. SOLIDS WITH LITHIUM TETRABORATE

Temperature (°C)	Time (min)	% Loss of X.R.F. Intensity		
		Pb(Lβ)	Br(Kα)	Zn(Kα)
1000	10	0	53.78	5.31
1100	10	0	80.60	0
1200	3	52.44	60.34	0
1200	5	79.27	71.94	2.65
1200	10	95.12	93.01	30.97
1200	15	100	98.72	51.33
1200	20	89.02	98.86	68.14
1300	10	71.95	96.86	78.76
Unfused	–	0	0	0

Both of these conditions were examined prior to the final development of analytical procedures. To check the linearity of calibration, a representative sample was selected from each of the four types of solid materials. Each laboratory made the selection independently. At ORF, 2 grams of the material was mixed with 0.5 grams of Methocel; at St. Lawrence Cement, 10 grams of the sample was used. The samples were placed on watch-glasses, to each was added a measured volume of each of four methanol solutions containing known amounts of Pb, Br, Zn and P. After drying, each mix was ground and pelletized as described above.

All substances used to prepare standard solutions were obtained as reagent grade chemicals except triphenyl phosphate which was an NBS Standard Reference Material (#1071 a). The concentration and composition of standard solutions used at both laboratories are given in Table A.5. In the case of the phosphorus calibration for clinker, a set of NBS Portland cements (Standard Reference Materials 633 to 639 and 1011 to 1016) was used at ORF.

Examination of these samples at both laboratories by measurement of X-ray emission intensities yielded linear calibration relationships when plotted against the amount of element added. The least-squares computations for each set of data gave the slopes intercepts and regression (correlation) coefficients listed in Tables A.6 and A.7.

At ORF, the investigation was extended to examine whether significant matrix absorption differences existed between various samples of the same type of process solid. In addition to those chosen for the work described above, three further samples of each of raw meal, clinker and conditioning tower solids and five further samples of by-pass dust were selected from the collected samples to be analyzed. To each of these, a 0.1% addition of Pb, Zn, Br and P was made by solution addition. The calibration constant for each sample and each element was measured and for each data set, a coefficient of variation was computed. The results are shown in Table A.8. The relatively large coefficients of variation observed for by-pass dust indicated that for the most precise analysis, it would be necessary to adjust calibration constants to suit the overall composition of each individual by-pass dust sample. The most

TABLE A.5. STANDARD STOCK SOLUTIONS

Solution #	Compound	Concentration
ORF-1	Zinc acetate, $Zn(C_2H_3O_2)_2 2H_2O$	0.6715 g/100 ml
ORF-2	Potassium bromide, KBr	0.2978 g/100 ml
ORF-3	Lead nitrate, $Pb(NO_3)_2$	0.3197 g/100 ml
ORF-4	Triphenyl phosphate, $(C_6H_5)_3PO_4$	2.1044 g/100 ml
SLC-1	Zinc nitrate, $Zn(NO_3)_2 6H_2O$	0.0910 g/litre
SLC-2	Zinc nitrate	1.8225 g/litre
SLC-3	Lead nitrate, $Pb(NO_3)_2$	0.3197 g/litre
SLC-4	Lead nitrate,	6.4350 g/litre
SLC-5	Potassium bromide, KBr	0.1489 g/litre
SLC-6	*Zinc bromide, $ZnBr_2$	11.4100 g/litre
SLC-7	Triphenyl phosphate $(C_6H_5)_3PO_4$	10.5344 g/litre

* Zinc bromide although extremely hygroscopic is freely soluble in
  methanol. The solution was standardized by performing triplicate
  additions of both this solution and solid potassium bromide to
  by-pass dust, the solid addition being considered standard.

TABLES A.6. LEAST SQUARES DATA FOR CALIBRATION LINES (ORF)

Material	Element	Correlation Coefficient	Slope	Intercept (%)
Raw meal	Pb	.9998	10613	.0011
	Br	.9999	31793	.0005
	Zn	.9999	17985	.0035
	P	.9986	5057	.038
Clinker	Pb	.9998	7799	.0007
	Br	.9999	23041	.0006
	Zn	.9999	12929	.0061
	P	.9998	5719	_____
Conditioning Tower Solids	Pb	.9997	8498	.035
	Br	.9992	22712	.063
	Zn	.9999	13748	.017
	P	.9969	6346	.029
By-pass Dust	Pb	.9997	7072	.069
	Br	.9997	19092	.39
	Zn	.9996	12330	.012
	P	.9990	6162	.013

TABLE A.7. LEAST SQUARES DATA FOR CALIBRATION LINES (SLC)

Material	Element	Correlation Coefficient	Slope	Intercept
Raw meal	lead	0.9977	5584	0.0005
	bromine	0.9972	8681	0.0012
	zinc	0.9998	3514	0.0053
	phosphorus	0.9986	716	0.037
Clinker	lead	0.9952	2612	0.0005
	bromine	0.9991	5950	0.0005
	zinc	0.9989	2150	0.0108
	phosphorus	0.9748	595	0.055
Conditioning Tower Solids	lead	0.9997	1904	0.0177
	bromine	0.9998	7117	0.0427
	zinc	0.9928	2018	0.015
	phosphorus	0.9935	782	0.039
By-pass Dust	lead	0.9999	1710	0.037
	bromine	0.9997	5436	0.35
	zinc	0.9996	2248	0.008
	phosphorus	0.9971	762	0.017

TABLE A.8.   WORKING STANDARDS CALIBRATION CONSTANTS (CPS/%)

		Pb	Br	Zn	P
Raw Meal	Average Value	25043	31855	18213	5060
	Coefficient of Variation	0.6%	1.2%	1.1%	3.0%
Clinker	Average Value	19318	23872	13507	**
	Coefficient of Variation	4.9%	3.3%	3.3%	**
C.T. Solids	Average Value	8379	22835	14164	6313
	Coefficient of Variation	1.1%	3.6%	3.4%	4.6%
B.P. Dust	Average Value	7057	18312	12220	5990
	Coefficient of Variation	9.0%	12.2%	3.1%	8.3%

**P in clinker was determined using NBS Standard Reference Materials

(see text).

convenient procedure depends upon a measurement of scattered X-ray intensity, as discussed below.

In this study, there were four different types of materials, each being analyzed for four elements, making a total of sixteen analytical situations. For ease of description, they are represented below by six letters. Each letter denotes a change in either instrumental conditions of analytical procedure at ORF for that particular analysis.

Classification of Analytical Situations

	Pb	Br	Zn	P
RM	C	A	A	D
CL	C	A	A	E
CTS	A	A	A	D
BPD	B	B	B	F

The final analytical procedures used at ORF are summarized below, referring to the classification of analytical situations given above.

(a) Types A, C and D Analyses

The four pairs of working standards were measured to obtain an average value of the calibration constant (cps/%). Measured intensities (cps) were divided directly by the calibration constant to obtain element percentage in the unknowns.

(b) Types B and F Analyses

Six pairs of working standards were used to obtain six values of the calibration constant. A linear least squares correlation was computed between the calibration constant and the scattered intensity measured at 17.60° under instrumental conditions for type A and B analyses. For each individual BPD sample, a value of the calibration constant was calculated from its scattered intensity and the least squares equation. Measured element intensities were divided by the calculated calibration constant to obtain element percentage in the unknowns.

(c)   Type E Analyses

NBS Standard Reference Materials were used to compute
a least squares linear relationship between % P and
measured intensities. This equation was used directly
to obtain % P in unknown clinker samples.

Since the method described for calibration of by-pass
dust analyses is somewhat time consuming and since the
by-pass dust generally contributes only a small
part to the mass balance, it was decided that the
analysis of unknowns carried out at St. Lawrence should
proceed without resort to this method. At St. Lawrence
Cement, one sample of each material type was spiked
with the elements to be analyzed giving a single
working standard calibration for each element in
each material. The calibration constants were then
used to obtain elemental percentages in the unknown
samples.

The instrumental conditions used at both laboratories
are given in Table A.9 Instrumental conditions reported
in this table for analyses done at ORF are related to
the various experimental types discussed above.

Lower limits of detection are defined as that concen-
tration which gives a count rate equivalent to A times
the standard deviation of the background.

$$L.L.D. = \frac{A}{m} \left[R_b/T_b \right]^{1/2}$$

where m = slope in cps per %

R_b = background count rate in cps

T_b = time for background count in seconds

Limits of detection for A = 3 (99 percent confidence) and A =
2 (95 percent confidence) are given in Table A.10.

A.8   Analysis of Waste Oils

The following spectrometric procedures were developed for the
analysis of 15 waste oil samples for lead, bromine, zinc and phosphorus.

TABLE A.9. INSTRUMENT CONDITIONS
AT ORF

	Type A and B	Type C	Type D,E and F
Tube/voltage	Cr/50kV-40mA	W/50kV-40mA	Cr/50kV-40mA
Crystal	LiF	LiF	Ge
Collimator	Fine	Fine	Coarse*
Detector/voltage setting	SC/.8+400	SC/.8+400	FC/1.4+460
Amplifier gain	128	32	128
Baseline/window	100/open	100/350	80/150
Counting Time	40 sec.	40 sec.	40 sec.
Vacuum	No	No	<0.5 Torr.
Angles	17.50 Scatter		
(* = background)	27.60*	27.60 *	138.00*
	28.23 PbLβ	28.23 PbLβ	141.05 PKα
	29.20*	29.20 *	
	29.94 BrKα		
	31.00*		
	41.00*		
	41.76 ZnKα		
	42.50		

TABLE A.9.   (CONTINUED)

AT SLC

Element	Pb	Br	Zn	P
Tube	Cr	Cr	Cr	Cr
Voltage	60kV-24mA	60kV-24mA	60kV-24mA	60kV-24mA
Detector	scintillation	scint.	scint.	flow
Counting Time				
Clinker	1000 sec.	100 sec.	100 sec.	100 sec.
Raw Meal	400 sec.	100 sec.	100 sec.	100 sec.
Others	100 sec.	100 sec.	100 sec.	100 sec.
Vacuum	<0.5 Torr.	<0.5 Torr.	<0.5 Torr.	<0.5 Torr.
Angles	27.76*	28.90*	40.95*	
	28.23PbLβ	29.94BrKα	41.76ZnKα	141.05 PKα
	28.90*	31.40*	42.80*	143.10*

(* = background)

† no vacuum used for oil analysis

TABLE A.10. LOWER LIMITS OF DETECTION

ORF Data

Material	Pb		Br		Zn		P	
	95%	99%	95%	99%	95%	99%	95%	99%
Raw meal	.0002	.0003	.0003	.0005	.0004	.0006	.0011	.002
Clinker	.0003	.0004	.0004	.0006	.0005	.0008	.0009	.001
C.T. Solids	.0012	.0018	.0004	.0006	.0005	.0007	.0009	.001
B.P. Dust	.0014	.0021	.0005	.0007	.0005	.0008	.0009	.001

SLC Data

Material	Pb		Br		Zn		P	
	95%	99%	95%	99%	95%	99%	95%	99%
Raw meal	.0003	.0004	.0003	.0004	.0004	.0006	.004	.005
Clinker	.0003	.0005	.0004	.0006	.0006	.0009	.004	.007
C.T. Solids	.0014	.0021	.0003	.0005	.0007	.0010	.003	.005
B.P. Dust	.0015	.0023	.0004	.0006	.0006	.0009	.003	.005

A.8.1   Sample Preparation

Prior to analysis, all samples were individually shaken in a
paint mixer apparatus to suspend all solids and allow representative
sampling. Immediately after mixing, a sample was poured into the usual
stainless steel holder and placed in the X-ray spectrograph for measurement.
Preliminary tests indicated that gradual intensity changes occur if the
sample is allowed to stand for prolonged periods, presumably due to the
settling of suspended particles. Table A.11 shows net intensity versus
time for a typical waste oil sample. Lead intensity shows a gradual
increase, bromine a corresponding decrease, while zinc shows very little
change.

During actual analysis, the total elapsed time required to
complete all the necessary measurements on any sample did not exceed 2
minutes. In each case, a second series of measurements was then made
on the same sample to check for any gross changes due to accelerated
settling. No instances of accelerated settling were found.

Other than for thorough mixing before sampling, the waste oils
were analysed directly, as received.

A.8.2   Standards and Analytical Methods

Preliminary tests indicated that standards prepared by adding
individual elements to clean oil were not satisfactory because of the
serious matrix absorption effects introduced by the lead content of the
waste oil. On the basis of these tests, standards were prepared by
addition of individual elements to representative waste oil samples.
Since all the waste oils being analysed came from two sources, the
samples were classified before analysis into two groups and one sample
from each group was used as a base for the addition procedure. The
substances used as addition materials were metallo-organic compounds
in either pure form or as a concentrated solution in a compatible
base oil. Information on these substances is given in Table A.12.

Bromine and zinc were analysed using separate calibration
constants for each group of oil. In the case of phosphorus, the two
calibrations were so similar that one combined constant was used for all

TABLE A.11.   EFFECT OF SETTLING ON XRF NET INTENSITIES IN WASTE OILS

Elapsed Time	Net Intensity (cps)		
(min)	Pb	Br	Zn
0	33567	14467	8914
5	33523	14397	8894
10	33538	14420	8881
15	33686	14406	8893
20	33843	14329	8874
25	33849	14204	8977
30	33956	14315	8960

TABLE A.12. SOURCE OF STANDARDIZING SUBSTANCES USED FOR WASTE OIL ANALYSES

Pb.	24.31%	National Spectrographic Labs 630-39-11
Br	92.47%	Fisher Scientific A-29 (s-tetra-bromoethane)
Zn	8.06%	National Spectrographic Labs 630-39-23
P	1.32%	National Spectrographic Labs 630-39-17

phosphorus determinations. In addition, it was necessary to correct all phosphorus net intenstities by subtracting a small residual net count which probably originates in the mylar film covering the bottom of the sample holder. This residual count was measured with a white oil sample in the holder. Final calibration constants for this group of elements, as determined by least squares methods, are included in Table A.13.

The analysis for lead presented some additional problems, in that the original calibration line produced by adding lead to waste oil was found to be non-linear. With a relatively large amount of lead present in the waste oil it was not possible to accurately extrapolate the line back to a zero point. For this reason a new calibration line was produced by adding lead to new oil rather than waste oil. This was also a curved line, but no extrapolation was required. Analytical results read directly off this graph are considered to be valid since the largest matrix effect is produced by lead itself. The absence in the standards of the other elements present in waste oil, should have only a minor effect on the accuracy of the lead analyses.

A.8.3   Instrumental Conditions

The instrumental conditions used for measurement of both standards and samples are given in Table A.14. For measurement of phosphorus, the spectrometer was divided into two sections by a .00015" polyester film at the collimator entrance. The crystal chamber section was evacuated to less than 0.5 Torr, while the sample chamber remained at atmospheric pressure. This avoided placing the oil into a vacuum, while still maintaining minimum absorption of the phosphorus Kα wavelength.

A.8.3   Detection Limits

Lower limits of detection for Pb, Br, Zn, and P in waste oil are included in Table A.13.

A.9   Analysis of Airborne Particulates

Filter deposits of two types were received for analysis, deposits collected on glass fibre filters by stack sampling, and probe

TABLE A.13.   CALIBRATION CONSTANTS AND DETECTION LIMITS FOR ANALYSIS OF OIL

	Calibration Constant		Lower Limit of Detection
Pb	(non-linear)		.002%
Br	Group 1	156,866 cps per %	.0003%
	Group 2	153,374 cps per %	
Zn	Group 1	110,242 cps per %	.0003%
	Group 2	116,981 cps per %	
P	792 cps per %		.006%

TABLE A.14.   INSTRUMENTAL CONDITIONS FOR ANALYSES OF WASTE OILS

	Pb, Br, Zn	P
Tube/operation	Cr/50 kV-40 mA	Cr/50kV-40 mA
Crystal	LiF	Ge
Collimator	Fine	Coarse
Detector/voltage setting	SC/.8 + 400	FC/1.4 + 460
Amplifier gain	128	128
Base line/window	100/open	65/200
Counting time	10 seconds	40 seconds
Vacuum	No	Crystal chamber <.5 torr Sample chamber in air.
Angles	26.10*	137.00*
(*=background)	28.21 PbLβ	141.00 PKα
	29.94 BrKα	
	32.00*	
	40.80*	
	41.76 ZnKα	
	43.00*	

rinse solids collected on membrane filters. Each deposit was analysed for lead, bromine, zinc and phosphorus. For analytical purposes both type of deposits were considered to be equivalent and were analysed by a single calibration procedure.

The deposits ranged from very thick to very thin layers, and in many cases the deposit did not adhere to the filter. Since it was not possible to analyse the deposits in situ and the amount of material available was not enough to produce a standard size pellet, a mini-pellet technique was adopted. A pellet diameter of 1/2" was used, and by preliminary experiment the weight of sample required to produce an infinitely thick layer for the most penetrating analytical radiation was determined as 0.1 gm. This thin layer of sample was backed by a thick layer of methocel to produce a strong pellet. Suitable masks and retaining rings of steel were devised to position the mini-pellets in the sample chamber. The same masks could be used with standard size pellets to present the equivalent sample area for analysis.

A.9.1   Sample Preparation

The powder deposits were carefully scraped off each filter and collected in plastic vials. 0.1 gm of sample was added to 0.025 gm of methocel, transferred to a clean plastic vial and shaken by hand until uniformly mixed. In those cases where the total sample available was less than 0.1 gm, the deficiency was made up by adding reagent calcium carbonate. The mixed powder was then pelletized with a backing of methocel to form a duplex pellet 1/2" diameter and about 1/8" thick. The pelletizing procedure follows. Pour about 1/2 ml of methocel powder in the 1/2" mould and tamp lightly to form a smooth surface. (Excess pressure at this time will result in poor interlayer adhesion.) Pour the mixed sample powder on top and spread evenly. Compress at 10 tons pressure for about 1 minute.

A.9.2   Standards

Standards were prepared by adding each of the analytical elements to a sample of precipitator dust which was as similar as possible to the filter deposits in chemical composition. The additions

were made using standard solutions. Four multi-element standards
were prepared by adding 0.5 ml, 1 ml, 1.5 ml, or 2 ml of the Pb, Br,
Zn, and P stock solutions to 2 gm of precipitator dust.

Intensity measurements on the above standards using instrumental
conditions listed in Table A.15, produced linear calibration curves.
In the case of phosphorus, the previously prepared NBS-SRM Portland
cements were used to determine the residual net count rate at the
phosphorus position, i.e., the intercept value of the least squares
equation when %P = 0. This value, 72.2 counts per second was treated
as a blank instrument reading, and was subtracted from all peak
measurements to give net peak intensities.

Least squares calibration equations, computed for each element,
gave the correlation coefficients, slopes and intercepts are listed in
Table A.16.

Net count rates for the unknown samples were converted to %
element using the calibration constants (slopes) given in Table A.16.
In those instances where $CaCO_3$ had been added to the powder mixture,
a correction was applied to compensate for the sample dilution. This
correction also took into account the fact that small amounts of the
analytical elements were detected in the calcium carbonate. For
example, using the procedure and standards described above, .0074%
Zn and .005% P, were detected in the reagent $CaCO_3$. No Pb was detected.
The correction took the form of the equation shown below for Zn.

$$\% \text{ Zn (corrected)} = .1 \times \% \text{ Zn (uncorrected)} - \frac{\% \text{ Zn } (CaCO_3) \times \text{wt. } CaCO_3}{\text{wt. sample}}$$

A.9.3   Detection Limits

Lower limits of detection are given below:

Pb	.007%
Br	.004%
Zn	.005%
P	.001%

TABLE A.15.   INSTRUMENTAL CONDITIONS FOR ANALYSES OF FILTER DEPOSIT

	Pb	Br, Zn	P	Cl
Tube/voltage	W/60kV-45 mA	Cr/60kV-45 mA	Cr/60kV-45 mA	Cr/50kV-40 mA
Crystal	LiF	LiF	Ge	FET
Collimator	Fine	Fine	Coarse	Coarse
Detector/voltage setting	SC/.8 + 400	SC/.8 + 400	FC/1.4 + 460	FC/1.4 + 460
Amplifier gain	32	32	128	128
Base line/window	100/350	100/350	80/150	100/200
Counting time	100 seconds	100 seconds	100 seconds	10 seconds
Vacuum	No	No	.5 torr	.5 torr
Angles	27.60*	26.00*	138.00*	65.55 ClK
(* = background)	28.24 PbLβ	29.94 BrKα	141.05 PKα	67.20*
	29.20*	32.00*		
		41.78 ZnKα		
		43.00*		
Sample Mask	Steel	Steel	Steel	Steel
	.485" dia.	.485" dia.	.485" dia.	.485" dia.

TABLE A.16.   LEAST SQUARES CALIBRATION DATA FOR ANALYSES OF FILTER DEPOSITS

Element	Correlation Coefficient	Slope cps per %	Intercept %
Pb	.9994	15,402	.0037%
Br	.9961	17,395	.028%
Zn	.9999	8,979	.0058%
P	.9904	4,090	.030%
Cl	.9766	2,477	1.34%

A.10   Analyses of Probe-Rinse and Impinger Solutions

Aqueous probe-rinse and impinger solutions were analyzed by identical methods. Phosphate was determined colorimetrically by A.P.H.A. standard method 223E (A 5), using stannous chloride and ammonium molybdate. Zinc and lead were determined by atomic absorption using spiking techniques. Estimated limits of detection for P, Zn and Pb are 0.04 ppm, 0.1 ppm and 0.1 ppm respectively.

The following procedure was used to analyse the solutions for trace amounts of bromine. The lower limit of detection for the method was found to be 0.5 ppm Br.

No sample preparation was required, since the samples were clear solutions. A standard solution containing 500 ppm Br was prepared by dissolving KBr in distilled water. Further dilution of this stock solution by factors of 10 X and 100 X yielded standard solutions containing 50 and 5 ppm Br resepectively. Measurement of the Net BrKα intensity for the three solutions resulted in the linear calibration.

Instrumental conditions are summarized in Table A.17. Full tube power was used to yield maximum sensitivity, with a tight pulse height discriminator setting to reduce background as much as possible. Background at the peak position was interpolated from measurements 1° on either side of the peak. This procedure was found to give a small negative net count (110 counts) with distilled water due to a gradual curvature of the background profile in this angle range. To correct for this error 110 counts were added to all net count determinations.

TABLE A.17. INSTRUMENTAL CONDITIONS FOR ANALYSIS OF Br IN SOLUTIONS

Tube/voltage	Cr/60kV – 45 mA
Crystal	Lif
Collimator	Fine
Detector/voltage setting	SC/.8 + 400
Amplifier gain	32
Base line/window	100/350
Counting time	100 seconds
Vacuum	No
Angles	28.94*
(* = background)	29.94 BrKα
	30.94*

REFERENCES FOR APPENDIX A

(A 1)   "Standard Reference Methods for Source Testing: Measurement
         of Emissions of Particulates from Stationary Sources"
         APCD/EPS, Report EPS 1-AP-74-1, Feb. 1974.

(A 2)   "Source Testing Code" Ministry of the Environment, Province
         of Ontario, Air Management Branch, Jan. 1973.

(A 3)   Blaine, R.L., Bean, L. and Hubbard, E.K., "Occurrence of
         Minor and Trace Elements in Portland Cement", "Interrelations
         Between Cement and Concrete Properties", Part 1, Section 3,
         Building Science Series 2, NBS. Aug. 1965, p 33.

(A 4)   Cowgill, U.M., "Use of X-Ray Emission Spectroscopy in the
         Chemical Analysis of Lake Sediments, Determining 41 Elements"
         in Pearson, L.R. and Grove, E.L., "Developments in Applied
         Spectroscopy", Vol. 5, p 3, Plenum Press, New York, 1966.

(A 5)   "Method 223E: Phosphate by the $SnCl_2$ method" in "Standard
         Methods for the Examination of Water and Waste Water" 13th
         Edn. Publ. by APHA-AWWA-WPCF, p 530, 1971.

APPENDIX B

APPENDIX B

RESULTS AND CALCULATIONS

B.1   Mass Balance Experimentation

B.1.1   Results of Analyses of Process Materials

Analyses of solid process materials (raw meal, clinker, by-pass dust, conditioning tower solids) were carried out at both St. Lawrence Cement and Ontario Research Foundation. Solids for the entire experiment were analyzed at St. Lawrence Cement, a limited number were analyzed at Ontario Research Foundation to check analytical agreement. Waste oil and bunker 'C' fuel oil were analyzed for lead content by the National Research Council, Mechanical Engineering Division, Fuels and Lubricants Laboratory section and by the Research and Development laboratories of the Canadian National Railways and three samples were analyzed at St. Lawrence Cement Co. to check analytical agreement between laboratories.

Tables B.1 to B.5 show the comparative results of analyses of materials carried out by more than one laboratory.

The analytical results reported by St. Lawrence Cement for process materials are given in Tables B.6 to B.9. All analyses are reported as percent by weight of the analyzed element.

Analyses of a limited number of samples of No. 6 fuel oil taken at intervals throughout the experiment showed none to contain detectable quantities of Pb, Br, Zn, or P.

B.1.2   Calculation of Material Balances

A daily record of production and materials consumption is given in Table B.10 for the period March 9, 1974 to May 30, 1974. Production was disrupted through this time by a kiln breakdown and repair lasting through the period March 31 to April 12. At some other times, by-pass system shutdowns were necessary, these are indicated in the Table B.10 by zero or low values of reported quantities for by-pass dust and conditioning tower solids. From the daily composite analysis of each material for each element, and the total daily quantity

TABLE B.1.   COMPARISON OF ORF AND SLC ELEMENTAL ANALYSES RESULTS FOR RAW MEAL

	% Pb		% Br		% Zn		% P	
Date	ORF	SLC	ORF	SLC	ORF	SLC	ORF	SLC
16/3	.0005	.0009	.0001	.0008	.0043	.0050	.035	.042
19/3	.0002	.0007	.0004	.0007	.0033	.0049	.038	.036
20/3	.0007	.0005	.0003	.0003	.0042	.0052	.036	.032
21/3	.0001	.0003	.0006	.0004	.0037	.0050	.037	.038
22/3	.0002	.0005	.0008	.0006	.0039	.0052	.035	.040
23/3	.0001	.0006	.0006	.0004	.0042	.0059	.036	.036
24/3	.0005	.0005	.0007	.0008	.0045	.0053	.037	.040
27/3	.0005	.0004	.0006	.0008	.0043	.0048	.035	.044
30/3	.0003	.0007	.0002	.0010	.0047	.0050	.036	.038
22/4	.0007	.0010	.0010	.0012	.0040	.0056	.036	.035
24/4	.0007	.0006	.0006	.0012	.0039	.0051	.035	.040
25/4	.0006	.0005	.0008	.0010	.0043	.0055	.037	.039
27/4	.0003	.0005	.0008	.0008	.0034	.0057	.036	.040
28/4	.0007	.0004	.0010	.0009	.0039	.0051	.037	.038
29/4	.0001	.0004	.0005	.0009	.0037	.0060	.039	.037
30/4	.0004	.0005	.0008	.0007	.0045	.0052	.036	.043
1/5	.0006	.0005	.0007	.0011	.0038	.0054	.037	.035
2/5	.0004	.0003	.0006	.0010	.0040	.0055	.037	.039
3/5	.0005	.0007	.0009	.0025	.0042	.0047	.039	.035
4/5	.0004	.0006	.0005	.0008	.0039	.0052	.036	.037
5/5	.0006	.0005	.0014	.0005	.0040	.0058	.035	.041
6/5	.0006	.0005	.0005	.0010	.0037	.0048	.037	.037
7/5	.0005	.0003	.0009	.0008	.0042	.0048	.037	.034
8/5	.0003	.0006	.0005	.0008	.0042	.0046	.038	.040
9/5	.0003	.0002	.0007	.0010	.0036	.0047	.039	.043
10/5	.0001	.0006	.0006	.0011	.0043	.0048	.039	.041

* ND = none detected.

TABLE B.2. COMPARISON OF ORF AND SLC ELEMENTAL ANALYSES RESULTS FOR CLINKER

Date	% Pb		% Br		% Zn		% P	
	ORF	SLC	ORF	SLC	ORF	SLC	ORF	SLC
11/3	.0006	.0004	.0004	.0008	.0053	.0075	.063	.074
19/3	.0008	.0010	.001	.0008	.0047	.0084	.063	.055
20/3	.0003	.0008	ND*	.0003	.0055	.0092	.058	.053
21/3	.0030	.0025	ND	.0004	.0057	.0098	.059	.059
22/3	.0032	.0036	.0001	.002	.0059	.0088	.060	.070
23/3	.0005	.0016	.0002	.001	.0061	.0086	.061	.055
24/3	.0008	.0013	.0002	.0008	.0055	.0086	.059	.054
27/3	.0082	.0072	.0003	.001	.0070	.010	.060	.057
30/3	.0010	.0012	.0005	.0004	.0060	.0083	.059	.055
22/4	.0129	.011	.0005	.0006	.0075	.011	.064	.057
24/4	.0036	.0035	.001	.001	.0054	.0090	.059	.063
25/4	.0004	.0017	.0004	.0009	.0058	.0093	.059	.060
27/4	.013	.011	.0004	.001	.0079	.011	.063	.062
28/4	.012	.012	.0002	.0007	.0065	.011	.062	.064
29/4	.012	.0094	.0006	.0002	.0075	.010	.064	.071
30/4	.0099	.0091	.0009	.002	.0071	.011	.062	.064
1/5	.0090	.0078	ND	.0007	.0067	.010	.060	.054
2/5	.010	.0088	.0003	.001	.0065	.010	.060	.062
3/5	.0095	.0085	.001	.002	.0069	.011	.065	.062
4/5	.0090	.0084	.001	.001	.0072	.011	.063	.055
5/5	.0086	.0076	.0007	.001	.0073	.012	.060	.061
6/5	.0069	.0067	.0001	.0006	.0067	.011	.060	.064
7/5	.0035	.0038	ND	.0005	.0055	.0093	.062	.056
8/5	.0010	.0012	.0001	.0007	.0056	.0094	.062	.056
9/5	.0004	.0011	.0008	.0009	.0058	.0089	.062	.066
10/5	.0003	.0013	.0003	.0007	.0057	.0088	.063	.069

* ND = none detected.

TABLE B.3. COMPARISON OF ORF AND SLC ELEMENTAL ANALYSIS RESULTS FOR
CONDITIONING TOWER SOLIDS

Date	% Pb		% Br		% Zn		% P	
	ORF	SLC	ORF	SLC	ORF	SLC	ORF	SLC
19/3	.020	.024	.045	.037	.012	.019	.027	.038
20/3	.017	.020	.037	.031	.012	.018	.028	.044
21/3	.019	.022	.034	.029	.012	.020	.028	.042
22/3	.11	.031	.071	.053	.013	.020	.030	.040
23/3	.051	.065	.064	.052	.016	.026	.029	.040
24/3	.027	.029	.055	.047	.013	.020	.028	.038
25/3	.037	.041	.066	.054	.016	.025	.026	.038
27/3	.23	.26	.076	.061	.020	.031	.027	.044
18/4	.11	.10	.076	.068	.009	.014	.029	.036
22/4	.23	.26	.13	.11	.014	.021	.030	.033
24/4	.043	.065	.10	.10	.007	.013	.029	.040
25/4	.027	.034	.087	.074	.008	.012	.028	.039
27/4	.22	.25	.18	.15	.015	.024	.030	.040
28/4	.19	.21	.20	.18	.013	.020	.031	.038
29/4	.20	.24	.19	.16	.014	.022	.031	.037
30/4	.19	.26	.15	.16	.014	.025	.029	.043
1/5	.18	.17	.16	.13	.013	.021	.030	.035
2/5	.27	.26	.17	.14	.018	.029	.029	.039
4/5	.15	.18	.19	.17	.019	.030	.033	.037
5/5	.19	.21	.19	.15	.020	.030	.033	.041
6/5	.19	.22	.13	.12	.014	.022	.031	.037
7/5	.11	.12	.10	.096	.010	.016	.026	.034
8/5	.040	.053	.080	.072	.008	.015	.025	.035
9/5	.027	.036	.073	.064	.009	.014	.028	.036

TABLE B.4. COMPARISON OF ORF AND SLC ELEMENTAL ANALYSES RESULTS FOR BY-PASS DUST

Date	% Pb		% Br		% Zn		% P	
	ORF	SLC	ORF	SLC	ORF	SLC	ORF	SLC
15/3	.037	.041	.33	.31	.009	.012	.016	.020
19/3	.051	.050	.44	.35	.011	.014	.008	.014
20/3	.042	.046	.29	.28	.013	.017	.015	.021
21/3	.027	.030	.14	.16	.014	.017	.028	.029
22/3	.21	.25	.38	.36	.016	.020	.021	.023
23/3	.082	.089	.47	.41	.012	.015	.012	.016
24/3	.15	.16	.37	.33	.014	.018	.021	.021
25/3	.065	.074	.43	.40	.011	.014	.013	.016
21/4	.23	.25	.91	.74	.008	.010	.014	.019
22/4	.35	.29	.91	.75	.009	.011	.014	.012
24/4	.32	.36	.67	.62	.010	.014	.018	.032
25/4	.10	.12	.58	.51	.007	.010	.017	.022
27/4	.13	.052	.73	.49	.008	.009	.013	.019
28/4	.22	.24	.94	.80	.009	.012	.015	.016
30/4	.22	.24	.89	.79	.011	.014	.021	.022
1/5	.25	.28	.78	.74	.012	.017	.021	.026
2/5	.33	.41	.96	.98	.013	.016	.016	.018
4/5	.36	.38	1.27	1.02	.010	.014	.011	.014
5/5	.40	.40	1.71	1.20	.010	.012	.004	.004
6/5	.45	.44	1.69	1.20	.009	.013	.003	.007
7/5	.35	.14	1.34	1.49	.011	.012	.009	.012
8/5	.15	.15	.90	.70	.008	.011	.013	.014
9/5	.076	.082	.71	.59	.007	.009	.013	.016
10/5	.082	.091	.72	.59	.007	.009	.011	.015

TABLE B.5. WASTE OIL ANALYSES

Date	Aver. Specific Gravity	% Pb				% Br		% Zn		%P
		ORF	NRC[1]	CN[2]	SLC	ORF	SLC	ORF	SLC	ORF
19/4	0.8897	0.53				0.093		0.080		0.092
20/4	0.8951	0.52	0.41	0.62		0.090		0.080		0.092
21/4	0.8944	0.53			0.61	0.095	0.095	0.081	0.075	0.103
22/4	0.8964	0.55	0.46	0.69		0.102		0.085		0.111
23/4	0.8974	0.48				0.135		0.104		0.091
27/4	0.9232	0.54	0.48	0.69	0.56	0.160	0.160	0.106	0.095	0.111
28/4	0.9068	0.54				0.146		0.099		0.102
29/4	0.9031	0.50				0.120		0.090		0.098
30/4	0.8935	0.47	0.41	0.62		0.119		0.087		0.093
1/5	0.8923	0.48				0.121		0.085		0.102
2/5	0.9000	0.47	0.47	0.64		0.131		0.088		0.097
3/5	0.8902	0.47				0.132		0.088		0.086
4/5	0.8903	0.46				0.134		0.088		0.093
5/5	0.9144	0.46	0.48	0.63	0.55	0.134	0.133	0.086	0.082	0.089
6/5	0.8925	0.45				0.133		0.083		0.092

TABLE B.6. RESULTS FROM ANALYSES OF RAW MEAL FEED SAMPLES
(ST. LAWRENCE CEMENT CO. DATA)

Date	% Pb	% Br	% Zn	% P
9/3	.0005	.0007	.0048	.038
10/3	.0006	.0010	.0048	.040
11/3	.0005	.0008	.0051	.039
12/3		No Sample		
13/3	.0003	.0007	.0048	.040
14/3	.0006	.0009	.0048	.040
15/3	.0006	.0011	.0047	.038
16/3	.0009	.0008	.0050	.042
17/3	.0003	.0005	.0044	.036
18/3	.0004	.0008	.0052	.038
19/3	.0007	.0007	.0049	.036
20/3	.0005	.0003	.0052	.032
21/3	.0003	.0004	.0050	.038
22/3	.0005	.0006	.0052	.040
23/3	.0006	.0004	.0059	.036
24/3	.0005	.0008	.0053	.040
25/3	.0004	.0011	.0051	.040
26/3	.0004	.0007	.0070	.040
27/3	.0004	.0008	.0048	.044
28/3	.0004	.0010	.0047	.038
29/3	.0003	.0011	.0050	.042
30/3	.0007	.0010	.0050	.038
13/4	.0005	.0010	.0050	.034
14/4	.0005	.0014	.0054	.040
15/4	.0003	.0010	.0053	.036
16/4	.0007	.0012	.0052	.030
17/4	.0004	.0011	.0051	.041
18/4	.0006	.0008	.0047	.037
19/4	.0010	.0015	.0048	.038
20/4	.0006	.0015	.0052	.038
21/4	.0009	.0016	.0050	.040
22/4	.0010	.0012	.0056	.035
23/4	.0008	.0016	.0048	.038

Date	% Pb	% Br	% Zn	% P
24/4	.0006	.0012	.0051	.040
25/4	.0005	.0010	.0055	.039
26/4	.0006	.0009	.0047	.036
27/4	.0005	.0008	.0047	.040
28/4	.0004	.0009	.0051	.038
29/4	.0004	.0009	.0060	.037
30/4	.0005	.0007	.0052	.043
1/5	.0005	.0011	.0054	.035
2/5	.0003	.0010	.0055	.039
3/5	.0007	.0006	.0047	.035
4/5	.0006	.0008	.0052	.037
5/5	.0005	.0005	.0058	.041
6/5	.0005	.0010	.0048	.037
7/5	.0003	.0008	.0048	.034
8/5	.0006	.0008	.0046	.040
9/5	.0002	.0010	.0047	.043
10/5	.0006	.0011	.0048	.041
11/5	.0005	.0008	.0052	.035
12/5	.0004	.0009	.0051	.036
13/5	.0003	.0008	.0056	.036
14/5	.0005	.0011	.0051	.034
15/5		Kiln down		
16/5				
17/5	.0004	.0012	.0051	.034
18/5	.0003	.0012	.0052	.035
19/5	.0003	.0014	.0050	.038
20/5	.0005	.0014	.0051	.039
21/5	.0004	.0013	.0044	.038
22/5	.0004	.0013	.0046	.035
23/5	.0003	.0012	.0049	.031
24/5	.0003	.0011	.0053	.040
25/5	.0005	.0013	.0045	.038
26/5	.0003	.0013	.0053	.037
27/5	.0003	.0011	.0054	.036
28/5	.0002	.0010	.0051	.036
29/5	.0003	.0005	.0048	.038
30/5	.0004	.0010	.0052	.032

TABLE B.7.   RESULTS FROM ANALYSES OF CLINKER SAMPLES
(ST. LAWRENCE CEMENT CO. DATA)

Date	% Pb	% Br	% Zn	% P
9/3	.0009	.0007	.0081	.056
10/3	.0006	.0001	.0089	.054
11/3	.0004	.0008	.0075	.074
12/3	.0009	.0003	.0083	.059
13/3	.0005	.0004	.0080	.055
14/3	.0009	.0003	.0085	.053
15/3	.0011	.0008	.0098	.058
16/3	.0014	.0007	.0086	.058
17/3	.0007	.0004	.0080	.053
18/3	.0010	.0019	.0087	.059
19/3	.0010	.0008	.0084	.055
20/3	.0008	.0003	.0092	.053
21/3	.0025	.0004	.0098	.059
22/3	.0036	.0015	.0088	.070
23/3	.0016	.0014	.0086	.055
24/3	.0013	.0008	.0086	.054
25/3	.0010	.0010	.0084	.054
26/3	.0023	.0008	.0088	.057
27/3	.0072	.0010	.0101	.057
28/3	.0038	.0008	.0092	.061
29/3	.0021	.0011	.0084	.057
30/3	.0012	.0004	.0083	.055
13/4	.0010	.0004	.0095	.062
14/4	.0011	.0006	.0091	.053
15/4	.0010	.0008	.0094	.055
16/4	.0009	.0005	.0083	.049
17/4	.0014	.0007	.0086	.047
18/4	.0050	.0002	.0110	.054
19/4	.0115	.0011	.0112	.062
20/4	.0112	.0008	.0104	.062
21/4	.0115	.0009	.0105	.065
22/4	.0111	.0006	.0112	.057
23/4	.0131	.0004	.0118	.064

TABLE B.7. (CONT'D)

Date	% Pb	% Br	% Zn	% P
24/4	.0035	.0012	.0090	.063
25/4	.0017	.0009	.0093	.060
26/4	.0068	.0006	.0102	.054
27/4	.0108	.0010	.0105	.062
28/4	.0117	.0007	.0111	.064
29/4	.0094	.0002	.0103	.071
30/4	.0091	.0018	.0110	.064
1/5	.0078	.0007	.0104	.054
2/5	.0088	.0012	.0101	.062
3/5	.0085	.0018	.0108	.062
4/5	.0084	.0014	.0110	.055
5/5	.0076	.0012	.0117	.061
6/5	.0067	.0006	.0106	.064
7/5	.0038	.0005	.0093	.056
8/5	.0012	.0007	.0094	.056
9/5	.0011	.0009	.0089	.066
10/5	.0013	.0007	.0088	.069
11/5	.0011	.0008	.0086	.048
12/5	.0010	.0009	.0090	.056
13/5	.0008	.0007	.0083	.054
14/5	.0007	.0007	.0091	.049
15/5		Kiln down		
16/5				
17/5	.0014	.0013	.0078	.052
18/5	.0009	.0008	.0083	.050
19/5	.0011	.0008	.0089	.057
20/5	.0012	.0006	.0085	.055
21/5	.0010	.0010	.0083	.048
22/5	.0011	.0010	.0085	.054
23/5	.0006	.0010	.0083	.061
24/5	.0004	.0009	.0087	.058
25/5	.0009	.0012	.0080	.053
26/5	.0009	.0013	.0088	.052
27/5	.0010	.0003	.0086	.053
28/5	.0010	.0008	.0089	.051
29/5	.0009	.0008	.0083	.051
30/5	.0004	.0002	.0081	.058

TABLE B.8.   RESULTS FROM ANALYSES OF CONDITIONING TOWER SOLIDS SAMPLES
(ST. LAWRENCE CEMENT CO. DATA)

Date	% Pb	% Br	% Zn	% P
9/3	.015	.034	.019	.038
10/3	.015	.024	.014	.038
11/3	.017	.036	.016	.040
12/3	.022	.041	.018	.040
13/3	.020	.055	.017	.034
14/3	.017	.045	.014	.034
15/3	.021	.046	.015	.039
16/3	.026	.044	.016	.037
17/3	.019	.037	.012	.041
18/3	.023	.032	.017	.036
19/3	.024	.037	.019	.038
20/3	.020	.031	.018	.044
21/3	.022	.029	.020	.042
22/3	.131	.053	.020	.040
23/3	.065	.052	.026	.040
24/3	.029	.047	.020	.038
25/3	.041	.054	.025	.038
26/3	.089	.056	.031	.036
27/3	.260	.061	.031	.044
28/3	.100	.087	.027	.037
29/3	.176	.063	.032	.027
16/4	.024	.050	.013	.037
17/4	.029	.054	.013	.032
18/4	.103	.068	.014	.036
19;4	.220	.092	.018	.032
20/4	.256	.099	.019	.035
21/4	.283	.117	.020	.035
22/4	.260	.110	.021	.033
23/4	.294	.128	.021	.030

TABLE B.8. (CONT'D)

Date	% Pb	% Br	% Zn	% P
24/4	.065	.100	.013	.040
25/4	.034	.074	.012	.039
26/4	.027	.060	.013	.036
27/4	.249	.148	.024	.040
28/4	.214	.176	.020	.038
29/4	.239	.161	.022	.037
30/4	.256	.155	.025	.043
1/5	.175	.133	.021	.035
2/5	.256	.145	.028	.039
3/5	———————————— By-pass Off ————————————			
4/5	.179	.165	.030	.037
5/5	.209	.155	.030	.041
6/5	.217	.117	.022	.037
7/5	.122	.096	.016	.034
8/5	.053	.072	.015	.035
9/5	.036	.064	.014	.036
10/5	———————————— By-pass Off ————————————			
11/5	————————————			
12/5	.021	.093	.013	.031
13/5	.015	.057	.013	.031
14/5	.019	.066	.013	.038
15/5	———————————— Kiln Down ————————————			
16/5	————————————			
17/5	.017	.058	.012	.034
18/5	.017	.077	.011	.029
19/5	.018	.073	.012	.038
20/5	.018	.075	.012	.038
21/5	.018	.055	.012	.044
22/5	.015	.045	.012	.035
23/5	.016	.044	.012	.037
24/5	.016	.058	.012	.034
25/5	.015	.059	.011	.028
26/5	.017	.052	.013	.032
27/5	———————————— No sample ————————————			
28/5	.015	.055	.012	.038
29/5	.016	.045	.012	.033
30/5	.018	.042	.013	.034

TABLE B.9.   RESULTS FROM ANALYSES OF BY-PASS DUST SAMPLES
(ST. LAWRENCE CEMENT CO. DATA)

Date	% Pb	% Br	% Zn	% P
9/3	-	-	-	-
10/3	.029	.083	.019	.035
11/3	.021	.169	.014	.029
12/3	.031	.300	.013	.018
13/3	.025	.305	.012	.020
14/3	.025	.198	.012	.029
15/3	.041	.309	.012	.020
16/3	.039	.238	.015	.021
17/3	.023	.180	.013	.028
18/3	.033	.282	.013	.020
19/3	.050	.352	.014	.014
20/3	.046	.279	.017	.021
21/3	.030	.156	.017	.029
22/3	.248	.360	.020	.023
23/3	.089	.413	.015	.016
24/3	.159	.329	.018	.021
25/3	.074	.395	.014	.016
15/4	.032	.344	.009	.015
16/4	.030	.351	.007	.019
17/4	.023	.350	.008	.016
18/4	.095	.406	.007	.013
19/4	.138	.457	.008	.029
20/4	.218	.617	.010	.020
21/4	.250	.738	.010	.019
22/4	.387	.750	.011	.012
23/4	No sample			
24/4	.363	.618	.014	.032
25/4	.115	.507	.010	.022
26/4	.054	.494	.009	.019
27/4	.052	.493	.008	.019
28/4	.237	.798	.012	.016
29/4	No sample			
30/4	.236	.790	.014	.022

TABLE B.9. (CONT'D)

Date	% Pb	% Br	% Zn	% P
1/5	.283	.742	.017	.026
2/5	.412	.975	.016	.018
3/5		By-pass Off		
4/5	.379	1.017	.014	.014
5/5	.402	1.204	.012	.004
6/5	.444	1.199	.013	.007
7/5	.144	1.487	.012	.012
8/5	.154	.698	.011	.014
9/5	.082	.588	.009	.016
10/5	.091	.588	.009	.015
11/5		By-pass off		
12/5	.161	.708	.010	.012
13/5	.062	.480	.008	.014
14/5	.036	.329	.009	.021
15/5		Kiln down		
16/5				
17/5	.035	.349	.009	.013
18/5	.041	.391	.009	.016
19/5	.040	.389	.009	.012
20/5	.040	.418	.008	.014
21/5	.038	.353	.008	.012
22/5	.031	.323	.009	.014
23/5	.032	.310	.009	.022
24/5	.023	.234	.010	.024
25/5	.023	.348	.007	.018
26/5	.025	.328	.008	.012
27/5	.027	.381	.007	.014
28/5	.031	.374	.007	.017
29/5	.031	.380	.008	.014
30/5	.029	.333	.008	.020

TABLE B.10.   DAILY RECORD OF PRODUCTION AND MATERIALS CONSUMPTION

Date	Raw Meal Feed (tons/24 hr)	Waste-Oil (gal/24 hr)	Clinker (tons/24 hr)	By-pass Dust (tons/24 hr)	C.T. Solids (tons/24 hr)
9/3/74	2097	0	1363	2.01	6.67
10/3/74	4798	0	3114	6.02	20.00
11/3/74	5328	0	3460	6.02	20.00
12/3/74	5311	0	3449	6.02	20.00
13/3/74	4100	0	2671	2.51	8.33
14/3/74	5335	0	3465	6.02	20.00
15/3/74	5329	0	3461	6.02	20.00
16/3/74	5375	0	3491	6.02	20.00
17/3/74	5357	0	3479	6.02	20.00
18/3/74	5188	0	3369	6.02	20.00
19/3/74	5129	0	3333	5.27	17.50
20/3/74	5022	0	3261	6.02	20.00
21/3/74	5092	4007	3306	6.02	20.00
22/3/74	5015	971	3257	6.02	20.00
23/3/74	4886	0	3188	1.50	5.00
24/3/74	4913	0	3189	6.02	20.00
25/3/74	4851	0	3149	6.02	20.00
26/3/74	4734	3345	3076	5.02	16.67
27/3/74	4891	18084	3186	2.76	9.17
28/3/74	4888	5038	3176	5.02	16.67
29/3/74	4902	3530	3188	4.52	15.00
30/3/74	4615	0	3015	0	0
31/3/74	34	0	22	0	0

TABLE B.10. (CONT'D)

Date	Raw Meal Feed (tons/24 hr)	Waste-Oil (gal/24 hr)	Clinker (tons/24 hr)	By-pass dust (tons/24 hr)	C.T. Solids (tons/24 hr)
Process shut down for kiln repairs 31/3/74 to 12/4/74 inclusive.					
13/4/74	3222	0	2088	5.02	16.67
14/4/74	4753	0	3084	6.02	20.00
15/4/74	4769	0	3097	5.52	18.33
16/4/74	4770	0	3098	5.27	17.50
17/4/74	4766	896	3093	6.02	20.00
18/4/74	4757	6288	3102	2.01	6.67
19/4/74	4798	22720	3114	6.02	20.00
20/4/74	4814	21439	3125	6.02	20.00
21/4/74	4757	21115	3087	6.02	20.00
22/4/74	4726	19883	3067	6.02	20.00
23/4/74	4814	21545	3125	6.02	20.00
24/4/74	4765	592	3105	2.26	7.50
25/4/74	4795	0	3112	6.02	20.00
26/4/74	4796	7130	3113	6.02	20.00
27/4/74	4577	18522	2970	6.02	20.00
28/4/74	4762	18198	3098	4.01	13.33
29/4/74	4761	18043	3090	6.02	20.00
30/4/74	4745	16876	3079	6.02	20.00
1/5/74	4786	16895	3106	6.02	20.00
2/5/74	4781	18565	3116	2.51	8.33
3/5/74	4749	16926	3103	0	0
4/5/74	4755	16546	3098	2.76	9.17
5/5/74	4722	14652	3065	6.02	20.00
6/5/74	4758	14895	3088	6.02	20.00
7/5/74	4772	3135	3097	6.02	20.00

TABLE B.10. (CONT'D)

Date	Raw Meal Feed (tons/24 hr)	Waste-Oil (gal/24 hr)	Clinker (tons/24 hr)	By-pass Dust (tons/24 hr)	C.T. Solids (tons/24 hr)
8/5/74	4784	0	3105	6.02	20.00
9/5/74	4603	0	2986	6.02	20.00
10/5/74	4745	0	3084	4.76	15.83
11/5/74	4795	0	3133	0	0
12/5/74	4783	0	3119	1.76	5.83
13/5/74	4812	0	3123	6.02	20.00
14/5/74	4784	0	3108	5.27	17.50
15/5/74	400	0	259	0.50	1.67
16/5/74	574	0	371	1.25	4.17
17/5/74	3219	0	2083	6.02	20.00
18/5/74	4856	0	3152	6.02	20.00
19/5/74	4856	0	3152	6.02	20.00
20/5/74	4904	0	3183	6.02	20.00
21/5/74	4760	0	3105	1.50	5.00
22/5/74	4746	0	3089	3.51	11.67
23/5/74	3984	0	2587	4.52	15.00
24/3/74	4760	0	3082	6.02	20.00
25/3/74	4784	0	3105	6.02	20.00
26/3/74	4736	0	3074	6.02	20.00
27/5/64	4711	0	3074	1.25	4.17
28/5/74	4820	0	3136	3.76	12.50
29/5/74	4688	0	3042	6.02	20.00
30/5/74	4640	0	3011	6.02	20.00

of each material, daily elemental quantities (as lb per 24-hour)
were determined from the relationship:

$$X_{ij} = M_{ij} \times \frac{C_{ij}}{100}$$

where X_{ij} = Total daily weight of element X reporting in
material i (1b/24 hr) on day j.

M_{ij} = total daily weight of material i (1b) on
day j.

C_{ij} = concentration of element X reporting in the
composite sample material i on day j.

These data were then used to form the separate individual
elemental balance accounts given in B.11 to B.18. Because of process
fluctuations and the very low concentrations of the elements in some
materials, little significance should be attached to individual daily
balance results except in that they indicate the responsiveness of the
system to major changes in input of waste oil. Significant assessment
of the balance is available by considering prolonged periods of plant
operation. Summary balances for this purpose are given in the body
of this report (see Discussion, Section 4.2 Tables 9 and 10).

The procedure for these calculations is illustrated in
Figure B.1. and in the example given below for lead balances.

Example Lead Balance

The following items are available from analysis and material
quantity for each day (units = lb/day):

$$Pb_{rmf,i}; \quad Pb_{ct,i}; \quad Pb_{wo,i}; \quad Pb_{c,i}$$

$Pb_{rm,i}$ is not available from analysis.

where rmf = raw meal feed

ct = conditioning tower solids

wo = waste oil

bpd = by-pass dust

c = clinker

rm = raw materials

For individual daily balance:

$$Pb_{rmf} + Pb_{wo} = Pb_{ct} + Pb_{bpd} + Pb_c$$

For long-term accumulated balance: (i >> 1)

$$\sum_i (Pb_{rm,i} + Pb_{wo,i}) = \sum_i (Pb_{bpd,i} + Pb_{c,})$$

$$Pb_{rm,i} = \sum (pb_{rmf,i} - Pb_{ct,i})$$

.
. . accumulated balance (i >> 1)

is given by:

$$\sum_i (Pb_{wo,i} + Pb_{rmf,i} - Pb_{ct,i}) = \sum (Pb_{bpd,i} + Pb_{c,i})$$

In calculating the bromine balance using SLC data, the clinker analysis for bromine for March 17 was considered improbably high. This may have been due to some unknown contamination. The data for clinker were subjected to a Dixon extreme value test (B.1) and it was found that the value 132 lb/24 hr for March 18 could be rejected with between a 0.05 and a 0.01 chance of error. The bromine balance therefore was accounted without consideration of either input or output data for March 18. This is justifiable since no plant changes or kiln upsets had preceeded this day for some considerable time and therefore it is valid to assume that a stable equilibrium of plant cycles was operative at this time.
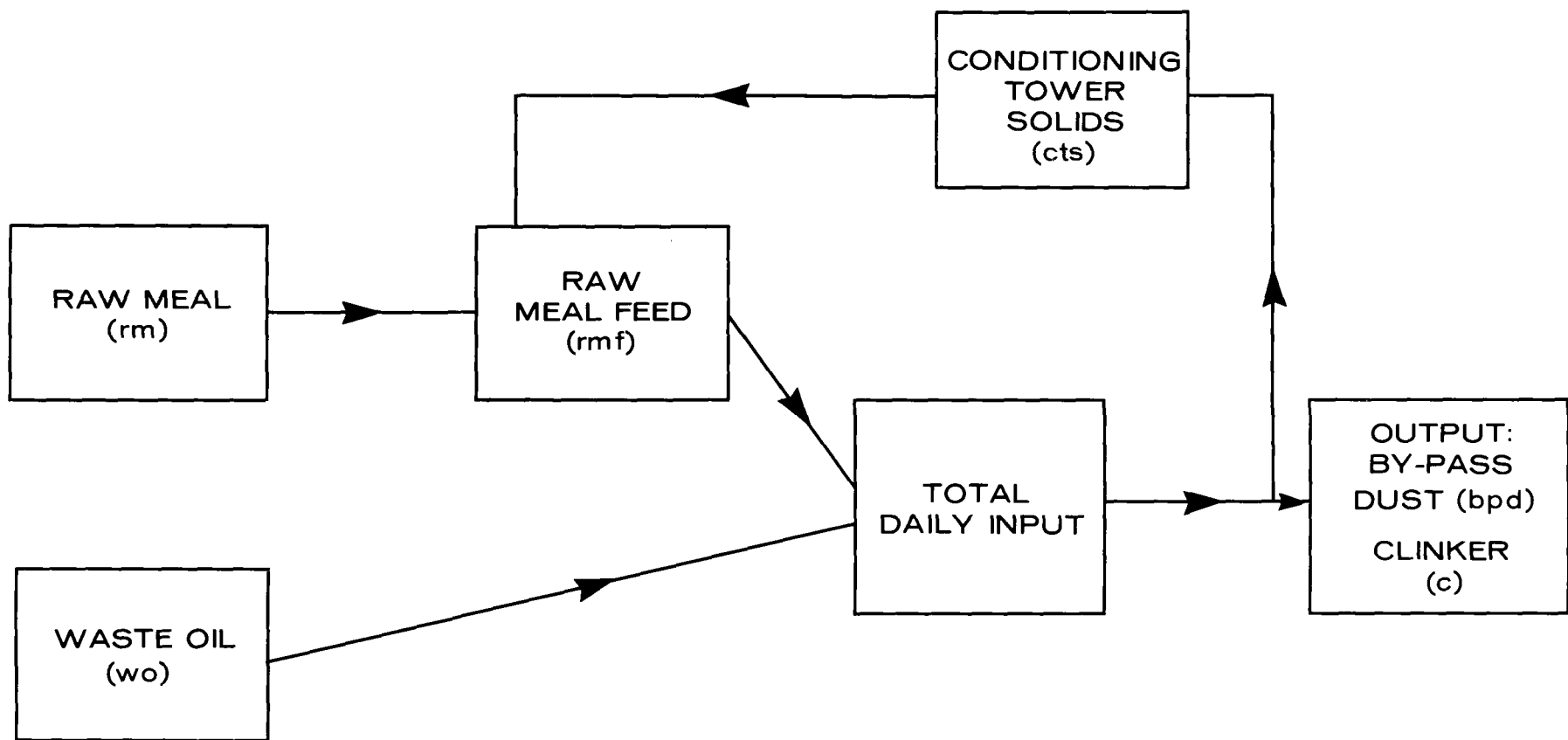
Figure B.1 Overall Material Balance

TABLE B.11. MATERIAL BALANCE FOR LEAD, USING ORF DATA

Date	Lead Input (1b/24 hr)			Lead Retained (1b/24 hr)				Total Retained (%)
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total	
27/4	27.5	923	951	87	760	16	863	90.8
28/4	76.2	891	967	75	743	17	835	86.4
29/4	9.5	815	825	55	717	(20)	792	96.0
30/4	38.0	709	747	78	610	26	714	95.6
1/5	57.4	724	781	74	559	30	663	84.9
2/5	38.2	785	823	106	629	16	751	91.3
3/5	47.5	708	756	0	590	0	590	78.0
4/5	38.0	678	716	25	558	20	603	82.2
5/5	56.7	616	673	35	527	49	611	90.8
6/5	57.1	598	655	74	426	54	554	84.6
7/5	47.7	126	174	42	217	42	301	165.3
8/5	28.7	0	29	16	62	18	96	331.0
9/5	27.6	0	28	11	24	9	44	157.4
10/5	9.5	0	10	(10)	19	8	37	389.5

TABLE B.12. MATERIAL BALANCE FOR BROMINE, USING ORF DATA

Date	Bromine Input (lb/24 hr)			Bromine Retained (lb/24 hr)				Total Retained (%)
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total	
27/4	73	274	347	70	24	88	182	52.5
28/4	95	240	335	80	12	75	167	50.0
29/4	48	196	244	51	37	(100)	188	77.1
30/4	76	179	255	62	55	108	225	88.2
1/5	67	182	249	64	0	94	158	63.5
2/5	57	219	276	69	19	48	136	49.3
3/5	85	199	284	0	81	0	81	*28.5
4/5	48	197	245	32	62	70	164	66.9
5/5	132	179	311	34	43	205	282	90.7
6/5	48	176	224	54	6	203	263	117.4
7/5	86	42	128	41	0	161	202	157.8
8/5	48	0	48	32	6	108	146	304.2
9/5	64	0	64	29	48	86	163	254.7
10/5	57	0	57	(20)	19	69	108	189.5

* Bypass Off 3/5/74

TABLE B.13. MATERIAL BALANCE FOR ZINC, USING ORF DATA

Date	Zinc Input (lb/24 hr)			Zinc Retained (lb/24 hr)				Total
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total	Retained (%)
27/4	311	184	495	5.8	469	0.9	476	96.3
28/4	271	164	435	5.2	403	0.7	409	76.4
29/4	352	147	499	3.6	464	(1)	469	93.9
30/4	427	131	558	5.8	437	1.3	444	79.6
1/5	364	128	492	5.3	416	1.5	423	85.6
2/5	382	147	529	7.3	405	0.6	413	78.1
3/5	399	133	532	0	428	0	428	80.5
4/5	371	129	500	3.2	446	0.6	450	90.0
5/5	378	115	493	3.6	447	1.2	452	91.6
6/5	352	109	461	5.6	414	1.1	421	91.3
7/5	401	24	425	3.8	341	1.4	346	81.5
8/5	402	0	402	3.3	348	0.9	352	87.6
9/5	331	0	331	3.6	346	0.8	350	105.9
10/5	408	0	408	(4)	352	0.7	357	87.5

TABLE B.14. MATERIAL BALANCE FOR PHOSPHORUS, USING ORF DATA

Date	Phosphorus Input (lb/24 hr)			Phosphorus Retained (lb/24 hr)				Total Retained (%)
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total	
27/4	3286	189	3475	5.8	3736	1.6	3744	107.7
28/4	3552	168	3720	5.2	3860	1.2	3866	103.9
29/4	3752	159	3911	3.6	3949	(1.5)	3954	101.1
30/4	3407	140	3547	5.8	3836	2.5	3844	108.4
1/5	3542	154	3696	5.3	3746	2.6	3754	101.6
2/5	3528	162	3690	7.3	3758	0.8	3766	102.1
3/5	3676	129	3805	0	4028	0	4028	105.9
4/5	3424	136	3560	3.2	3879	0.6	3883	109.1
5/5	3296	119	3415	3.6	3666	0.5	3670	107.5
6/5	3559	122	3681	5.6	3730	0.4	3736	101.5
7/5	3484	27	3511	3.8	3809	1.1	3814	108.6
8/5	3626	0	3626	3.3	3840	1.5	3855	106.3
9/5	3572	0	3572	3.6	3679	1.6	3684	103.1
10/5	3682	0	3682	(3.5)	3898	1.1	3903	106.0

TABLE B.15. MATERIAL BALANCE FOR LEAD USING SLC DATA

| Date | Lead Input (lb/24 hr) | | | Lead Retention (lb/24 hr) | | | |
	Raw Meal	Waste Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
9/3	21	0	21	2	25	-	27
10/3	58	0	58	6	37	4	47
11/3	53	0	53	7	28	3	38
12/3	--	-	--	-	--	-	--
13/3	25	0	24	3	27	1	31
14/3	64	0	64	7	62	3	72
15/3	64	0	64	8	76	5	89
16/3	97	0	97	10	98	5	113
17/3	32	0	32	8	49	3	60
18/3	42	0	42	9	67	4	80
19/3	72	0	72	8	67	5	80
20/3	50	0	50	8	52	6	66
21/3	31	(188)	(219)	9	165	4	178
22/3	50	(46)	(96)	52	235	30	317
23/3	59	0	59	7	102	3	111
24/3	49	0	49	12	83	19	114
25/3	39	0	39	16	63	9	88
26/3	38	(157)	(195)	30	142	-	172
27/3	39	(848)	(887)	48	459	-	507
28/3	39	(236)	(275)	33	241	-	275
29/3	29	(165)	(194)	53	134	-	187
30/3	65	0	65	0	72	0	72

Date	Lead Input (lb/24 hr)			C.T. Solids	Lead Retention (lb/24 hr)		Total
	Raw Meal	Waste Oil	Total		Clinker	B.P. Dust	
13/4	32	0	32	–	42	–	62
14/4	48	0	48	–	68	–	68
15/4	29	0	29	–	62	4	65
16/4	67	0	67	8	56	3	67
17/4	38	(42)	(80)	12	87	3	102
18/4	57	(296)	(353)	14	310	4	348
19/4	96	1071	1167	88	716	17	821
20/4	58	998	1056	102	700	26	828
21/4	86	1001	1087	113	709	30	852
22/4	95	980	1075	104	680	46	830
23/4	77	928	1005	118	819	(30)	967
24/4	57	27	84	10	217	16	243
25/4	48	0	48	14	106	14	134
26/4	58	355	413	11	423	7	441
27/4	46	923	969	100	642	6	748
28/4	38	891	929	57	725	19	801
29/4	38	815	853	96	581	(30)	707
30/4	47	709	756	102	560	28	690
1/5	48	724	772	70	484	34	588
2/5	29	785	814	43	548	21	612
3/5	66	708	774	0	528	0	528
4/5	57	678	735	33	521	21	575
5/5	47	616	663	84	466	48	598
6/5	48	598	646	87	414	53	554
7/5	29	126	155	49	235	17	301

Date	Lead Input (1b/24 hr)				Lead Retention (1b/24 hr)		
	Raw Meal	Waste Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
8/5	57	0	57	21	75	19	115
9/5	18	0	18	14	65	10	89
10/5	57	0	57	(10)	80	9	99
11/5	48	0	48	0	69	0	69
12/5	38	0	38	2	62	6	70
13/5	29	0	29	6	50	7	63
14/5	48	0	48	7	44	4	55
15/5	–	–	–	–	–	–	–
16/5	–	–	–	–	–	–	–
17/5	26	0	26	7	58	4	69
18/5	29	0	29	7	57	5	69
19/5	29	0	29	7	69	5	81
20/5	49	0	49	7	76	5	88
21/5	38	0	38	2	62	1	65
22/5	38	0	38	4	68	2	74
23/5	24	0	24	5	31	3	39
24/5	29	0	29	6	25	3	34
25/5	48	0	48	6	56	3	65
26/5	28	0	28	7	55	3	65
27/5	28	0	28	(6)	61	1	67
28/5	19	0	19	4	63	2	69
29/5	28	0	28	6	55	4	65
30/5	37	0	37	7	24	4	35

TABLE B.16. MATERIAL BALANCE FOR BROMINE USING SLC DATA

Date	Bromine Input (lb/24 hr)			Bromine Retention (lb/24 hr)			
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
9/3	29	0	29	5	19	(10)	34
10/3	96	0	96	10	6	10	26
11/3	85	0	85	14	55	20	89
12/3	–	–	–	–	–	–	–
13/3	57	0	57	9	21	15	45
14/3	96	0	96	18	21	24	63
15/3	117	0	117	18	55	37	110
16/3	86	0	86	18	49	29	96
17/3	54	0	54	15	28	22	65
18/3*	83	0	83	13	128	34	175
19/3	72	0	72	13	53	37	103
20/3	30	0	30	12	20	33	65
21/3	41	33	74	11	26	19	56
22/3	60	8	68	21	98	43	162
23/3	39	0	39	5	89	12	106
24/3	79	0	79	19	51	39	109
25/3	107	0	107	22	63	47	132
26/3	66	28	94	19	49	–	–
27/3	78	149	227	11	64	–	–
28/3	98	41	139	29	51	–	–
29/3	108	29	137	19	70	–	–
30/3	92	0	92	0	24	0	24

*Not included in balance -- see text.

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| Date | Bromine Input (lb/24 hr) | | | Bromine Retained (lb/24 hr) | | | Total |
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	
13/4	64	0	64	–	17	–	17
14/4	67	0	67	–	37	–	37
15/4	95	0	95	–	50	38	88
16/4	114	0	114	18	31	37	85
17/4	105	7	112	22	43	42	107
18/4	76	52	128	9	12	16	37
19/4	144	187	331	37	69	55	161
20/4	144	173	317	40	50	74	164
21/4	152	180	332	47	56	89	192
22/4	113	181	294	44	37	90	171
23/4	154	261	415	51	25	(100)	176
24/4	114	8	122	15	74	28	117
25/4	96	0	96	30	56	61	147
26/4	86	105	191	24	37	59	120
27/4	73	274	347	59	59	59	177
28/4	86	240	326	47	43	64	154
29/4	86	196	282	64	12	(70)	146
30/4	66	179	245	62	111	95	268
1/5	105	182	287	53	43	89	185
2/5	96	219	315	24	75	49	148
3/5	57	199	256	0	111	0	111
4/5	76	198	274	30	86	56	172
5/5	47	179	226	62	74	144	280
6/5	95	176	271	47	37	144	228
7/5	76	37	113	38	31	178	247
8/5	77	0	77	29	43	84	156

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Date	Bromine Input (lb/24 hr)			Bromine Retention (lb/24 hr)			
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
9/5	92	0	92	25	54	71	150
10/5	104	0	104	(20)	43	56	119
11/5	77	0	77	0	50	0	50
12/5	86	0	86	11	56	25	92
13/5	77	0	77	23	44	58	125
14/4	105	0	105	23	44	35	102
15/5		-					
16/5		-					
17/5	77	0	77	23	54	42	119
18/5	117	0	117	31	50	47	128
19/5	136	0	136	29	50	47	126
20/5	137	0	137	30	38	50	118
21/5	124	0	124	5	62	11	78
22/5	123	0	123	10	62	23	95
23/5	96	0	96	13	52	28	93
24/5	105	0	105	23	56	28	107
25/5	124	0	124	23	75	42	140
26/5	123	0	123	21	80	39	140
27/5	104	0	104	(20)	18	10	48
28/5	96	0	96	14	50	28	92
29/5	47	0	47	18	49	46	113
30/5	93	0	93	17	12	40	69

TABLE B.17. MATERIAL BALANCE FOR ZINC USING SLC DATA

Date	Zinc Input (lb/24 hr) Raw Meal	Waste-Oil	Total	Zinc Retention (lb/24 hr) C.T. Solids	Clinker	B.P. Dust	Total
9/3	201	0	201	2.5	221	(2)	226
10/3	461	0	461	5.6	554	2.2	562
11/3	543	0	543	6.4	519	1.6	527
13/3	394	0	394	2.8	427	0.6	430
14/3	512	0	512	5.6	589	1.5	596
15/3	501	0	501	6.0	678	1.4	685
16/3	538	0	538	6.4	600	1.8	608
17/3	471	0	471	4.8	557	1.5	563
18/3	540	0	540	6.8	586	1.5	594
19/3	503	0	503	6.7	560	1.5	568
20/3	522	0	522	7.2	600	2.0	609
21/3	509	28	537	8.0	648	2.0	658
22/3	522	7	529	8.0	573	2.4	583
23/3	577	0	577	3.0	548	0.5	551
24/3	521	0	521	8.0	549	2.1	559
25/3	495	0	495	10.0	529	1.7	540
26/3	663	23	686	10.3	541	(1)	552
27/3	470	126	596	5.7	643	(1)	650
28/3	459	35	494	9.0	584	(1)	594
29/3	490	25	515	9.6	535	(1)	546
30/3	461	0	461	0	500	0	500

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Date	Zinc Input (lb/24 hr)			Zinc Retention (lb/24 hr)			
	Raw Meal	Waste Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
13/4	322	0	322	–	397	–	397
14/4	513	0	513	–	561	–	561
15/4	506	0	506	–	582	1.0	583
16/4	496	0	496	4.6	514	0.8	519
17/4	487	6	492	5.2	532	0.9	538
18/4	447	45	492	1.9	682	0.3	684
19/4	461	162	623	7.2	698	1.0	706
20/4	501	154	655	7.6	650	1.2	659
21/4	476	154	630	8.0	648	1.2	657
22/4	529	151	680	8.4	687	1.3	697
23/4	462	201	663	8.4	738	(1)	747
24/4	485	5	490	2.0	559	0.6	562
25/4	527	0	527	4.8	579	1.2	584
26/4	451	70	521	5.2	635	1.1	641
27/4	430	183	613	9.6	624	0.9	635
28/4	486	164	650	5.3	688	1.0	694
29/4	571	147	718	8.8	637	(1)	647
30/4	493	131	624	10.0	677	1.7	689
1/5	517	128	645	8.5	646	2	657
2/5	526	147	673	4.8	629	0.8	635
3/5	446	133	579	0	670	0	670
4/5	495	129	624	5.4	682	0.8	688
5/5	548	115	663	12.0	717	1.4	730
6/5	457	109	566	8.7	655	1.6	665
7/5	458	24	482	6.3	576	1.5	584
8/5	440	0	440	6.1	584	1.3	591

Date	Zinc Input (lb/24 hr)			Zinc Retention (lb/24 hr)			
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
9/5	433	0	433	5.4	532	1.1	539
10/5	456	0	456	(6)	543	0.9	550
11/5	499	0	499	0	539	0	539
12/5	488	0	488	1.5	561	0.3	563
13/5	539	0	539	5.1	518	0.9	524
14/5	488	0	488	4.6	566	0.9	572
15/5	–	–	–	–	–	–	–
16/5	–	–	–	–	–	–	–
17/5	328	0	328	5.0	325	1.1	331
18/5	505	0	505	4.2	523	1.1	528
19/5	486	0	486	5.0	561	1.0	567
20/5	500	0	500	4.7	541	1.0	547
21/5	419	0	419	1.2	515	0.3	517
22/5	437	0	437	2.9	525	0.6	529
23/5	390	0	390	3.5	429	0.8	433
24/5	505	0	505	4.9	537	1.2	543
25/5	431	0	431	4.2	497	0.9	502
26/5	502	0	502	5.1	541	0.9	547
27/5	509	0	509	(2)	529	0.2	531
28/5	492	0	492	3.0	558	0.6	562
29/5	450	0	450	4.6	505	0.9	511
30/5	483	0	483	5.4	488	0.9	494

TABLE B.18.   MATERIAL BALANCE FOR PHOSPHORUS USING SLC DATA

Date	Phosphorus Input (lb/24 hr)			Phosphorus Retention (lb/24 hr)			
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
9/3	1593	0	1593	5.1	1526	(1)	1532
10/3	3838	0	3838	15.2	3363	4.2	3382
11/3	4156	0	4156	16.0	5121	3.4	5140
13/3	3280	0	3280	5.7	2938	1.0	2945
14/3	4268	0	4268	13.6	3673	3.5	3690
15/3	4050	0	4050	15.6	4015	2.4	4033
16/3	4515	0	4515	14.8	4050	2.5	4067
17/3	3857	0	3857	16.4	3688	3.4	3708
18/3	3943	0	3943	14.4	3975	2.4	3992
19/3	3693	0	3698	13.3	3666	1.5	3681
20/3	3214	0	3214	17.6	3457	2.5	3477
21/3	3870	35	3905	16.8	3902	3.5	3922
22/3	4012	8	4020	16.0	4558	2.8	4577
23/3	3518	0	3518	4.0	3507	0.5	3512
24/3	3930	0	3930	15.2	3444	2.5	3462
25/3	3881	0	3881	15.2	3401	1.9	3418
26/3	3787	29	3816	12.0	3507	2.0	3521
27/3	4304	159	4463	8.1	3632	1.1	3641
28/3	3715	44	3759	12.3	3875	2.0	3889
29/3	4118	31	4149	8.1	3634	1.8	3644
30/3	3507	0	3507	0	3316	0	3316

Date	Phosphorus Input (lb/24 hr)			Phosphorus Retention (lb/24 hr)			
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
13/4	2191	0	2191	–	2589	–	2589
14/4	3802	0	3802	–	3269	–	3269
15/4	3434	0	3434	–	3407	1.7	3407
16/4	2862	0	2862	13.0	3036	2.0	3051
17/4	3908	7	3915	12.8	2907	1.9	2922
18/4	3520	51	3571	4.8	3350	0.5	3355
19/4	3646	185	3831	12.8	3861	3.5	3877
20/4	3659	176	3835	14.0	3875	2.4	3891
21/4	3806	194	4000	14.0	4013	2.3	4029
22/4	3308	198	3506	13.2	3496	1.4	3511
23/4	3659	176	3835	12.0	4000	(2)	4014
24/4	3812	4	3816	6.0	3912	1.4	3919
25/4	3740	0	3740	15.6	3734	2.6	3752
26/4	3453	61	3514	14.4	3362	2.3	3379
27/4	3662	189	3851	16.0	3683	2.3	3701
28/4	3619	169	3788	10.1	3965	1.3	3976
29/4	3523	159	3682	14.8	4387	(2)	4404
30/4	4081	140	4221	17.2	3941	2.6	3961
1/5	3350	154	3504	14.0	3354	3.1	3371
2/5	3729	162	3891	6.5	3863	0.9	3870
3/5	3324	129	3453	0	3847	0	3847
4/5	3519	136	3655	6.8	3407	0.7	3445
5/5	3872	119	3991	16.4	3739	0.8	3756
6/5	3521	122	3643	14.8	3953	0.5	3968
7/5	3245	27	3272	13.6	3469	1.4	3484
8/5	3827	0	3827	14.0	3478	1.7	3494

Date	Phosphorus Input (lb/24 hr)			Phosphorus Retention (lb/24 hr)			
	Raw Meal	Waste-Oil	Total	C.T. Solids	Clinker	B.P. Dust	Total
9/5	3959	0	3959	14.4	3942	1.9	3958
10/5	3891	0	3891	0	4256	1.4	4257
11/5	3357	0	3357	0	3008	0	3008
12/5	3444	0	3444	3.6	3493	0.4	3497
13/5	3465	0	3465	12.4	3372	1.7	3386
14/5	3253	0	3253	13.3	3045	2.2	3061
15/5	-	-	-	-	-	-	-
16/5	-	-	-	-	-	-	-
17/5	2189	0	2189	13.6	2166	1.6	2181
18/5	3399	0	3399	11.6	3152	1.9	3166
19/5	3691	0	3691	15.2	3593	1.4	3610
20/5	3825	0	3825	15.2	3501	1.7	3518
21/5	3618	0	3618	4.4	2981	0.4	2986
22/5	3322	0	3322	8.2	3336	1.0	3345
23/5	2470	0	2470	11.1	3156	2.0	3169
24/5	3808	0	3808	13.6	3575	2.9	3592
25/5	3636	0	3636	11.2	3291	2.2	3302
26/5	3505	0	3505	12.8	3197	1.4	3211
27/5	3392	0	3392	(10)	3258	0.4	3268
28/5	3470	0	3470	9.5	3199	1.3	3210
29/5	3563	0	3563	13.2	3103	1.7	3118
30/5	2970	0	2970	13.6	3493	2.4	3509

B.2   Emissions Testing

B.2.1   Results of Emissions Testing Experiments

Tables B.19 to B.27 give the measured stack gas velocities together with wind conditions which were obtained from Toronto International Airport, meteorological office.

Tables B.28 to B.33 give the results for particulates, lead, bromide, zinc and phosphorus emissions. Particulate data are reported in mg units, elemental data are reported in μg units. Individual test loadings and average loadings for groups of tests are also recorded in these tables. Some data were not available for the following reasons:

(a) Probe wash solutions for the test during the period 11/3 - 15/3 were obtained as acetone washes according to the Ontario testing code. On evaporation, these were found to contain resinous residues. Discussion with ARB indicated that this was a phenomenon previously observed in some tests. Clearly particulate or elemental analysis of these solutions would be invalid. Since very little of the emissions expected from a cement plant would be acetone soluble, these solutions were not examined further. Subsequent probe washings were made using distilled water.

(b) Filter material quantities collected from the south east stack were too small for analysis at ORF. Lead and zinc were determined by Dubois, Piquette, Pupp and Zdrojewski. No phosphorus analyses were available on these filters.

(c) Probe wash solids from the south east stack were also only available in quantities too small for analysis.

Individual analytical data are given in Tables B.34 to B.37 Analytical data relating to filter solids for SE stack tests are reported separately in Appendix E. These data were obtained by Dubois, Piqueete, Pupp and Zdrojewski, the full report of these workers is given in Appendix E.

TABLE B.19. N.W. STACK: TEST PERIOD, MARCH 11-15, 1974: FUEL – BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	March 11, 1974 Wind: ESE/6 mph; N/11 mph		March 12, 1974 Wind: NNW/20 mph		March 12, 1974 Wind: NNW/20 mph	
		N S	W E	N S	W E	N S	W E
1	0.93	45	49	48	50	47	48
2	2.70	45	49	54	50	52	50
3	4.65	53	54	54	52	52	50
4	6.67	56	54	57	54	58	52
5	8.87	58	56	60	56	60	54
6	11.15	59	56	61	59	62	59
7	13.60	64	59	63	59	63	61
8	16.39	65	59	64	60	63	61
9	19.43	65	61	65	63	64	63
10	22.98	62	61	65	63	66	63
11	27.29	64	63	64	64	65	64
12	33.62	55	63	64	64	65	65
13	50.86	60	58	64	64	64	65
14	57.19	60	56	64	63	63	64
15	61.50	60	59	63	64	63	64
16	65.05	60	59	63	63	59	62
17	68.09	61	55	62	61	59	59
18	70.88	59	55	62	60	55	59
19	73.33	59	53	59	58	54	59
20	75.95	57	49	55	55	54	54
21	77.81	57	49	52	55	52	52
22	79.83	54	49	52	49	49	49
23	81.78	52	45	42	44	43	45
24	83.55	45	45	39	43	40	42

TABLE B.20. N.E. STACK: TEST PERIOD, MARCH 11-15, 1974: FUEL – BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	March 11, 1974 Wind: ESE/6 mph; N/11 mph		March 12, 1974 Wind: NNW/20 mph		March 12, 1974 Wind: NNW/20 mph	
		N S	W E	N S	W E	N S	W E
1	0.93	45	52	48	48	48	48
2	2.70	47	51	48	48	48	49
3	4.65	44	54	57	58	58	57
4	6.67	43	58	60	60	60	60
5	8.87	63	59	62	62	65	64
6	11.15	66	60	67	63	65	67
7	13.60	68	60	68	64	67	69
8	16.39	68	62	69	66	67	69
9	19.43	68	64	70	67	69	67
10	22.98	68	65	70	67	69	65
11	27.29	68	65	70	67	70	69
12	33.62	67	66	67	69	67	69
13	50.86	65	66	67	67	67	67
14	57.19	65	66	66	67	65	65
15	61.50	65	66	65	67	64	65
16	65.05	65	62	65	64	65	62
17	68.09	65	59	65	63	62	62
18	70.88	65	60	62	60	60	60
19	73.33	64	58	62	53	59	60
20	75.95	62	57	60	50	53	58
21	77.81	60	53	60	46	50	58
22	79.83	56	53	49	43	48	53
23	81.78	49	51	48	41	48	48
24	83.55	34	51	43	38	48	48

TABLE B.21. S.E. STACK: TEST PERIOD, MARCH 11-15, 1974: FUEL – BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	March 14, 1974 Wind: NNW/15 mph			March 14, 1974 Wind: NNW/15 mph			March 15, 1974 Wind: SE/7 mph		
		S N		E W	S N		E W	S N		E W
1	0.72	47		36	45		24	35		15
2	2.20	47		38	47		28	37		15
3	3.83	44		40	45		28	37		18
4	5.63	44		41	44		31	33		24
5	7.61	39		33	39		31	30		25
6	9.90	35		39	34		28	28		25
7	12.74	31		44	31		28	24		25
8	16.88	26		47	24		22	21		25
9	28.31	17		40	20		23	19		22
10	32.27	17		41	20		24	16		22
11	35.10	17		30	17		28	14		22
12	37.40	17		31	17		28	14		26
13	39.38	17		33	17		31	14		26
14	41.18	17		37	14		30	14		26
15	42.80	17		31	14		29	14		25
16	44.28	14		25	14		28	12		24

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TABLE B.22. N.W. STACK: TEST PERIOD, APR 22 - MAY 2, 1974: FUEL - WASTE OIL/BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	April 22, 1974 Wind: SW/11 mph N S	W E	April 23, 1974 Wind: W/17 mph N S	W E	April 30, 1974 Wind: SW/11 mph N S	W E	April 30, 1974 Wind: SW/13 mph N S	W E	May 1, 1974 Wind:NW/25 mph N S	W E	May 2, 1974 Wind:ESE/15 mph N S	W E
1	0.93	58	48	58	48	51	46	58	49	55	50	52	47
2	2.70	60	48	58	48	52	49	58	49	56	55	54	48
3	4.65	60	51	60	51	52	49	58	51	57	55	54	50
4	6.67	60	51	60	52	54	50	61	53	58	55	55	52
5	8.87	60	54	61	56	61	52	62	53	59	57	59	52
6	11.15	62	56	62	56	63	53	65	56	61	59	59	54
7	13.60	63	58	62	58	64	53	66	56	61	62	62	56
8	16.39	66	60	63	60	64	57	68	59	63	64	62	57
9	19.43	67	62	63	61	65	59	68	62	66	65	63	59
10	22.98	54	64	64	61	62	62	68	62	69	65	63	60
11	27.29	64	64	65	64	64	64	68	62	67	65	63	60
12	33.62	62	65	65	65	63	64	66	64	65	64	63	61
13	50.86	67	65	62	65	62	64	66	64	63	64	62	59
14	57.19	66	65	62	62	62	62	64	62	61	63	61	59
15	61.50	63	64	62	62	61	62	64	62	61	62	60	59
16	65.05	64	64	61	60	61	60	63	62	61	60	59	58
17	68.09	65	61	60	59	61	59	62	58	60	56	59	57
18	70.88	62	59	60	56	60	57	62	58	60	56	58	56
19	73.33	59	59	60	54	60	53	62	55	58	56	57	54
20	75.95	55	56	57	54	58	53	61	53	58	55	57	51
21	77.81	55	54	57	51	55	51	59	49	55	55	54	49
22	79.83	55	49	55	49	51	49	52	49	54	51	52	49
23	81.78	55	47	52	49	50	48	49	48	54	49	52	46
24	83.55	49	42	49	48	49	46	49	47	52	49	49	43

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TABLE B.23. N.E. STACK: TEST PERIOD, APR 22 – MAY 2, 1974: FUEL – WASTE OIL/BUNKER 'C' GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	April 22, 1974 Wind: SW/11 mph		April 23, 1974 Wind: W/17 mph		April 30, 1974 Wind: SW/11 mph		April 30, 1974 Wind: SW/13 mph		May 1, 1974 Wind: NW/25 mph		May 2, 1974 Wind: ESE/15 mph	
		N S	W E	N S	W E	N S	W E	N S	W E	N S	W E	N S	W E
1	0.93	60	53	60	52	53	50	50	48	55	53	53	52
2	2.70	60	53	62	52	53	50	51	50	57	53	55	52
3	4.65	62	56	62	55	58	53	53	53	59	54	57	53
4	6.67	62	59	60	56	61	53	57	54	59	55	57	56
5	8.87	63	61	60	60	65	56	60	54	62	57	60	59
6	11.15	66	63	64	60	66	58	62	56	64	58	64	60
7	13.60	67	63	69	62	67	61	65	58	67	61	67	61
8	16.39	70	66	67	65	68	63	66	60	67	63	68	63
9	19.43	68	66	67	65	68	65	66	61	69	63	68	64
10	22.98	66	67	67	66	68	66	66	63	70	66	68	67
11	27.29	66	66	68	66	68	68	67	64	67	67	67	67
12	33.62	66	67	67	66	68	68	66	64	67	67	61	68
13	50.86	65	67	67	66	65	67	62	63	65	65	58	67
14	57.19	63	67	67	65	66	67	63	62	63	65	58	66
15	61.50	63	64	64	64	66	65	63	62	63	63	63	64
16	65.05	63	64	65	63	66	63	63	60	65	62	64	62
17	68.09	63	60	65	62	65	61	63	56	64	59	63	60
18	70.88	61	60	65	60	64	60	61	55	61	57	61	55
19	73.33	59	54	64	59	63	57	62	54	59	55	60	52
20	75.95	57	50	61	53	61	57	54	51	56	55	58	50
21	77.81	55	54	55	54	57	52	55	49	56	52	58	50
22	79.83	49	50	50	49	52	50	50	41	55	50	51	46
23	81.78	44	43	43	43	43	43	51	36	50	43	43	40
24	83.55	44	43	43	43	43	43	41	35	46	43	43	40

TABLE B.24. S.E. STACK: TEST PERIOD APR 22 - MAY 2, 1974: FUEL - WASTE OIL/BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	April 22, 1974 Wind: SW/11 mph S N	E W	April 23, 1974 Wind: W/17 mph S N	E W	April 30, 1974 Wind: SW/11 mph S N	E W	April 30, 1974 Wind: SW/13 mph S N	E W	May 1, 1974 Wind: NW/25 mph S N	E W	May 2, 1974 Wind:ESE/15 mph S N	E W
1	0.72	54	38	61	45	49	32	46	31	38	22	37	*
2	2.20	54	38	61	45	49	32	46	31	38	22	37	
3	3.83	54	38	61	45	45	33	44	31	38	24	35	
4	5.63	48	35	57	45	41	33	39	32	38	25	33	
5	7.61	44	35	48	42	34	32	38	34	34	25	27	
6	9.90	37	32	42	35	32	32	38	31	32	25	22	
7	12.74	31	27	39	32	25	28	27	29	28	23	22	
8	16.88	31	27	27	22	25	25	22	22	25	23	22	
9	28.31	21	22	16	22	17	25	15	22	16	23	20	
10	32.27	18	24	16	31	17	25	15	23	16	23	21	
11	35.10	16	27	16	32	17	28	15	28	16	23	20	
12	37.40	16	30	16	32	17	29	15	28	16	24	18	
13	39.38	16	31	16	32	17	30	15	28	16	25	16	
14	41.18	15	31	16	32	17	30	15	29	16	25	16	
15	42.80	14	31	16	32	17	30	15	29	16	25	16	
16	44.28	14	31	32	32	17	30	15	29	16	25	16	

*Traverse incomplete due to unscheduled by-pass shutdown.

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TABLE B.25. N.W. STACK: TEST PERIOD, MAY 29-30, 1974: FUEL – BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	May 29, 1974 Wind: SE/ 5 mph		May 29, 1974 Wind: SE/5 mph		May 30 1974 Wind:SE/10 mph	
		W E	N S	W E	N S	W E	N S
1	0.93	45	49	47	48	45	50
2	2.70	45	49	47	48	47	50
3	4.65	47	50	49	52	48	53
4	6.67	48	53	52	55	49	55
5	8.87	51	56	52	57	44	59
6	11.15	52	58	54	60	52	61
7	13.60	53	59	55	62	55	63
8	16.39	55	60	56	62	55	63
9	19.43	57	60	59	62	56	63
10	22.98	58	60	59	62	59	63
11	27.29	60	60	62	62	61	63
12	33.62	60	60	62	62	63	63
13	50.86	59	60	61	60	60	61
14	57.19	59	58	61	59	60	61
15	61.50	59	58	60	59	60	61
16	65.05	57	58	59	59	60	61
17	68.09	56	58	57	59	58	61
18	70.88	56	47	55	58	56	60
19	73.33	52	47	54	58	53	59
20	75.95	50	56	52	55	51	54
21	77.81	49	55	49	55	49	56
22	79.83	44	52	48	50	45	53
23	81.78	44	49	43	49	44	51
24	83.55	44	48	43	48	43	51

TABLE B.26. N.E. STACK: TEST PERIOD, MAY 29-30, 1974: FUEL - BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	May 29, 1974 Wind:SE/5 mph		May 29, 1974 Wind: SE/5 mph		May 30, 1974 Wind:SE/10 mph	
		E W	N S	E W	N S	E W	N S
1	0.93	55	56	55	56	57	55
2	2.70	55	56	55	56	57	55
3	4.65	57	59	59	59	60	59
4	6.67	59	62	59	61	62	64
5	8.87	60	65	59	67	62	64
6	11.15	62	68	61	68	65	66
7	13.60	64	72	65	62	67	69
8	16.39	65	72	66	71	68	70
9	19.43	67	72	70	70	70	70
10	22.98	69	71	70	70	70	70
11	27.29	69	56	70	56	71	70
12	33.62	69	67	70	65	71	67
13	50.86	67	66	67	65	71	67
14	57.19	65	66	68	65	70	67
15	61.50	65	66	68	67	67	67
16	65.05	61	66	67	67	64	66
17	68.09	58	65	61	67	61	66
18	70.88	55	65	59	65	57	64
19	73.33	55	64	55	65	57	64
20	75.95	51	60	50	62	52	61
21	77.81	49	55	48	60	48	58
22	79.83	46	50	45	51	48	54
23	81.78	43	45	45	49	44	43
24	83.55	43	45	45	49	43	43

TABLE B.27.   S.E. STACK: TEST PERIOD MAY 29-30, 1974:   FUEL – BUNKER 'C'
GAS VELOCITIES (FT/SEC)

Test Point #	Distance from Stack Wall (inches)	May 29, 1974 Wind: SE/5 mph				May 29, 1974 Wind: SE/5 mph				May 30, 1974 Wind:SE/10 mph			
		E	W	S	N	E	W	S	N	E	W	S	N
1	0.72	46		69		49		70		53		54	
2	2.20	46		69		49		70		53		54	
3	3.83	47		67		49		68		53		54	
4	5.63	49		60		49		62		53		49	
5	7.61	46		46		44		52		49		49	
6	9.90	41		41		44		44		49		43	
7	12.74	35		35		38		38		38		43	
8	16.88	26		24		27		27		31		38	
9	28.31	26		20		27		20		31		33	
10	32.27	32		18		31		18		38		32	
11	35.10	38		17		38		17		43		32	
12	37.40	41		17		38		17		49		34	
13	39.38	42		17		38		17		49		31	
14	41.18	44		17		39		17		51		30	
15	42.80	41		12		31		14		46		28	
16	44.28	41		12		31		14		49		27	

TABLE B.28. PARTICULATE EMISSION DATA

Test Date	Stack	Filter (mg)	Probe Solids (mg)	Probe Wash (mg)	Total Collected Particulate (mg)	Gas Sampled (dscf)	Particulate Loading (mg/m^3)	
11/3	NW	686.5	327.0	N.A.*	1013.5	124.1	288.5	
12/3	NW	901.7	276.7	N.A.	1178.4	127.8	325.6	Av. 320.4
12/3	NW	808.0	446.1	N.A.	1254.1	127.6	347.1	
22/4	NW	783.4	282.0	109.2	1174.6	133.0	311.8	
23/4	NW	718.9	132.5	91.2	942.6	125.3	265.6	
30/4	NW	805.8	212.1	140.4	1158.3	128.9	317.5	Av.
30/4	NW	818.8	42.5	60.0	921.3	133.3	244.0	251.8
1/5	NW	629.2	232.7	94.8	956.7	130.8	259.6	
2/5	NW	173.4	171.0	67.2	411.6	129.3	112.3	
29/5	NW	154.0	23.3	144.0	321.3	127.7	89.0	
29/5	NW	157.3	22.0	97.2	276.5	131.3	74.5	Av. 87.9
30/5	NW	189.8	71.0	114.0	374.8	132.0	100.3	
11/3	NE	378.7	142.7	N.A.	521.4	129.3	142.3	
12/3	NE	413.6	107.5	N.A.	521.1	132.9	138.4	Av. 162.0
12/3	NE	639.7	146.6	N.A.	786.3	135.3	205.2	
22/4	NE	213.4	91.3	44.4	349.1	134.8	91.5	
23/4	NE	258.7	14.5	56.4	329.6	128.7	90.4	
30/4	NE	250.9	22.9	32.4	306.2	133.4	81.2	Av.
30/4	NE	214.1	48.6	36.0	298.7	126.9	83.0	103.0
1/5	NE	225.0	84.1	48.0	357.1	132.8	95.0	
2/5	NE	588.9	46.2	22.8	657.9	131.5	176.6	
29/5	NE	1506.5	497.7	93.6	2097.8	140.4	527.6	
29/5	NE	1340.4	559.2	72.0	1971.6	142.2	489.8	Av. 547.6
30/5	NE	1625.3	850.1	115.2	2590.6	146.3	625.4	

TABLE B.28. (CONT'D)

Test Date	Stack	Filter (mg)	Probe Solids (mg)	Probe Wash (mg)	Total Collected Particulate (mg)	Gas Sampled (dscf)	Particulate Loading (mg/m^3)	
14/3	SE	144.2	22.1	N.A.*	166.3	71.8	81.9	Av.
14/3	SE	119.9	19.4	N.A.	139.3	62.2	79.1	89.0
15/3	SE	121.4	15.9	N.A.	137.3	45.7	105.9	
22/4	SE	7.2	5.6	14.4	27.2	62.1	15.5	
23/4	SE	150.7	2.9	54.0	207.6	67.0	109.5	
30/4	SE	21.0	1.9	9.6	32.5	57.7	19.8	
30/4	SE	78.9	0.4	7.2	86.5	57.4	53.3	Av. 86.6
1/5	SE	55.1	1.3	9.6	66.0	48.5	48.0	
2/5	SE	9.2	5.0	0	14.2	36.3	13.8	
29/5	SE	483.4	8.5	55.2	547.1	81.1	238.4	Av.
29/5	SE	1073.3	5.5	102.0	1180.8	81.5	511.7	264.3
30/5	SE	90.8	1.3	21.6	113.7	93.7	42.7	

*N.A. = Not analysed due to acetone residue.

TABLE B.29. LEAD EMISSION DATA

Test Date	Stack	Filter Pb (µg)	Probe Solids Pb (µg)	Probe Wash Pb (µg)	Impinger Pb (µg)	Total Pb Collected (µg)	Gas Sampled (dscf)	Pb Loading (µg/m^3)	
11/3	NW	24.0	110.9	N.A.*	N.D.	134.9	124.1	38.5	
12/3	NW	18.9	11.3	N.A.	75	105.2	128.8	29.0	Av.
12/3	NW	17.8	7.1	N.A.	225	249.9	127.6	69.2	45.6
22/4	NW	65.8	80.7	N.D.**	N.D.	146.5	133.0	38.8	
23/4	NW	58.9	30.1	N.D.	N.D.	89.1	125.3	25.1	
30/4	NW	52.4	27.6	N.D.	N.D.	80.0	128.9	21.9	Av.
30/4	NW	53.2	6.4	N.D.	75	134.6	133.3	35.7	29.7
1/5	NW	46.6	28.9	N.D.	N.D.	75.5	130.8	20.5	
2/5	NW	9.5	17.4	30	75	131.9	129.3	36.0	
29/5	NW	5.5	7.2	N.D.	N.D.	12.7	127.7	3.53	
29/5	NW	5.2	7.2	N.D.	N.D.	12.4	131.3	3.18	Av.
30/5	NW	5.5	7.3	60	150	222.8	132.0	59.7	22.1
11/3	NE	27.6	20.8	N.A.	N.D.	48.4	129.3	13.1	
12/3	NE	14.9	8.3	N.A.	75	98.2	132.9	26.1	Av.
12/3	NE	12.8	3.8	N.A.	N.D.	16.6	135.3	4.24	14.5
22/4	NE	28.8	44.8	N.D.	N.D.	73.6	134.8	19.4	
23/4	NE	54.3	13.4	N.D.	N.D.	67.7	128.7	18.7	
30/4	NE	19.6	7.8	N.D.	N.D.	27.4	133.4	7.42	Av.
30/4	NE	14.8	16.9	N.D.	N.D.	31.7	126.9	8.83	14.0
1/5	NE	15.8	42.6	N.D.	N.D.	58.4	132.8	15.5	
2/5	NE	40.6	***	N.D.	N.D.	***	131.5	***	
29/5	NE	30.1	25.4	N.D.	75	130.5	140.4	32.8	
29/5	NE	29.5	21.2	N.D.	150	200.7	142.2	49.8	Av.
30/5	NE	42.3	36.6	N.D.	75	153.9	146.3	37.1	39.9

TABLE B.29. (CONT'D)

Test Date	Stack	Filter Pb(μg)	Probe Solids Pb (μg)	Probe Wash Pb (μg)	Impinger Pb (μg)	Total Pb Collected (μg)	Gas Sampled (dscf)	Pb Loading (μg/ m³)	
14/3	SE	8.6	*	N.A.	N.D.	8.6	71.8	4.24	
14/3	SE	44.5		N.A.	N.D.	44.5	62.2	25.4	Av.
15/3	SE	80.2		N.A.	N.D.	80.2	45.7	61.8	30.5
22/4	SE	24.5		N.D.	N.D.	24.5	62.1	13.8	
23/4	SE	95.7		30	N.D.	125.7	67.0	66.4	
30/4	SE	46.8		60	N.D.	106.8	57.7	65.3	Av.
30/4	SE	82.4		N.D.	N.D.	82.4	57.4	50.9	90.1
1/5	SE	292		60	N.D.	352.0	48.5	256.4	
2/5	SE	30.1		60	N.D.	90.1	36.3	87.6	
29/5	SE	289		30	N.D.	319	81.1	135.3	
29/5	SE	504		N.D.	N.D.	504	81.5	18.2	Av. 123.0
30/5	SE	41.2		N.D.	N.D.	41.2	93.7	15.5	

*No analyses carried out due to very small quantities of probe solids collected.

TABLE B.30. BROMINE EMISSION DATA

Test Date	Stack	Filter Br (μg)	Probe Solids Br (μg)	Probe Wash Br (μg)	Impinger Br (μg)	Total Br Collected (μg)	Gas Sampled (dscf)	Loading (μg/m^3)	
11/3	NW	213.5	36.6	N.A.	ND	250.1	124.1	71.0	Aver. 78.4
12/3	NW	317.4	38.5	N.A.	ND	355.9	128.8	97.5	
12/3	NW	206.0	34.8	N.A.	ND	240.8	127.6	66.7	
22/4	NW	684.7	4.5	270	ND	959.2	133.0	254.6	
23/4	NW	547.1	3.4	ND	ND	550.5	125.3	155.0	
30/4	NW	838.0	4.7	210	ND	1052.7	128.9	288.5	Aver. 249.6
30/4	NW	707.4	1.1	210	ND	918.5	133.3	243.3	
1/5	NW	741.2	4.7	420	ND	1165.9	130.8	314.7	
2/5	NW	221.1	3.8	660	ND	884.9	129.3	241.6	
29/5	NW	68.7	1.4	210	ND	280.1	127.7	77.3	
29/5	NW	81.2	2.2	ND	ND	83.4	131.3	22.6	Aver. 41.1
30/5	NW	85.8	1.3	ND	ND	87.1	132.0	23.3	
11/3	NE	107.6	12.6	N.A.	ND	120.2	129.3	32.8	
12/3	NE	109.2	13.4	N.A.	ND	122.6	132.9	32.5	Aver. 37.4
12/3	NE	159.9	20.5	N.A.	ND	180.4	135.3	47.0	
22/4	NE	218.9	2.3	ND	ND	221.2	134.8	57.9	
23/4	NE	224.0	2.2	ND	ND	226.2	128.7	62.2	
30/4	NE	307.1	0.5	ND	ND	307.6	133.4	81.6	Aver. 86.6
30/4	NE	221.8	1.2	ND	ND	223.0	126.9	62.2	
1/5	NE	302.0	4.9	ND	ND	306.9	132.8	81.6	
2/5	NE	648.4	–	ND	ND	648.4	131.5	174.1	

TABLE B.30 (CONT'D)

Test Date	Stack	Filter Br (μg)	Probe Solids Br (μg)	Probe Wash Br (μg)	Impinger Br (μg)	Total Br Collected (μg)	Gas Sampled (dscf)	Br Loading (μg/ m³)	
29/5	NE	498.7	8.0	180	ND	686.7	140.4	172.7	
29/5	NE	528.1	8.9	ND	ND	537.0	142.2	133.5	Aver.
30/5	NE	590.0	6.0	210	ND	806.0	146.3	194.6	166.9
14/5	SE	686	N.A.	N.A.	ND	686	71.8	337.3	
14/5	SE	626	N.A.	N.A.	825	1451	62.2	823.5	Aver.
15/5	SE	617	N.A.	N.A.	ND	617	45.7	476.7	545.8
22/4	SE	174	N.A.	ND	ND	174	62.1	98.9	
23/4	SE	1740	N.A.	1800	ND	3540	67.0	1866.0	
30/4	SE	400	N.A.	ND	ND	400	57.7	244.7	Aver.
30/4	SE	1141	N.A.	ND	ND	1141	57.4	702.1	601.7
1/5	SE	744	N.A.	ND	ND	744	48.5	541.7	
2/5	SE	161	N.A.	ND	ND	161	36.3	156.8	
29/5	SE	2086	N.A.	240	577	2903	81.1	1264.3	Aver.
29/5	SE	3590	N.A.	720	525	4835	81.5	2095.2	1173.2
30/5	SE	424	N.A.	ND	ND	424	93.7	160.0	

TABLE B.31. ZINC EMISSION DATA

Test Date	Stack	Filter Zn(μg)	Probe Solids Zn (μg)	Probe Wash Zn (μg)	Impinger Zn (μg)	Total Zn Collected (μg)	Gas Sampled (dscf)	Zn Loading (μg/m³)	
11/3	NW	56.9	27.8	N.A.	N.D.	84.7	124.1	24.0	Av.
12/3	NW	89.3	26.8	N.A.	N.D.	116.1	128.8	31.8	27.9
12/3	NW	67.9	33.5	N.A.	N.D.	101.4	127.6	27.9	
22/4	NW	72.1	39.5	9	30	150.6	133.0	39.9	
23/4	NW	53.9	24.2	N.D.	N.D.	78.1	125.3	21.9	
30/4	NW	77.4	45.2	N.D.	22.5	145.1	128.9	39.9	Av.
30/4	NW	68.8	11.6	N.D.	N.D.	80.4	133.3	21.2	26.7
1/5	NW	49.7	40.5	N.D.	N.D.	90.2	130.8	24.4	
2/5	NW	17.0	30.4	N.D.	N.D.	47.4	129.3	13.1	
29/5	NW	10.0	16.9	N.D.	N.D.	26.9	127.7	7.42	Av.
29/5	NW	17.9	23.9	N.D.	N.D.	41.8	131.3	11.3	10.0
30/5	NW	13.1	29.5	N.D.	N.D.	42.6	132.0	11.3	
11/3	NE	38.6	13.6	N.D.	N.D.	52.2	129.3	14.1	
12/3	NE	35.6	12.1	N.D.	N.D.	47.7	132.9	19.8	Av. 17.5
12/3	NE	60.1	11.9	N.D.	N.D.	72.0	135.3	18.7	
22/4	NE	21.8	35.1	N.D.	N.D.	56.9	134.8	14.8	
23/4	NE	35.7	8.0	N.D.	N.D.	43.7	128.7	12.0	Av.
30/4	NE	24.3	7.8	N.D.	N.D.	32.1	133.4	8.48	
30/4	NE	18.4	12.8	N.D.	N.D.	31.2	126.9	8.12	11.6
1/5	NE	23.2	30.9	N.D.	N.D.	54.1	132.8	14.5	
2/5	NE	47.7	***	N.D.	N.D.	***	131.5	***	
29/5	NE	122.0	73.7	N.D.	N.D.	195.7	140.4	49.1	
29/5	NE	124.7	113.5	N.D.	N.D.	238.2	142.2	59.3	Av.
30/5	NE	159.3	115.6	N.D.	N.D.	274.9	146.3	66.4	58.3

TABLE B.31. (CONT'D)

Test Date	Stack	Filter Zn (μg)	Probe Solids Zn (μg)	Probe Wash Zn (μg)	Impinger Zn (μg)	Total Zn collected (μg)	Gas Sampled (dscf)	Zn Loading (μg/m^3)	
14/3	SE	N.D.	*	N.A.	N.D.	Nil	71.8	0	
14/3	SE	N.D.		N.A.	N.D.	Nil	66.2	0	Av.
15/3	SE	N.D.		N.A.	N.D.	Nil	45.7	0	0
22/4	SE	N.D.		45	N.D.	45	6.21	25.4	
23/4	SE	N.D.		75	6	81	67.0	42.7	
30/4	SE	N.D.		N.D.	N.D.	Nil	57.7	0	Av.
30/4	SE	16.7		12	3	32	57.4	19.8	16.6
1/5	SE	15.6		N.D.	N.D.	16	48.5	11.7	
2/5	SE	N.D.		N.D.	N.D.	Nil	36.3	0	
29/5	SE	N.D.		N.D.	N.D.	Nil	81.1	0	
29/5	SE	13.4		N.D.	N.D.	13	81.5	5.7	Av.
30/5	SE	N.D.		N.D.	N.D.	Nil	93.7	0	1.90

TABLE B.32. PHOSPHORUS EMISSION DATA

Test Date	Stack	Filter P (μg)	Probe Solids P (μg)	Probe Wash P (μg)	Impinger P (μg)	Total P Collected (μg)	Gas Sampled (dscf)	P Loading (μg/m^3)	
11/3	NW	238.2	107.9	N.A.	N.D.	346.1	124.1	98.5	
12/3	NW	372.4	106.8	N.A.	N.D.	479.2	128.8	131.4	Av. 116.9
12/3	NW	306.2	129.8	N.A.	N.D.	436.0	127.6	120.8	
22/4	NW	237.4	118.4	N.D.	N.D.	355.8	133.0	94.6	
23/4	NW	236.5	50.0	N.D.	N.D.	286.5	125.3	80.9	
30/4	NW	319.9	86.7	N.D.	N.D.	406.6	128.9	111.2	Av.
30/4	NW	303.0	15.5	N.D.	N.D.	318.5	133.3	84.4	79.2
1/5	NW	193.8	72.4	N.D.	N.D.	266.2	130.8	72.0	
2/5	NW	62.6	53.2	N.D.	N.D.	115.8	129.3	31.8	
29/5	NW	64.7	12.0	N.D.	N.D.	76.7	127.7	21.2	
29/5	NW	53.0	12.9	N.D.	N.D.	65.9	131.3	17.7	Av. 22.3
30/5	NW	70.0	34.6	N.D.	N.D.	104.6	132.0	27.9	
11/3	NE	117.0	51.7	N.A.	N.D.	168.7	129.3	45.9	
12/3	NE	127.4	31.9	N.A.	N.D.	159.3	132.9	42.4	Av. 51.9
12/3	NE	213.7	44.9	N.A.	N.D.	258.6	135.3	67.5	
22/4	NE	70.0	46.0	N.D.	N.D.	116.0	134.8	30.4	
23/4	NE	115.9	11.8	N.D.	N.D.	127.7	128.7	35.0	
30/4	NE	106.1	4.0	N.D.	N.D.	110.1	133.4	29.3	Av.
30/4	NE	80.9	19.2	N.D.	N.D.	100.1	126.9	27.9	30.7
1/5	NE	84.8	32.0	N.D.	N.D.	116.8	132.8	31.1	
2/5	NE	177.3	***	N.D.	N.D.	***	131.5	***	
29/5	NE	581.5	152.8	N.D.	N.D.	734.3	140.4	184.7	Av.
29/5	NE	445.0	145.4	N.D.	N.D.	590.4	142.2	146.6	167.8
30/5	NE	473.0	238.9	N.D.	N.D.	711.9	146.3	172.0	

TABLE B.33.   TOTAL FILTER BROMIDE (μg, Br) CALCULATED FROM XRF NET
              INTENSITY MEASUREMENTS FOR SE STACK FILTERS

Test Date	XRF net intensity (counts/sec)	Calculated Bromide Quantities (μg, Br per total filter)
14/5	6015	686
14/5	5462	626
15/5	5378	617
22/4	1277	174
23/4	15769	1740
30/4	3379	400
30/4	10226	1141
1/5	6548	744
2/5	1161	161
29/5	18964	2086
29/5	32883	3590
30/5	3586	424

TABLE B.34. FILTER SOLIDS ANALYSES
(DATA FROM ORF, XRF ANALYSES)

Test Date	Stack	Weight % of Element Indicated			
		Pb	Zn	Br	P
11/3	NW	.0035	.0083	.031	.035
12/3	NW	.0021	.0099	.035	.041
12/3	NW	.0022	.0084	.026	.038
22/4	NW	.0084	.0092	.087	.030
23/4	NW	.0082	.0075	.076	.033
30/4	NW	.0065	.0096	.104	.040
30/4	NW	.0065	.0084	.086	.037
1/5	NW	.0074	.0079	.12	.031
2/5	NW	.0055	.0098	.13	.036
29/5	NW	.0036	.0070	.045	.042
29/5	NW	.0033	.011	.052	.034
30/5	NW	.0029	.0069	.045	.036
11/3	NE	.0073	.010	.028	.031
12/3	NE	.0036	.0086	.026	.031
12/3	NE	.0020	.0094	.025	.033
22/4	NE	.014	.010	.10	.033
23/4	NE	.021	.014	.087	.045
30/4	NE	.0078	.0097	.122	.042
30/4	NE	.0069	.0086	.10	.038
1/5	NE	.0070	.010	.134	.038
2/5	NE	.0069	.0081	.11	.030
29/5	NE	.0020	.0081	.033	.039
29/5	NE	.0022	.0093	.039	.033
30/5	NE	.0026	.0098	.036	.029

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TABLE B.35.   PROBE SOLIDS ANALYSES
(DATA FROM ORD, XRF ANALYSES)

Test Date	Stack	Weight % of Element Indicated			
		Pb	Zn	Br	P
11/3 *	NW	.034	.0085	.011	.033
12/3 *	NW	.0041	.0097	.014	.039
12/3 *	NW	.0016	.0075	.0078	.029
22/4	NW	.029	.014	.0016	.042
23/4	NW	.023	.018	.0026	.038
30/4	NW	.013	.021	.0022	.041
30/4	NW	.015	.027	.0026	.036
1/5	NW	.012	.017	.0020	.031
2/5	NW	.010	.018	.0022	.031
29/5	NW	.031	.073	.0060	.052
29/5	NW	.033	.11	.0099	.059
30/5	NW	.010	.042	.0018	.049
11/3*	NE	.015	.0095	.0088	.036
12/3*	NE	.0077	.011	.013	.030
12/3*	NE	.0026	.0081	.014	.031
22/4	NE	.049	.038	.0025	.050
23/4	NE	.093	.055	.015	.081
30/4	NE	.034	.034	.0021	.017
30/4	NE	.035	.026	.0025	.040
1/5	NE	.051	.037	.0058	.038
2/5 **	NE				
29/5	NE	.0051	.015	.0016	.031
29/5	NE	.0038	.03	.0016	.026
30/5	NE	.0043	.014	.0007	.028

*   Samples from acetone washing

** Sample contaminated during analysis

TABLE B.36.   IMPINGER SOLUTIONS ANALYSES
(DATA FROM ORF, XRF, AA XRF
AND CHEMICAL ANALYSES)

Test Date	Stack	Total Dissolved Solids (mg)	p.p.m. of Element Indicated			
			Pb	Zn	Br	P
11/3	NW	1089	ND	ND	ND	ND
12/3	NW	1149	ND	ND	ND	ND
12/3	NW	657	0.3	ND	ND	ND
22/4	NW	1032	ND	0.04	ND	ND
23/4	NW	921	ND	ND	ND	ND
30/4	NW	1035	ND	0.03	ND	ND
30/4	NW	981	0.1	ND	ND	ND
1/5	NW	1038	ND	ND	ND	ND
2/5	NW	1083	0.1	ND	ND	ND
29/5	NW	826	ND	ND	ND	ND
29/5	NW	972	ND	ND	ND	ND
30/5	NW	1242	0.2	ND	ND	ND
11/3	NE	924	ND	ND	ND	ND
12/3	NE	714	0.1	ND	ND	ND
12/3	NE	543	ND	ND	ND	ND
22/4	NE	1091	ND	ND	ND	ND
23/4	NE	828	ND	ND	ND	ND
30/4	NE	891	ND	ND	ND	ND
30/4	NE	1077	ND	ND	ND	ND
1/5	NE	1017	ND	ND	ND	ND
2/5	NE	1092	ND	ND	ND	ND
29/5	NE	1080	0.1	ND	ND	ND
29/5	NE	1017	0.2	ND	ND	ND
30/5	NE	983	0.1	ND	ND	ND

TABLE B.36. (CONT'D)

Test Date	Stack	Total Dissolved Solids(μg)	ppm of Element Indicated			
			Pb	Zn	Br	P
14/5	SE	15	ND	ND	ND	ND
14/5	SE	10	ND	ND	1.1	ND
15/5	SE	18	ND	ND	ND	ND
22/4	SE	12	ND	ND	ND	ND
23/4	SE	9	ND	ND	ND	ND
30/4	SE	6	ND	ND	ND	ND
30/4	SE	15	ND	ND	ND	ND
1/5	SE	6	ND	ND	ND	ND
2/5	SE	0	ND	ND	ND	ND
29/5	SE	59	ND	ND	0.7	ND
29/5	SE	30	ND	ND	0.7	ND
30/5	SE	32	ND	ND	ND	ND

TABLE B.37. PROBE RINSE SOLUTIONS ANALYSES
(DATA FROM ORF, XRF ANALYSES)

Test Date	Stack	ppm of Element Indicated			
		Pb	Zn	Br	P
11/3	NW				
12/3	NW	←———————— Acetone ————————→			
12/3	NW				
22/4	NW	ND	0.03	0.9	ND
23/4	NW	ND	ND	ND	ND
30/4	NW	ND	ND	0.7	ND
30/4	NW	ND	ND	0.7	ND
1/5	NW	ND	ND	1.4	ND
2/5	NW	0.1	ND	2.2	ND
29/5	NW	ND	ND	0.7	ND
29/5	NW	ND	ND	ND	ND
30/5	NW	0.2	ND	ND	ND
11/3	NE				
12/3	NE	←———————— Acetone ————————→			
12/3	NE				
22/4	NE	ND	ND	ND	ND
23/4	NE	ND	ND	ND	ND
30/4	NE	ND	ND	ND	ND
30/4	NE	ND	ND	ND	ND
1/5	NE	ND	ND	ND	ND
2/5	NE	ND	ND	ND	ND
29/5	NE	ND	ND	0.6	ND
29/5	NE	ND	ND	ND	ND
30/5	NE	ND	ND	0.7	ND

TABLE B.37. (CONT'D)

Test Date	Stack	Pb	Zn	Br	P
		ppm	of Element	Indicated	
14/3	SE				
14/3	SE	← —————— Acetone —————— →			
15/3	SE				
22/4	SE	ND	0.15	ND	ND
23/4	SE	0.1	0.25	6.0	ND
30/4	SE	0.2	ND	ND	ND
30/4	SE	ND	0.04	ND	ND
1/5	SE	0.2	ND	ND	ND
2/5	SE	0.2	ND	ND	ND
29/5	SE	0.1	ND	0.8	ND
29/5	SE	ND	ND	2.4	ND
30/5	SE	ND	ND	ND	ND

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REFERENCES FOR APPENDIX B

(B 1)   Dixon, W.J. Ann. Math. Statis. $\underline{22}$, 68, (1951)

<u>APPENDIX C</u>

APPENDIX C

EXAMINATION OF CEMENT PROPERTIES

Seventeen cement samples were collected during regular production cement grinding and were analyzed by X-ray fluorescence for lead content. Lead was found in the range 0.0014 to 0.0070 percent. These samples were then tested for compressive strength, normal consistency and vicat setting times. A linear regression analysis was performed by least squares to determine whether there was significant correlation between percent lead and the measured parameters. The test data and the correlation parameters are given in Table C.1. Figures C.1 to C.4 show the compressive strength results graphically. The calculated t-statistics for each pair of correlation tests show that there is very little evidence of any correlation between percent lead and any of the performance test results. Had any effect been noted, it would of course not necessarily have been related only to lead but a correlation with amount of waste oil burned would have been indicated.

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TABLE C.1. CEMENT PROPERTIES

% Lead	Vicat Time of Set		Normal Consistency Water Percent	Compressive Strength			
	Initial	Final		1 day	3 days	7 days	28 days
0.0038	124	251	25.0	2062	3100	3762	4450
0.0058	119	239	24.0	1956	2993	3362	4033
0.0028	128	228	25.0	1962	2850	3525	4000
0.0070	117	227	25.0	2012	2918	3368	3946
0.0032	115	220	24.5	1950	2775	3243	3900
0.0019	128	243	25.0	2056	2875	3250	4054
0.0015	120	237	25.0	2037	2881	3393	4092
0.0032	115	240	25.0	1943	2537	3206	3833
0.0043	124	264	25.0	1968	2831	3293	4021
0.0047	129	239	25.0	1993	3031	3675	4166
0.0042	132	244	25.0	1812	2806	3237	4016
0.0033	118	222	25.0	2300	2950	3575	4200
0.0032	117	230	25.0	2237	2662	3343	4133
0.0044	115	255	25.0	2093	2675	3331	4050
0.0017	115	230	25.0	2030	2818	3387	4129
0.0014	110	235	25.0	2056	2831	3412	3962
0.0033	120	240	24.5	1987	2862	3668	4375
b	614	1621	-56	-14777	22246	4803	-6087
a	118	234	25.1	2079	2769	3397	4101
r	0.150	0.238	-0.300	-0.198	0.242	0.043	-0.058
t	0.586	0.947	-1.218	-0.782	0.965	0.166	-0.226
*P	55	45	35	45	35	85	85

*P indicates the approximate probability (as %) that a greater value of r could occur in sampling from a population with ρ (correlation coefficient) = 0.
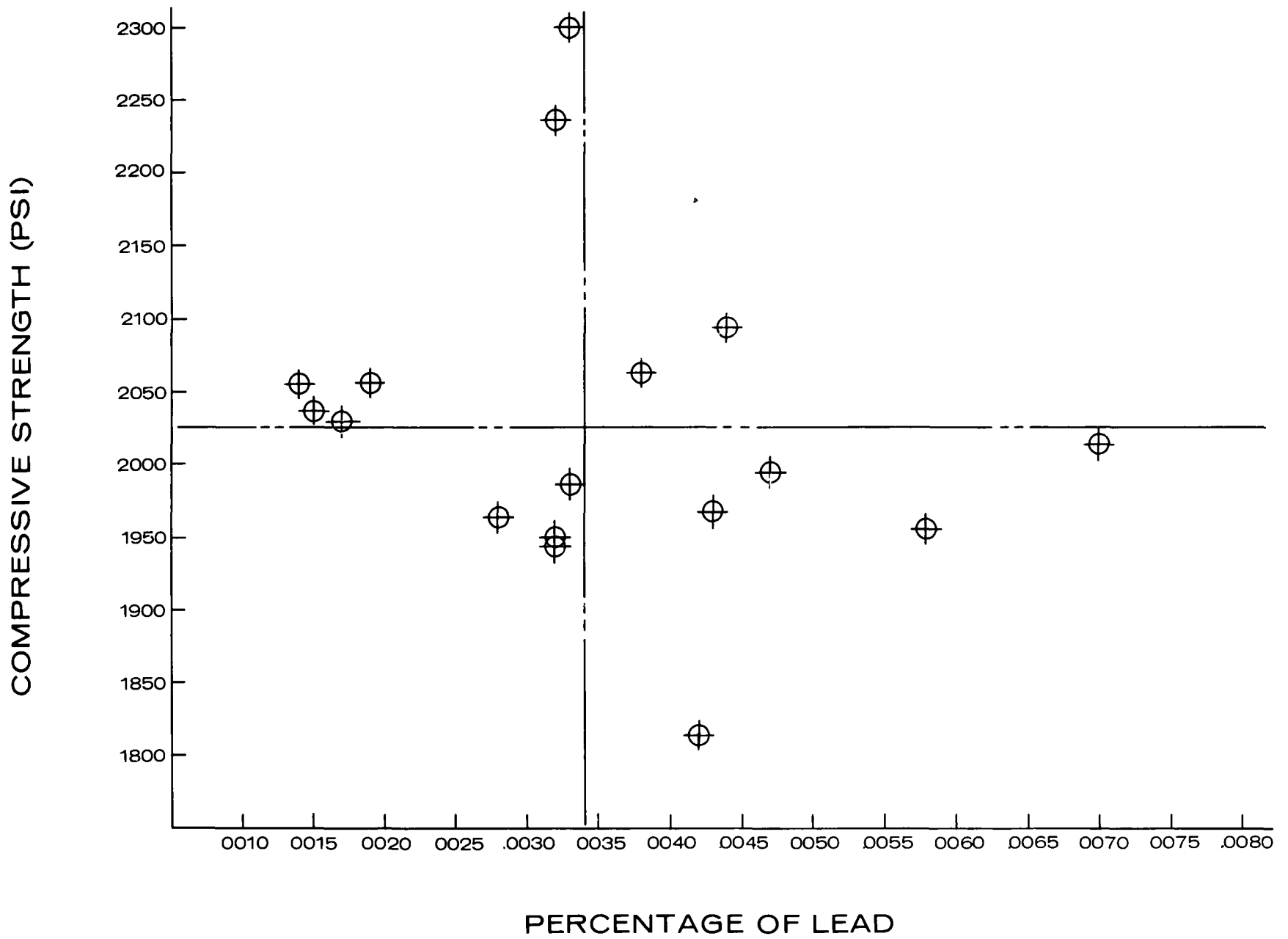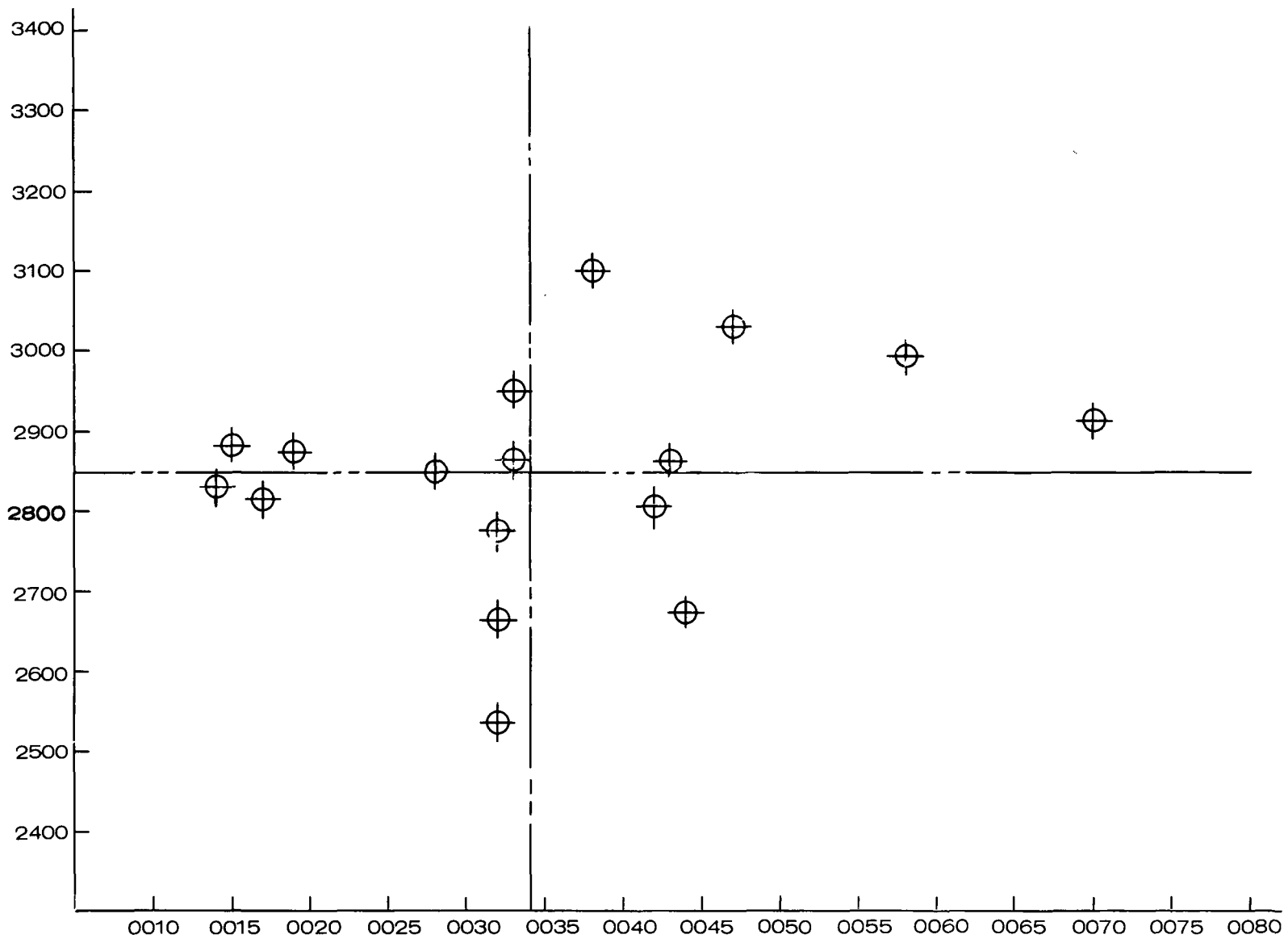
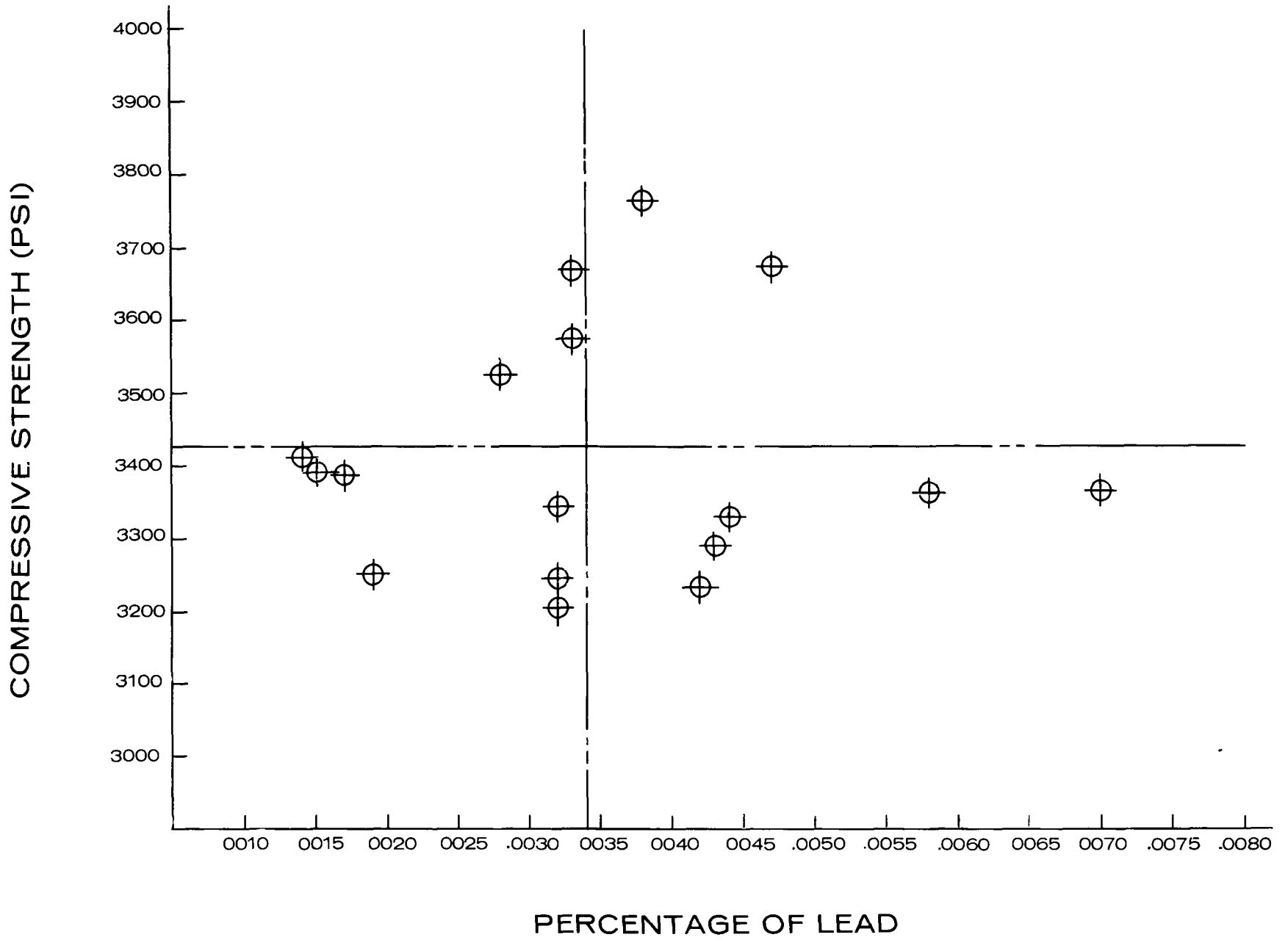Figure C.1   Compressive Strength Results (1 Day Strength)

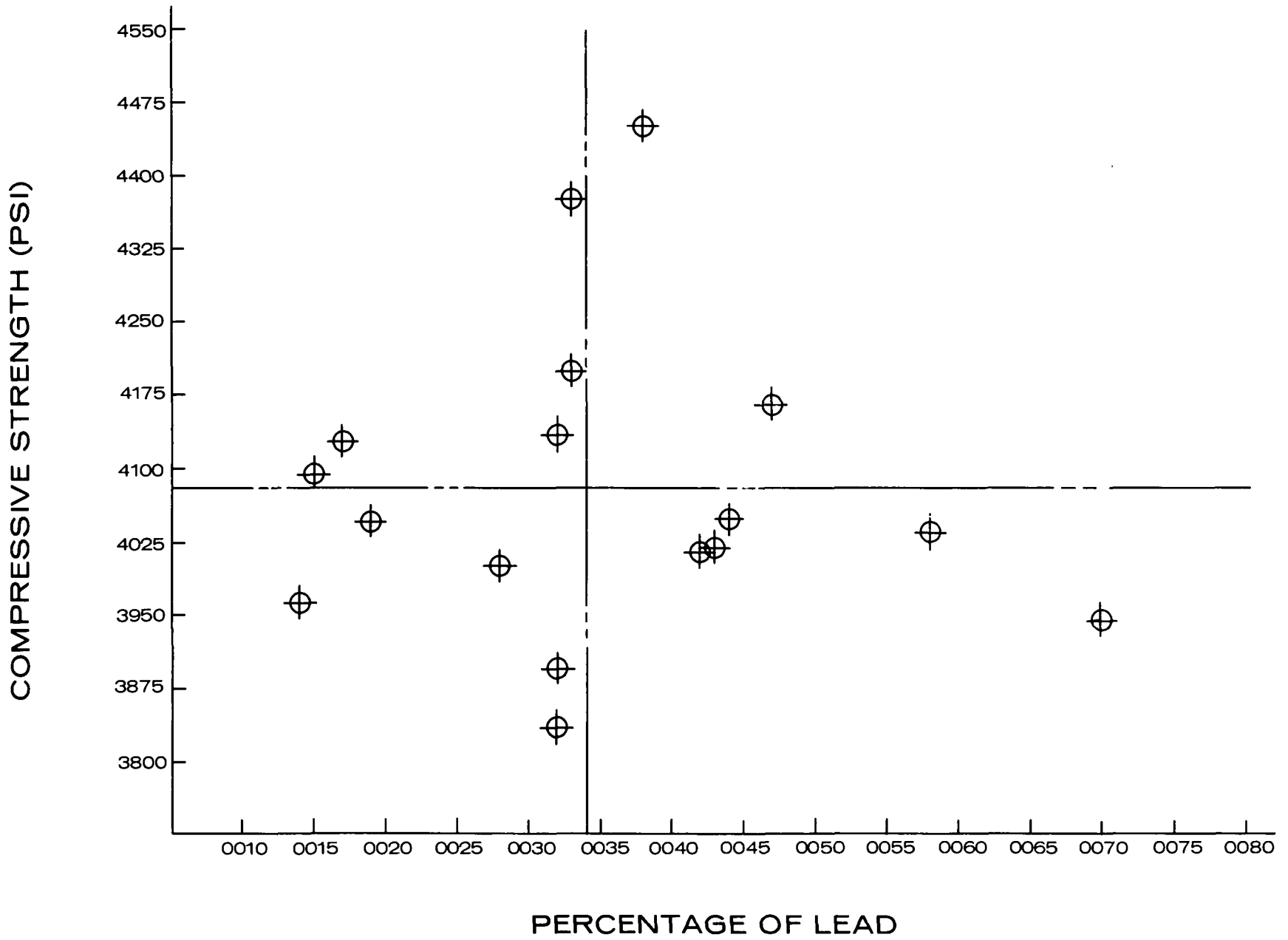Figure C.3   Compressive Strength Results (7 Day Strength)

Figure C.4   Compressive Strength Results (28 Day Strength)

APPENDIX D

APPENDIX D

DESCRIPTION OF THE USED OIL HANDLING SYSTEM

For the used oil experiments, a prototype oil handling
system (Figure D.1) was built from three 10,000 gallon tanks, thus
allowing storage of a one-day supply of the oil. Only essential features
of the system as regards kiln operation will be described, safety check
valves, relief valves, etc. although present will be ignored. Trucks
delivering oil pumped through a 3" line in which were installed filters
(double basket strainers, 30 mesh) into tank I. Tanks II and III are
gravity fed from tank I. From either tank II or III, 2" lines convey
the oil through a second filter to the pump. (Positive displacement
triple screw pump).

The oil is conveyed to the kiln or recirculated through 2"
lines some sections of which are equipped with heaters. The recirculating
feature whereby the oil is returned to tank I is essential since the
oil on storage in the tanks separates into a water layer and an oil
layer. It also allows some heating of the oil by passing it through
the line heaters. The amount of oil used was measured on the kiln
burner floor by target meter which could control the oil rate via a
motorized flow control valve.

Normally, number 6 (Bunker "C") fuel oil is burned using a
standard Pillard "Triplex" Tube containing three separate Pillard MY
Type mechanical atomization burners. During the experiment, one of the
MY burners was fueled with the used lubricating oil, while the remaining
two burners continued burning number 6 fuel. Pillard recommend the use
of these nozzles if burning oil in conjunction with either coal or
natural gas, hence used lubricating oil could be burned in kilns other
than oil fired kilns.

During the trial burn, several problems were encountered with
this system. The meter suddenly started giving extremely erratic results,
a problem which caused severe operating difficulties on the kiln. A
second problem encountered was a gradual decrease in the oil pressure
after the pump and in the flow rate which could be achieved.

TARGET METER

MOTORIZED FLOW
CONTROL VALVE

PRESSURE
SWITCH

10,000
GAL

BYPASS

BYPASS

10,000
GAL

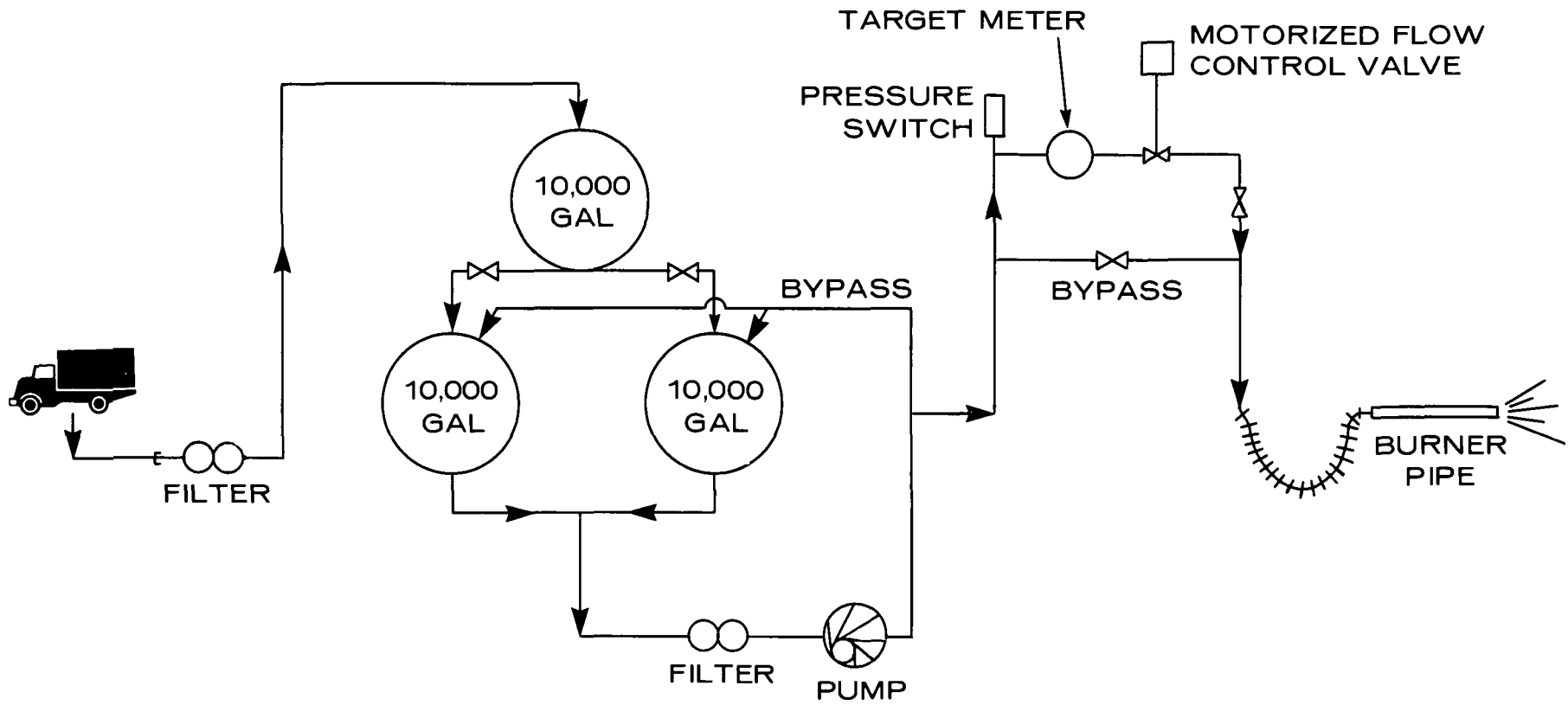10,000
GAL

BURNER
PIPE

FILTER

FILTER

PUMP

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Figure D.1   Waste Oil Flow Sheet

As indicated elsewhere in this report, this equipment was successfully used during previous trials, and operated well during parts of this burn, the fault is not believed due to equipment. Some of the oil delivered during the experiment had a large amount of both water and particulate matter present (this also required very frequent strainer cleanings as well as long truck unloading times due to strainer plugging). It is presently believed that particulate matter caused excessive wear in the pump and a mixture of oil/water and/or particulate caused build-up in the meter.

It would seem that at least the high amount of water in the oil (D 1) results from handling after collection, something which may also occur with particulate matter. If so, improvements in the collection procedure could result in a better quality oil for utilization in cement kilns and possibly overcome the equipment problems noted. Severe fluctuations in the heating value of this oil due to water were noted during this experiment.

Since the requirements for road oiling are not stringent, it may be that the oil collectors could take more care of this aspect fairly easily. At any rate, the quality of the oil delivered to cement plants must be carefully monitored if successful operation is to be maintained.

REFERENCES FOR APPENDIX D

(D 1)   Chansky, S., McCoy, W., Surprenant, N. and Salaginn, J.,
          "Waste Automotive Lubricating Oil as a Municipal Incinerator
          Fuel" in Proc. of Int. Conf. on Waste Oil Recovery and Reuse
          Feb. 12-14, 1974, Washington, D.C. Published by Information
          Transfer Inc., Washington, D.C. 1974, p 327.

APPENDIX E

APPENDIX E

REPORT ON ANALYSES OF STACK SAMPLES

FROM THE ST. LAWRENCE CEMENT COMPANY

BY

C. Pupp, A. Zdrojewski, J. Piquette, L. Dubois

Chemistry Division
Air Pollution Control Directorate
Environmental Protection Service
Environment Canada

E.1   Objective

Lead, zinc and possibly bromine had to be determined in stack samples collected on glass fibre filters of 125 mm diameter. One quarter of a filter was available for analysis. The results were to serve as comparison or to supplement analytical data obtained by the Ontario Research Foundation.

E.2   Approach

Preliminary results had shown that concentrations of lead and zinc in the samples were of the order of background levels and near the limits of detection. Thus, interferences and variations in background levels were expected to have significant effects upon the measured values. An average from different analytical methods, where feasible, were expected to give the most reliable results because effects of interferences and backgrounds due to a specific method would tend to average out.

E.3   Methods

E.3.1   X-ray Fluorescence Analysis

We had developed a XRF (X-ray Fluorescence) method to measure lead directly on ambient air filters (glass fibre filters). Concentrations were determined from an empirical calibration curve relating net X-ray intensities to concentrations. This was to be the first method of analysis. While it appeared to be an ideal method for

filters with light loading, it had to be determined by a comparison with other methods, if the same relationship of X-ray intensities versus concentration would hold for filters with heavy loading. This was established with reasonable certainty for lead and the conclusion was drawn that it would also be true for zinc and bromine. This is quite reasonable, especially for bromine, whose fluorescent wavelength is quite close to that of lead. In all cases a number of blank measurements were necessary, because glass fibre filters are contaminated with lead as well as with zinc.

A Siemens SRS instrument with a molybdenum tube, lithium fluoride crystal, scintillation counter and pulse height discriminator was used, and the Lβ - line of lead, the Kα - line of bromine and zinc were measured.

E.3.2   Atomic Absorption

For atomic absorption (AA) analysis it is necessary to bring the elements to be analyzed into solution. In order to separate from the sample, at least partially, the background zinc and lead present in the filter material, we extracted the sample by heating with nitric acid, rather than use our standard procedure of digestion of the whole filter with $HF + HNO_3$. From a repetition of this extraction we established that the first treatment had extracted all but an insignificant fraction of zinc and lead. These extracts were then analyzed by two different atomic absorption methods:

(a)   flame atomic absorption with an air-acetylene flame

(b)   flameless atomic absorption using a graphite atomizer and a deuterium arc background corrector.

For lead the absorption line at 283.3 nm and for zinc the line at 213.9 nm was used. The use of the background corrector significantly improved the agreement between AA and the other methods. This was to be expected as it is known that the presence of alkali and alkaline earth metals is a source of background in AA spectroscopy that is significant at low concentrations. In addition to the background corrector, spiking with the element to be analyzed was used as a check of the method.

E.4   Results and Conclusions

E.4.1   Lead

        The results for lead are given in Table E.1. The results
obtained by the Ontario Research Foundation by an X-ray analysis of
pelletized sample are shown in the column labelled ORF. Exact values
for the uncertainties of these figures are difficult to give, as they
depend on a variety of factors, like the variation of the filter blank,
uncertainty of the method proper etc. An estimate of the 95% uncertainty
based mainly on filter blanks and known uncertainties of the method
would be 5-10 µg per filter for the results obtained by any method in
our laboratory. It can be seen that some of the total amounts of lead
given in the table are not very much larger than these uncertainties.
It also can be seen that almost all values obtained by different methods
and different laboratories agree to better than a factor of 2. The
very good agreement between the two different X-ray methods seems to
indicate that they are less subject to interferences and may give
somewhat better results, but we have not investigated this any further.
At this stage one should probably choose an average from all methods
from all laboratories. We would consider such an average to be reliable
to better than a factor of 2 or $\pm$ 10 µg per filter, whichever is larger.

E.4.2   Zinc

        The high background of zinc and its large variability made
X-ray analysis directly on the filter impossible. Also, flameless
atomic absorption spectroscopy gave rather irreproducible results. Thus,
only our results by flame atomic absorption and ORF X-ray measurements
of pellets could be compared, as shown in Table E.2. Again we estimate
that our results are uncertain by about $\pm$ 10 µg per filter. It can be
seen from the table that these uncertainties are again of almost the
same magnitude as the total amount of zinc. It can also be seen that
almost all values from ORF are higher by factors up to 2 and 3. While
the reason for this difference may be found with – probably considerably –
additional work, we think that at these levels so close to the limits
of detection such differences should be acceptable. The lower value is

probably close to the lower, the higher value close to the upper limit and an average would most likely be reliable within a factor of 2 to 3.

E.4.3   Bromine

Net X-ray intensities measured directly on the filter are shown in Table E.3 (after blank corrections) together with X-ray values from ORF for the NW and NE stack. We did not have any calibration for bromine, but the ORF values can be used to calibrate our X-ray intensities and from that calibration the values of the SE stack can be calculated. It can be seen from the ratios in the last column of Table E.3 that the correlation is quite good. Assuming a linear relationship (with zero intercept) one can calculate values for the SE stack with an average ratio of 8.1 ± 1.2 counts/sec per μg/filer. By analogy with the results on lead one may also estimate an uncertainty of a factor of 2.

TABLE E.1. LEAD IN MICROGRAMS PER FILTER

Stack	Experiment Number	XRF	Flameless AA	Flame AA	ORF
NW	1	–	7.3	64.6	24.0
NW	2	–	5.2	64.6	19.0
NW	3	–	8.5	51.0	18.0
NW	4	72.4	124.0	99.1	66.0
NW	5	61.2	38.0	133.6	59.0
NW	6	57.9	18.9	110.2	52.0
NW	7	51.2	21.2	121.4	53.0
NW	8	–	15.6	92.4	47.0
NW	9	6.5	4.9	13.4	9.5
NW	10	–	1.7	6.7	5.5
NW	11	4.7	3.5	6.7	5.2
NW	12	6.1	3.6	26.7	5.5
NE	1	18.9	22.3	50.1	28.0
NE	2	9.5	11.7	60.1	15.0
NE	3	–	8.5	49.0	13.0
NE	4	27.8	16.7	27.8	29.0
NE	5	64.6	10.9	93.5	54.0
NE	6	15.6	6.5	42.3	20.0
NE	7	8.6	8.1	33.4	15.0
NE	8	11.1	6.5	39.0	15.0
NE	9	–	17.8	63.5	41.0
NE	10	–	3.1	72.4	30.0
NE	11	–	94.6	64.6	29.0
NE	12	–	8.5	75.7	42.0
SE	1	7.9	8.6	6.9	–
SE	2	7.9	8.6	44.5	–
SE	3	65.7	22.3	80.2	–
SE	4	24.5	16.7	24.5	–
SE	5	95.7	27.8	75.7	–
SE	6	34.5	16.7	46.8	–
SE	7	63.5	66.8	82.4	–
SE	8	292.0	105.8	241.6	–
SE	9	30.1	12.2	24.5	–
SE	10	223.0	289.5	232.7	–
SE	11	347.0	496.6	504.4	–
SE	12	40.1	15.6	41.2	–

TABLE E.2.   ZINC IN MICROGRAMS PER FILTER

Stack	Experiment Number	Flame AA	ORF
NW	1	20.0	57.0
NW	2	39.0	89.0
NW	3	39.0	68.0
NW	4	18.9	72.0
NW	5	20.0	54.0
NW	6	24.5	77.0
NW	7	33.4	69.0
NW	8	16.7	50.0
NW	9	N.M.	17.0
·NW	10	N.M.	10.0
NW	11	N.M.	18.0
NW	12	N.M.	13.0
NE	1	6.7	39.0
NE	2	10.0	36.0
NE	3	22.3	60.0
NE	4	3.3	22.0
NE	5	4.5	36.0
NE	6	4.5	24.0
NE	7	31.2	18.0
NE	8	21.2	23.0
NE	9	13.4	48.0
NE	10	43.4	122.0
NE	11	33.4	125.0
NE	12	47.9	159.0
SE	1	N.M.	–
SE	2	N.M.	–
SE	3	N.M.	–
SE	4	N.M.	–
SE	5	N.M.	–
SE	6	N.M.	–
SE	7	16.7	–
SE	8	15.6	–
SE	9	N.M.	–
SE	10	N.M.	–
SE	11	13.4	–
SE	12	N.M.	–

TABLE E.3. BROMINE NET X-RAY INTENSITIES AND μg PER FILTER RESPECTIVELY

Stack	Experiment Number	Net XRF Int. Counts/sec	ORF Values μg/Filter	Ratios XRF Int./ORF Values
NW	1	–	213.3	
NW	2	–	317.4	
NW	3	–	206.0	
NW	4	5215	684.7	7.62
NW	5	4312	547.1	7.88
NW	6	8467	838.0	10.10
NW	7	5343	707.4	7.55
NW	8	–	741.2	–
NW	9	1534	221.1	6.94
NW	10	798	68.7	11.6
NW	11	606	81.2	7.46
NW	12	807	85.8	9.41
NE	1	772	107.6	7.17
NE	2	730	109.2	6.68
NE	3	–	159.9	–
NE	4	1800	218.9	8.22
NE	5	1630	224.0	7.23
NE	6	2785	307.1	9.07
NE	7	1113	221.1	5.02
NE	8	2744	302.0	9.09
NE	9	–	648.4	–
NE	10	–	498.7	–
NE	11	–	528.1	–
NE	12	–	590.0	–
SE	1	6015	741	
SE	2	5462	673	
SE	3	5378	663	
SE	4	1277	159	
SE	5	15769	1940	
SE	6	3379	417	Calculated from
SE	7	10226	1259	net intensity
SE	8	6548	807	
SE	9	1161	145	
SE	10	18964	2332	
SE	11	32883	4042	
SE	12	3586	443	

APPENDIX F

APPENDIX F

PORTLAND CEMENT MANUFACTURING

F.1   Introduction

Portland cement is manufactured principally for use in the construction industry as a component of concrete. A number of technical terms are in common use in the industry. The following definitions apply.

Clinker: is the product discharged from the kiln after the raw materials have been burned.

Portland cement: is the product obtained when clinker is ground to specified fineness with gypsum. Portland cements are hydraulic since they harden to a stone-like mass by reacting with water. This chemical reaction is called hydration.

Neat-paste: is a mixture of cement and water.

Mortar: is a mixture of cement, sand and water.

F.2   Manufacture

Summary:

The most common raw materials are limstone and clay or shale. The raw mix is finely ground and heated to about $2600^{\circ}F$ ($1430\ ^{\circ}C$) to decompose the calcium carbonate and combine the calcium oxide with silica, alumina and iron to form a partly fused clinker. The clinker is then ground, usually with a small proportion of calcium sulphate (gypsum), which regulates set. Cements with special properties are produced by varying the oxide composition and also by adding small amounts of chemical agents at the clinker-grinding stage or later.

Raw Materials:

The raw materials for cement are chosen to supply:

a) Lime component (calcareous)

b) silica component (siliceous)

c) alumina component (argillaceous)

d) iron component (ferriferous)

and in Canada and USA about 30 different raw materials are used to supply the required oxides. (taken from Encyclopedia Britannica)
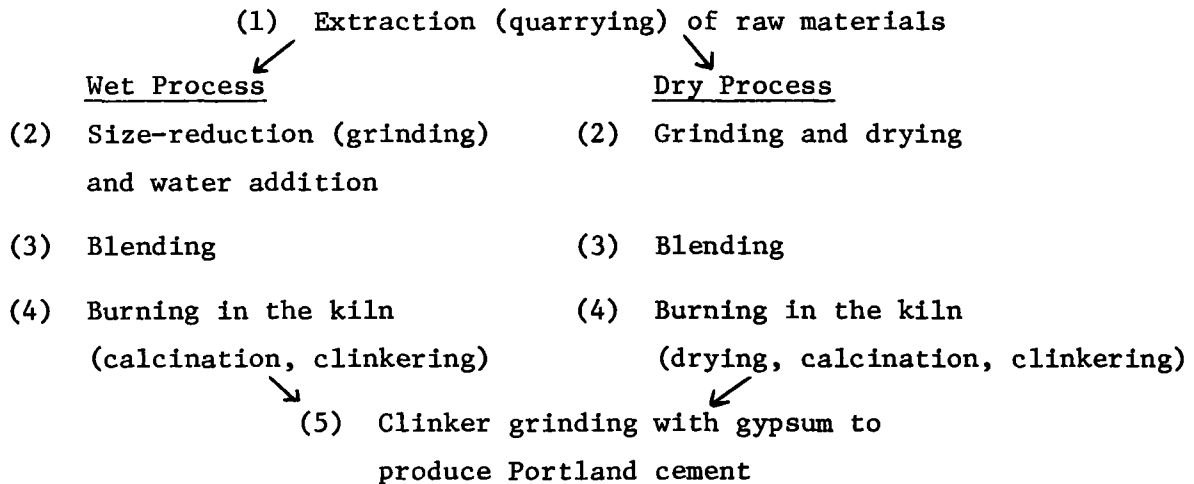
TABLE F.1. RAW MATERIAL FOR CEMENT

Calcareous	Argillaceous	Siliceous	Ferriferous
Cement rock Limestone Marl Alkali waste Oyster shell Coquina shell Chalk Marble	Clay Shale Slag Fly ash Copper slag Aluminium ore refuse Staurolite Diaspore clay Granodiorite Kaolin	Sand "Traprock" Calcium silicate Quartzite Fuller's earth	Iron ore Iron calcine Iron dust Iron pyrite Iron sinters Iron oxide Blast-furnace flue dust

TABLE F.2. TYPICAL OXIDE COMPOSITION OF RAW MATERIAL FOR CEMENT

Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Ignition loss
Limestone	1.2	0.5	0.4	54.0	0.6	43.2
Limestone	5.6	1.0	0.5	50.7	0.8	41.2
Cement rock	14.2	4.8	1.6	40.2	2.8	34.2
Sand	89.7	2.4	0.7	0.6	0.7	5.9
Clay	67.8	14.3	4.5	0.9	1.2	8.0
Shale	63.0	20.0	5.5	0.7	2.7	6.0
Pyrite cinders	6.3	2.1	86.7	0.02	0.1	2.6
Slag	37.8	11.4	1.0	46.1	2.0	--
Sea shells (washed)	1.5	0.4	1.2	52.28	0.7	41.8
Fly ash	51.2	25.6	8.5	1.6	0.9	8.6

These materials must be prepared and correctly blended to give the required composition of each component in the cement. After blending the material is ready to feed to the kiln.

Clinker is manufactured by either wet or dry process methods. In the wet process, raw materials are prepared, blended and fed to the kiln as a water slurry (about 30-35% water). In the dry process, raw materials are prepared, blended and fed to the kiln as a dry powder (about 0.5% water). The procedures and the distinctions between the processes are illustrated below:

(1) Extraction (quarrying) of raw materials

Wet Process	Dry Process
(2) Size-reduction (grinding) and water addition	(2) Grinding and drying
(3) Blending	(3) Blending
(4) Burning in the kiln (calcination, clinkering)	(4) Burning in the kiln (drying, calcination, clinkering)

(5) Clinker grinding with gypsum to produce Portland cement

The kilns used are long, cylindrical, fire brick lined vessels, 8 to 20 ft in diameter and 150 to 400 ft long. The dry process kilns are shorter - 150 to 300 ft, whereas the wet process kiln needs an additional drying zone (water removal which amounts to about 15-25% of the length). The kilns are direct fired (flame is in contact with the material) from the lower of discharge end. Due to the slope and rotation of these cylinders, the material moves from the higher elevation, feed end, to the lower hot discharge end. The retention time in the kiln is a function of the length, diameter, slope and speed of rotation.

The raw meal or raw mix enters the kiln, in the wet process, as a slurry and to avoid lumping, bridging, and breaching a network of heavy chains is installed inside the kilns to keep the material broken up and moving. These chains also enhance the heat transfer between the direct fired combustion gases and the material in the kiln. The hot gases flow up the kiln countercurrent to the downward flow of the solids. For a wet kiln the exit gas temperature is around $500^{\circ}F$ ($260-310^{\circ}C$) whereas with a dry process kiln the exit gas temperature is around $600-100^{\circ}F$ (310 to $540^{\circ}C$) as there is no slurry water removal zone.

As the material moves down the kiln into progressively hotter zones two distinct phenomena take place:

a) liberation of carbon dioxide from the limestone thus forming calcium oxide. This is called calcination and begins at $700^\circ F$ $(370^\circ C)$.

b) burning zone in which the lime combines with the silica and alumina, facilitated by the fluxing action of the alkalies and the iron oxide, to form a partially fused material called cement clinker. This is a complex mixture of such compounds as tricalcium silicate $(3CaO \cdot SiO_2)$ $(C_3S)*$, dicalcium silicate $(2\ CaO \cdot SiO_2)$ (C_2S), tricalcium aluminate $(3CaO \cdot Al_2O_3)$ (C_3A) and tricalcium alumnate $(4CaO \cdot Al_2O_3 \cdot Fe_2O_3)$, (C_4Af). The burning, fluxing, chemical reaction zone takes place at 2580 to $3000^\circ F$ $(1400-1600^\circ C)$.

The cement clinker leaves the kiln at a temperature of 2400 to $2600^\circ F$ $(1300-1400^\circ C)$. This temperature is quickly lowered with air in what is called a "clinker cooler". For economy of fuel, part of the hot air from the cooler is fed to the kiln for secondary combustion air. The cooled clinker is very stable and may be stored for months without deterioration.

In order to regulate the setting times of the cement, gypsum (calcium sulphate) is usually added to the clinker and the mixture ground to an extremely fine powder. The size of the particulate matter is less than 74 microns. In some specifications the required fineness is expressed in terms of surface area per gram. The final product is then stored in large vessels called cement silo, from which it is drawn as needed for packaging and/or shipment.

There are many different Portland cements each with its own special qualities, such as rapid hardening cements, low heat of hydration cements, and sulphate resisting cements. The unique properties of each are obtained by varying chemical and physical composition (See Table F.3).

* Note: C_3S, C_2S, C_3A and C_4Af are abbreviations used in the industry and are not chemical formulae.

TABLE F.3.   TYPICAL CALCULATED COMPOUND COMPOSITIONS

CSA designation	Symbol	Major Compound Composition %			
		C_3S	C_2S	C_3A	C_4AF
Normal	10	52	20	12	8
Moderate	20	46	33	7	11
High Early Strength	30	60	11	11	8
Low Heat	40	30	46	4	13
Suphate Resistant	50	38	42	2	11

APPENDIX G

APPENDIX G

DISPERSION OF AIR POLLUTANTS

by

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Atmospheric emissions released from point sources or chimneys
are subject to various phenomena occurring between the point of release
at the chimney exit to their final destination. Emissions are usually
subjected to some degree of vertical rise above their point of release.
This plume is thought of as having two components: that due to gas temper-
ature and that due to the gas exit velocity. The magnitude of this rise
is also affected by the meterological conditions of the ambient space
to which the gas or plumes is released. Of the meteorological parameters
affecting ground or receptor level concentrations of pollutants, the most
important are the influences of wind direction, wind speed, turbulence,
temperature and stability.

Wind, which can be considered to be air motion in three directions,
is the prime factor in the transport of any released pollutants to their
final destination. The prevailing wind direction is indicative of the
direction of the travel of the pollutants. Since the wind is seldom
constant for any length of time, turbulence (or frequent fluctuations)
in the wind is responsible for the movement and diffusion of the pollu-
tants about the mean wind path. The wind speed is the determining factor
for the time of travel of the pollutant from its point of release or
source to a receptor which can be considered to be its point of impinge-
ment. More important then this time factor is the dilution effect which
it has upon the plume. In general, pollutant concentrations downwind
from ground level sources are inversely proportional to wind speed, but
for high level stacks as in the case of the cement kiln stacks: an increase
in wind speed lowers the plume rise to a critical point where ground level

concentrations are increased and maximized at what is known as the critical wind speed.

The variation in atmospheric temperature with height is important in determining plume behaviours and pollution concentrations. The temperature variation with height is termed the lapse rate and under adiabatic or neutral atmospheric conditions is $1^{\circ}C$ per 100 meters. This concept of lapse rate is the basis of the five classes of stability (designated A to F) used for air pollution dispersion analyses.

The lapse rate of $1^{\circ}C$ per 100 meters is the "D" class or adiabatic condition. The air is considered unstable or superadiabatic when the temperature decreases with height at a greater rate than this. Solar heating and light winds are necessary for this to occur. Higher winds cause this instability to break down and the degree of breakdown is dependent upon the heating from the sun. Very stable conditions of E and F are prevalent with the absence of solar insolation and occur at night and on overcast days. The Key to Stability Categories, best summarizes these classifications.

TABLE G.1. KEY TO STABILITY CATEGORIES

Surface Wind Speed (at 10 m) M/sec	Insolation Strong	Moderate	Slight	Night Thinly Overcast or > 4/8 Low Cloud	$\leq$ 3/8 Cloud
< 2	A	A-B	B	-	-
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
> 6	C	D	D	D	D

The neutral category, Category D, should be assumed for overcast conditions during day or night

The Air Management approach to Air Pollution Control is based upon the precept that the contribution to ground level concentration (GLC) for any pollutant is within a specified concentration level for a given time period.

Atmospheric dispersion calculations are made for either maximum
ground level concentrations or impingement concentrations, depending
upon the point of plume contact of interest. These calculations consider
the emission and meteorological variables for the model under considera-
tion. The C & D stability classes are representative of the most common
naturally occurring conditions, and therefore are frequently examined.