EXPERIMENTAL BURNING OF USED AUTOMOTIVE CRANKCASE OIL IN A DRY-PROCESS CEMENT KILN

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Summary

An experimental program was carried out at the St. Lawrence Cement Company Limited, Mississauga, Ontario, in which 330,000 gallons of used lubricating oil was burned as a portion of the total fuel requirement for a dry-process cement kiln. The plant uses a dual four-stage preheater with a by-pass system. The oil was primarily composed of automotive crankcase drainings and contained approximately 0.6% lead, 0.15% bromine, 0.1% zinc and 0.1% 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 found to occur during the waste-oil burn. A material balance was carried out for lead, bromine, zinc and phosphorus which indicated that these elements were retained in the process solids. Lead, zinc, phosphorus and some of the bromine were retained in the cement clinker. Most of the bromine was retained in the collected dust from the precipitator on the by-pass system.

Introduction

The disposal of waste lubricating oil shares many features with other major resource and environmental concerns. It originates in a non-renewable resource that should be conserved and, like other industrial and municipal wastes, presents significant health and environmental hazards in its disposal. The problem is of concern in all major industrial countries and in recent times has been examined in Canada [1], the United States [2], and Western Europe [3].

Used lubricating oils originate from automotive, railway, marine, farm and industrial sources. The study reported in this paper was concerned with waste automotive lubricating oils (crankcase drainings). Automotive crankcase drainings are perhaps the most problematic waste oils. They are heavily contaminated with toxic components; they originate in a consumer product and thus tend not to be centrally located; they are the least amenable to recycling

back to the base-stock required to formulate new lubricating oil. In 1972, some 73,000,000 imp. gals. of automotive oils were sold in Canada, of which it has been estimated up to 41,000,000 gallons could be recovered (56%) [1]. Very little is known of the true proportion recovered. Re-refining (recycling) plants are able to treat 5—6 million gallons. The remainder is subject to largely uncontrolled disposal, principally as road-oil for dust control.

Used automotive oils contain both portions of the original additives and impurities acquired during service. A summary of the generally reported contaminants of used lubricating oils is given in Table 1, together with their expected ranges of concentration. In addition to these contaminants, analyses of samples at the Ontario Research Foundation and the St. Lawrence Cement Co. has shown that bromine is a significant contaminant in automobile crankcase drainings. Analytical work associated with combustion tests at Gulf Researc and Development Co. in 1969 also showed bromine as a significant constituent of boiler deposits after waste oils had been used as fuels.

TABLE 1

Elements found as contaminants in used automotive oils (1)

Element	Reported concentration range (ppm)		
	Min.		Max.
Si	10		875
Ca	700		3000
Na	16		300
Fe	50		2000
Mg	10		1108
Pb	800		21700
V	3		39
Cu	5		348
Ba	10		2000
Zn	300		3000
P	500		2000
Sn	5		112
Cr	8		50
Be		6	
Mn	5		10
Ni	3		30
Cd		4	
Ag		1	
Sr	10		30
Al	10		800
B	3		20
Mo	2		3
Ti	5		30
Br		0.15%*	
S	0.21%		0.65%

* ORF/SLC analyses

The thermal value of used oils (140,000—160,000 BTU/gal.) makes the concept of heat recovery combined with disposal an attractive proposition. However, unless controls are applied to combustion emissions, burning automotive crankcase drainings may be expected to present an environmental hazard through the emission of contaminant elements to the atmosphere.

The concept of using waste oil as a fuel in cement processing derives from the action of cement kilns in containing sulphur from the kiln gases [4]. It was believed that this scrubbing action would be effective as a means of removing other chemical elements. This concept was examined through a full-scale plant experiment in which 330,000 gallons of used lubricating oil were burned as a partial fuel in the St. Lawrence Cement Co. dry-process cement kiln at Mississauga, Ontario. This experiment was conducted to determine whether the gas-scrubbing action of the kiln would permit waste oil to be burned without an adverse effect on air pollution.

Atmospheric emission measurements were made before, during and after a test period of waste-oil burning. Emission measurements were supported by carrying out a mass balance on lead, bromine, zinc and phosphorus in all of the process materials.

Cement manufacturing — The St. Lawrence Cement Co. dry-process plant

Portland cement is produced by igniting a mixture of finely ground limestone, silica, alumina, and iron oxide (raw feed). The kiln discharge (clinker) is a chemically complex mixture of calcium silicates, aluminates and ferrites which, when ground and blended with 2—5% of calcium sulphate, is sold as Portland cement. Detailed descriptions of cement manufacturing methods are available from many literature sources [5]. Procedures described in this paper will be limited to those relevant to the St. Lawrence Cement Co. dry-process plant. General information on the company and the plant has been published in two articles [6,7].

The process system comprises a dual, Fuller—Humboldt suspension preheater, a by-pass and a 17 ft. × 276 ft. Traylor rotary kiln. Normal production capacity requires the burning of approximately 4500—5000 tons per day of raw meal to produce some 3000—3200 tons of clinker.

The suspension preheater consists of a system of cyclones, with connecting pipes, through which the hot exit gases from the kiln are drawn. The general flow of materials and gases in the preheater is illustrated in Fig. 1. Kiln feed is introduced into the duct between the first and second stage cyclones. It is swept with the hot exhaust gas into the uppermost (Stage I) cyclones where gas and material are separated. The raw feed material drops into the duct between the second and third stage cyclones and is again suspended and separated. This procedure is repeated in Stages III and IV 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 Schroth [8].
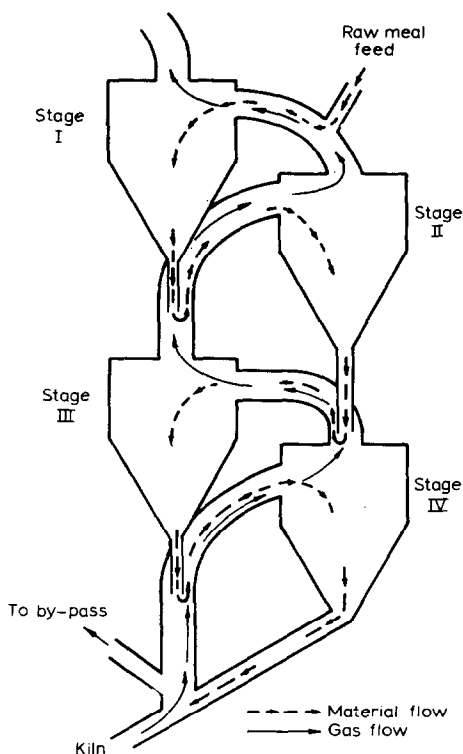
Fig. 1. Principal of operation of a suspension preheater.

The raw material enters Stage I and is preheated to approximately 600°F while the gas temperature drops from 990° to 650° F. Corresponding heat exchanges occur in Stages II, III and IV such that the material enters the rotary kiln at approximately 1475°F. The gas temperature at the point of exit from the kiln into the preheater is 1900°–2000°F.

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 waste oil, which are volatile at kiln and flame temperature will be expected also to travel with the gas stream. The mass transfer of these elements in the total production system is the key to understanding the successful containment of potentially volatile contaminants found during this study.

The concepts of kiln-gas reaction chemistry have been summarized by Locher Sprung and Opitz [9]. To illustrate the general principles, consider a kiln—preheater combination operating at normal clinkering temperature using a raw mix containing alkali 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° 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 be volatilized again, thereby setting up an internal cycle [10]. 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.

In process plants using suspension preheaters, special measures have to be taken to reduce the build-up of chlorides and alkali metals in the clinker and the preheater cyclones. At the St. Lawrence plant, a fraction of the kiln exhaust gas is by-passed through a conditioning tower in which the gas velocity is reduced and water is sprayed into the gas stream to lower the temperature and condition the gases for precipitation. 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.
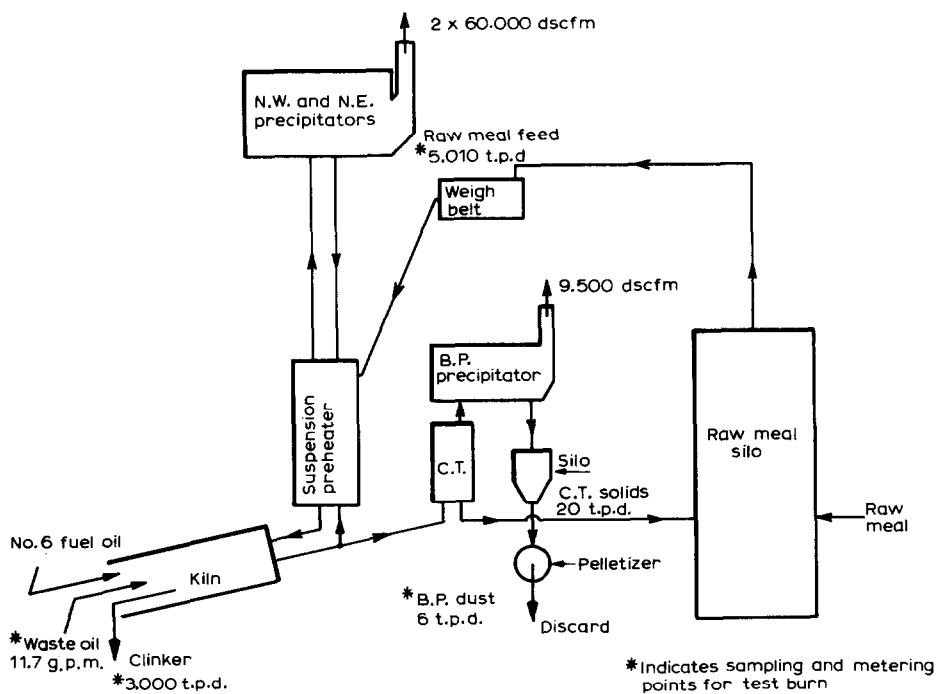

Fig. 2. Schematic of the material flow.

Experimental

A schematic illustration of material flow through the production system is shown in Fig. 2. Kiln emissions were sampled at the three exit stacks (NE, NW and SE) after the electrostatic precipitators. To obtain the material balance, raw feed, clinker, bypass precipitator dust, conditioning tower solids, No. 6 fuel oil and waste oil were all sampled as 24-hour, composite samples. These same materials were weighed or metered on a 24-hour basis. For details of sampling and metering procedures the reader is referred to the full report [11] of this experiment.

Emissions sampling was carried out according to the schedule given in Table 2. Sampling was isokinetic using the Joy EPA, Model CU—2 commercial source sampling train, in accordance with Environment Canada [12] and the Ontario Ministry of the Environment [13] source testing codes. Particulate samples were collected on Reeve Angel 900AF, 12.5 cm glass fiber filters. The first two impingers of the sampling train were filled with 250 ml of distilled water; the third impinger was empty and the fourth impinger contained silica gel.

Analyses for lead, bromine, zinc and phosphorus in emissions samples and process materials were carried out using X-ray fluorescence techniques. Detailed analytical procedures are available in the full report [11].

Emissions calculations were computed by the standard methods given in the

TABLE 2

Schedule of emissions testing

Test no.	Test date	Stacks tested	Fuel conditions
1	March 11	NW, NE*	No. 6 only
1 (a)	March 14	SE	
2	March 12	NW, NE*	
2 (a)	March 14	SE	
3	March 12	NW, NE*	
3 (a)	March 15	SE	
4	April 22	NW, NE, SE*	No. 6 + waste oil
5	April 23	NW, NE, SE*	
6	April 30	NW, NE, SE*	
7	April 30	NW, NE, SE*	
8	May 1	NW, NE, SE*	
9	May 2	NW, NE, SE*	
10	May	NW, NE, SE*	No. 6 only
11	May	NW, NE, SE*	
12	May	NW, NE, SE*	

* Simultaneous tests

relevant source testing codes [12]. Mass balance calculations were made as follows. From the daily composite analysis of each material for each element and the total daily quantity of each material:

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

where X_{ij} = total daily weight of element X reporting in material i (lb./24 hour) on day j; M_{ij} = total daily weight of material i (lb.) on day j; C_{ij} = concentration of X in the composite sample of material i on day j.

The X_{ij} values were then used to form individual elemental balances for the process. For daily balance calculations, conditioning tower solids were counted as an output stream because of the long duration of the return cycle. For long-term accumulated balances, accumulated conditioning tower contributions were subtracted from the input account and not included in the output account to avoid multiple accounting in the balance.

Results

Space does not permit the inclusion of all of the very large quantities of data collected during this experiment. A complete record is available in the final report of this work [11] and the reader is referred to this source for detailed data. For the purposes of this paper, reported results have been limited to the pertinent summaries provided below. Emission rates (measured at the stack by direct sampling) are recorded in Table 3. These data are summarized as average emissions for each of the three test periods in Table 4.

An illustration of typical elemental analysis data for the process materials is given in Table 5. The analysis results for waste-oil samples are given in Table 6. No. 6 fuel oil was not found to contain detectable quantities of Pb, Zn, Br or P.

Accumulated mass balances for the first baseline period (March 9, 1974— March 20, 1974) and a period comprising the test period and second baseline combined, are given in Table 7.

Discussion

This experiment 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 principal test of such an hypothesis resides in the measurement of kiln emissions. In the present experiment, these were supplemented by an extensive mass balance on the elements Pb, Br, Zn and P.

TABLE 3

Emission rates

Test Date	Stack	Stack gas conditions				Emission rates (lb./h)					% Isokinetic
		Flow (dscfm)	Velocity (ft./s)	Temperature (°F)	Moisture (%)	Particulate	Pb	Br	Zn	P	
First baseline period											
11/3	NW	60700	56.09	580	8.5	65.61	0.0087	0.0161	0.0055	0.0224	97.63
12/3	NW	61800	57.67	589	8.5	75.38	0.0067	0.0226	0.0074	0.0304	98.69
12/3	NW	61100	57.10	591	8.4	79.46	0.0158	0.0153	0.0057	0.0276	99.44
11/3	NE	62600	58.82	598	8.3	33.37	0.0031	0.0077	0.0033	0.0108	98.16
12/3	NE	63800	59.43	600	7.5	33.09	0.0062	0.0078	0.0047	0.0101	99.25
12/3	NE	64700	60.16	599	7.3	49.73	0.0010	0.0114	0.0045	0.0163	100.00
14/3	SE	12100	32.15	272	22.5	3.71	0.0002	0.0153	0	*	102.05
14/3	SE	10400	27.13	274	22.1	3.08	0.0010	0.0321	0	*	103.98
15/3	SE	8800	22.45	269	19.7	3.49	0.0020	0.0157	0	*	89.86
Test period											
22/4	NW	60900	58.75	588	10.3	71.14	0.0089	0.0581	0.0091	0.0216	104.08
23/4	NW	59900	58.09	588	9.3	59.59	0.0056	0.0348	0.0049	0.0181	98.41
30/4	NW	59600	56.79	601	8.4	70.89	0.0049	0.0644	0.0089	0.0248	102.97
30/4	NW	60100	60.00	599	11.2	54.94	0.0080	0.0548	0.0048	0.0190	105.76
1/5	NW	60100	58.94	600	11.0	58.12	0.0046	0.0708	0.0055	0.0162	103.53
2/5	NW	59400	56.09	594	8.9	24.99	0.0080	0.0538	0.0029	0.0071	103.68
22/4	NE	62100	59.93	607	8.7	21.28	0.0045	0.0135	0.0035	0.0071	103.38
23/4	NE	62900	60.30	593	8.9	21.30	0.0044	0.0146	0.0028	0.0082	97.51
30/4	NE	62200	59.75	613	8.0	18.93	0.0017	0.0190	0.0020	0.0068	102.03
30/4	NE	58200	56.79	609	9.9	18.09	0.0019	0.0136	0.0018	0.0061	104.40
1/5	NE	61400	59.32	606	9.1	21.85	0.0036	0.0188	0.0033	0.0071	103.18
2/5	NE	61100	58.33	606	9.0	40.42	*	0.0398	*	*	102.28
22/4	SE	11400	30.63	278	21.5	0.66	0.0006	0.0042	0.0011	*	93.56
23/4	SE	12000	33.69	291	23.5	4.92	0.0030	0.0839	0.0019	*	95.69
30/4	SE	10300	28.45	305	21.6	0.76	0.0025	0.0094	0	*	96.57
30/4	SE	9830	27.25	310	21.3	1.96	0.0019	0.0259	0.0007	*	101.59
1/5	SE	8780	24.01	300	21.1	1.58	0.0084	0.0178	0.0004	*	95.15
2/5	SE	8220	21.23	293	18.0	0.42	0.0027	0.0048	0	*	105.53

TABLE 3 (continued)

Test Date	Stack	Stack gas conditions				Emission rates (lb./h)					% Isokinetic
		Flow (dscfm)	Velocity (ft./s)	Temperature (°F)	Moisture (%)	Particulate	Pb	Br	Zn	P	
Second baseline period											
29/5	NE	61100	60.48	619	9.5	120.77	0.0113	0.0395	0.0112	0.0423	109.39
29/5	NE	62200	61.38	620	9.0	114.14	0.0117	0.0311	0.0138	0.0342	108.70
30/5	NE	64000	61.63	600	9.0	149.95	0.0124	0.0467	0.0152	0.0412	108.89
29/5	NW	56300	54.34	604	8.5	18.77	0.0007	0.0163	0.0016	0.0045	107.94
29/5	NW	57500	55.43	600	8.7	16.05	0.0007	0.0049	0.0024	0.0038	108.71
30/5	NW	57700	55.84	611	8.5	21.68	0.0129	0.0050	0.0024	0.0060	108.84
29/5	SE	14500	36.93	261	18.9	12.95	0.0075	0.0687	0	*	97.16
29/5	SE	14400	37.01	265	19.0	27.61	0.0118	0.1130	0.0003	*	97.46
30/5	SE	16700	42.64	255	20.1	2.67	0.0010	0.0100	0	*	97.07

* No data available

TABLE 4

Average emissions

Stack	Test period	Fuel	Mean flow (dscfm)	Mean emission rate (lb./h)				
				Particulate	Pb	Zn	Br	P
NW	11/3/74—15/3/74	No. 6	61000	73.5	0.0104	0.0062	0.0180	0.0268
NE			63000	38.7	0.0034	0.0042	0.0090	0.0125
SE			9500	3.42	0.0011	0	0.0210	*
NW	22/4/74—2/5/74	No. 6 + waste oil	60000	56.6	0.0067	0.0060	0.0561	0.0178
NE			61300	25.0	0.0032	0.0027	0.0199	0.0071
SE			10500	1.72	0.0032	0.0007	0.0234	*
NW	28/5/74—30/5/74	No. 6	57200	18.8	0.0048	0.0021	0.0087	0.0048
NE			62500	128.3	0.0118	0.0134	0.0391	0.0392
SE			15200	14.4	0.0068	0.0001	0.0639	*

* No data available

TABLE 5

Ranges of Pb, Br, Zn and P concentrations in process solids

Fuel	Process material	Concentration ranges							
		% Pb		% Br		% Zn		% P	
		Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
No. 6 fuel oil only	Raw meal feed	<0.0002	0.001	0.0003	0.001	0.004	0.006	0.03	0.04
	Clinker	0.0004	0.0015	0.0003	0.001	0.007	0.008	0.05	0.07
	B.P. dust	0.03	0.05	0.1	0.3	0.01	0.02	0.01	0.03
	C.T. solids	0.015	0.025	0.02	0.06	0.014	0.019	0.035	0.040
No. 6 fuel oil + waste oil	Raw meal feed	<0.0002	0.001	0.0005	0.001	0.004	0.006	0.03	0.04
	Clinker	0.006	0.01	0.0006	0.001	0.009	0.012	0.05	0.07
	B.P. dust	0.1	0.5	0.5	1.5	0.008	0.013	0.01	0.03
	C.T. solids	0.12	0.25	0.10	0.17	0.013	0.03	0.03	0.04

TABLE 6

Waste oil analyses

Date	Average specific gravity (g/cc)	% (weight/weight)			
		Pb	Br	Zn	P
19/4	0.8897	0.53	0.09	0.08	0.09
20/4	0.8951	0.52	0.09	0.08	0.09
21/4	0.8944	0.53	0.10	0.08	0.10
22/4	0.8964	0.55	0.10	0.08	0.11
23/4	0.8974	0.48	0.14	0.10	0.09
27/4	0.9232	0.54	0.16	0.11	0.11
28/4	0.9068	0.54	0.15	0.10	0.10
29/4	0.9031	0.50	0.12	0.09	0.10
30/4	0.8935	0.47	0.12	0.09	0.09
1/5	0.8923	0.48	0.12	0.09	0.10
2/5	0.9000	0.47	0.13	0.09	0.10
3/5	0.8902	0.47	0.13	0.09	0.09
4/5	0.8903	0.46	0.13	0.09	0.09
5/5	0.9144	0.46	0.13	0.09	0.09
6/5	0.8925	0.45	0.13	0.09	0.09

Emissions

Three sets of data are available from the present test program. The first was taken 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 minor disturbance 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. This is attributed to electrostatic precipitator problems that were not associated with waste-oil burning.

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 with used oil. White has shown that water can improve precipitator efficiency even at $660°$ F in the cement manufacturing process [14].

No significant changes were noted in the measured average 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 slightly increased concentrations in the particulate materials collected during used-oil burning. This effect is not reflected in the emission rates for these elements due to the reduction in total particulate emissions discussed above.

TABLE 7

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
9/3–20/3	"C"	Pb	502	0	627	117.1	7.8	124.9
		Br	590	0	564	55.4	40.2	95.6
		Zn	5125	0	5909	114.9	0.3	115.2
		P	40260	0	39500	98.0	0.1	98.1
17/4–7/5	"C" +	Pb	13731	96.6	12246	85.0	4.2	89.2
and	WO	Br	6187	52.3	4466	35.3	36.9	72.2
8/5–30/5	"C"	Zn	22168	10.6	24526	110.6	0.2	110.8
		P	150135	1.7	147833	98.2	0.1	98.3

** "C": bunker "C" fuel oil as the only fuel
"C" + WO: bunker "C" fuel oil and waste oil as fuels

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 waste oil.

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 common with other material balance experiments on large-scale production systems, the material accounting in this experiment shows apparent losses and gains. 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 analyzing 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)	1b./24 h equivalent to 0.0001%
Raw meal feed	5,000	10
Clinker	3,000	6

Thus, an analytical error of ±0.0001% imposes an uncertainty of approximately ±10 lb./24 h on the material account for the analyzed element. 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 experiment. The material balance serves to show the overall order of retention and the material stream to which the elements studied ultimately report.

The results of the mass balance show that 90% of the total lead in the system, most of which originates from waste oil, is retained in the process solids; from 70% to 80% in the clinker and 9% in the conditioning tower solids. The by-pass dust, the only material discarded (in pelletized form), was found to retain less than 4% of the total lead.

Despite levels so low as to make analyses extremely difficult, a fairly good balance was obtained for bromine. Some 72% of the total bromide was found in the process solids. As would be expected, the majority of the bromide was found in the 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. Both phosphorus and zinc were found to be completely contained within the clinker.

Comparison of cement-kiln burning with other uses and disposal methods for waste oils

Of the estimated 73 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 a 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.

While perhaps the most desirable means of disposal from a resource conservation viewpoint, re-refining back to a lube-oil stock is becoming less competitive and economically viable [15] and is declining in North America. Further, the most widely used process, acid-clay treatment, produces an acid sludge which contains in concentrated form the bulk of the contaminants from the oil and hence poses a difficult disposal problem.

Road oiling is the end use of most of the used oil picked up by waste-oil collectors in North America. To date, this appears to have been economically attractive. However, a study by EPA [16] on one particular road found that
(a) 70—75% leaves the road by dust movement and run-off;
(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 automotive 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. This 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 this use subject to considerable pollution hazards.

An extensive review of experimental studies on burning 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 only quantitative studies 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 8 for lead emissions. The very substantial differences in the ratio Pb out/Pb in (%) between the conventional burner tests and the cement plant

TABLE 8

Comparison of lead emissions during waste-oil burning at St. Lawrence Cement with conventional combustion

Test location	Sample identification	Pb (lb./h)		Out/In (%)
		Total in	Total out	
St. Lawrence Cement	22/4	45	0.014	0.031
	23/4	42	0.013	0.031
	30/4(1)	32	0.009	0.029
	30/4(2)	32	0.012	0.037
	1/5	32	0.017	0.052
Humble, Baltimore Terminal (3)	15/8/72(1)	0.235	0.104	44.8
	15/8/72(2)	0.235	0.156	66.4
	18/9/72	0.227	0.160	70.5
	22/9/72	1.17	0.504	45.1
	23/9/72	1.17	0.389	33.2
	6/9/72	1.14	0.400	35.1
	8/9/72	0.914	0.424	46.4
	11/9/72	0.933	0.480	51.4
	13/9/72	1.05	0.496	47.2
	11/10/72	3.77	0.806	21.4
	17/10/72	3.11	0.746	24.0
	18/10/72	3.57	0.849	23.8
Shell Oil (7)	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	<0.007	0.167

* Included 3-min. soot blower operation

experiment shows the potential overall improvement in terms of environmental impact to be gained by burning in the cement kiln rather than conventional burning. In addition, there is an advantage in cement-kiln burning that is not immediately apparent from much of the literature data. In the results shown in Table 8 only on one test are the effects of soot-blowing indicated. Test No. 10 reported for the Shell oil experiment showed over 100% of the lead to be emitted during soot blowing. The manufacture of cement 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 at Northern States Power Company in which some 29,000 gallons of used oil was burned. Oil was fed at 155 gal/h and was computed to introduce lead at 4.036 lb./h with 0.159 lb./h from coal to give a total of 4.19 lb./h. Lead emissions were monitored and found to be less than 6.99×10^{-3} lb./h. 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. A report published by the American Petroleum Institute [2] concluded that: "The burning of used lubricating oils, blended (<25%) with residual fuel oil, be encouraged as an effective way of solving the problem (of waste-oil disposal)". The present authors consider that such burning in conventional oil-fired burners merely serves to dilute the pollution from inorganic oil contaminants. On the other hand, this work has shown that use in the cement kiln contains most of these elements in a non-polluting form.

Cement quality

It has been shown by other workers that additions of lead [17], zinc [18] and phosphorus [19] as salts can alter substantially the physical characteristics of cement.

These reported effects made it necessary to examine the hydraulic properties of the cements produced from clinkers manufactured during waste-oil burning. The results of the experimental work carried out to this purpose are given in Table 9. 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.

TABLE 9

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	428	25.0	1962	2850	3525	4000
0.0070	117	437	25.0	2012	2918	3368	3946
0.0032	115	320	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 σ (correlation coefficient) = 0.
** By ASTM C—109

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 kiln types is difficult. However, some broad generalizations may be made by considering the ways in which some elements are trapped in the kiln system.

(a) 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.

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

(c) 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 a slight increase in levels at the precipitator of straight kilns will occur.

Conclusións

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 boiler equipment is considered to result in practically all of the lead, and an 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 restricted to approximately 0.03% of the lead and 0.7% of the bromine put in with the waste oil.

To supplement these findings, a mass balance was carried out on trace quantities of these elements in the cement kiln. The results of the study showed that 89% of the lead, 72% of the bromine and 100% 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. No deterioration was found in the properties of the clinker produced or in the production plant during this experiment.

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