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Experimental Burning of Delayed Coke in a Wet Process Cement Kiln

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Report EPS 4-WP-77-5

Water Pollution Control Directorate

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EXPERIMENTAL BURNING OF DELAYED COKE IN A WET PROCESS CEMENT KILN

by

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A joint Government-Industry project conducted under the Development and Demonstration of Pollution Abatement Technology (DPAT) Program.

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ABSTRACT

The Great Canadian Oil Sands (GCOS) plant north of Fort McMurray, Alberta, generates approximately 2500 tons per day of delayed coke in the production of synthetic crude oil from bitumen. A major portion of the coke is used to produce steam for power generation; approximately 500 tons per day are stockpiled. Future processing of tar sands is expected to generate even larger quantities of coke.

During 1976, 3500 tons of GCOS delayed coke were burned in a wet process cement kiln at the St. Lawrence Cement Co. plant in Mississauga, Ontario. The burning of this coke constituted an experimental trial to determine the maximum rate of coke burning possible with available equipment, and the effect of the burn on both air and product quality. For an initial evaluation of these parameters, coke was burned at the rate of 50 percent of the fuel input to the kiln. During the final phase, coke supplied as much as 87.4 percent of the total heat required by the kiln. Both values are based on gross calorific heat requirement of the kiln.

Atmospheric emission measurements were conducted while burning fuel oil only and during both rates of coke burning. Data from these tests showed that the burning of coke did not contribute significant emissions of the metallic contaminants nickel and vanadium to the atmosphere. Emission rates during maximum rate of coke burning were 0.003 pound per hour of nickel and 0.01 pound per hour of vanadium. A mass balance revealed that nickel and vanadium were largely retained in the clinker produced.

Sulphur dioxide emissions increased from an average of 90 pounds per hour when burning fuel oil only to an average of 595 pounds per hour when burning coke at the maximum rate. This latter value represents 35 percent of the total sulphur input to the kiln. At no time did the emissions exceed the requirements of the Ontario air pollution regulations. A marked reduction in SO_2 emissions might be obtained by changing the kiln operating conditions during coke burning.

Burning of coke at the maximum level caused some minor detrimental effects on the setting characteristics of the cement, possibly due to vanadium. It is likely that this problem could be controlled by varying the quantity of gypsum added.

Changing kiln operating conditions to reduce SO_2 emissions would cause more sulphur to be retained in the product. The effect this would have on cement quality is unknown.

RESUMÉ

L'usine de la société Great Canadian Oil Sands (GCOS), située au nord de Fort McMurray (Alberta), donne quotidiennement, par cokéfaction différée, environ 2500 tonnes de coke; le procédé accompagne la production du pétrole brut synthétique à partir du bitume. Une partie importante de ce coke sert à produire de la vapeur comme source d'énergie; on en accumule une provision d'environ 500 tonnes par jour. A l'avenir, on escompte tirer des sables bitumineux des quantités encore plus importantes de coke.

En 1976, 3500 tonnes de ce combustible venant de la Great Canadian Oil Sands on été brûlées par voie humide dans un four de cimenterie, celui de la St. Lawrence Cement Co., à Mississauga (Ontario). Il s'aggissait de déterminer expérimentalement le taux maximal de combustion du coke que permettent les installations actuelles et les conséquences qu'elle peut avoir sur la qualité de l'air et du produit. Au début, le coke alimentait le four à 50 p. 100 et, à la fin, il constituait jusqu'à 87,4 p. 100 du combustible. Ces deux valeurs relèvent des besoins calorifiques bruts du four.

Les émissions atmosphériques ont été mesurées pendant la combustion du mazout seulement et pour les deux taux de combustion du coke. Les épreuves ont montré que ce dernier n'entraîne pas d'émissions importantes de métaux polluants (nickel et vanadium). En effet, le taux maximal de combustion du coke n'a donné que 0,003 lb de nickel à l'heure et 0,01 lb de vanadium à l'heure. Le bilan des matières consumées a montré que ces deux métaux étaient en grande partie retenus dans les scories.

Les émissions de dioxyde de soufre sont passées d'une moyenne de 90 lb à l'heure pendant la combustion exclusive du mazout à 595 lb à l'heure pendant la combustion maximale du coke, cette dernière quantité représentant 35 p. 100 de tout le soufre entrant dans le four. Les émissions n'ont dépassé en aucun temps les limites que prescrit le règlement de l'Ontario sur la pollution atmosphérique. On pourrait réduire considérablement les émissions de SO_2 en modifiant les conditions accompagnant la combustion du coke dans le four.

Au taux maximal, la combustion du coke a quelque peu altéré les caractérisques de solidification du ciment, peut-être à cause du vanadium. On pourrait probablement corriger cette situation en variant la quantité de gypse ajoutée.

On pourrait modifier les conditions de fonctionement du four pour réduire les émissions de SO_2; toutefois, le produit contiendrait alors plus de soufre et l'on ignore l'effet que cela pourrait avoir sur la qualité du ciment.

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

CONCLUSIONS AND RECOMMENDATIONS

This study demonstrated that burning delayed coke from the Athabasca tar sands in a wet process cement kiln is technically feasible. It is important, however, that the grinding system be capable of reducing coke to a sufficiently small size (approximately 5 percent retained on a 200 mesh sieve).

Emissions from the cement kiln were restricted to 0.06 percent of the total nickel and vanadium input to the kiln. A mass balance showed these metals to be retained preferentially in the clinker.

Sulphur dioxide emissions increased from an average of 90 pounds per hour when burning fuel oil to an average of 595 pounds per hour when burning coke at the maximum rate.

When burning the coke, emissions of SO_2 were controlled to a considerable extent by adjusting the operating conditions of the kiln. Lower kiln temperatures and higher levels of excess oxygen reduced these emissions considerably by causing more sulphur to be retained in the process solids. To conserve fuel, it is also desirable that kiln temperatures be reduced as far as possible without impairing clinker quality. Increasing excess O_2 to reduce SO_2 emissions would cause higher fuel consumption; however, since the coke under consideration is not presently being put to a beneficial use, this may be a viable method of operation.

Detrimental effects were noted in the setting characteristics of cements produced from coke burned clinker. It is expected that these effects can be countered by varying the quantity of gypsum added while grinding the cement. Effects seen, therefore, should not be an impediment to burning this coke in a cement kiln.

If measures to reduce SO_2 emissions are taken, the effect of retaining greater quantities of sulphur in the clinker is unknown.

It is concluded that delayed coke from the Athabasca tar sands can be burned in a cement kiln where due consideration is given to the control of SO_2 emissions. It is recommended that further study be made of the effects of reducing SO_2 emissions, and the quality of cement produced when burning high sulphur fuel.

1 INTRODUCTION

At the Sun Oil-controlled Great Canadian Oil Sands Ltd. (GCOS) plant north of Fort McMurray in Alberta, 50,000 - 60,000 barrels of oil are produced daily by the only commercial oil sands treatment process currently in operation [1]. The mined sand is first slurried with hot water, steam and caustic in rotary drums. Bitumen froth is skimmed off after charging the pulped material into vertical cone-bottomed separators. A middlings stream is withdrawn from the centre of the separator and processed through air-flotation scavenger cells, in which additional bitumen is recovered. The two bitumen streams are combined, diluted with naphtha and centrifuged to remove residual solids and water. "Spent" sand and liquid effluents from the extraction process are sent to a tailings disposal pond.

After distillation to recover naphtha, the crude bitumen is subjected to delayed coking at around 480°C (900°F), and the overhead hydrocarbon vapours are separated into wet gas, naphtha, kerosene and gas oil. Approximately 65% by weight of the bitumen appears in the synthetic crude from this process.

Coking of the bitumen can be carried out in a number of ways [2], including direct coking, fluid coking, delayed coking and destructive batch distillation of bitumen. In all cases, the charge is converted to distillate oil and coke. The coke distillate is a suitable feed for hydrodesulphurization to produce a sweet synthetic crude. As the temperature of coking is decreased in the range 540°C to 430°C (1000°F to 800°F) and the residence time correspondingly increased, operating conditions shift from fluid coking and approach once-through or delayed coking. In delayed coking, the charge oil is heated to a temperature of 480°C to 510°C (900°F to 950°F) to initiate the coking reactions. The heated oil is then fed to large drums where the volatile material is allowed to vapourize. The residue is left behind to polymerize to coke. Delayed coking in this manner favours higher coke yields. Sulphur is distributed throughout the boiling range of the delayed coke distillate, whereas heavy metals such as vanadium remain predominantly in the coke.

At GCOS some 2500-2700 tons of delayed coke are produced daily. About 2000 tons are used daily in three boilers to produce steam for power generation. Surplus coke is stockpiled.

It is anticipated that future processes to recover oil from the tar sands, such as the Syncrude project, will produce even larger quantities of coke, all of which will be high in sulphur and heavy metal content. Conventional boilers and other combustion systems using such material as a fuel will generate significant quantities of pollutants such as sulphur dioxide, vanadium, nickel and other metal oxides. Even with sophisticated pollution control equipment to control emissions, disposal of collected materials containing relatively high concentrations of heavy metals constitutes a problem.

Previous studies of the use of waste oil as supplemental fuel in a cement kiln have shown that the major portion of heavy metal contaminants are retained in the clinker [3]. It has been suggested, therefore, that delayed coke could also be used as fuel in a cement kiln, thus conserving fossil fuels, using a potential waste material, and also disposing of it in a manner which would not create additional air, water or solid waste pollution problems.

This research program was carried out to determine the maximum quantity of coke which could be burned in a wet process kiln and whether burning could take place without detrimental effects on air quality. The approach taken was to monitor kiln emissions for selected elements: nickel, vanadium and sulphur, present as contaminants in the coke. A material balance on these elements was made to determine their distribution in the process materials.

A supplement is available containing the detailed data which are summarized in this report. The supplement may be obtained by contacting:

Training and Technology Transfer Division (Water)
Environmental Protection Service
Fisheries and Environment Canada
Ottawa, Canada   K1A 1C8

A related report, EPS 4-WP-77-2, "Burning Waste Chlorinated Hydrocarbons in a Cement Kiln" is also available and may be of interest to the readers of this report.

This joint government-industry project was supported by a cost sharing contract under Fisheries and Environment Canada's Development and Demonstration of Pollution Abatement Technology (DPAT) Program. For more information on this technology development incentive program contact:

The DPAT Secretariat
Environmental Protection Service
Fisheries and Environment Canada
Ottawa, Canada K1A 1C8

2 CEMENT MANUFACTURE

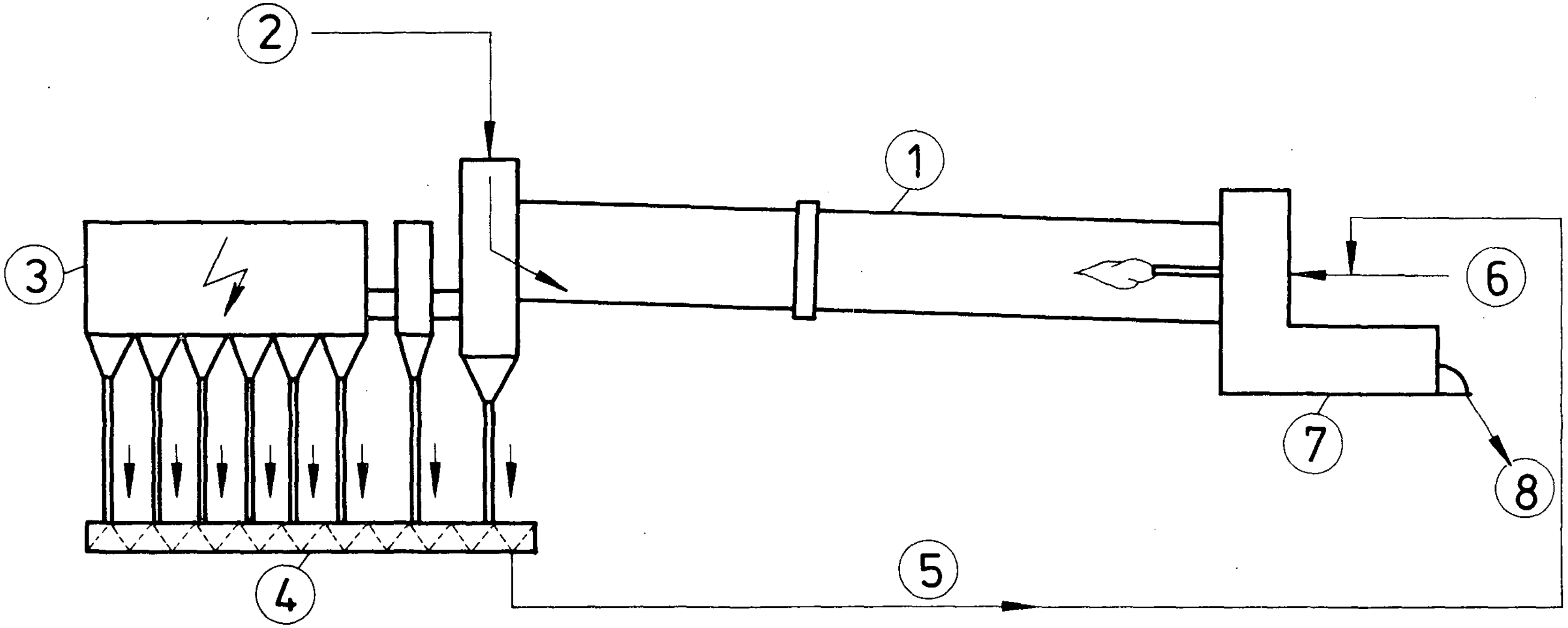
2.1 General Principles

While a variety of raw materials may be used in cement manufacture, materials containing calcium, silicon, aluminum and iron without an excess of certain other elements are required. These materials are ground to a fine powder called raw meal, the chemical composition of which is carefully controlled by proper blending of the various materials. Normally, blending is achieved by grinding the raw materials together (intergrinding). Raw meals required for wet and dry processes are similar except that the raw meal for the wet process is in the form of a slurry containing approximately 35% water, while raw meal for the dry process contains less than 0.5% water.

The raw meal is fed into the kiln (see Figure 1) and is burned to produce an intermediate product called clinker. The kiln slopes towards the burning zone and rotates slowly, causing the raw material to gradually move into the burning zone. Reactions which occur during gradual heating in the kiln are: evaporation of free water, evolution of combined water, evolution of carbon dioxide from carbonates, and combination of lime with silica, alumina and iron to form the desired compounds in the clinker. These reactions require a final material temperature of 1450°C (2650°F). Four main compounds are present in Portland cement clinker.

Name of Compound	Chemical Formula	Common Abbreviation Used in the Cement Industry
Tricalcium Silicate	$3\ CaO \cdot SiO_2$	C_3S
Dicalcium Silicate	$2\ CaO \cdot SiO_2$	C_2S
Tricalcium Aluminate	$3\ CaO \cdot Al_2O_3$	C_3A
Tetracalcium Aluminoferrite	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

Minor compounds are also formed in clinker, e.g., magnesia (MgO), potassium sulphate (K_2SO_4), and sodium sulphate (Na_2SO_4). Traces of other elements present in either the raw materials or fuel are also found in clinker. Upon leaving the kiln, the clinker is rapidly cooled to prevent the formation of undesirable crystal forms of the above compounds.



1 - KILN
2 - SLURRY FEED
3 - PRECIPITATOR
4 - PRECIPITATOR DUST SCREW
5 - DUST RETURN
6 - FUEL
7 - CLINKER COOLER
8 - CLINKER

WET PROCESS KILN

FIGURE 1

After cooling, the clinker is ground and blended with gypsum, normally by intergrinding, to a fine powder. This final product, called Portland cement, is the basic ingredient of concrete.

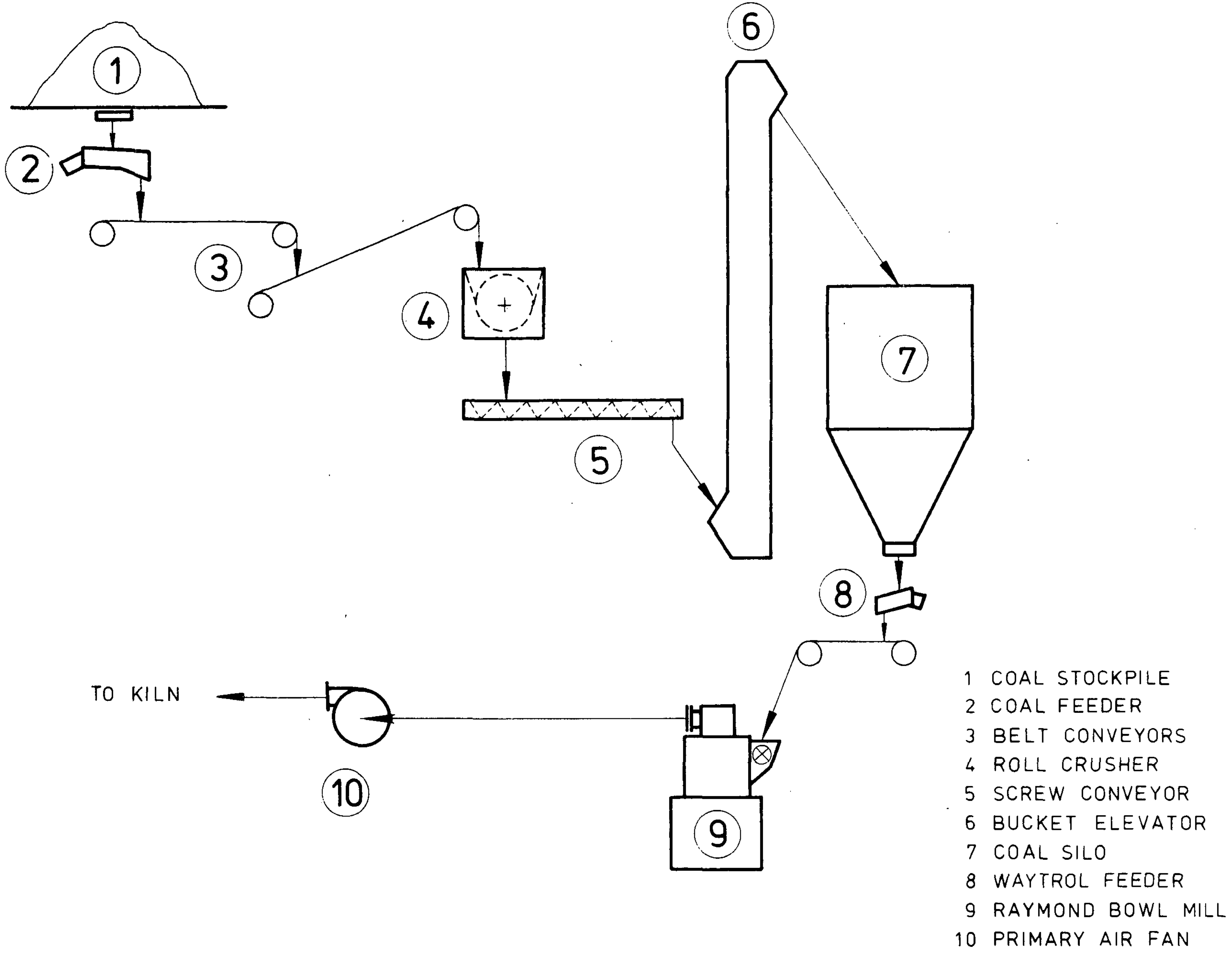
2.2 The St. Lawrence Cement Co.

The St. Lawrence Cement Co., Mississauga Plant, has a nominal production capacity of 1,750,000 short tons per year. The company operates two wet process and one dry process suspension preheater kilns.

2.2.1 Relevant unit processes - wet process kiln

The kiln used in this study is an Allis Chalmers wet process kiln (Figure 1). It is 122 m (402') long, dumb-bell shaped with a diameter of 3.5 m (11'6") in the centre and 4 m (13'2") at each end, and having nominal capacity of 1050 short tons per day. The drying zone contains 57 tons of loose hung carbon steel chains with a radiation curtain of stainless steel chains at the front or flame end. Slurry is fed by a bucket wheel conveyor with variable speed drive from a constant level box. Exhaust gases (maximum capacity 150,000 cfm at 230°C [450°F]) pass through a six-section precipitator built by Western Precipitation. These gases are then vented to a stack 168 m (554') in height with 4 m (13') exit inside diameter.

The coal preparation system was used to convey the coke to the kiln (Figure 2). Coke was fed from the stockpile via a Syntron 30 tph capacity vibratory feeder equipped with a Merrick weigh scale to a Williams 35 tph capacity roll crusher. After being crushed, the coke was stored in a silo which gravity feeds a Waytrol feeder. This feeder maintained the required rate of feed to a Raymond bowl mill. The 125 hp bowl mill has a capacity of 8.5 tph when grinding coal to 80% passing a 200 mesh sieve. Ground coke was conveyed by air through the primary air fan to the kiln.



FLOW SHEET FOR COAL PREPARATION

FIGURE 2

3 SELECTION OF ELEMENTS FOR STUDY

Fuels commonly in use in the cement industry are residual or No. 6 fuel oil and bituminous to subbituminous coals. Typical analyses of these fuels and the GCOS coke are given in Table 1. Typical coal and coke ash analyses are presented in Table 2.

The selection of an element for study was based on:

- the relative concentration of the element in the coke compared to that in fuels normally employed;
- the effect of the element on the environment; and,
- the effect on the quality of the cement produced.

Thus, elements for which the contribution due to coke burning is small, relative to concentrations normally present in cement raw materials (Si, Al, Fe, Ca, Mg, K and Na), were rejected. Also rejected were those elements present at extremely low concentrations in the coke (Cl, Mo, Mn and Cr).

Oxides of both sulphur and nitrogen are noxious pollutants. Nitrogen was not studied because it is present in all fuels at approximately the same concentration level. It is known that copious quantities of sulphur can be absorbed in the process solids of the cement kiln [7]. However, sulphur is present in the coke at a high concentration level and hence this element was selected for study. The retention of vanadium and nickel in the kiln and their effect on cement quality was largely unknown. Therefore, the elements chosen for study were sulphur, vanadium and nickel.

TABLE 1. RELEVANT FUEL CHARACTERISTICS

Fuel Characteristics	GCOS [4]	Bituminous [5]	Coal [6] (Typical)	No. 6 [6] Fuel Oil (Typical)
Moisture (%)	2 - 10	2.6 - 12.4	-	-
Volatile Combustible Matter (%)	7 - 12	18.2 - 40.2	30	-
Fixed Carbon (%)	80 - 90	39.1 - 74.4	-	-
Ash (%)	2.5 - 4	3.0 - 9.1	8.5	-
Sulphur (%)	5 - 6	0.6 - 4.3	1	2*
Nitrogen (%)	1 - 1.5	1.0 - 1.6	1.5	1
Hydrogen (%)	3 - 4	4.8 - 5.9	5	12
Gross Calorific Value (Btu/lb)	13,000 - 15,000	11,420 - 14,550	13,000	18,700
Hardgrove Grindability Index	40 - 60	-	-	-

*From present report

Note: To convert from Btu/lb to kilojoules/kilogram, multiply by 2.324.

TABLE 2. FUEL ASH ANALYSIS

Constituent (% by weight)	GCOS [4] Coke Ash (Typical)	Bituminous [5] Coal Ash
SiO_2	36.77	46.2 - 58.5
Al_2O_3	25.70	22.9 - 30.6
SO_3	10.08	0.9 - 8.9
Fe_2O_3	8.26	4.2 - 7.7
CaO	5.51	2.0 - 10.1
MgO	4.58	0.4 - 1.6
V_2O_5	3.49	-
TiO_2	1.93	1.0 - 1.8
K_2O	1.87	1.5 - 1.6*
Na_2O	0.43	
NiO	1.16	-
P_2O_5	0.21	-
Cl	0.04	-
MoO_3	0.03	-
MnO_2	0.01	-
Cr_2O_3	0.02	-

* Total K_2O + Na_2O

4 DISCUSSION

The experimental work for this study was designed to determine to what extent delayed coke, obtained from the Great Canadian Oil Sands process of upgrading bitumen extracted from tar sands, could replace normal fuel in a cement kiln. Parameters under consideration were kiln operation, environmental impact and product quality.

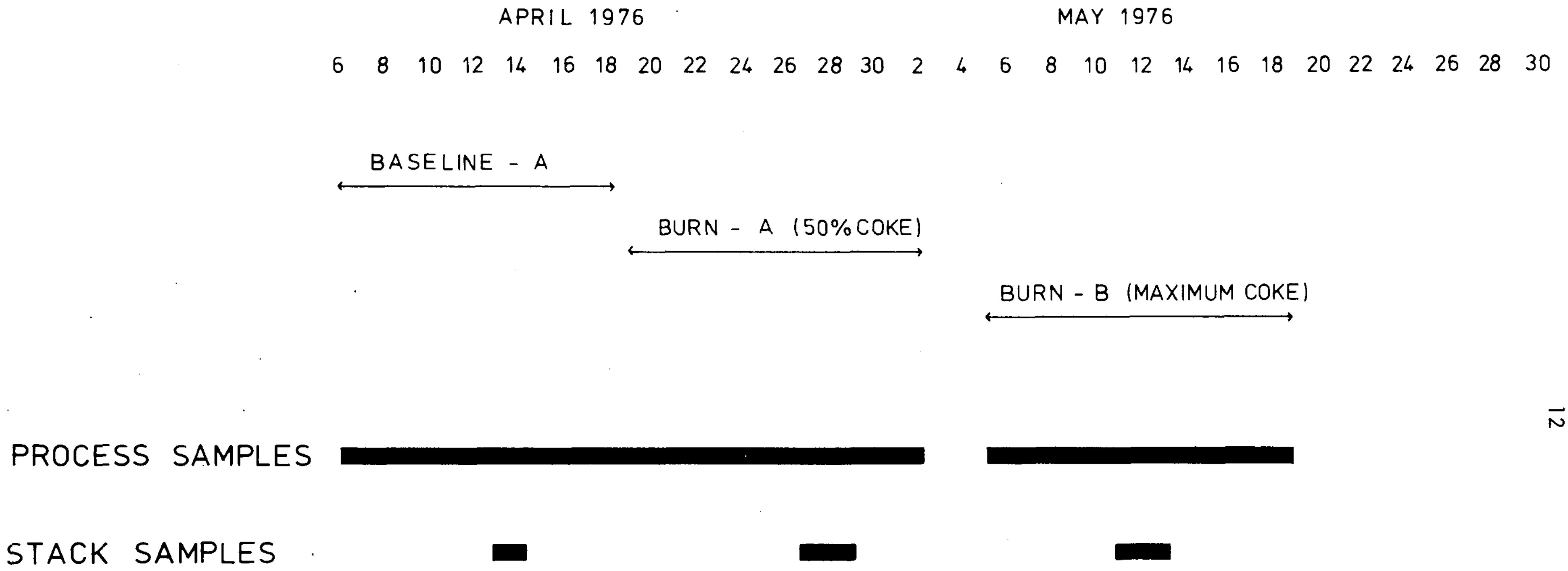
Figure 3 outlines the program schedule. In the first phase, (Burn A), coke was burned at a rate representing between 52.9 and 55.8 percent of the total gross heat supplied to the kiln; this phase allowed a preliminary evaluation of the above three parameters. On the same basis, between 76.1 and 87.4 percent of the heat was supplied by coke burning during the second phase (Burn B), the limiting factor in this case being kiln operation. At higher rates of coke burning, the flame was extremely unstable.

Kiln emissions were monitored before, during each phase, and after the coke burning to determine the effect of coke burning on air quality. In addition, a mass balance on the elements sulphur, vanadium and nickel was carried out to determine the relative distribution of each element in the process materials. Cement made from clinker produced during coke burning was compared to cement made from normal clinker to evaluate product quality.

Process samples during normal operation of the kiln burning No. 6 fuel oil (Baseline A) were collected over the period April 6 to April 18, 1976. The first phase of burning coke took place from April 19 to May 2, and the second phase, with maximum coke input, occurred over the period May 6 to May 19. The total amount of coke burned in the kiln was 3,603 tons. Final tests were made during June 22 to June 24, with the kiln once again operating on No. 6 fuel oil (Baseline B). Emission concentrations of sulphur dioxide were continuously monitored while particulate samples were being collected.

4.1 Emission Data - Particulate Material

An earlier report [3], which described a study of burning waste oil in a dry process cement kiln, referred to a recent survey [8] of emissions made from Canadian cement plants to illustrate that the particulate emissions from the St. Lawrence plant are much lower than



NOTE FOR BASELINE - B : Stack sampling tests only were performed for final baseline on June 23 through 24, 1976

SCHEDULE OF TEST PROGRAM

FIGURE 3

the average for the nation. Particulate emission rates from the wet process kiln obtained in this study confirmed previously collected data; mean emission rates were 0.5 to 0.8 lb/ton of clinker. Stack gas concentration and emission rates for particulate material and the elements nickel, vanadium and sulphur are summarized in Table 3.

It is quite evident that burning delayed coke in the kiln instead of No. 6 fuel oil did not significantly alter the concentration of particulate material in the kiln gases. The average particulate loadings and emission rates for each test series, as seen in Table 3, were quite similar. The greatest difference in actual values was obtained for the two baseline test series, with higher emissions occurring during the final series of tests. A variation of this magnitude could have been caused by a slight change in precipitator collection efficiency.

As the total amount of coke burned in the kiln increased, the concentration of both nickel and vanadium in emitted particulate increased. With coke representing almost 90% of the fuel input, maximum average emission rates of 3×10^{-3} lb/hr and 1×10^{-2} lb/hr of nickel and vanadium, respectively, were determined. While these levels are extremely low, the emitted quantities of these metals increased in direct proportion to their total input to the kiln. The maximum emission rates of nickel and vanadium given above were 0.06 and 0.07 percent, respectively, of the kiln input levels for these elements. The emission rate of sulphur as particulate material did not increase with increasing usage of coke; an average emission rate of 3.6 pounds per hour was determined.

4.2 Emission Data - Sulphur Oxides

Concentrations of sulphur dioxide and sulphur trioxide, as measured during each test series in this study, are summarized in Table 4. Sulphur trioxide levels were generally in the region of 10-20 ppm for all four test series and appear to be independent of the ratio of coke to oil burned in the kiln. Sulphur dioxide levels, however, increased with increasing coke input to the kiln. A maximum concentration of 1700 ppm was recorded when burning 90% coke. The mean concentration of SO_2 during this test period was 890 ppm. This latter value corresponds to an emission rate of 595 lb/hr as sulphur

TABLE 3. AVERAGE CONCENTRATIONS AND EMISSION RATES DURING EACH TEST SERIES

Test Period	Fuel	Mean Flow (dscfm)	Stack Gas Concentration (grains/scf)				Mean Emission Rate (lb/hr)			
			Particulate $\times 10^{-2}$	Nickel $\times 10^{-6}$	Vanadium $\times 10^{-6}$	Sulphur* $\times 10^{-3}$	Particulate	Nickel $\times 10^{-4}$	Vanadium $\times 10^{-3}$	Sulphur*
April 12-14	No. 6 Oil	67,400	3.95	1.25	1.86	6.30	22.7	7.17	1.07	3.63
April 27-29	50/50 Coke & No. 6 Oil	65,770	3.83	2.96	8.57	6.66	21.6	1.67	4.84	3.76
May 11-13	90/10 Coke & No. 6 Oil	67,330	3.35	5.24	1.72	4.16	19.3	3.03	9.90	2.40
June 22-24	No. 6 Oil	65,970	5.79	1.57	2.94	7.97	32.8	8.99	1.67	4.51

*Sulphur contained in total particulate.

NOTE: To convert from lb/hr to kilograms/hr, multiply by 0.454.
To convert from grains/scf to g/m^3, multiply by 2.29.

TABLE 4. KILN EMISSION SO_2 AND SO_3 CONCENTRATIONS
(Ontario Research Foundation Data)

Test Series	Test No.	SO_2 Concentration Range* (ppm)	Concentration** (ppm) SO_2	Concentration** (ppm) SO_3	SO_2 Emission Rates** lb/hr
Baseline A	1		207	-	138.4
	2	100 - 350	249	-	166.5
	3		215	-	143.7
		Average	224		149.8
Burn A	1		577	6	385.7
	2	300 - 1000	670	10	447.9
	3		633	11	423.2
		Average	627	9	419.2
Burn B	1		1142	22	763.5
	2	400 - 1700	727	19	486.0
	3		801	18	535.5
		Average	890	20	595.0
Baseline B	1		37	15	24.7
	2	50 - 250	23	9	15.4
	3		119	10	79.6
		Average	60	11	40.1

* Continuous monitor read-out

** Wet chemical analysis

Note: To convert from lb/hr to kilograms/hr, multiply by 0.454.

dioxide. Corresponding emission rates for other SO_2 levels are also found in Table 4.

In comparison, when burning No. 6 fuel oil only, recorded SO_2 concentrations varied from 50-350 ppm, with an average value of 142 ppm over both baseline test series. This average SO_2 concentration corresponds to an average SO_2 emission rate of 95 lb/hr.

4.3 The Mass Balance

A mass balance was determined with slurry feed, No. 6 oil and coke as the input streams. Output streams were the product clinker and kiln dust, which is normally pelletized and wasted. Since emission tests were conducted on only three days during each phase, it was not considered valid to include emission data in the mass balance calculated over 14 days.

To calculate the mass balance, each stream was sampled and quantified using a period of 24 hours as the time base for calculation. Table 5 summarizes the mass balance findings. Methods of sampling and quantifying material streams are detailed in Appendix A. Details of analytical results and mass balance calculations are given in Appendix B.

4.3.1 Significance of mass balance

In common with other material balance experiments on large scale production units, 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 fluctuations or minor systematic errors in weighing and quantifying very large quantities of materials and in analyzing samples.

Initially, atomic absorption was planned as the standard analytical method. However, the analysis of vanadium by atomic absorption with flame excitation is subject to severe interference for cement process materials. Complications also arise when analyzing vanadium with the carbon rod furnace due to the high concentration of calcium present. For these reasons, total reliance was placed on the results of the X-ray fluorescence analyses, along with some comparative atomic absorption analyses performed by the Ontario Ministry of the Environment and the Ontario Research Foundation. A comparison of the results obtained is given in Table 6. A systematic error is apparent

TABLE 5. ACCUMULATED MASS BALANCES

Accumulation Period	Fuel	Element	Laboratory	Accumulated Input (lb) T_I	% of T_I Derived from Coke	Accumulated Retention (lb)	% of T_I Retained in		
							Clinker	Dust	Total
6/4/76-18/4/76	Oil	V	SLC	1,202	0	1,017	81.8	2.8	84.6
(Baseline A)		V	ORF	1,128	0	842	73.0	1.7	74.7
		Ni	SLC	1,037	0	1,085	102.5	2.1	104.6
		Ni	ORF	817	0	1,019	122.6	2.1	124.7
		S	SLC	171,427	0	137,835	68.0	12.4	80.4
		S	ORF	150,654	0	131,034	71.9	15.1	87.0
19/4/76-2/5/76	Oil	V	SLC	3,890	68.6	2,706	66.9	2.6	69.5
(Burn A)	+	V	ORF	3,484	68.0	2,704	75.2	2.4	77.6
	Coke	Ni	SLC	1,250	70.4	1,395	108.4	3.2	111.6
		Ni	ORF	1,316	67.8	1,234	91.3	2.4	93.7
		S	SLC	244,279	56.4	127,085	36.8	15.2	52.0
		S	ORF	243,640	57.0	119,534	34.0	15.1	49.1
5/5/76-19/5/76	Oil	V	SLC	5,484	75.0	4,113	69.5	5.5	75.0
(Burn B)	+	V	ORF	4,863	76.5	3,966	76.0	5.5	81.5
	Coke	Ni	SLC	1,780	76.8	1,831	96.7	6.2	102.9
		Ni	ORF	1,757	79.8	1,678	90.2	5.4	95.6
		S	SLC	304,431	72.6	159,290	31.9	20.4	52.3
		S	ORF	299,379	72.5	150,431	29.0	21.2	50.2

TABLE 6. COMPARISON OF ANALYTICAL DATA FOR SPECIFIC CLINKER SAMPLES

Data Collected		ORF*		SLC**	MOE***
		X-Ray ppm	AA ppm	X-Ray ppm	AA ppm
April 10, 1976	Nickel	13	18	11	34
	Vanadium	32	52	36	61
April 25, 1976	Nickel	41	46	43	61
	Vanadium	93	136	81	164
May 10, 1976	Nickel	51	59	48	66
	Vanadium	115	193	111	180

* Ontario Research Foundation

** St. Lawrence Cement Co.

*** Ontario Ministry of Environment

between X-ray and atomic absorption methods, with atomic absorption yielding consistently higher results.

An analytical error of ±20 μg/g on clinker alone imposes a quantitative uncertainty of approximately ±40 lb/24 hours on the material balance. That such uncertainty exists is obvious from the data obtained by the different techniques.

Clearly, no attempt should be made to equate material balance losses with true losses from the process. Losses due to emissions were determined in separate source sampling tests in this study. The material balance shows the overall order of retention and the material stream in which the selected elements were found, and confirms the emission data.

4.3.2 Nickel retention

Nickel was found to be completely contained in the system. Over 90 percent of the nickel was retained in the clinker and 2 to 6 percent in the dust.

4.3.3 Vanadium retention

The results of the mass balance for the highest level of coke burning show that 81 percent of the total vanadium in the system, 75 percent of which originated from the coke, was retained in the process solids, 76 percent in clinker and five percent in the dust.

It is obvious from the data that vanadium formed compounds which did not volatilize in the cement kiln. The vanadium concentration in clinker increased immediately when coke burning was started or increased. This is consistent with the finding that vanadium was concentrated in the clinker.

4.3.4 Sulphur retention

Emission tests were performed on three days of each phase of the study. The mass balance was calculated over 13 to 15 days in each case. The variations in SO_2 emission rate (Table 4) were large; thus, it was not considered valid to use these data in the mass balance.

If the range of SO_2 concentrations monitored is considered, however, the total emitted sulphur and the loss from the mass balance are in reasonable agreement. For example, during the maximum coke burn, approximately 50 percent of the sulphur was retained in the process solids. The reported values of 400 ppm and 1700 ppm emitted SO_2 correspond to 16 and 68 percent, respectively, of the total input sulphur during this burn.

4.4 Relationship of SO_2 Emissions and Kiln Operating Parameters

The capacity of the raw materials in a cement kiln to absorb sulphur input through fuel burning is well known [7]. During this study, average emitted SO_2 levels increased during coke burning, consistent with greater sulphur input. During each phase of the burn, large variations in emitted SO_2 concentrations were apparent and the emitted SO_2 concentrations were higher at times during Burn A than they were during Burn B. Also anomalous was a decrease in the total quantity of sulphur retained in the process materials despite higher input quantities when burning coke. Available literature and data from the coke burning test were studied in an attempt to find causes for these anomalies.

According to Duda [9], only sulphur in excess of the quantity used to form alkali sulphates results in SO_2 emissions. Data from the present study indicated that the alkali level was not a factor in the variations of retained sulphur. The alkali contents of both the slurry feed and clinker produced were identical through all phases of the study and the clinker contained sufficient alkali at all times to bind at least 0.52 percent sulphur. On this basis, the clinker alone should have retained at least 84 percent of the sulphur input during baseline tests, 63 percent during Burn A and 50 percent during Burn B. Such levels were attained for several days during Baseline A but were not achieved at any time while burning coke.

To react with the process materials in a cement kiln, SO_2 must first be converted to SO_3. Higher levels of excess oxygen in the kiln increase the degree of conversion to SO_3, thus causing more sulphur to be retained in the materials. This topic is dealt with at length in a paper by Verbeck [10] in which the rate of SO_2 emission is correlated with excess oxygen. In one kiln, considered typical, emissions of about 450 ppm SO_2 were measured with 0.4 percent excess oxygen, but only 20 ppm SO_2 were measured when the excess oxygen was about 3.2 percent. During the present study, the excess oxygen (Table 7) was generally about 0.4 percent. No correlation could be found between excess oxygen and emitted SO_2 values in the present study, probably because

TABLE 7. SO_2 LEVELS AND CORRESPONDING KILN OPERATING DATA

(St. Lawrence Cement Co. Data)

Date	Time	SO_2* (ppm)	Litre Weight (g/l)	O_2 (%)	Burning Zone Temp. °C (°F)	Calcining Zone Temp. °C (°F)	Chain Zone Temp. °C (°F)
BASELINE-A							
April 13	1000	128	1420	0.3	1310 (2400)	1060 (1940)	870 (1600)
"	1200	116	1400	0.3	1310 (2400)	1060 (1940)	860 (1580)
"	1600	260	1480	0.3	1310 (2400)	1060 (1940)	870 (1600)
April 14	1000	171	1405	0.4	1230 (2250)	1070 (1960)	860 (1580)
"	1200	148	1425	0.5	1230 (2250)	1060 (1940)	860 (1580)
BURN - A							
April 27	1200	668	1260	0.5	1260 (2300)	905 (1660)	840 (1540)
"	1400	355	1265	0.5	1260 (2300)	980 (1800)	825 (1520)
April 28	1200	822	1220	0.7	1175 (2150)	1040 (1900)	860 (1580)
"	1400	1262	1310	0.4	1310 (2400)	1040 (1900)	840 (1540)
April 29	1400	1070	1265	0.5	1310 (2400)	960 (1760)	840 (1540)
"	1600	762	1375	0.4	1260 (2300)	940 (1720)	820 (1510)
BURN - B							
May 11	1200	1225	1430	0.3	1260 (2300)	980 (1800)	850 (1560)
"	1400	1425	1445	0.3	1260 (2300)	980 (1800)	850 (1560)
May 12	1200	712	1265	0.4	1200 (2200)	925 (1700)	815 (1500)
"	1400	862	1330	0.4	1200 (2200)	980 (1800)	805 (1480)
May 13	1000	250	1245	0.5	1065 (1950)	950 (1740)	795 (1460)
"	1200	630	1170	0.3	1285 (2350)	905 (1660)	795 (1460)
"	1400	638	1260	0.4	1285 (2350)	890 (1640)	815 (1500)

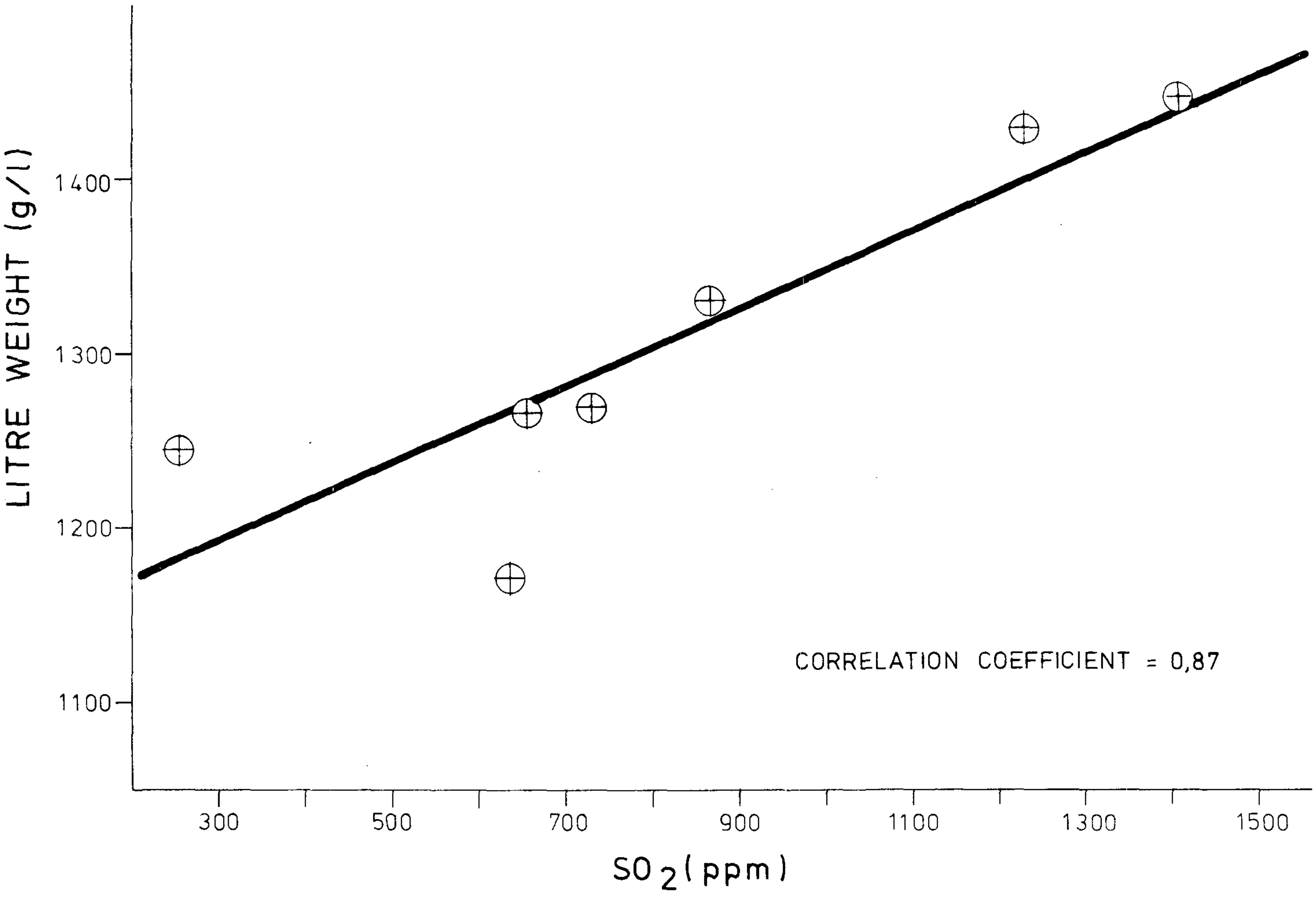
*SO_2 results average of 10 minutes each side of hour

the range of excess oxygen was too narrow to give significant differences. From the data of Verbeck, it would appear that lower SO_2 emissions would have resulted if the present study had been conducted with higher excess oxygen levels.

Higher kiln temperatures inhibit the conversion of SO_2 to SO_3 [10] and it would, therefore, be expected that higher temperatures could contribute to greater emissions of SO_2. While burning coke, the flame extended through a greater section of the kiln and the operators tended to burn at higher temperatures than when burning with oil.

To investigate the effect of kiln operation on emitted SO_2 levels, correlation coefficients were calculated relating emitted SO_2 levels and the various kiln operating parameters given in Table 7. One parameter which yielded good correlation with emitted SO_2 was the litre weight of the clinker. The plotted data are shown graphically in Figures 4 and 5. The litre weight is the weight in grammes of one litre of clinker after passing through sieves to obtain the 5 to 7 mm size fraction. Clinker burned at a higher temperature or for a longer time is heavier due to a decrease in porosity, thus higher litre weight indicates higher burning temperature. A coefficient of correlation of 0.87 was found between clinker litre weight and emitted SO_2 concentration during Burn B. The combined data of Burn A and Burn B also gave fair correlation between these two parameters. The coefficient of correlation between clinker litre weight and emitted SO_2 levels was 0.67 when all data obtained while burning coke were accounted for.

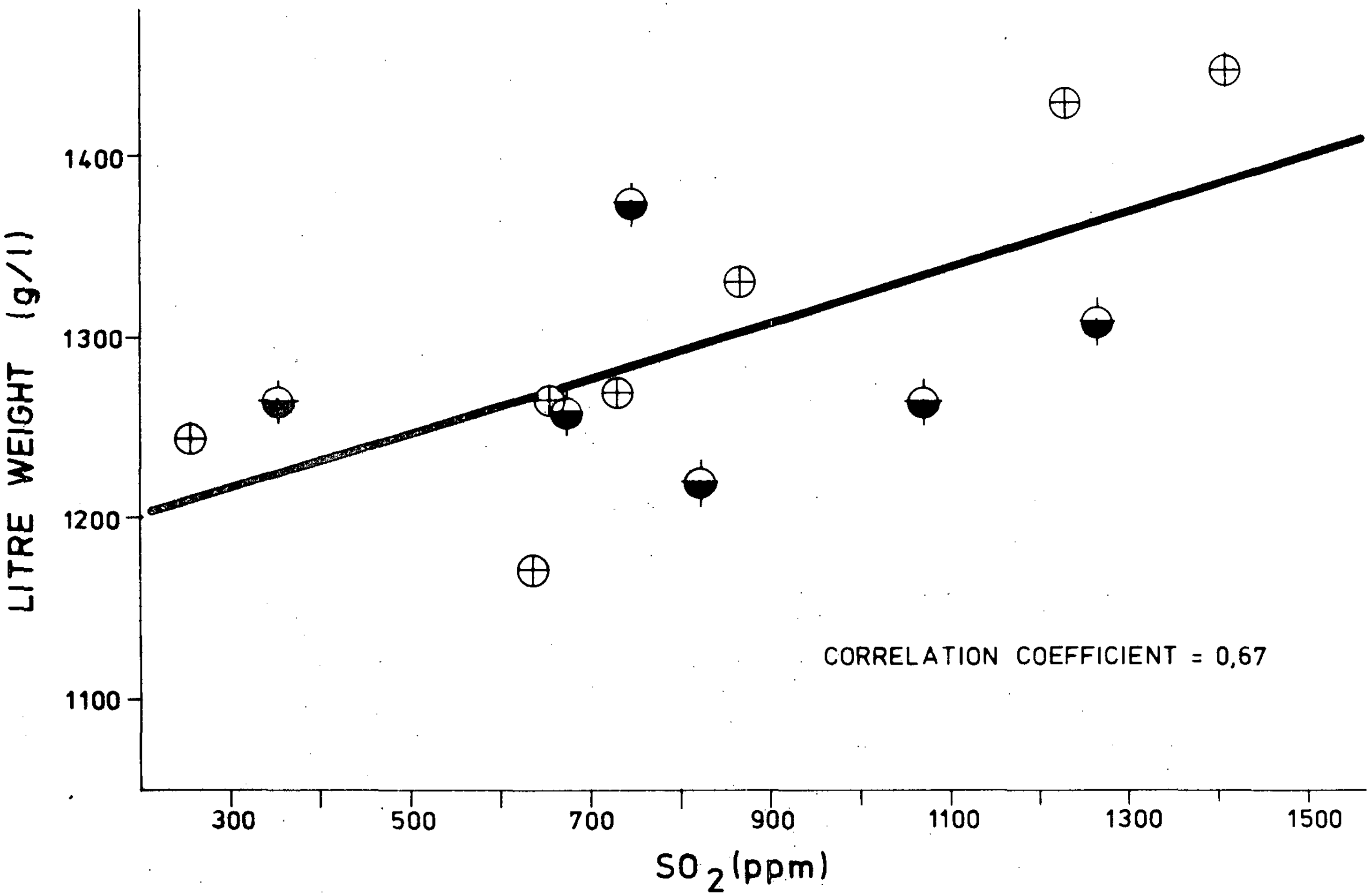
A similar degree of correlation was found between emitted SO_2 concentration and the temperature at the chain zone of the kiln. While a relationship appeared to exist between burning zone temperature and emitted SO_2, this relationship was not as well defined as the two previously cited. However, the monitoring of the burning zone temperature is subject to large errors caused by such variables as the amount of dust in the burning zone and the actual configuration of the flame and clinker bed. While the data are few, indications are that emitted SO_2 is dependent upon the temperature profile of the kiln. The data, with the calculated least squares correlation lines, are plotted in Figures 6 and 7.



SO_2 EMISSIONS vs LITRE WEIGHT

MAXIMUM COKE BURN

FIGURE 4

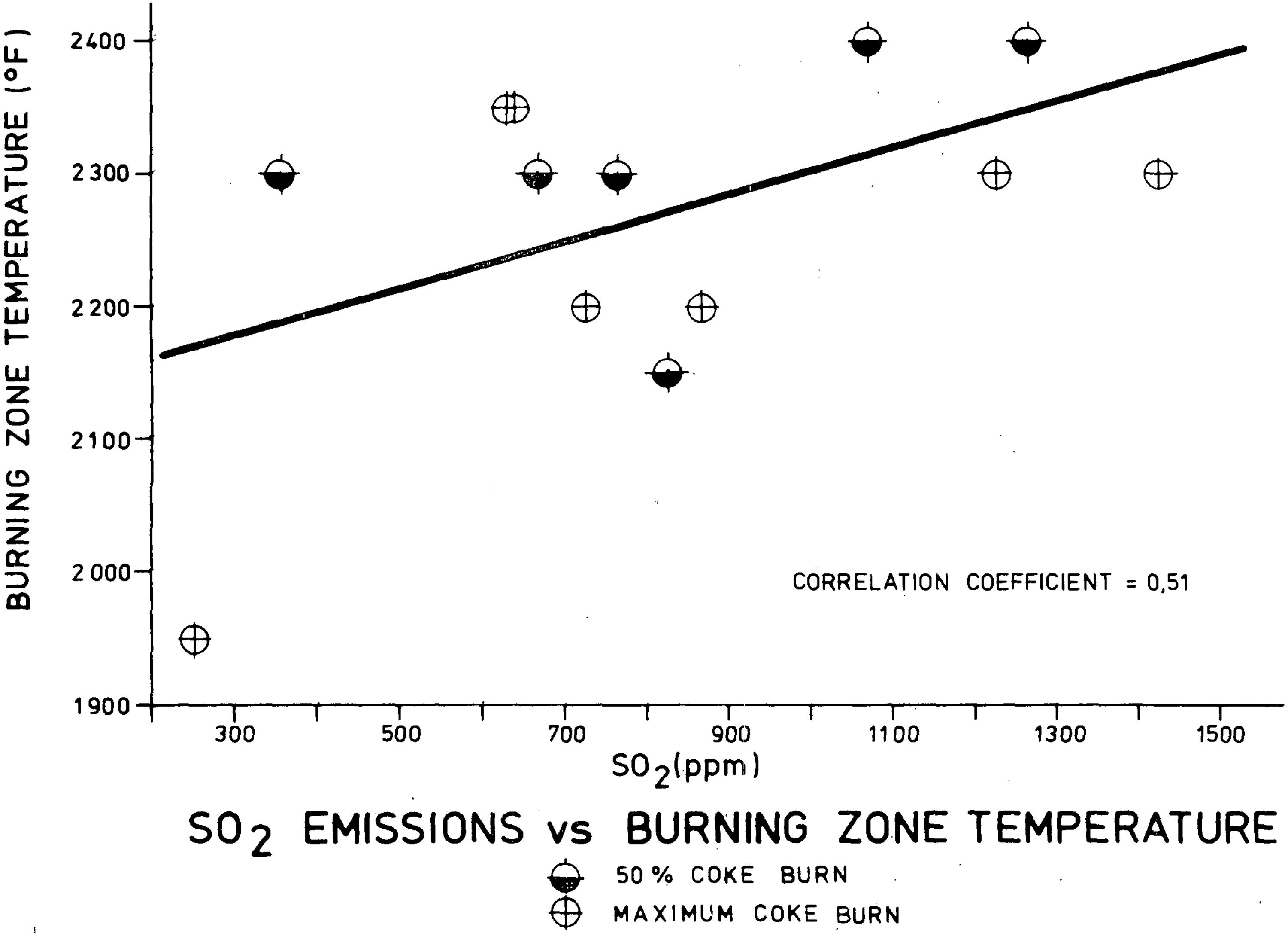


SO_2 EMISSIONS vs LITRE WEIGHT

◓ 50 % COKE BURN

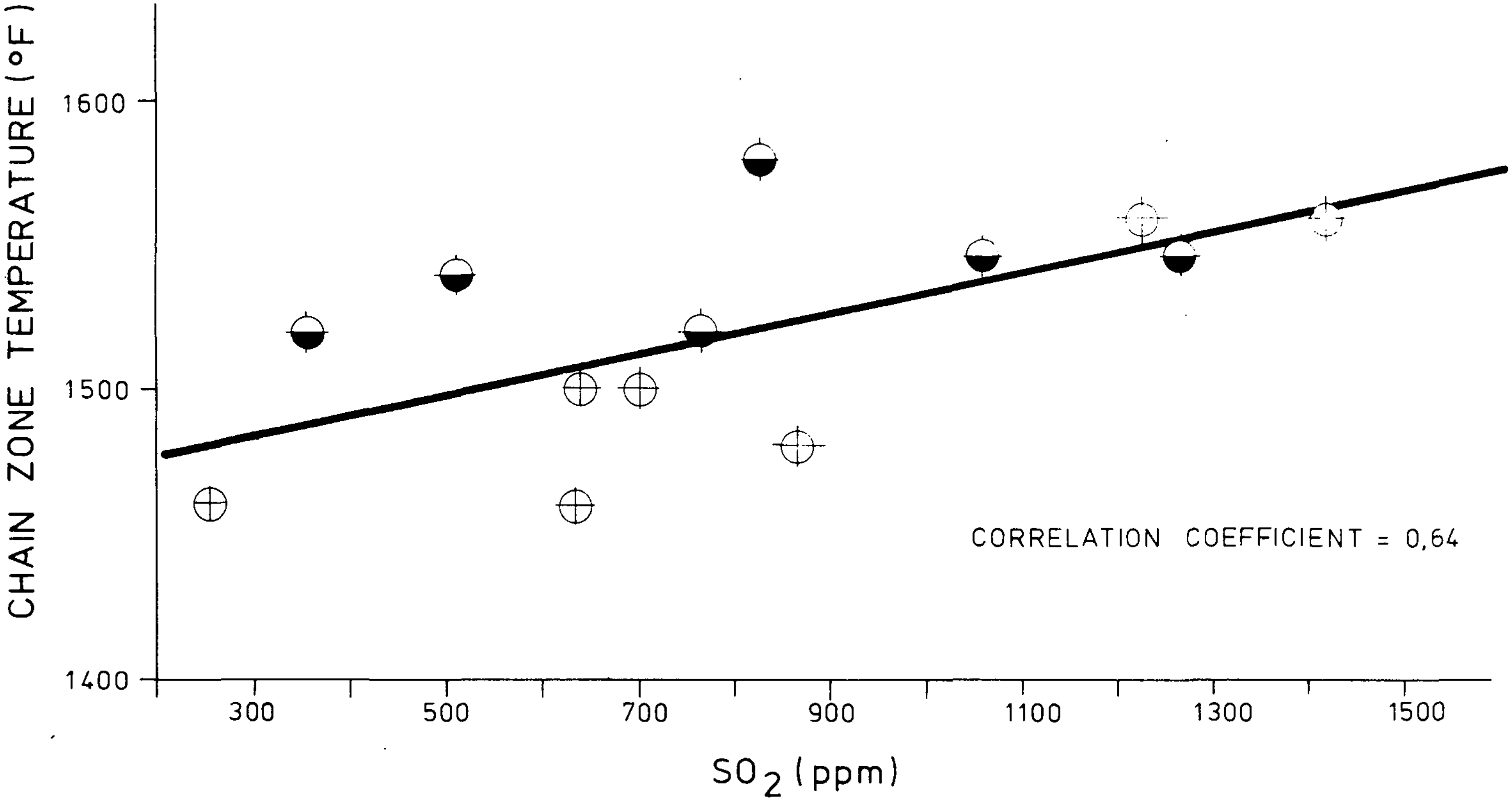
⊕ MAXIMUM COKE BURN

FIGURE 5



SO_2 EMISSIONS vs BURNING ZONE TEMPERATURE

FIGURE 6



SO_2 EMISSIONS vs CHAIN ZONE TEMPERATURE

◒ 50 % COKE BURN

⊕ MAXIMUM COKE BURN

FIGURE 7

Attempts to correlate litre weight and emitted SO_2 while burning only oil were unsuccessful. One possible reason is that the shorter flame observed while burning oil influences the retention of sulphur.

It would appear that the emissions of SO_2 could be reduced by appropriate changes in kiln operation. However, it must be emphasized that these hypotheses are based on extremely limited data. Further studies while burning high sulphur fuels could determine whether and to what extent SO_2 emissions could be controlled through kiln operation.

4.5 Cement Quality

Clinker is ground and blended with gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$), normally by intergrinding, to produce cement. The sulphate added controls the setting time and has a pronounced beneficial effect on other properties of the cement. Sulphate added to cement is considerably more effective than sulphate present in clinker for the control of the cement characteristics [11]. The quantity of total sulphate in cement must, however, be carefully controlled because excessive sulphate can cause deleterious expansion. Thus, maximum sulphate levels are general requirements of cement specifications. With cement produced from clinker containing a high percentage of sulphate, it may not be possible to add sufficient sulphate as gypsum or anhydrite to attain the optimum cement properties. It was anticipated that a large quantity of sulphate would be retained in the clinker when burning coke. Trace elements can also influence the characteristics of the cement; for example, vanadium reduces the setting time and can improve the compressive strength levels of cements.

To study the overall effects on cement quality as a result of burning coke, separate daily lots of production clinker were retained during each phase of the study. Each lot of clinker was separately ground into cement and composite samples of the cement produced were retained. The same production mill was used and the fineness and sulphate content were controlled to the same values for all cements produced. In this manner, six composite samples were obtained for each phase of the burn.

Sample 3, prepared from oil burned clinker, was not large enough for a complete testing program and this sample was blended with sample 4. The following tests were conducted on all cement samples:

- fineness on No. 200 sieve,
- normal consistency,
- setting time, Vicat method,
- soundness by autoclave expansion test,
- compressive strength,
- air content (ASTM method C185),
- false set, mortar method (ASTM method C359),
- Blaine fineness by air premeability (ASTM method C204).

Tests, with the exception of those noted as ASTM methods [12] were conducted in accordance with the methods of CSA Standard A5 - Portland Cements [13].

Averaged data are given in Table 8. While the compressive strength levels increased slightly in cements made from clinker produced while burning coke, the increase is not considered large enough to be significant. However, significant differences were noted with regard to setting characteristics of the cements produced. The initial setting time, which is the time required for normal hardening to attain a certain consistency, was shorter in cements produced from coke-burned clinker. The shorter setting times are within the acceptable and competitive range of Canadian cements.

The false set test is a measure of premature stiffening after the addition of water. A false set is usually associated with precipitation of gypsum crystals. Precipitated crystals form a network giving undesirable rigidity to the mortar. Breaking of this network by remixing generally relieves the problem. The test involves mixing cement, sand and water and placing this mortar into a container 50 mm deep. A needle of exact weight and diameter is released above the mortar at various times. The penetration into the mortar is measured in millimetres. Thus a reading of 50 mm indicates complete penetration and hence no premature stiffening. After 11 minutes, the mortar is remixed and retested. Values less than 25 mm or failure to obtain a 50 mm penetration after remixing are undesirable. While premature stiffening occurred in cements produced from all phases of the study, the occurence is much more severe in cements made from clinker produced while burning

TABLE 8. AVERAGE TEST RESULTS FOR CEMENTS

Test	Clinker Produced While Burning Oil	Clinker Produced While Burning 50% Coke	Clinker Produced While Burning Maximum Coke
Blaine Fineness (cm^2/g)	3482	3515	3512
Retained on 200 Mesh Sieve (%)	2.3	2.2	2.0
Normal Consistency, Water (%)	25.3	25.0	25.5
Initial Setting Time (minutes)	147	128	118
Final Setting Time (minutes)	283	251	229
Air Content (%)	9.5	9.0	8.6
False Set, Penetration (mm)			
3 minutes	46	50	43
5 minutes	42	47	37
8 minutes	37	38	28
11 minutes	33	35	24
Remix	50	50	40
Compressive Strength (psi)			
1 day	2053	2150	2076
3 days	3286	3401	3350
7 days	3988	4048	4124
28 days	4829	4873	4919

Note: To convert from psi to kilograms/cm^2, multiply by 0.070.

coke at the maximum rate. The premature stiffening reported in this study could undoubtedly be alleviated simply; possibly an adjustment in the quantity of added gypsum would suffice.

While V_2O_5 can alter the setting time of cement, other factors such as burning temperature in the kiln and slightly different sulphate concentration of the clinker may also have contributed to the shorter setting times found.

Operation of the kiln to retain more sulphur would, of course, yield higher sulphate levels in the clinker. The extent to which the clinker can retain additional sulphur is unknown. While it was intended to study the effect of high sulphur clinker on cement quality, the failure to retain sulphur in the clinker made this impossible.

5 BURNING OF COKE FROM AN OPERATIONAL STANDPOINT

5.1 General Considerations

The satisfactory burning of solid fuels in a cement kiln is highly dependent upon the volatile combustible matter. According to Duda [9], volatile combustible matter burns off immediately, leaving the particles highly porous. Thus, the reaction with oxygen can proceed rapidly. A low content of volatile matter causes slow combustion along an extended kiln section, thereby generating a long flame. As a general rule, a shorter flame is desirable as this may increase the production capabilities of the kiln [6]. To counteract slower burning of fuels containing less volatile matter, the fuel must be more finely ground. The grinding of the fuel has a dramatic effect on flame length since the burning time increases approximately by the square of the diameter of the fuel particle.

While extremely important, volatile matter and fineness are not the only parameters controlling the rate of burning. Clinker leaving the kiln must be rapidly cooled. In a grate cooler, the cooling is achieved by drawing air through the bed of clinker. Hot air from the clinker cooler, usually around 815°C (1500°F), is drawn into the kiln to supply oxygen for combustion. Some of the air from the clinker cooler is blended with ambient air to control the temperature at safe operating levels, then is drawn through the coal grinding mill where it dries the fuel and entrains the smaller fuel particles. This air stream, laden with finely ground fuel is transported through the burner pipe into the kiln. The temperature of each air stream, the velocity of the air stream carrying the fuel, and the efficiency of mixing of the two air streams also alter the time for ignition. Other factors are also involved, some under control of the operator, others inherent in the design of the kiln and auxiliary equipment.

When burning oil, the correct size nozzle must be used for proper atomization of the oil. Smaller nozzles are required for lower flow rates. Therefore, when burning a solid fuel and oil together, it becomes necessary to stop the burning and change the nozzle when changing the ratio of the two fuels. This entails a risk of damage to the kiln brick, since, with each stop, cooling and reheating with the related shrinkage and expansion of the bricks takes place.

The plume of the flame, that is the area between the burner and the actual point of ignition of the fuel, is seen as a black cloud or jet in the kiln. Fuels which ignite more rapidly have a shorter visible plume; therefore, the plume is a valuable indicator of the rate of ignition.

5.2 Burning of GCOS Coke

Analyses indicated the content of volatile matter in the GCOS coke to be between 7 and 12 percent (Table 1), as compared to over 30 percent in the coals normally burned in the St. Lawrence Cement Co. plant. While grindability was given with the analytical data, a comparison of the grindability of GCOS coke and the coal normally used was made. The results obtained were:

	Coke	Coal
Work Index according to the Bond formula	17.7	19.5
Kilowatt hours per short ton of product at -100 mesh	13.5	15.2

The coke is more easily ground than coal. Thus, it was anticipated that proper grinding of the coke was possible in the present coal mill.

As expected, when burning coke at the rate required to give 52.9 to 55.8 percent (planned, 50 percent) of the gross heat supplied to the kiln, operation of the system was smooth and stable. The operators, being unaccustomed to the dense black plume from the coke, tended to burn the clinker at too high a temperature. As indicated earlier, high temperatures in the kiln adversely affect the emission of SO_2. Overburning, combined with the planned stops to change oil nozzles as the rate of oil burning was decreased, also caused weakening of the brick and visible red spots on the kiln shell. However, these problems were not associated with coke burning but rather with the lack of familiarity with the fuel. The flame was stable and of fairly good length with coke of fineness to obtain residues retained on a 200 mesh sieve ranging from 1.5 to 13.5 percent, the average value being 5.1 percent.

It was planned to increase the ratio of coke to oil in increments to the point that a stable flame was no longer possible. Through a fortuitous error, a smaller oil nozzle than desired was installed after completion of the 50 percent coke burn. To stop and change to the correct nozzle immediately would have entailed further risk to already weakened kiln brick. Even with extremely high oil pressures, a maximum of 10 percent of the heat requirement could be input as oil. For a period of several hours, coke represented 90.5 percent of the gross heat to the kiln. The residue on a 200 mesh sieve was 12.2 percent, indicating insufficient grinding for the low volatile content fuel. At slightly over six tons per hour, it was not possible to increase the fineness. Attempts to do so caused the mill to overload. The flame was extremely unstable with a long plume. Occasionally, as the plume became thinner through turbulence in the kiln, the oil could be seen burning in the centre of the plume but having little effect on the ignition of the coke. Clouds of coke could be seen drifting unburned for a considerable distance along the kiln and then igniting when impinging upon the inside of the kiln or the feed bed.

On May 7, the kiln was stopped because of a power failure and the opportunity was taken to install a slightly larger oil nozzle. With the larger oil nozzle, it was possible to increase oil and decrease coke. With the decrease in coke (to about 5.9 tons per hour), the fineness was increased so that the residue retained on a 200 mesh sieve was 6 percent. As the coke burn progressed, the operators became more accustomed to the long plume of the coke. The tendency was still to burn at too high a temperature although not to the same extent as earlier in the program. The flame at this level was stable and kiln operation smooth. This level of coke was burned until May 19.

After completion of the maximum coke burn the kiln bricks had been weakened to the extent that another shutdown to change oil nozzles was not possible. At this point the kiln was shut down for rebricking. Therefore, it was not possible to carry out the final baseline test.

The method used for reporting the percentage heat supplied by the coke requires clarification. All values cited throughout this report were calculated by determining the percentage of gross heat supplied by coke compared to the total gross heat input to the kiln at that moment. Because of the lower hydrogen content of coke in comparison with oil, lower quantities of gas were generated through combustion. This, in turn, resulted in lower heat losses and better heat exchange [9] when burning coke. Thus, the actual reduction in oil was greater than indicated by the method of calculation used in this report. Because of this effect, the calculated value of 90.5 percent gross heat input as coke cited above gave an actual reduction of oil consumed per ton of clinker of 92.4 percent, when compared to the baseline while burning only oil.

The volatile content of the coke was somewhat higher than reported in the analysis received from GCOS. The average content of volatile matter obtained through analyses performed for this study was 14.5 percent, compared with the 7 to 12 percent provided. Other values, such as gross heat, ash and sulphur content, agreed well with the values reported by GCOS. Thus, while those parameters relating to the effect of burning coke on the environment and quality of clinker produced can be considered representative, a lower volatile matter content would undoubtedly have decreased the maximum rate of coke burning by a small amount.

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APPENDIX A

SAMPLING AND ANALYTICAL METHODOLOGY

APPENDIX A

SAMPLING AND ANALYTICAL METHODOLOGY

A.1 Quantifying and Sampling Slurry Feed and Clinker

Ground slurry is stored in basins equipped with air agitators for the purpose of blending the slurry and maintaining a uniform suspension of solids in liquid. Slurry is pumped from one of these basins to the constant level box of the slurry feed system. The material which overflows from the constant level box is returned to the slurry basins. Slurry feed for the kiln is taken from the constant level box by an Allis Chalmers "Ferris Wheel" bucket wheel feeder with variable speed drive. From the bucket wheel feeder, the slurry flows into a small basin with an outlet at the bottom from which the slurry is gravity fed to the kiln.

The slurry feed samples were taken every two hours from the overflow of the constant level box and blended into a daily composite. A portion of the daily composite then was dried at 120°C for analysis.

Slurry feed quantities were obtained by multiplying the total number of revolutions of the "Ferris Wheel" per day by a factor relating revolutions to quantity. Measuring the slurry basin level during periods of feeding the kiln from a basin, while not allowing the slurry produced to be fed to the basin, was one method of calibration used during the study. A second method, performed every two hours, was to close a valve on the small basin fed by the Ferris Wheel. By determining the time to fill this basin, the quantity per unit time was established.

The clinker is fed to a bucket elevator by gravity through a chute from the cooler. Clinker samples were taken from this chute at intervals of two hours to form a 24-hour composite. The clinker composite sample was mixed, reduced by "cone and quartering", and a portion ground for analysis.

In common with general practice in the industry, there was no provision in the plant for continuous weighing of clinker. The clinker quantity can be calculated from the slurry quantity by considering the reactions taking place within the kiln. Reactions taking place are:

1) evolution of free water (drying),
2) evolution of combined water,
3) evolution of CO_2 from $CaCO_3$ and $MgCO_3$,
4) reaction of CaO with SiO_2, Al_2O_3 and Fe_2O_3,
5) absorption into clinker of SO_3 and ash from fuel,
6) loss of dust generated by abrasion and from volatile compounds.

If the percentage of water contained in the slurry is known, the quantity of dry slurry remaining after reaction (1) can be determined by:

$$\mathrm{SFD} = \mathrm{SF}\left(\frac{100 - H_2O}{100}\right)$$

where: SFD = quantity of slurry feed on a dry basis,
SF = quantity of slurry feed including water,
H_2O = % water in the slurry feed.

The loss occurring in reactions (2) and (3) can be found by determining the loss on ignition of the slurry. The quantity of material remaining after these reactions is given by:

$$\text{Ignited Material} = \mathrm{SFD}\left(\frac{100 - \mathrm{LOI}_{\mathrm{SFD}}}{100}\right)$$

where: SFD = quantity of slurry feed on dry basis,
$\mathrm{LOI}_{\mathrm{SFD}}$ = % loss on ignition of slurry feed on dry basis.

Reaction (4) does not alter the quantity of material. The quantity of material represented by reaction (5) is small relative to total quantities and is generally ignored. However, dust discarded from the precipitator represents a significant proportion of total material quantities. Since the dust quantity is subtracted from the ignited material, it must also be converted in the same manner as the ignited material above. Subtracting this quantity gives the final calculation for clinker quantity:

$$\text{Clinker} = \mathrm{SFD}\left(\frac{100 - \mathrm{LOI}_{\mathrm{SFD}}}{100}\right) - \mathrm{DD}\left(\frac{100 - \mathrm{LOI}_{\mathrm{DD}}}{100}\right)$$

where: SFD = quantity of slurry feed on dry basis,

LOI_{SFD} = % loss on ignition of slurry feed on dry basis,

DD = quantity of dust discarded,

LOI_{DD} = % loss on ignition of dust discarded.

A.2 Weighing and Sampling Precipitator Dust

Dust from the precipitator is separated into two portions by a system of screw conveyers under the precipitator. The major portion (approximately 90 percent) is returned via a conveyor belt into a small holding silo, from which the dust is returned almost immediately into the burning zone of the kiln. The rest of the dust is fed into a second holding silo from which trucks are loaded directly. A sample of this dust is taken from each truck load, and all samples for each day are blended into a 24-hour composite. Each load of dust is weighed on the truck weigh scales before being disposed of.

A.3 Measurement and Sampling No. 6 Fuel Oil

A daily sample of No. 6 fuel was bled from the line feeding the kiln. Fuel quantities were continuously monitored and recorded in the production data but are not given in this report.

A.4 Measurement and Sampling Coke

Crushed coke was fed to the coal mill by a belt feeder equipped with a weighing device and integrator which gave the total number of tons fed to the mill and, hence, the kiln. Samples were taken from the belt feeder at two-hour intervals and combined into 24-hour composites. After drying and blending each composite, a portion was ground for analysis.

A.5 Sampling Kiln Gas Emissions

Gases from each of two wet process kilns at the St. Lawrence Cement Co. plant pass through identical six-section electrostatic precipitators, and are exhausted through a common stack via rectangular ducts. Sampling of the kiln emissions could only be made in the duct between the precipitator and stack.

The experimental program required that emission tests be performed during the following four test periods:

1. Normal kiln operation burning No. 6 fuel oil - Designated Baseline A
2. Burning a 50/50 delayed coke/oil mixture - Designated Burn A
3. Burning a maximum quantity of coke - Designated Burn B
4. Normal kiln operation burning No. 6 fuel oil - Designated Baseline B

Three tests in each period were to be made in accordance with procedures specified in the Environmental Protection Service, Fisheries and Environment Canada [A.1], and Ontario Ministry of the Environment [A.2] source testing codes. Testing was to be carried out to determine stack gas concentrations and emission rates of total particulate material and of the elements nickel, vanadium and sulphur. Concentrations of gaseous sulphur oxides were also to be determined.

A.5.1 Sampling location

Emissions from both #1 and #2 wet process kilns pass through electrostatic precipitators (Joy Manufacturing Co.) and then sections of rectangular breeching before mixing in a common section of duct entering the stack. The stack, which is of height 169 m (554 ft) and has an exit diameter of 4 m (13 ft), vents the exhaust gases, at a temperature of about 200°C (400°F) and a velocity of almost 12 m/s (40 ft/sec), to the atmosphere.

The rectangular breeching from the precipitator makes a 90° bend and then angles at about 30° upwards from the horizontal for a distance of approximately 14 m (45 ft) to the common header which leads into the stack. This 14 m section of duct was considered the most suitable for installation of sampling ports at a location which would meet both Federal and Provincial source testing codes. It was subsequently decided, therefore, to install five 10 cm (4 in) diameter ports in the vertical side of the duct at a position 3.7 m (12 ft) upstream to the bend into the header, and positioned on a line perpendicular to the gas flow. The port locations are shown schematically in Figure A.1.

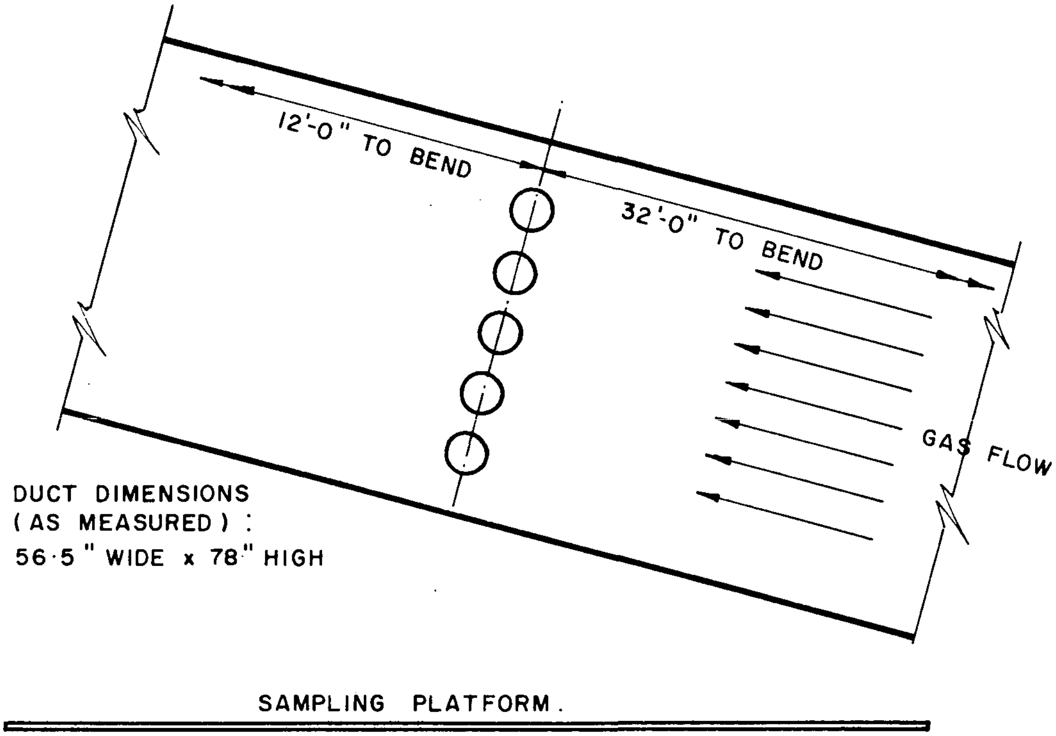


FIGURE A.1 SCHEMATIC OF PORT LOCATIONS.

As agreed by the Ontario Ministry of Environment, and Fisheries and Environment Canada, sampling was carried out at eight points on each of the five duct traverses for a minimum of five minutes per point. The sampling points were located at the centres of equal rectangular areas in the duct.

A.6 Sample Analysis

The samples collected for analysis for nickel, vanadium and sulphur included the following types:

Emission Samples:
- filter particulate catch,
- probe rinse insolubles,
- probe rinse solution.

Process samples:
- raw meal feed,
- clinker,
- precipitator dust.

Fuel samples:
- no. 6 fuel oil,
- delayed coke.

X-ray fluorescence techniques have been used extensively in the past at St. Lawrence Cement Co. (SLC) and Ontario Research Foundation (ORF) to analyze for trace amounts or low concentrations of specific elements in cement clinker and related products. Due in part to the experience gained in this analytical method, X-ray fluorescence was selected for the analyses, by SLC and ORF, of all process and fuel samples.

The amount of material collected on the filter and the quantity of solids insoluble in the probe rinse were found to be quite small in preliminary tests, precluding any division into aliquots for referee analyses. It was decided that ORF would analyze these samples using X-ray fluorescence and, where possible, provide a small portion to the Ontario Ministry of the Environment (MOE) laboratory for checks to be made. The MOE analysts used atomic absorption spectroscopy for these analyses. A portion of all of the filter catches was analyzed by MOE using flameless AA. However, the probe rinse insolubles for some test series had to be combined, even for X-ray analysis by ORF.

All probe rinse solutions were analyzed by ORF and MOE using flameless AA techniques. Specific clinker and dust samples were also analyzed by both ORF and MOE using AA spectroscopy. Table A.1 summarizes the analytical methods used by different analytical groups for all samples collected.

TABLE A.1 SUMMARY OF ANALYTICAL METHODS AND ANALYTICAL GROUPS FOR ALL COLLECTED SAMPLES

Sample Type	Laboratory		
	ORF	SLC	MOE
Filter Catch	XRF	-	AA
Probe Rinse Insoluble	XRF	-	-
Probe Rinse Soluble	AA	-	AA
Raw Meal	XRF	XRF	-
Clinker	XRF AA*	XRF	AA*
Dust	XRF	-	-
Fuel Oil	XRF	XRF	-
Coke	XRF	XRF	-

* For a few specific samples.

REFERENCES FOR APPENDIX A

A.1 "Standard Reference Methods for Source Testing: Measurement of Emissions of Particulates from Stationary Sources", Air Pollution Control Directorate, Fisheries and Environment Canada, 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 "Standard Reference Methods for Source Testing: Measurement of Emissions of Sulphur Dioxide from Stationary Sources", Air Pollution Control Directorate, Fisheries and Environment Canada, Report EPS 1-AP-74-3, Sept., 1975.

APPENDIX B

RESULTS AND CALCULATIONS

APPENDIX B

RESULTS AND CALCULATIONS

B.1 Mass Balance Experimentation

B.1.1 Results of analyses of process materials

Analyses of all process materials were carried out at both St. Lawrence Cement Co. and Ontario Research Foundation.

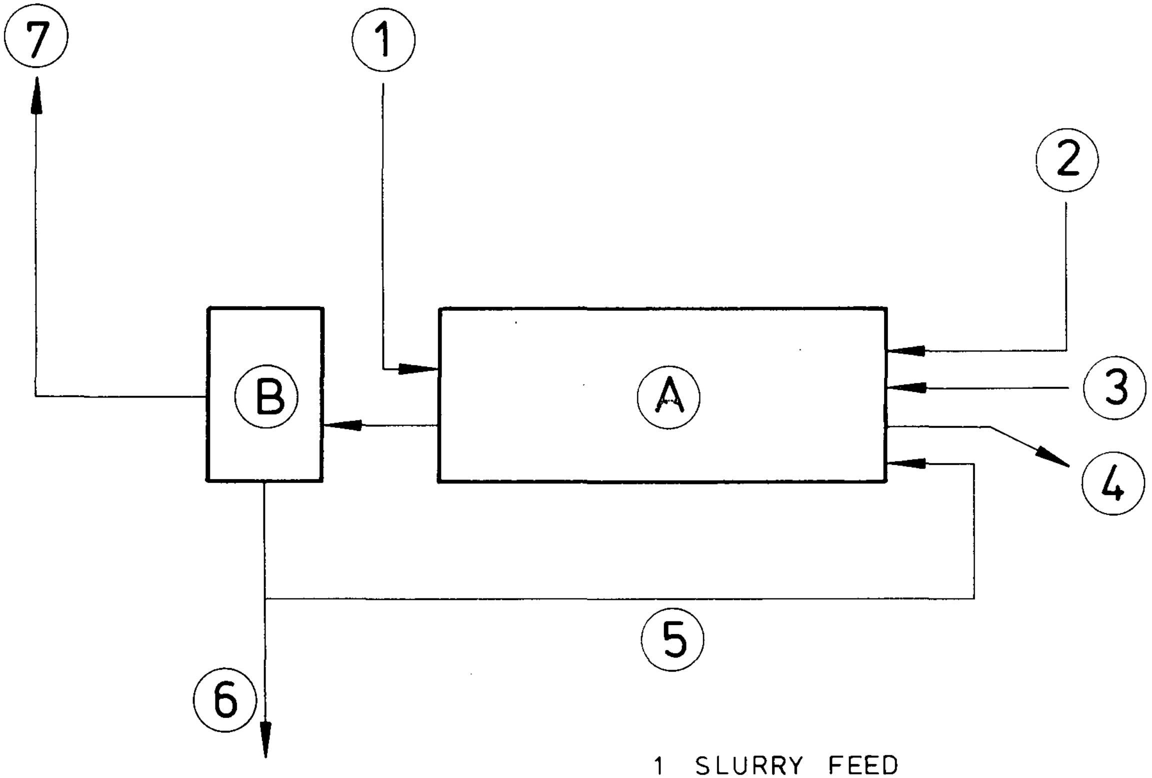
Several clinker samples were analyzed by atomic absorption spectroscopy at both the Ontario Ministry of the Environment and the Ontario Research Foundation. These comparative results were reported in Table 6 in the body of the report.

B.1.2 Calculation of material balance

Materials input to the process (see Figure B.1) were slurry feed, No. 6 fuel oil and coke. Output streams were the product, clinker and precipitator dust, which was wasted. The major portion of the precipitator dust was returned, almost immediately, to the kiln and was not considered as either an input or output stream.

It was anticipated that a minimum of a week would be required to determine the maximum rate of coke burning during which a material balance was not to be determined. Only two days were required to attain this maximum rate of burning (May 3 and 4) and these two days did not constitute a part of the program.

From the daily composite analysis of each material for each element, and the total quantity of each material, daily elemental quantities as pounds per 24 hours were computed. Coke was fed to the grinding mill wet. Since analyses were done on dry coke, daily elemental quantities input by this material as calculated on a dry basis were reduced by 8.6 percent, the average moisture content of this material. These data were then used to form the separate individual mass balance accounts. The mass balance for prolonged periods can be assessed using the cumulative mass balances given in the body of the report (Section 4).



1 SLURRY FEED
2 AIR
3 FUEL (OIL, COKE)
4 CLINKER
5 DUST RETURN
6 PRECIPITATOR DUST WASTED
7 STACK GAS

A KILN
B PRECIPITATOR

SCHEMATIC OF THE MATERIAL BALANCE

FIGURE B.1